

## THESE

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pour la détermination des propriétés moléculaires :  
Application au trifluorosilane



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# Sommaire

|                                                                            |           |
|----------------------------------------------------------------------------|-----------|
| <b>Introduction</b>                                                        | <b>9</b>  |
| <b>1<sup>ère</sup> partie : Méthodologie</b>                               | <b>13</b> |
| <b>Chapitre 1 : Réduction des Hamiltoniens de rotation-vibration</b>       | <b>15</b> |
| I) De l'équation de Schrödinger à l'Hamiltonien effectif                   | 15        |
| 1) Surface de potentiel                                                    | 15        |
| 2) Développement en série de l'Hamiltonien                                 | 16        |
| 3) La transformation de Van Vleck                                          | 18        |
| 4) Les corrélations entre paramètres                                       | 19        |
| II) Les toupies asymétriques                                               | 21        |
| 1) Réduction A                                                             | 22        |
| 2) Réduction S                                                             | 23        |
| III) Les toupies symétriques                                               | 23        |
| 1) Etat non dégénéré                                                       | 24        |
| a) Réduction A                                                             | 25        |
| b) Réduction B                                                             | 25        |
| 2) Etat de vibration isolé et dégénéré                                     | 26        |
| a) Réduction Q                                                             | 28        |
| b) Réduction D                                                             | 28        |
| c) Toupie quasi-sphérique : la réduction QD                                | 30        |
| IV) Conclusion                                                             | 31        |
| <b>Chapitre 2 : Détermination expérimentale des paramètres</b>             | <b>33</b> |
| I) Description des spectromètres                                           | 33        |
| 1) Spectromètre microonde à transformée de Fourier (Kiel, Allemagne)       | 33        |
| 2) Spectromètres millimétrique et submillimétrique (Lille)                 | 34        |
| 3) Spectromètre submillimétrique à bandes latérales (Lille)                | 34        |
| 4) Spectromètre infrarouge à transformée de Fourier (Wuppertal, Allemagne) | 37        |
| II) Analyse du spectre                                                     | 37        |
| 1) Analyse combinée des données                                            | 37        |
| 2) Détermination expérimentale du champ de force                           | 40        |
| <b>Chapitre 3 : Structure et champ de force <i>ab initio</i></b>           | <b>47</b> |
| I) Méthodes et bases                                                       | 48        |
| 1) La méthode Hartree-Fock                                                 | 48        |
| 2) Les méthodes post Hartree-Fock                                          | 49        |
| a) Traitement perturbatif : la méthode Møller-Plesset                      | 49        |
| b) Les méthodes "Coupled-Cluster"                                          | 50        |
| 3) Bases                                                                   | 50        |

|                                                                                                |                |
|------------------------------------------------------------------------------------------------|----------------|
| II) Calcul de structures <i>ab initio</i>                                                      | 51             |
| 1) Effets des méthodes et bases sur la structure                                               | 52             |
| a) La corrélation électronique dans la méthode de calcul                                       | 53             |
| b) Influence de la taille de la base                                                           | 54             |
| c) Les atomes de la 2 <sup>ème</sup> ligne                                                     | 59             |
| d) L'effet des fonctions diffuses                                                              | 61             |
| e) La corrélation électronique cœur-valence                                                    | 63             |
| f) Applications                                                                                | 64             |
| 2) Calibration                                                                                 | 64             |
| 3) Conclusion                                                                                  | 66             |
| III) Détermination <i>ab initio</i> du champ de force                                          | 66             |
| 1) Précision du champ de force                                                                 | 66             |
| a) Les systèmes de coordonnées                                                                 | 67             |
| b) La géométrie de référence                                                                   | 67             |
| c) Dérivées analytiques et numériques                                                          | 68             |
| 2) Applications                                                                                | 68             |
| a) Structure combinée expérimentale et <i>ab initio</i>                                        | 68             |
| b) Utilisation des paramètres <i>ab initio</i>                                                 | 69             |
| <br><b>2<sup>ème</sup> partie : Résultats</b>                                                  | <br><b>71</b>  |
| <b>Chapitre 4 : Détermination de structures géométriques par les méthodes <i>ab initio</i></b> | <b>73</b>      |
| I) Etude de la liaison C-F                                                                     | 73             |
| II) Calculs <i>ab initio</i> des angles de liaison                                             | 73             |
| <br><b>Chapitre 5 : Analyse des états de vibration du trifluorosilane</b>                      | <b>117</b>     |
| I) Présentation de la molécule                                                                 | 117            |
| II) Analyse des spectres                                                                       | 119            |
| 1) Etats non dégénérés                                                                         | 119            |
| 2) L'état dégénéré $\nu_5 = 1$                                                                 | 121            |
| 3) Les états dégénérés $\nu_4$ et $\nu_6 = 1$                                                  | 121            |
| <br><b>Chapitre 6 : Calcul du champ de force et applications</b>                               | <b>187</b>     |
| I) Détermination des paramètres moléculaires du trifluorosilane                                | 187            |
| II) Structure à l'équilibre de SiF <sub>4</sub>                                                | 188            |
| <br><b>Conclusion</b>                                                                          | <br><b>223</b> |
| <br><b>Bibliographie</b>                                                                       | <br><b>227</b> |

# Tableaux

- Tableau 1 :** Les paramètres effectifs et leur dépendance en fonction des paramètres de l'opérateur de la transformation unitaire
- Tableau 2 :** Détermination des paramètres spectroscopiques (en MHz) pour l'état dégénéré  $v_6 = 1$  de  $\text{SiHF}_3$  avec différents types de mesure
- Tableau 3 :** Dépendance des paramètres en fonction des constantes de force
- Tableau 4 :** Nombre de constantes de force indépendantes pour quelques molécules
- Tableau 5 :** Les différents types de transition mesurés pour chaque spectromètre
- Tableau 6 :** L'erreur moyenne des valeurs absolues des écarts entre valeurs expérimentales et *ab initio* pour différentes méthodes et bases
- Tableau 7 :** Evolution de la convergence avec l'ajout d'une fonction de polarisation pour les atomes de la 2<sup>ème</sup> ligne
- Tableau 8 :** Calcul des corrections dues aux fonctions diffuses avec les méthodes CCSD(T) et MP2
- Tableau 9 :** Valeur de la corrélation électronique de cœur-valence pour différentes liaisons
- Tableau 10 :** Application de la méthode de convergence
- Tableau 11 :** Détermination d'un "offset" pour la liaison C-F
- Tableau 12 :** Fréquences de vibration fondamentale du trifluorosilane

# Figures

- Figure 1 :** Courbe de gain du laser submillimétrique à 634 GHz
- Figure 2 :** Stabilisation du laser submillimétrique
- Figure 3 :** Nombre de paramètres déterminés par spectromètre
- Figure 4 :** Schéma des niveaux d'énergie  $(K-\ell) = 3$  pour une toupie symétrique  $C_{3v}$
- Figure 5 :** Gamme et précisions des spectromètres
- Figure 6 :** Illustration de quelques évolutions de longueurs de liaison avec l'augmentation de la taille de la base
- Figure 7 :** Amélioration de la convergence pour les atomes de la 2<sup>ème</sup> ligne avec les bases cc-pVnZ+1
- Figure 8 :** Niveaux d'énergie de vibration en  $\text{cm}^{-1}$



# Introduction

La spectroscopie moléculaire à haute résolution a fait des progrès gigantesques ces cinquante dernières années. Tout d'abord dans les gammes de fréquences accessibles qui se sont considérablement élargies, en particulier dans les domaines submillimétrique et infrarouge proche. Ceci a été rendu possible grâce à l'apparition des carcinotrons et des lasers qui peuvent être utilisés en différence de fréquence, ou les lasers moléculaires optiquement pompés. La sensibilité des spectromètres a été aussi très nettement améliorée avec l'utilisation de détecteurs plus performants (par exemple les bolomètres), mais aussi avec les traitements informatiques du signal plus perfectionnés. En particulier la transformée de Fourier a permis d'accroître énormément les capacités des spectromètres.

Ces progrès techniques permettent une analyse beaucoup plus détaillée des spectres de ro-vibration, ce qui nécessite des progrès théoriques, les modèles existants n'étant plus assez précis pour analyser de manière quantitative les spectres. Alors que dans les années cinquante un spectre de rovibration était défini par une dizaine de paramètres (beaucoup moins pour un spectre de rotation pure), il faut aujourd'hui plus de paramètres : par exemples vingt-sept paramètres ont été déterminés expérimentalement lors de l'étude de l'état fondamental de vibration dégénéré et isolé  $v_6 = 1$  pour  $\text{SiHF}_3$ . Cela pose évidemment des problèmes numériques mais aussi des problèmes théoriques plus fondamentaux liés à la signification des paramètres, car dans les Hamiltoniens utilisés pour l'ajustement des données expérimentales, tous les paramètres ne sont pas déterminables. Il faut contraindre la valeur de certains paramètres pour lever les corrélations qui existent entre eux : c'est la théorie des réductions. Nous aborderons ces problèmes dans le premier chapitre, d'abord pour les toupies asymétriques car ils sont plus simples à saisir puis pour les toupies symétriques où les travaux sont plus récents et nous concernent plus directement.

Nous décrivons d'abord dans le chapitre 2, les spectromètres que nous avons utilisés pour l'enregistrement des spectres des états de rovibration du trifluorosilane. Nous verrons que l'intérêt de l'utilisation de ces différents spectromètres réside dans l'analyse combinée des données provenant des différentes gammes de fréquence, qui est le moyen le plus efficace de déterminer avec précision l'ensemble des paramètres spectroscopiques.

On peut remarquer dans le premier chapitre que les paramètres moléculaires peuvent s'exprimer en fonction du champ de force et de la structure de la molécule. Mais nous verrons à la fin de ce deuxième chapitre que le problème "d'inversion", c'est-à-dire le calcul du champ de force à partir des paramètres expérimentaux, reste extrêmement difficile car les constantes de force sont en général trop nombreuses pour qu'elles soient toutes déterminables expérimentalement.

Toutefois ce problème de détermination d'un champ de force est depuis peu soluble grâce aux calculs *ab initio*. L'apparition d'ordinateurs puissants et de programmes (méthodes et bases) sophistiqués permet maintenant de calculer un champ de force anharmonique (jusqu'aux termes quartiques) avec une excellente précision.

Le chapitre 3 est consacré à la détermination *ab initio* des paramètres moléculaires. Dans la première partie, nous étudions les calculs de structure des molécules. La structure à l'équilibre qui correspond au minimum de l'énergie potentielle est la plus intéressante, mais elle est très difficile à obtenir expérimentalement car elle nécessite l'analyse de toutes les bandes fondamentales de vibration. Les calculs *ab initio* se présentent comme une bonne alternative pour la détermination de ces structures. Nous ferons le bilan des possibilités et des précisions que l'on peut atteindre avec les niveaux de calcul actuellement utilisables. Nous aborderons les différentes techniques de calcul de structures : une première qui est strictement théorique, et deux autres semi-expérimentales. Nous verrons les avantages et les inconvénients, ainsi que leurs précisions respectives pour chacune de ces méthodes de calcul. Parmi les deux méthodes semi-expérimentales, l'une fait intervenir des données provenant des champs de force *ab initio* et sera donc plus particulièrement discutée à la fin de ce chapitre dédiée aux calculs et applications des champs de force *ab initio*.

Dans la deuxième partie de ce manuscrit, nous présenterons les résultats que nous avons obtenus. Le chapitre 4 reporte les résultats relatifs aux calculs de structures. L'étude sur la liaison C-F est d'abord abordée : l'atome de fluor étant très électronégatif, il faut utiliser des bases très étendues, ce qui explique qu'il n'y ait pas encore d'études précises sur cette liaison. Puis nous avons entrepris une étude systématique pour les angles de liaison afin d'estimer la précision des calculs avec les moyens actuels.

Dans le chapitre 5 nous exposerons l'analyse des spectres de vibration du trifluorosilane après une présentation rapide de la molécule. Les deux états dégénérés  $\nu_4 = 1$  et  $\nu_6 = 1$  sont plus particulièrement discutés.

Le chapitre 6 est consacré aux résultats obtenus à l'aide du champ de force, tout d'abord celui du trifluorosilane avec lequel nous avons calculé les paramètres spectroscopiques : d'une part pour estimer la précision de ce champ de force, et aussi pour confirmer les relations entre les paramètres réduits et les constantes de force.

Nous avons aussi calculé des structures géométriques par combinaison des moments d'inertie expérimentaux et des corrections harmoniques et anharmoniques obtenues à partir du champ de force. Nous avons déterminé la précision de ces structures en les comparant à celles obtenues avec d'autres méthodes.



1 ère Partie :

Méthodologie



# Réductions des Hamiltoniens de rotation-vibration

L'énergie des niveaux d'un atome ou d'une molécule est obtenue en utilisant l'équation de Schrödinger, mais la résolution exacte de cette équation n'est possible que pour les systèmes à un seul électron : l'atome d'hydrogène et  $H_2^+$ . On doit faire un certain nombre de simplifications afin d'obtenir un modèle qui puisse reproduire les données provenant de la spectroscopie haute résolution actuelle. Nous verrons plus ou moins en détail quelques étapes qui conduisent à l'Hamiltonien de rotation-vibration d'une molécule polyatomique (plus de deux atomes) utilisé pour l'identification des spectres.

Nous nous consacrerons essentiellement aux transformations unitaires qui permettent de découpler les états de vibration qui ne sont pas en interaction. Mais cela n'est pas sans conséquences, car c'est la cause de corrélations entre les paramètres déterminables expérimentalement. La théorie des réductions qui prédit ces corrélations est bien connue pour les toupies asymétriques [67Wat], mais elle est en revanche plus récente pour les états excités des toupies symétriques. La compréhension et la résolution des problèmes de réductions ne datent que de 1987 [87Lob], et les confirmations expérimentales de 1994 [94Har] pour l'état dégénéré  $v_{10} = 1$  de  $CF_3CCH$ .

## I) De l'équation de Schrödinger à l'Hamiltonien effectif

### 1) Surface de potentiel

En se plaçant dans l'approximation adiabatique de Born-Oppenheimer qui permet la séparation des mouvements des électrons et des noyaux, on peut résoudre indépendamment les équations de Schrödinger pour les noyaux et les électrons [98Bun]. On ne verra ici que la résolution de la partie "noyau". Les niveaux d'énergie de l'Hamiltonien de rotation-vibration sont donnés par les valeurs propres de :

$$\mathbf{H} = T_{\text{nuc}} + V \quad (1)$$

où  $T_{\text{nuc}}$  est l'énergie cinétique des noyaux et  $V$  l'énergie potentielle :

$$V = V_{\text{NN}} + E_e \quad (2)$$

composée de  $V_{\text{NN}}$  qui est la somme de l'énergie de répulsion électrostatique noyau-noyau et  $E_e$  la valeur propre de l'Hamiltonien électronique calculée en supposant les noyaux fixes.

La surface d'énergie potentielle ( $V$ ) qui représente l'énergie des électrons en fonction des coordonnées nucléaires constitue la source de renseignements la plus complète. Elle résume les caractéristiques essentielles de la molécule, et apporte des connaissances beaucoup plus larges que les simples paramètres spectroscopiques. Il est ainsi possible de prédire les spectres rovibrationnels, de déterminer les propriétés thermodynamiques, d'obtenir la structure à l'équilibre et de prédire les chemins réactionnels. Mais la détermination complète de la surface de potentiel de la position d'équilibre à la dissociation de la molécule, n'est possible que pour des systèmes présentant un nombre limité de degrés de liberté (deux ou trois atomes). Pour la plupart des applications spectroscopiques on peut néanmoins se limiter à l'étude autour de l'équilibre et considérer des mouvements de faible amplitude. Ceci autorise un développement analytique en série du potentiel autour de cette position d'équilibre. Le développement de l'énergie potentielle utilisé s'exprime :

$$V(Q) = V_0 + f_i q_i + \frac{1}{2} \sum_{ij} f_{ij} Q_i Q_j + \frac{1}{6} \sum_{ijk} f_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} Q_i Q_j Q_k Q_l + \dots \quad (3)$$

Les constantes  $f_{ij}, f_{ijk}, f_{ijkl}$  sont respectivement les constantes de force quadratiques, cubiques, et quartiques. Elles sont les dérivées à l'ordre deux, trois et quatre du potentiel par rapport aux coordonnées normales  $Q_k$  qui représentent les déplacements des noyaux. L'origine  $V_0$  du potentiel peut être choisie comme nulle, le second terme qui représente la dérivée à l'ordre un du potentiel est lui aussi nul si l'on se place à la position d'équilibre de la molécule, c'est à dire au minimum du potentiel.

## 2) Développement en série de l'Hamiltonien

Nous donnons ci-dessous la version compacte de l'Hamiltonien complet de rotation-vibration proposée par Watson [68Wat]. Si l'on veut plus de détail sur la construction de l'Hamiltonien quantique, on peut trouver une bonne présentation des problèmes dans [55Wil].

$$\mathbf{H}_{vr} = \frac{\hbar^2}{2} \sum_{\alpha, \beta=x, y, z} \mu_{\alpha\beta} (J_\alpha - \pi_\alpha)(J_\beta - \pi_\beta) + \frac{1}{2} \sum_k P_k^2 + V(Q) - \frac{\hbar^2}{8} \sum_{\alpha=x, y, z} \mu_{\alpha\alpha} \quad (4)$$

Les différents termes présents dans cet Hamiltonien sont les suivants :  $\mu_{\alpha\beta}$  est l'élément de la matrice inverse du tenseur d'inertie effectif. Le déterminant de cette matrice est noté  $\mu$ .  $J_\alpha$  est le moment cinétique de rotation selon l'axe  $\alpha$ .  $\pi_\alpha$  est la composante du moment

cinétique interne de vibration selon l'axe  $\alpha$ , et  $P_k$  est le moment conjugué de la coordonnée normale de vibration  $Q_k$ .

La forme de l'Hamiltonien est encore simplifiée en utilisant le développement du tenseur d'inertie  $\mu_{\alpha\beta}$  [68Wat]:

$$\mu_{\alpha\beta} = (I_\alpha)^{-1} I_\alpha \delta_{\alpha\beta} - \sum_k a_k^{\alpha\beta} Q_k + \frac{3}{4} \sum_{kl\gamma} a_k^{\alpha\gamma} Q_k I_\gamma^{-1} a_l^{\gamma\beta} Q_\gamma - \dots \} (I_\beta)^{-1} \quad (5)$$

en remplaçant (3) et (5) dans (4), on obtient un Hamiltonien qui peut être décomposé en une somme de termes que l'on peut ordonner en fonction des puissances des opérateurs de vibration  $\pi$  et de rotation  $J$ . L'Hamiltonien se présente comme une série de termes notés  $H_{mn}$  [76Ali] où les valeurs de  $m$  et  $n$  sont respectivement les puissances des opérateurs  $\pi$  et  $J$  présents dans les différents termes. Elles définissent l'ordre du développement de l'Hamiltonien en fonction de ces opérateurs.

$$\mathbf{H}_{vr} = \sum \mathbf{H}_{mn}$$

$$\begin{aligned} \mathbf{H}_{vr} &= \mathbf{H}_{20} + \mathbf{H}_{30} + \mathbf{H}_{40} + \dots && \text{termes de vibration} \\ &+ \mathbf{H}_{21} + \mathbf{H}_{31} + \mathbf{H}_{41} + \dots && \text{termes de Coriolis} \\ &+ \mathbf{H}_{02} + \mathbf{H}_{12} + \mathbf{H}_{22} + \dots && \text{termes de rotation} \end{aligned} \quad (6)$$

L'ordre de grandeur des différents termes est donné par :  $\mathbf{H}_{mn} = \kappa^{m+n-2} \omega_{vib}$ , où  $\kappa$  est le rapport d'expansion de Born-Oppenheimer, sa valeur est de l'ordre de 1/30 [71Ama]. On ne donnera pas ici les expressions des différents termes que l'on peut trouver dans [85Ali]. Néanmoins on s'arrêtera sur les termes de vibration harmonique  $\mathbf{H}_{20}$  et du rotateur rigide  $\mathbf{H}_{02}$ , qui représentent l'ordre zéro du développement de l'Hamiltonien :

$$\mathbf{H}_{20} = \frac{1}{2} \sum_k \omega_k (Q_k^2 + P_k^2) \quad (7)$$

Ce terme est décomposable en une somme d'oscillateurs harmoniques à une dimension selon chaque coordonnée normale de vibration, dont les valeurs propres sont bien connues [55Wil]. Il dépend de la partie quadratique de  $V(q)$ . Ainsi cette partie du potentiel est aussi appelée champ de force harmonique. Le terme du rotateur rigide s'écrit :

$$\mathbf{H}_{02} = \sum B_\alpha^e J_\alpha^2 \quad (8)$$

$$\text{avec les constantes de rotation : } B_\alpha^e = \frac{\hbar^2}{2hcI_\alpha}$$

Lorsque l'on détermine les constantes de rotation de la molécule, on peut en déduire les moments d'inertie et donc calculer sa structure. Pour une toupie asymétrique, les trois constantes de rotation sont différentes, alors que dans le cas d'une toupie symétrique, deux des constantes de rotations sont identiques :  $B_x^e = B_y^e$ .

Enfin, on peut observer dans le tableau I de [85Ali] que les différents termes de l'Hamiltonien développé s'expriment en fonction des constantes de force. On comprend ainsi qu'avec le champ de force d'une molécule, on peut en déduire les paramètres spectroscopiques et inversement.

### 3) La transformation de Van Vleck

Les éléments de matrice de l'Hamiltonien s'expriment dans la base des états propres de l'oscillateur harmonique et du rotateur rigide. Chaque bloc de matrice pour un  $J$  donné est infini en fonction des nombres quantiques de vibration. Des simplifications sont nécessaires afin de déterminer les valeurs propres de cet Hamiltonien. Il existe des techniques variationnelles qui consistent à tronquer l'Hamiltonien pour pouvoir le diagonaliser, mais elles nécessitent des calculs assez lourds. On peut aussi avoir recours à des méthodes perturbatives, comme la transformation de Rayleigh-Schrödinger utilisée par Oka [67Oka] et Mills [72Mil] ou la transformation de contact de Van Vleck employée par Amat, Nielsen et Tarrago [71Ama] ainsi que par Aliev et Watson [85Ali]. Pour reproduire la précision des données expérimentales actuelles il est nécessaire d'utiliser des ordres élevés de perturbation, la transformation de contact s'avère être dans ce cas la méthode la plus simple à mettre en œuvre. Voici un très bref résumé du principe de la transformation de Van Vleck.

Tout d'abord, on écrit les termes de l'Hamiltonien en les ordonnant suivant leur ordre de grandeur :

$$\mathbf{H} = \mathbf{H}_0 + \lambda \mathbf{H}_1 + \lambda^2 \mathbf{H}_2 + \dots \quad (9)$$

puis on applique une première transformations de Van Vleck à l'Hamiltonien :

$$\mathbf{H}' = e^{iS_1} \mathbf{H} e^{-iS_1} = \mathbf{H}'_0 + \lambda \mathbf{H}'_1 + \lambda^2 \mathbf{H}'_2 + \dots \quad (10)$$

le choix de l'opérateur  $S_1$  doit être tel que :  $\mathbf{H}'_0 = \mathbf{H}_0$  et l'Hamiltonien  $\mathbf{H}_1$  doit être bloc diagonal dans l'état de vibration considéré (ou la polyade). On peut ensuite utiliser une deuxième transformation :

$$\mathbf{H}'' = e^{iS_2} \mathbf{H}' e^{-iS_2} = \mathbf{H}_0'' + \lambda \mathbf{H}_1'' + \lambda^2 \mathbf{H}_2'' + \dots \quad (11)$$

qui doit laisser  $\mathbf{H}_0'' = \mathbf{H}_0'$  et  $\mathbf{H}_1'' = \mathbf{H}_1'$  et rendre de même  $\mathbf{H}_2''$  diagonal suivant le nombre quantique de vibration.

Il est possible d'appliquer autant de transformations que l'ordre de développement de l'Hamiltonien le nécessite. On évalue donc les opérateurs de transformation suivant l'ordre du développement auquel ils apparaissent. L'intérêt de ces transformations est d'éliminer à un certain ordre d'approximation les termes de couplage entre les états qui ne sont pas en interaction.

Le détail sur la technique de calcul des opérateurs  $S$  est donné dans l'article de revue de Aliev et Watson [85Ali]. On notera cependant que les paramètres de transformation doivent être petits et respecter un certain ordre de grandeur afin d'assurer une bonne convergence de l'Hamiltonien effectif [97Sar] :

$$s_{mn} \leq \kappa^{m+2n-2} \quad (12)$$

Le calcul de  $S$  est très important si l'on veut comprendre les conséquences de cette transformation sur les problèmes de corrélations entre paramètres, et les liens entre les paramètres effectifs et les constantes de force. Ces constantes de force sont les vrais paramètres physiques auxquels on a accès lorsque l'on calcule un champ de force expérimental ou *ab initio*.

#### 4) Les corrélations entre paramètres

L'avantage de cette transformation de Van Vleck est évident. Cette dernière permet de traiter chaque état de vibration isolé séparément des autres. Mais une corrélation linéaire entre les paramètres existe lorsqu'ils ont la même dépendance en fonction des nombres quantiques [97Sar]. Cela conduit à un système mal conditionné que l'on ne peut pas résoudre, on ne peut alors déterminer qu'une combinaison linéaire de ces paramètres. Les problèmes de conditionnement d'un système ne se limitent pas aux corrélations linéaires, et ne sont d'ailleurs pas toujours facilement détectables.

Les paramètres effectifs qui sont obtenus à la suite de l'application de la transformation de Van Vleck peuvent être écrits sous la forme :

$$\tilde{X}_i = X_i + f_i(X_1, \dots, X_m; s_1, \dots, s_p) = X_i + \Delta X_i \quad (13)$$

où  $\tilde{X}_i$  est le paramètre effectif obtenu à l'issue de la transformation de contact,  $X_i$  est quant à lui le paramètre présent dans l'Hamiltonien  $H_{mn}$  (6), enfin  $\Delta X_i$  représente la modification du paramètre  $X_i$  lors de la transformation de contact. Les paramètres  $s_k$  sont les termes présents dans les opérateurs de transformation.

Le mauvais conditionnement du système est dû aux paramètres  $s_k$  qui peuvent avoir un nombre infini de valeurs et satisfaire aux propriétés générales de l'opérateur de transformation  $S$ . C'est la valeur de  $\Delta X_i$  qui nous renseigne sur l'affectation du paramètre par la transformation. On peut distinguer trois groupes :

$$\begin{aligned} \text{a) } \Delta X_i &= 0 \\ \text{b) } \Delta X_i &\approx 0 \\ \text{c) } \Delta X_i &\approx X_i \end{aligned} \quad (14)$$

En ce qui concerne les deux premiers groupes, les paramètres ne sont pas (cas a) ou peu (cas b) affectés par la transformation et ne posent pas de problèmes de corrélations. En revanche les paramètres du 3<sup>ème</sup> groupe ne sont pas indépendants, des corrélations existent pour ceux-ci. La solution est de réduire le nombre de paramètres présents dans l'Hamiltonien. Ainsi la théorie des réductions fournit des contraintes appropriées sur les paramètres  $s_k$ .

La théorie des réductions peut se résumer par la méthode générale suivante, qui conduit à l'Hamiltonien réduit utilisé pour ajuster les données expérimentales. Il s'agit d'abord de trouver un opérateur de transformation  $S$  qui possède les propriétés générales requises (physique et de symétrie), puis de déterminer les variations des différents paramètres créées par l'application des transformations unitaires, et enfin de fixer les contraintes qui lèvent les corrélations.

Le plus souvent la contrainte proposée consiste à fixer un des paramètres à zéro. Les paramètres effectifs sont alors affectés par cette contrainte et il est important de noter qu'ils ne sont plus alors identiques aux paramètres physiques présents dans l'Hamiltonien développé  $H_{mn}$ . Il n'est donc pas possible de comparer directement les paramètres expérimentaux (réduits) à ceux obtenus par le calcul d'un champ de force.

Voyons sur un modèle simple à deux paramètres l'application des contraintes, et leurs effets sur les paramètres. On suppose deux paramètres  $a$  et  $b$  présents dans un Hamiltonien effectif :

$$\begin{aligned}\tilde{a} &= a + Xs \\ \tilde{b} &= b + Ys\end{aligned}\tag{15}$$

Comme nous l'avons dit, il existe a priori une infinité de valeurs pour  $s$ . On propose deux réductions possibles :  $\tilde{a} = 0$  (réduction A) et  $\tilde{b} = 0$  (réduction B) qui déterminent une valeur du paramètre  $s$ .

**réduction A :**

$$\begin{aligned}\tilde{a} = 0 &\Rightarrow s = -\frac{a}{X} \\ \tilde{b}^a &= b - \frac{Y}{X}a\end{aligned}\tag{16}$$

**réduction B :**

$$\begin{aligned}\tilde{b} = 0 &\Rightarrow s = -\frac{b}{Y} \\ \tilde{a}^b &= a - \frac{X}{Y}b\end{aligned}\tag{17}$$

Dans chacune des deux réductions on obtient des paramètres réduits que l'on note  $\tilde{a}^b$  et  $\tilde{b}^a$ . Ce sont ces paramètres réduits qui seront calculés à partir des données expérimentales.

Le choix des contraintes ne doit pas avoir de conséquences sur la qualité de l'ajustement des paramètres sur les données expérimentales, on doit donc pouvoir utiliser sans distinction les différentes réductions : c'est l'équivalence unitaire des réductions. Ceci a été vérifié expérimentalement en 1994 pour un état de vibration dégénéré d'une toupie de symétrie  $C_{3v}$  [94Har] : c'est la technique des régressions multiples qui permet de vérifier les relations de passage entre les réductions afin de tester leur équivalence. Les relations de passage relient les paramètres obtenus expérimentalement à partir des différentes réductions utilisées. Avec notre exemple, on peut en établir une très simplement à partir des équations (16) et (17). L'utilisation simultanée de plusieurs réductions permet de tester tout d'abord la cohérence interne de la théorie, mais aussi celle des données expérimentales :

$$\tilde{a}^b = \tilde{b}^a \frac{X}{Y}(X-1) \quad \text{relation de passage}\tag{18}$$

## II) Toupies asymétriques

La première mise en évidence de ces problèmes de corrélation dans les Hamiltoniens effectifs date de 1965 [65Dre], et concernait les constantes de distorsion centrifuge quartiques d'une toupie asymétrique. Il n'a pas été possible de déterminer séparément les six constantes

de distorsion centrifuge quartiques du dimethylsulfoxyde ((CH<sub>3</sub>)<sub>2</sub>SO), une molécule toupie asymétrique non plane, car elles étaient complètement corrélées. L'observation de l'Hamiltonien de rotation pour la molécule concernée ne permet pas de mettre en évidence les corrélations, nous présentons l'Hamiltonien de rotation sous sa forme tensorielle (cylindrique) incluant la distorsion centrifuge jusqu'à l'ordre quatre de l'opérateur de rotation  $J$ .

$$\begin{aligned} \mathbf{H}_{\text{rot}} = & B_{200}J^2 + B_{020}J_z^2 + T_{400}(J^2)^2 + T_{220}J^2J_z^2 + T_{040}J_z^4 \\ & + \frac{1}{2}[B_{002} + T_{202}J^2 + T_{022}J_z^2, J_+^2 + J_-^2]_+ + T_{004}(J_+^4 + J_-^4) \end{aligned} \quad (19)$$

C'est Watson [67Wat], [77Wat] qui apportera la solution : ces corrélations sont la conséquence directe de la transformation de contact appliquée à l'Hamiltonien. Les paramètres  $\tilde{T}_{202}, \tilde{B}_{200}, \tilde{B}_{020}, \tilde{B}_{002}$  font partie des deux premiers groupes de paramètres définis précédemment (14) et sont donc déterminables. Les problèmes de corrélation proviennent des paramètres suivants affectés par la transformation de contact :

$$\begin{aligned} \tilde{T}_{400} &= T_{400} - 2d \\ \tilde{T}_{220} &= T_{220} + 12d \\ \tilde{T}_{040} &= T_{040} - 10d \\ \tilde{T}_{022} &= T_{022} - 4r \\ \tilde{T}_{004} &= T_{004} + d \end{aligned} \quad \text{où} \quad \begin{aligned} d &= B_{002} s_{111} = \frac{1}{4} s_{111} (B_x - B_y) \\ r &= \frac{1}{2} s_{111} B_{020} = \frac{1}{4} s_{111} (2B_z - B_x - B_y) \end{aligned} \quad (20)$$

$B_x, B_y, B_z$  sont les constantes de rotation dans le système de coordonnées cartésiennes, on peut trouver les relations pour les paramètres entre les systèmes de coordonnées cylindriques et cartésiens dans [77Wat].

Pour lever les problèmes de corrélation, il faut fixer la valeur de  $s_{111}$  à l'aide d'une contrainte sur un des paramètres.

### 1) Réduction A

La réduction la plus souvent utilisée est la réduction A de Watson (ou asymétrique), elle consiste à adopter la contrainte suivante :

$$\tilde{T}_{004} = 0$$

$$\text{d'où} \quad d = -T_{004} \quad \text{et} \quad s_{111} = -\frac{4T_{004}}{B_x - B_y} \quad (21)$$

La valeur de  $s_{111}$  est ainsi parfaitement définie. Les paramètres réduits peuvent se calculer sans problème. Cette réduction peut être adoptée dans les cas où les constantes de rotation ont des valeurs assez différentes :  $B_x - B_y \approx B$  (ordre de grandeur d'une constante de rotation), ainsi  $s_{111} \approx \kappa^4$ , l'ordre de grandeur est bien respecté. Mais ceci n'est plus valable pour une molécule proche d'une toupie symétrique, car les valeurs de  $B_x$  et  $B_y$  sont alors voisines, la valeur de  $s_{111}$  donnée par l'équation (21) n'a plus alors le bon ordre de grandeur [67Wat]. Il y a des problèmes de convergence de l'Hamiltonien, on doit utiliser des ordres de développement plus élevés pour reproduire les données expérimentales.

## 2) Réduction S :

Il semble plus judicieux lorsque deux constantes de rotation sont proches d'utiliser la réduction S (ou symétrique):

$$\begin{aligned} & \tilde{T}_{022} = 0 \\ \text{d'où} \quad & r = \frac{T_{022}}{4} \quad \text{et} \quad s_{111} = \frac{T_{022}}{2B_z - B_x - B_y} \end{aligned} \quad (22)$$

on peut en déduire facilement les cinq constantes de distorsion centrifuge quartiques déterminables expérimentalement. On peut noter une application intéressante de la réduction S pour la molécule  $D_2S_2$  [72Win] où l'on a  $B_x - B_y = \kappa^4 B$ , dans ce cas l'Hamiltonien dans la réduction A diverge, alors que la réduction S a pu être appliquée avec succès.

## III) Toupies symétriques

Nous allons appliquer la théorie des réductions aux toupies symétriques de symétrie de type  $C_{3v}$  que nous avons étudiées. L'Hamiltonien est plus simple pour une toupie symétrique car il y a un nombre moins important de paramètres : deux constantes de rotation, trois constantes de distorsion centrifuge quartiques... Mais ceci se complique pour les états de vibration doublement dégénérés, pour lesquels intervient l'interaction de Coriolis. Nous verrons tout d'abord le cas de ces états non dégénérés, les réductions adoptées seront aussi valables pour les états de vibration dégénérés que nous aborderons ensuite.

## 1) Etat non dégénéré

On peut séparer l'Hamiltonien de rotation en deux parties. Une partie diagonale en  $J$  et  $K$  puis une autre partie non diagonale que l'on appellera  $\mathbf{H}_{\text{split}}$  et qui rend compte de la levée de dégénérescence des niveaux  $K = 3n$  ( $n$  entier), ceci se traduit par des dédoublements des raies observés dans le spectre. Mais cette interaction est assez faible et n'est observable que pour des valeurs de  $J$  élevées.

Nous avons considéré le développement de l'Hamiltonien jusqu'à l'ordre 6 de l'opérateur de rotation :

$$\begin{aligned} \mathbf{H}_{\text{diag}} = & BJ^2 + (C - B)J_z^2 - D_J(J^2)^2 - D_{JK}J^2J_z^2 - D_KJ_z^4 + H_J(J^2)^3 \\ & + H_{JK}(J^2)^2J_z^2 + H_{KJ}J^2J_z^4 + H_KJ_z^6 \end{aligned} \quad (23)$$

$C$  est la constante de rotation axiale pour une toupie symétrique aplatie (oblate), ce qui est le cas de la molécule que nous avons étudiée :  $\text{SiHF}_3$ . Cet Hamiltonien est aussi utilisable pour une toupie allongée (prolate), il suffit de remplacer  $C$  par  $A$ .

La partie non diagonale s'écrit :

$$\begin{aligned} \mathbf{H}_{\text{split}} = & h_3(J_+^6 + J_-^6) + \varepsilon [J_z, J_+^3 + J_-^3] + \varepsilon_J J^2[J_z, J_+^3 + J_-^3] + \varepsilon_K [J_z^3, J_+^3 + J_-^3] \\ & + \text{termes octiques } (h_{3J}, h_{3K}) \end{aligned} \quad (24)$$

Le premier terme et les termes octiques ont des éléments de matrice non nuls pour  $\Delta K = \pm 6$ , alors que les trois termes intermédiaires sont eux non nuls pour  $\Delta K = \pm 3$

Le seul opérateur de transformation  $S$  qui respecte les propriétés requises déjà évoquées est le suivant [77Wat], [97Sar] :

$$S = S_{03} + S_{05} = t(J_+^3 - J_-^3) + x(J_+^3 - J_-^3)J^2 + y[J_z^2, J_+^3 + J_-^3] \quad (25)$$

On voit dans l'opérateur (25) qu'il y a trois paramètres libres  $t$ ,  $x$ , et  $y$ . Il va donc falloir pour cet ordre de développement de l'Hamiltonien fixer trois contraintes afin de lever les corrélations existantes entre les paramètres effectifs. Il convient d'abord de noter quels sont les paramètres corrélés.

Les constantes de rotation et de distorsion centrifuge quartiques :  $B$ ,  $C$ ,  $D_J$ ,  $D_{JK}$  et  $D_K$  ne sont pas affectées par la transformation. Ce n'est pas le cas des termes de distorsion

centrifuge sextiques, qui seront sensibles au choix de la réduction. Les paramètres de l'opérateur S doivent respecter les ordres de grandeur suivants :

$$t \approx \kappa^4 \quad x, y \approx \kappa^8 \quad (26)$$

Les deux réductions employées consistent à éliminer les termes non diagonaux de l'Hamiltonien (24). Voici l'expression des paramètres effectifs de ces éléments non diagonaux, les autres paramètres sont dans [98Wat] :

$$\begin{aligned} \tilde{h}_3 &= h_3 - 6t\tau_{xxxz} + 9t^2(C - B) \\ \tilde{\tau}_{xxxz} &= \tau_{xxxz} + 12t(C - B) \\ \tilde{\epsilon}_J &= \epsilon_J - 3t D_{JK} + 3x(C - B) \\ \tilde{\epsilon}_K &= \epsilon_K - 6t D_K + 6y(C - B) \end{aligned} \quad (27)$$

#### a) Réduction A

Le premier cas s'applique aux molécules dont les constantes de rotation vérifient :  $(C - B) \approx B$ . On élimine les éléments de matrice en  $\Delta K = \pm 3$  correspondant aux termes  $\epsilon$ ,  $\xi$  et  $\epsilon_K$  provenant de la partie non diagonale de l'Hamiltonien (21). Les seuls termes présents dans l'Hamiltonien  $\mathbf{H}_{\text{split}}$  sont alors ceux avec des éléments  $\Delta K = \pm 6$

$$\tilde{\tau}_{xxxz} = 0 \quad \tilde{\epsilon}_J = 0 \quad \tilde{\epsilon}_K = 0 \quad (28)$$

les paramètres libres valent :

$$\begin{aligned} t &= -\frac{\tau_{xxxz}}{12(C - B)} & x &= -\frac{\epsilon_J}{3(C - B)} - \frac{\tau_{xxxz} D_{JK}}{12(C - B)^2} \\ y &= -\frac{\epsilon_K}{6(C - B)} - \frac{\tau_{xxxz} D_K}{12(C - B)^2} \end{aligned} \quad (29)$$

Lorsque l'on observe les transitions dues aux dédoublements des niveaux  $K = 3$ , dans cette réduction on peut déterminer les paramètres  $\tilde{h}_3$ ,  $\tilde{h}_{3J}$ , et  $\tilde{h}_{3K}$ . On peut trouver plus de détails sur cette réduction jusqu'aux termes octiques dans [89Sar2].

#### b) Réduction B

Dans le cas de molécules quasi-sphériques  $(C - B) \approx 0$ , les ordres de grandeur des paramètres  $t$ ,  $x$  et  $y$  de la réduction A ne sont plus respectés. La solution proposée par Sarka [89Sar] consiste à éliminer les termes non diagonaux  $\Delta K = \pm 6$ .

$$\tilde{h}_3 = 0 \quad \tilde{h}_{3J} = 0 \quad \tilde{h}_{3K} = 0 \quad (30)$$

Ces contraintes, comme précédemment, fixent les valeurs des trois paramètres de transformation. Dans cette réduction, ce sont les paramètres des termes  $\Delta K = \pm 3 : \tilde{\tau}_{xxxz}$ ,  $\tilde{\epsilon}_J$ , et  $\tilde{\epsilon}_K$  qui seront déterminés. Styger et coll. [92Sty] ont vérifié expérimentalement la nécessité de l'utilisation de cette réduction B pour une toupie quasi-sphérique en analysant le spectre de OPF<sub>3</sub>.

## 2) Etat de vibration isolé et dégénéré

On ne considère ici que des dégénérescences essentielles dues à la symétrie de la molécule. Dans ce cas, il apparaît des forces de Coriolis dues à l'interaction entre les deux composantes du mouvement de vibration dégénéré. Il y a une séparation des niveaux d'énergie avec l'interaction entre le moment cinétique de vibration  $\ell$  et celui dû à la rotation autour de l'axe :  $J_z$ . La séparation des niveaux augmente avec la vitesse de rotation autour de l'axe de symétrie, donc lorsque le nombre quantique  $K$  augmente, et est nulle pour  $K = 0$ . Pour les états dégénérés, le bon nombre quantique n'est plus  $K$  comme précédemment, mais  $(K-\ell)$ . Ce nombre quantique de vibration  $\ell$  vaut  $[-v_i, -v_i+2, \dots, v_i]$ . Donc pour un état simplement excité où  $v_i = 1$ , on a deux valeurs possibles :  $\ell = \pm 1$ . Ceci se caractérise dans les spectres par l'observation de deux branches correspondant à ces deux valeurs de  $\ell$ .

Les éléments diagonaux de l'Hamiltonien comprennent la partie strictement rotationnelle déjà indiquée pour l'état non dégénéré (23), à laquelle s'ajoute une partie provenant de l'interaction de Coriolis.

$$\begin{aligned} \langle v_i = 1, \ell, J, k | H | v_i = 1, \ell, J, k \rangle = & E_v + BJ(J+1) + (C-B)k^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)k^2 \\ & - D_K k^4 + H_J J^3(J+1)^3 + H_{JK} J^2(J+1)k^4 \\ & - 2C\zeta k\ell + \eta_J k\ell J(J+1) + \eta_K k^3\ell \\ & - \tau_J k\ell J^2(J+1)^2 - \tau_{JK} k^3\ell J(J+1) + \tau_K k^5\ell + \dots \end{aligned} \quad (31)$$

En plus des termes non diagonaux présents dans  $\mathbf{H}_{\text{split}}$  (24), il faut considérer ceux provenant de plusieurs interactions rotationnelles. Ces éléments doivent satisfaire la règle d'Amat  $\Delta(k-\ell) = \pm 3n$  ( $n$  entier) [71Ama]. Les interactions généralement les plus importantes sont les suivantes :

### interaction de type $\ell$ :

\*  $\Delta k = \Delta \ell = \mp 2$  :

$$\begin{aligned} \langle v_t = 1, \ell = -1, J, k | \mathbf{H}_{22} + \mathbf{H}_{24} | v_t = 1, \ell = 1, J, k + 2 \rangle = 2 \{ q_{22} + f_{22}^J J(J+1) + f_{22}^K k(k+2) \} \\ \times F(J, k) F(J, k+1) \end{aligned} \quad (32)$$

C'est cette forte interaction qui permet l'observation des transitions de dédoublements- $\ell$  direct.

\*  $\Delta k = \mp 1, \Delta \ell = \pm 2$  :

$$\begin{aligned} \langle v_t = 1, \ell = 1, J, k | \mathbf{H}_{22} + \mathbf{H}_{24} | v_t = 1, \ell = -1, J, k + 1 \rangle = 2 \{ [q_{12} + f_{12}^J J(J+1)] \\ + f_{12}^K [k^3 + (k+1)^3] \} F(J, k) \end{aligned} \quad (33)$$

\*  $\Delta k = \mp 4, \Delta \ell = \pm 2$ :

$$\begin{aligned} \langle v_t = 1, \ell = +1, J, k | \mathbf{H}_{22} + \mathbf{H}_{24} | v_t = 1, \ell = -1, J, k + 4 \rangle = 2 f_{42} F(J, k) F(J, k+1) \\ \times F(J, k+2) F(J, k+3) \end{aligned} \quad (34)$$

ce terme rend compte du dédoublement des niveaux  $kl = -2$

### interaction de type $k$ :

\*  $\Delta k = \pm 3, \Delta \ell = 0$ :

$$\begin{aligned} \langle v_t = 1, \ell, J, k | \mathbf{H}_{22} + \mathbf{H}_{24} | v_t = 1, \ell, J, k + 3 \rangle = \ell \{ d_t + d_t^J J(J+1) + d_t^K [k^2 + (k+3)^2] \} \\ \times F(J, k) F(J, k+1) F(J, k+2) \end{aligned} \quad (35)$$

avec  $F(J, k) = [J(J+1) - k(k+1)]^{\frac{1}{2}}$

Dans le premier article concernant la théorie des réductions pour un état  $v_t = 1$  dégénéré et isolé [87Lob], le développement de l'Hamiltonien était limité au terme  $H_{24}$  pour la partie diagonale et  $H_{23}$  pour les termes non diagonaux. Lobodenko et coll. ont observé qu'il n'était pas possible de déterminer simultanément les paramètres :  $\tilde{q}_{12}, \tilde{d}_t, \tilde{\eta}_J, \tilde{\eta}_K$ . Pour ce niveau de développement, seul le premier ordre de l'opérateur de transformation S apparaît : la seule contrainte à fixer concerne le paramètre s. Mais pour reproduire la précision actuelle des mesures expérimentales il faut étendre le développement de l'Hamiltonien au moins jusqu'à  $\mathbf{H}_{06}$  et  $\mathbf{H}_{25}$  respectivement pour les parties diagonales et non diagonales. Dans ce cas, l'opérateur de transformation sera composé des termes suivants :

$$\mathbf{S} = \mathbf{S}_{21}(s) + \mathbf{S}_{03}(t) + \mathbf{S}_{23}(u, v, w) + \mathbf{S}_{05}(x, y) + \mathbf{S}_{24}(z) \quad (36)$$

Nous ne donnons pour cet opérateur de transformations que le nom des termes et les paramètres libres dont ils dépendent. Nous avons adopté la notation de l'article de Watson [98Wat], dans lequel on peut retrouver la forme complète de l'opérateur  $\mathbf{S}$ .

Il y a huit paramètres libres à fixer. Les trois paramètres  $t$ ,  $x$  et  $y$  proviennent de la partie purement rotationnelle de l'opérateur de transformation. Les contraintes utilisées pour les déterminer ont déjà été étudiées dans la partie sur les états non dégénérés.

Nous allons voir en détail le choix et les conséquences de la contrainte à effectuer sur le premier ordre de l'opérateur de transformation qui concerne le paramètre  $s$ . Pour cela nous allons écrire les paramètres effectifs  $\tilde{q}_{12}$ ,  $\tilde{d}_t$ ,  $\tilde{\eta}_J$ ,  $\tilde{\eta}_K$

$$\begin{aligned} \tilde{q}_{12} &= q_{12} + \frac{1}{2}sF \\ \tilde{d}_t &= d_t + 2sq_{22} - 6tC\zeta \\ \tilde{\eta}_J &= \eta_J + 8sq_{12} + 2s^2F \\ \tilde{\eta}_K &= \eta_K + 8sq_{12} + 2s^2F \end{aligned} \quad \text{avec : } F = C - B + 2C\zeta \quad (37)$$

Deux autres paramètres ne dépendent aussi que de  $s$  :  $f_{22}^J, f_{42}$ . Les contraintes choisies par Lobodenko portent sur  $q_{12}$  et  $d_t$ , car elles permettent d'éliminer des termes non diagonaux. Les calculs sont ainsi simplifiés : ce sont les deux réductions Q et D.

#### a) Réduction Q :

Dans cette réduction, on élimine le paramètre effectif  $\tilde{q}_{12}$  à l'aide de la contrainte :

$$\tilde{q}_{12} = 0 \quad (38)$$

la valeur de  $s$  est fixée sans ambiguïté et vaut :

$$s^Q = -\frac{2q_{12}}{F} \quad (39)$$

Il suffit de remplacer la valeur de  $s$  dans (37) pour obtenir la forme des paramètres réduits :  $d^Q$ ,  $\eta_J^Q$ ,  $\eta_K^Q$ .

#### b) Réduction D :

Dans cette réduction, la contrainte porte sur le paramètre  $\tilde{d}_t$  :

$$\tilde{d}_t = 0 \quad (40)$$

d'où la valeur de  $s$  :

$$s^D = -\frac{d_t - 6tC\zeta}{2q_{22}} \tag{41}$$

On obtient ainsi en remplaçant (41) dans (37) les paramètres réduits  $q_{12}^D, \eta_J^D, \eta_K^D$ .

Pour les autres paramètres issus du développement aux ordres supérieurs de l'Hamiltonien, on se limitera dans le tableau 1 à donner leur dépendance en fonction des paramètres de transformation, ainsi que les contraintes pour lesquelles ils peuvent être utilisés. Leur expression complète est dans [98Wat]. On trouvera aussi dans ce tableau les ordres de grandeur que doivent respecter ces paramètres de transformation pour que la convergence de l'Hamiltonien reste rapide.

**Tableau 1** : Les paramètres effectifs et leur dépendance en fonction des paramètres de la transformation unitaire

| paramètres effectifs                                               | dépendance   | contrainte utilisable pour définir : | ordre de grandeur des paramètres              |
|--------------------------------------------------------------------|--------------|--------------------------------------|-----------------------------------------------|
| $\tilde{\eta}_J, \tilde{\eta}_K, \tilde{f}_{22}^J, \tilde{f}_{42}$ | $s$          | *a)                                  | * a)                                          |
| $\tilde{q}_{12}, \tilde{d}_t$                                      | $s$          | $s$                                  | $\leq \kappa^2$                               |
| $\tilde{f}_{12}^J, \tilde{d}_t^J$                                  | $s, u$       | $u$                                  | $\leq \kappa^6$                               |
| $\tilde{d}_t^K$                                                    | $s, v, w, z$ | $v, w, z$                            | $\leq \kappa^6, \leq \kappa^6, \leq \kappa^8$ |
| $\tilde{f}_{12}^K$                                                 | $s, v$       | $v$                                  | $\leq \kappa^6$                               |
| $\tilde{f}_{22}^K$                                                 | $s, w$       | $w$                                  | $\leq \kappa^6$                               |
| $\tilde{\tau}_J$                                                   | $s, u, w$    | $u, w$                               | $\leq \kappa^6$                               |
| $\tilde{\tau}_{JK}$                                                | $s, u, v, w$ | $u, v, w$                            | $\leq \kappa^6$                               |
| $\tilde{\tau}_K$                                                   | $s, v, w$    | $v, w$                               | $\leq \kappa^6$                               |

a) paramètres non utilisés pour définir des contraintes

On notera que le choix de la contrainte pour  $u$  parmi les deux possibles est guidé par la réduction utilisée Q ou D, ce qui n'est pas le cas de  $v, w$  et  $z$ .

Comme nous l'avons déjà évoqué dans notre exemple simplifié à deux paramètres, les différentes réductions sont équivalentes. On doit donc obtenir les mêmes qualités d'ajustement avec les données expérimentales dans les deux réduction Q et D. On peut en principe utiliser au choix l'une ou l'autre des réductions, mais il est conseillé d'utiliser les

deux indépendamment. Ceci a déjà été appliqué par exemple aux états :  $v_4 = 1$  de  $\text{AsF}_3$  [96Bür],  $v_8 = 1$  de  $\text{CF}_3\text{CN}$  [97Fri]. En plus de tester la cohérence de la théorie et des mesures, l'une des deux réductions peut ne pas être utilisable même si les données expérimentales sont correctes. C'est le cas lorsque le terme  $F$  est trop petit, on ne peut alors pas utiliser la réduction  $Q$ . Il est de même lorsque  $q_{22}$  est lui aussi trop petit, c'est dans ce cas la réduction  $D$  qui n'est plus applicable, car l'ordre de grandeur du paramètre de transformation n'est pas respecté. Cela a été observé pour l'état  $v_5 = 1$  de  $\text{CDF}_3$  [97Pra].

Dans les différentes réductions, les paramètres suivants :  $B, C, C\zeta, D_J, D_{JK}, D_K, q_{22}$  qui ne sont pas affectés par la transformation de Van Vleck doivent être identiques. Il en est de même pour les constantes de distorsion centrifuge sextiques, si dans les deux cas la même réduction est appliquée pour les paramètres de rotation  $t, x$  et  $y$ .

Enfin, comme dans l'exemple de notre modèle simple à deux paramètres, on peut trouver des relations de passage entre les deux réductions :

$$\begin{aligned} q_{12}^D &= -\frac{d_t^Q F}{4q_{22}} \\ \eta_J^D - \eta_J^Q &= -(\eta_K^D - \eta_K^Q) = \frac{(d_t^Q)^2 F}{4(q_{22})^2} \end{aligned} \tag{42}$$

D'autres relations existent pour les termes d'ordres supérieurs que l'on peut trouver dans [98Wat].

### c) Toupie quasi-sphérique : Réduction QD

Harder [99Har] a très récemment proposé une nouvelle réduction pour le cas particulier des molécules quasi-sphériques. En effet, la réduction  $B$  n'est plus adaptée lorsque  $B \approx C$  pour les états dégénérés : dans ce cas les deux réductions  $Q$  et  $D$  sont mises en échec. Mais on peut voir dans les expressions de  $\tilde{d}_t$ ,  $\tilde{q}_{12}$  des équations (37), qu'il est possible de fixer les valeurs de  $s$  et  $t$  en appliquant des contraintes sur ces deux paramètres. Cette réduction est appelée QD. Il est possible comme pour les réductions précédentes de trouver des relations liant les paramètres dans les réductions QD et  $Q$ . Pour la réduction QD, la contrainte sur  $t$  étant différente des deux autres, les constantes de distorsion sextiques seront distinctes de celles obtenues avec les réductions  $Q$  et  $D$ . Voici quelques unes des relations existantes entre les réductions  $Q$  et QD, les autres peuvent se trouver dans [99Har] :

$$d_t^Q = \frac{C\zeta}{2(C-B)} \tau_{xxxz}^{QD} \quad (43)$$

$$\Delta H_J = \frac{1}{9} \Delta H_{JK} = \frac{1}{15} \Delta H_{KJ} = \frac{1}{7} \Delta H_K = 2\Delta h_3 = \frac{1}{8} \frac{(\tau_{xxxz}^D)^2}{(C-B)} = \frac{(d_t^Q)^2 (C-B)}{2(C\zeta)^2}$$

Nous avons vérifié expérimentalement l'équivalence de cette réduction avec les deux autres dans notre étude sur l'état  $v_6=1$  de  $\text{SiDF}_3$  et  $\text{SiHF}_3$ .

## IV) Conclusion

Nous avons abordé dans cette partie les différentes étapes qui nous permettent d'obtenir un Hamiltonien utilisable pour reproduire les données expérimentales. Si l'on se limite à la détermination expérimentale des paramètres, la connaissance de la signification des paramètres réduits n'est pas indispensable. Ce n'est pas le cas si on veut les relier aux constantes qui ont un réel sens physique : les constantes de force. Il faut tout d'abord connaître les relations qui existent entre les paramètres effectifs et les constantes de force, ces relations pouvant être très compliquées, comme on peut le voir pour  $\eta_J$  et  $\eta_K$  dans [79Ali], puis ensuite relier les paramètres observables (réduits) aux paramètres effectifs issus de la transformation de contact.

La compréhension des réductions utilisées a donc été une étape très importante qui donne une signification claire des paramètres spectroscopiques déterminés.

Nous allons voir dans la partie suivante quelles sont les moyens que nous avons utilisés pour déterminer expérimentalement les constantes spectroscopiques.



# Détermination expérimentale des paramètres

La détermination des paramètres comprend deux étapes essentielles qui sont d'une part l'enregistrement des spectres puis leur analyse. Nous aborderons d'abord la description des spectromètres que nous avons utilisés pour l'étude des différents états de vibration. Outre les spectromètres du laboratoire qui opèrent dans les gammes millimétrique et submillimétrique, nous avons eu recours à d'autres spectromètres que nous présentons brièvement : le but n'étant pas de détailler les aspects techniques de ces spectromètres, ceux-ci peuvent se trouver dans des références que nous préciserons. Nous ne développerons plus en détail que le spectromètre submillimétrique (ou infrarouge lointain) auquel nous avons apporté quelques modifications afin d'améliorer la précision des mesures.

Les principales raisons de l'utilisation de tous ces spectromètres sont :

- dans le domaine centimétrique les spectres des molécules sont moins denses car ils font intervenir des valeurs de  $J$  plus faibles, l'identification de spectres est facilitée. On peut au contraire atteindre des valeurs de  $J$  et  $K$  élevées dans le domaine infrarouge.
- comme nous le montre le tableau 2, l'analyse combinée de données provenant de différentes spectromètres travaillant à des longueurs d'onde distinctes est le meilleur moyen pour une détermination correcte de paramètres. Chaque type de données ne fait pas intervenir les mêmes règles de sélection et permet donc la détermination de paramètres différents.

## I) Description des spectromètres

### 1) Spectromètre microonde à transformée de Fourier (Kiel, Allemagne) :

Il est basé sur l'observation du signal temporel de résonance réémis par les molécules préalablement excitées par une courte impulsion micro-onde. Cette technique est très sensible, elle nécessite des pressions de gaz beaucoup plus faibles qu'en spectroscopie d'absorption classique, et la largeur Doppler est plus petite à ces fréquences que dans le domaine millimétrique : ainsi les raies sont beaucoup plus fines, la précision de mesure est meilleure que 5 kHz. L'intensité des raies est ici proportionnelle au moment dipolaire et non pas à son carré comme en spectroscopie d'absorption classique. Des molécules avec un moment dipolaire faible peuvent donc être observées avec ces spectromètres [97Sar], [93Krü],

[83Bes], [95Köh]. Deux spectromètres à guide d'onde circulaire permettent de couvrir la gamme 8-26.5 GHz.

La même technique existe couplée à un jet moléculaire supersonique introduit dans une cavité Fabry-Pérot [94And]. La température rotationnelle est faible (de l'ordre de quelques Kelvin) : seuls les états les plus bas en énergie sont peuplés, on n'observe donc que des transitions correspondant à des  $J$  faibles et ce essentiellement pour l'état fondamental.

Une technique basée sur la double résonance est aussi utilisée avec les spectromètres à guides d'onde en envoyant deux impulsions successives. [97Sar], [89Jäg]. Ceci permet la mesure de transitions accessibles uniquement dans le domaine des radiofréquences (RF).

## **2) Spectromètres millimétrique et submillimétrique (Lille) :**

Le spectromètre millimétrique du laboratoire utilise comme source des klystrons ou diodes Gunn de gammes 48-53 GHz et 74-80 GHz. Les harmoniques (2, 3 et 4) de ces sources sont générés par une diode Schottky placée dans un guide croisé. La détection est de type super-hétérodyne [82Bur] ou bolométrique. La gamme de ce spectromètre est de 100-300 GHz.

Les sources pour le spectromètre submillimétrique sont des carcinotrons Thomson-CSF pour la gamme 340-475 GHz, et de 500 à 700 GHz ce sont des carcinotrons ISTOK russes. Avec ces carcinotrons, la détection est assurée par un bolomètre InSb refroidi à l'hélium liquide.

## **3) Spectromètre submillimétrique à bandes latérales (Lille) :**

Au delà de 1100 GHz, il n'existe pas de carcinotrons. Dans ce domaine de fréquence de l'infrarouge lointain jusque 2500 GHz, les trois principales méthodes existantes sont :

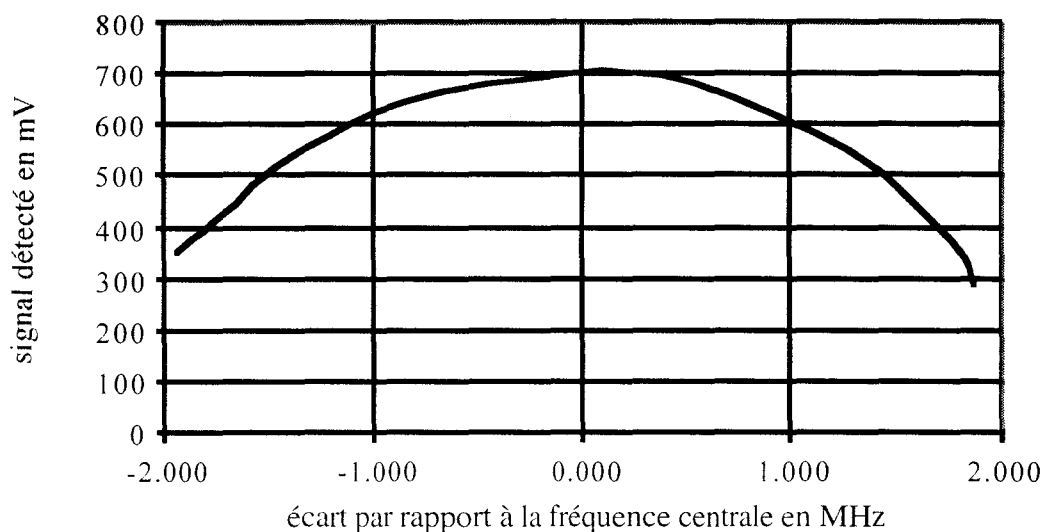
- la transformée de Fourier dont la sensibilité est assez faible  $10^{-3} \text{ cm}^{-1}$  et la précision de l'ordre de 3 MHz.
- le mélange de deux lasers  $\text{CO}_2$  travaillant dans l'infrarouge : cette technique intéressante nécessite une mise en place assez lourde, mais les principaux problèmes sont la sensibilité moyenne :  $10^{-4} \text{ cm}^{-1}$  et la puissance délivrée assez faible inférieure au  $\mu\text{W}$ .
- le laser moléculaire se présente comme une bonne solution : la sensibilité est bonne,  $10^{-5} \text{ cm}^{-1}$ , et une dizaine de raies sont assez puissantes (environ 5mW) pour être employées en spectroscopie ( $\text{CH}_2\text{CHF}$ ,  $\text{CH}_3\text{F}_2$ ,...). Les raies d'émission sont obtenues en pompant le laser moléculaire avec un laser  $\text{CO}_2$  de puissance élevée (environ 100W). La fréquence du

laser est rendue accordable en mélangeant le rayonnement submillimétrique avec celui d'un synthétiseur 2-20 GHz. On obtient des bandes latérales [94Bou] :

$$V_{BL} = V_{sub} \pm V_{synth} \tag{44}$$

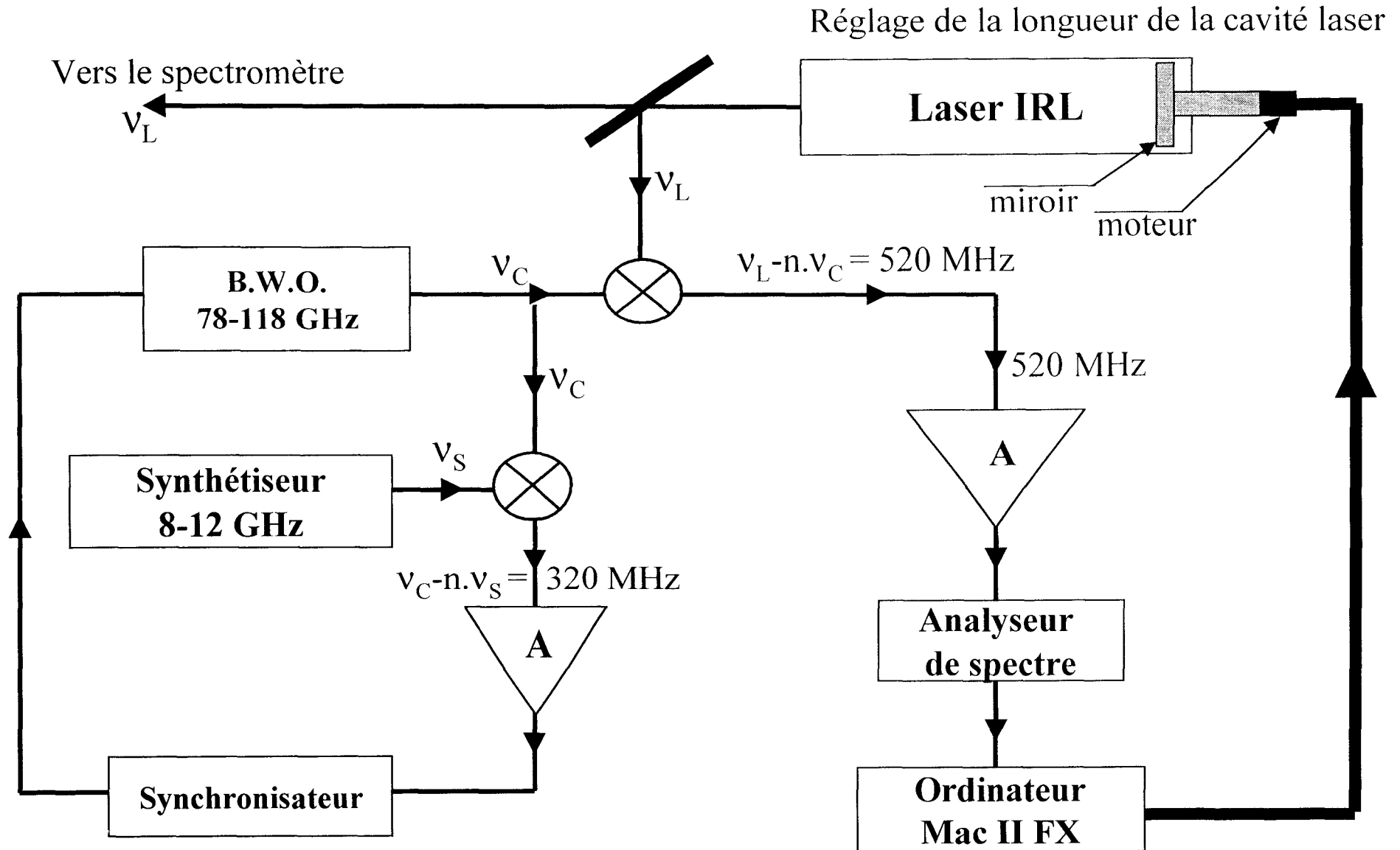
Mais le principal problème jusqu'alors était le manque de précision des mesures, avec des erreurs pouvant atteindre 2 à 3 MHz. Les deux principales causes sont la dérive thermique du laser submillimétrique, et la difficulté de la détermination précise de la fréquence d'émission du laser. Le laser est une cavité Fabry-Pérot dont on ajuste la longueur en modifiant la position du miroir de sortie : c'est ce réglage qui fait varier la fréquence d'émission du laser. On doit se placer sur le maximum de la courbe de gain de la cavité. Or des mesures ont montré (figure 1) que cette courbe de gain avait un sommet assez plat : une erreur sur la fréquence du laser de quelques MHz est alors possible.

**Figure 1 : Courbe de gain du laser à 634 GHz**



Nous avons entrepris de stabiliser le laser submillimétrique [99Mar] en comparant sa fréquence avec une source de fréquence connue. On prélève une partie du rayonnement submillimétrique que l'on mélange sur une diode Shottky à l'harmonique d'une source millimétrique (klystron, diode Gunn ou carcinotron) stabilisée en fréquence. Le battement issu de ce mélange (à 525 MHz) est mesuré et traité numériquement (figure 2). Lorsqu'il y a un

**Figure 2 : Stabilisation du Laser Submillimétrique (IRL)**



décalage en fréquence du battement, une correction est envoyée au moteur de la cavité submillimétrique corrigeant ainsi la fréquence d'émission du laser. Le pas du moteur permet une correction de 50 kHz, la fréquence du laser est donc stabilisée à 100 kHz près. La précision de mesure du spectromètre peut être estimée meilleure que 300 kHz.

#### **4) Spectromètre Infra-Rouge à transformée de Fourier (Wuppertal, Allemagne) :**

Le spectromètre est un interféromètre Bruker 120HR dont il est possible de changer le type de détecteurs afin de couvrir une gamme totale de 30 à 4000  $\text{cm}^{-1}$ . L'avantage des spectromètres à transformée de Fourier est de pouvoir enregistrer des grandes parties de spectres en un temps court : le temps d'enregistrement dépend de la résolution que l'on veut obtenir. Typiquement, la mesure d'une bande de vibration ne nécessite que quelques heures [89Bir].

## **II) Analyse du spectre**

Il est important de noter que la détermination des paramètres est liée non seulement aux règles de sélection mais aussi à la précision de mesure. Il faut que la contribution des paramètres sur les transitions concernées soit supérieure à l'erreur de mesure. La diminution des incertitudes expérimentales et l'exploration du domaine submillimétrique avec des mesures de transitions de  $J$  et  $K$  élevées a impliqué l'introduction de termes d'ordre supérieur dans le développement des Hamiltoniens pour que le modèle reproduise les mesures. On peut citer à titre d'exemple les termes d'ordre supérieur de l'interaction de Coriolis :  $\tau$  et  $\sigma$  pour les toupies symétriques  $C_{3v}$  [98Wat].

### **1) Analyse combinée des données**

Les spectromètres de notre laboratoire opèrent dans une gamme de fréquence de 100 à 2500 GHz. Nous observons des spectres de rotation pure de molécules dans leurs états fondamentaux et excités. L'analyse de ces spectres permet d'obtenir des constantes de rotation très précises, des constantes de distorsion centrifuge, ainsi que les termes de l'interaction de Coriolis pour un état excité dégénéré. Le recours à d'autres spectromètres permet d'une part l'accès à d'autres paramètres grâce à des règles de sélection différentes dans les autres gammes de fréquences, mais aussi de lever les corrélations entre les paramètres.

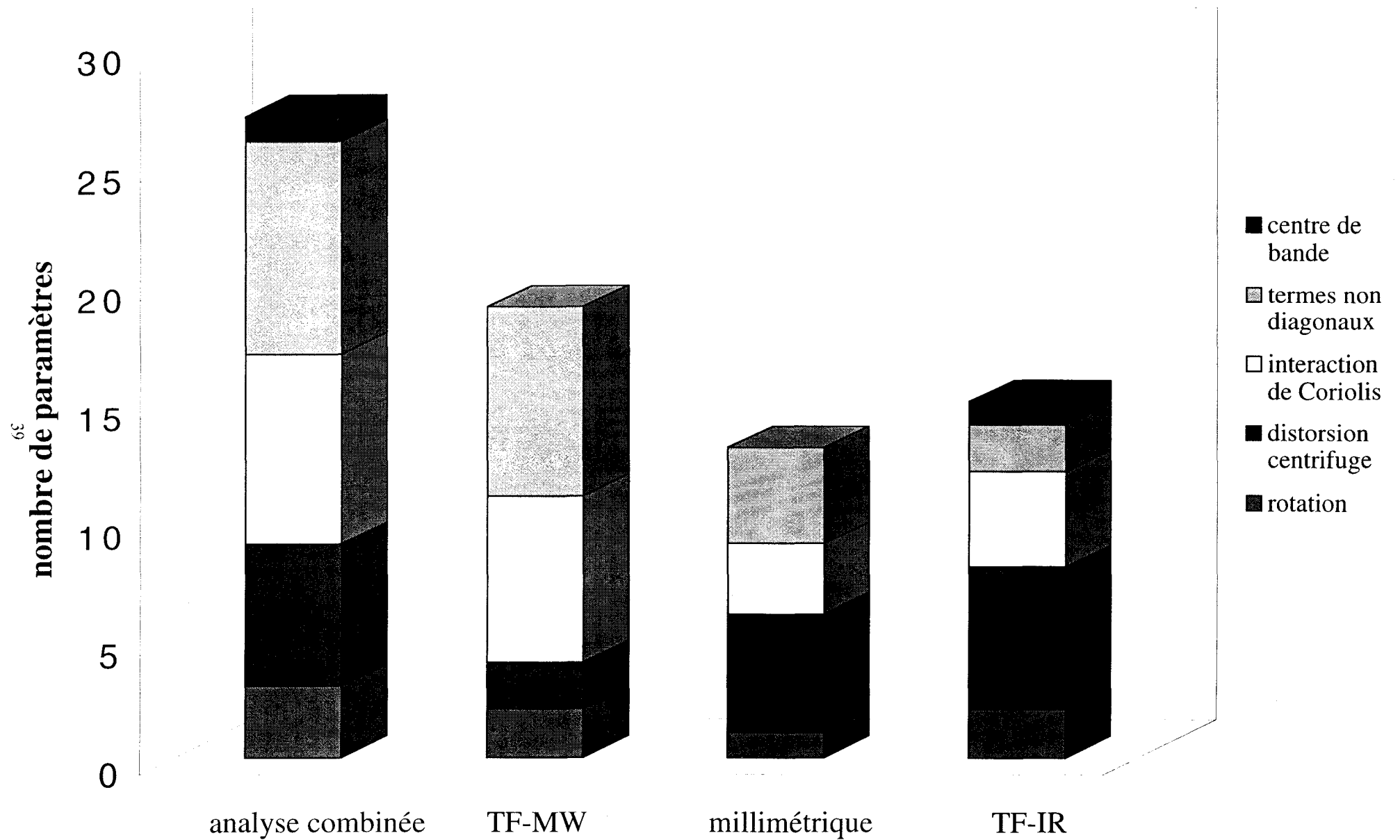
**Tableau 2** : Détermination de paramètres (en MHz) pour  $\text{SiHF}_3$  dans l'état excité  $v_6 = 1$ , pour différents types de mesures (dans la réduction D)

|                               | total                      | TF-microonde     | Millimétrique   | TF-infra-rouge  |
|-------------------------------|----------------------------|------------------|-----------------|-----------------|
| $C_o$                         | 4134.127 (15) <sup>a</sup> | *                | *               | *               |
| $E$ $\text{cm}^{-1}$          | 305.455403 (29)            | *                | *               | 305.455357 (33) |
| $B$                           | 7214.87004 (26)            | 7214.87049 (72)  | 7214.87394 (82) | 7214.8821 (44)  |
| $C$                           | 4130.35353 (62)            | 4130.119(46)     | *               | 4130.3157 (30)  |
| $D_J$ $\cdot 10^3$            | 7.60603 (20)               | *                | 7.6068 (15)     | 7.6115 (48)     |
| $D_{JK}$ $\cdot 10^3$         | -12.67325 (61)             | -12.989 (29)     | -12.6766 (43)   | -12.681 (11)    |
| $D_K$ $\cdot 10^3$            | 5.8727 (22)                | *                | *               | 5.8714 (66)     |
| $H_J$ $\cdot 10^8$            | 2.2231 (36)                | *                | 2.244 (84)      | 2.30 (12)       |
| $H_{JK}$ $\cdot 10^8$         | -8.648 (27)                | -18.540 (35)     | -8.79 (24)      | -8.51 (32)      |
| $H_{KJ}$ $\cdot 10^8$         | 10.951 (54)                | *                | 11.19 (33)      | 10.20 (23)      |
| $C\zeta$                      | -2345.47104 (54)           | -2345.706 (46)   | -2341.81 (19)   | -2345.559 (26)  |
| $\eta_J$ $\cdot 10^2$         | -4.13198 (12)              | -4.1951 (58)     | -3.3938 (22)    | -3.400 (12)     |
| $\eta_K$ $\cdot 10^2$         | 3.88865 (88)               | 3.88961 (26)     | 5.73 (29)       | 3.167 (14)      |
| $\tau_J$ $\cdot 10^7$         | -1.9763 (55)               | 0.               | 0.              | -1.65 (14)      |
| $\tau_{JK}$ $\cdot 10^7$      | 4.387 (33)                 | 4. 817 (53)      | 0.              | 0.              |
| $\tau_K$ $\cdot 10^7$         | -1.654 (56)                | -5.39 (23)       | 0.              | 0.              |
| $\sigma_J$ $\cdot 10^{11}$    | 1.1270 (69)                | 1.141 (12)       | 0.              | 0.              |
| $\sigma_{JK}$ $\cdot 10^{11}$ | -2.42 (16)                 | -3.45 (37)       | 0.              | 0.              |
| $q_{22}$                      | -3.29296369 (12)           | -3.29296313 (23) | -3.29203 (53)   | -3.2944 (54)    |
| $f_{22J}$ $\cdot 10^5$        | 2.231635 (19)              | 2.231576 (37)    | 2.392 (28)      | 2.55 (32)       |
| $f_{22JJ}$ $\cdot 10^{10}$    | -1.21047 (68)              | -1.20991 (17)    | 0.              | 0.              |
| $f_{42}$ $\cdot 10^6$         | -5.14565 (13)              | -5.14551 (28)    | -2.26 (40)      | 0.              |
| $f_{42J}$ $\cdot 10^{11}$     | 3.8333 (80)                | -3.825 (19)      | 0.              | 0.              |
| $h_3$ $\cdot 10^9$            | -1.1773 (17)               | -1.165 (33)      | -2.17 (24)      | 0.              |
| $h_{3J}$ $\cdot 10^{14}$      | 2.05 (10)                  | *                | 0.              | 0.              |
| $q_{12}$                      | 2.687534 (18)              | 2.68747 (12)     | 0.              | 0.              |
| $f_{12J}$ $\cdot 10^5$        | -2.31929 (99)              | -2.317 (11)      | 0.              | 0.              |
| <b>paramètres libres</b>      | <b>27</b>                  | <b>19</b>        | <b>13</b>       | <b>15</b>       |

\* : valeurs contraintes à celles de l'ajustement global

<sup>a</sup> : les erreurs portent sur les deux derniers chiffres des paramètres

**Figure 3 :** Nombre de paramètres déterminés par type de données



La spectroscopie infrarouge par ses règles de sélection,  $\Delta v = 0, \pm 1$ ,  $\Delta J = 0, \pm 1$ , ( $\Delta K - \Delta \ell = 3n$ ), fournit les centres de bande de vibration et permet d'améliorer la détermination des constantes de distorsion avec l'accès à des valeurs élevées de  $J$  et  $K$ .

Lorsque l'on étudie des états de vibration dégénérés, il existe une résonance de type  $\ell$  qui, lorsqu'elle est assez forte, rend observable des transitions de dédoublement- $\ell$  directes avec le spectromètre micro-onde à transformée de Fourier. Ceci est le cas quand on a :  $C - B - C\zeta \approx 0$ , car la séparation des niveaux d'énergie en interaction est alors petite. La règle de sélection de ces transitions est :  $\Delta J = 0$ ,  $\Delta K = \Delta \ell = 2$ . Elles déterminent aussi les termes d'ordre supérieur  $\tau$  et  $\sigma$  de l'interaction de Coriolis. Ces mesures de dédoublement- $\ell$  directes font intervenir la combinaison linéaire  $C - B - C\zeta$ , la corrélation entre  $C$  et  $C\zeta$  est levée lorsque l'on mesure des transitions dues à des résonances provenant de termes non diagonaux.

Les niveaux  $kl = -2$  et  $kl = 4$  forment un système très intéressant car ils font intervenir cinq interactions, dont les plus importantes sont  $(\Delta \ell, \Delta K) = (2, 2)$ ,  $(2, -4)$  et  $(0, 6)$ . Deux types de mesures sont possibles pour ce système avec les spectromètres à transformée de Fourier. On peut les observer sur la figure 6 : il y a les transitions de dédoublement- $\ell$  directes entre les niveaux  $kl = -2 \leftrightarrow kl = 4$ . Et avec le spectromètre à 2 dimensions, on peut mesurer les transitions entre les composantes  $A_1-A_2$  des doublets des niveaux  $kl = -2$  et  $kl = 4$  ( $\Delta K - \Delta \ell = 3$ ), ces transitions sont particulièrement liées au terme "0, 6" et déterminent le paramètre  $h_3$ .

Des dédoublements des niveaux  $K = 3$  ont aussi été observés pour l'état fondamental dans le domaine submillimétrique, avec le spectromètre IRL, car la contribution du terme  $h_3$  n'est observable que pour des valeurs de  $J$  élevées.

## 2) Détermination expérimentale du champ de force

L'obtention du champ de force est d'un grand intérêt, mais nous allons voir que le calcul du champ de force harmonique et anharmonique à partir des seules données expérimentales est un exercice compliqué qui nécessite souvent des simplifications. Les problèmes pour une bonne détermination expérimentale sont dus au nombre élevé de

constantes de force à déterminer et aux paramètres spectroscopiques qui sont souvent perturbés à cause des états de vibration en interaction.

On ne reviendra pas sur les difficultés pour relier les paramètres effectifs aux constantes de force. La procédure peut se trouver dans [85Ali], [72Mil]. Nous donnons dans le tableau 3 la dépendance des paramètres en fonction de l'ordre du développement du champ de force, ainsi que les références où l'on peut trouver l'expression complète des paramètres.

Mis à part les états les plus bas en énergie, les états de vibration sont très souvent en interaction, les paramètres spectroscopiques obtenus sont alors effectifs car ils sont affectés

**Tableau 3 :** Dépendance des paramètres en fonction des constantes de force

|                                            | harmonique | anharmonique |            | réf.    |
|--------------------------------------------|------------|--------------|------------|---------|
|                                            | $f_{ij}$   | $f_{ijk}$    | $f_{ijkl}$ |         |
| vibration harmonique $\omega_i$            | x          |              |            | [82Pap] |
| distorsion centrifuge quartique $D_e$      | x          |              |            | [82Pap] |
| constante de Coriolis $\zeta$              | x          |              |            | [82Pap] |
| dépendance vibrationnelle $\alpha_i^B$     | x          | x            |            | [72Mil] |
| distorsion centrifuge sextique $H_e$       | x          | x            |            | [82Pap] |
| constante de dédoublement- $\ell$ $q_{22}$ | x          | x            |            | [72Mil] |
| interaction de Coriolis $\eta_j, \eta_K$   | x          | x            |            | [79Ali] |
| fréquence de vibration $\nu_i$             | x          | x            | x          | [82Pap] |

par des résonances : Fermi, Coriolis... Dans le cas d'une résonance de Fermi, l'effet sur les niveaux d'énergie est un déplacement global. Avec des résonances de type Coriolis, les niveaux affectés dépendent des nombres quantiques. Pour "déperturber" les paramètres il faut analyser tous les états qui sont en interaction. Cela est long et difficile, donc souvent on utilise les paramètres perturbés, ce qui conduit à des constantes de force biaisées. De plus on peut ne pas détecter la présence d'une perturbation comme ce fut le cas pour  $\nu_4 = 1$  de  $\text{SiHF}_3$  et  $\text{SiDF}_3$ , rien dans l'identification du spectre ni les paramètres obtenus n'indiquaient la présence d'interaction entre les états. C'est la différence assez importante entre les paramètres obtenus à partir des données *ab initio* et ceux expérimentaux qui nous a signalé que les paramètres expérimentaux étaient perturbés [99Dem]

Même si les relations entre les paramètres et les constantes de force sont connues, le calcul de ces constantes n'est pas trivial. Pour déterminer les constantes de force à partir des

données expérimentales il faut utiliser une procédure de moindres carrés non linéaires, mais il est assez difficile de déterminer toutes les constantes de force en même temps, essentiellement à cause des problèmes de conditionnement du système [96Car]. La procédure la plus courante consiste à déterminer dans un premier temps les constantes de force harmoniques. Puis celles ci sont maintenues fixes lors de l'ajustement de la partie anharmonique. Cela simplifie très nettement les calculs, mais on induit des erreurs systématiques dans les valeurs des constantes ainsi déterminées.

Dans la plupart des études, seule la partie harmonique est calculée. Cela est dû à l'augmentation très rapide du nombre de constantes de force avec le nombre d'atomes et la perte de symétrie de la molécule. On peut en voir l'illustration dans le tableau 4. On se retrouve rapidement dans une situation où l'on a plus de constantes de force à déterminer que de paramètres spectroscopiques disponibles. Les données provenant de l'étude des espèces isotopiques sont la plupart du temps inutilisables car la dépendance isotopique des constantes anharmoniques est souvent faible.

**Tableau 4 :** Nombres de constantes de force indépendantes pour quelques molécules

|                                                  | $r_e$ | $f_{ij}$ | $f_{ijk}$ | $f_{ijkl}$ |
|--------------------------------------------------|-------|----------|-----------|------------|
| diatomique                                       | 1     | 1        | 1         | 1          |
| linéaire XY <sub>2</sub>                         | 1     | 3        | 3         | 6          |
| pliée XY <sub>2</sub>                            | 2     | 4        | 6         | 9          |
| plane XY <sub>3</sub>                            | 2     | 5        | 9         | 20         |
| pyramidale XY <sub>3</sub> Z (C <sub>3v</sub> )  | 3     | 12       | 38        | 102        |
| X <sub>6</sub> H <sub>6</sub> (D <sub>6h</sub> ) | 2     | 34       | 237       | 1890       |

Mais nous allons voir que même la détermination d'un champ de force harmonique précis n'est pas simple. Si le nombre de données expérimentales est suffisant pour calculer les constantes de force quadratiques, les paramètres qui ne dépendent que de la partie harmonique du potentiel sont : les fréquences de vibration harmonique  $\omega_i$ , les constantes de distortion centrifuge  $D_e$  et le terme d'interaction de Coriolis pour un état dégénéré. Les procédures de calcul des constantes de force quadratiques sont bien connues et sont résumées dans [93Hed].

Le problème est le suivant : les données spectroscopiques obtenues ne sont pas celles de la molécule à l'équilibre qui sont reliées aux constantes de force, mais celles dans l'état fondamental ou dans des états excités de vibration. Pour en déduire les constantes à l'équilibre il faut aussi connaître leur dépendance vibrationnelle qui peut se mettre sous la forme :

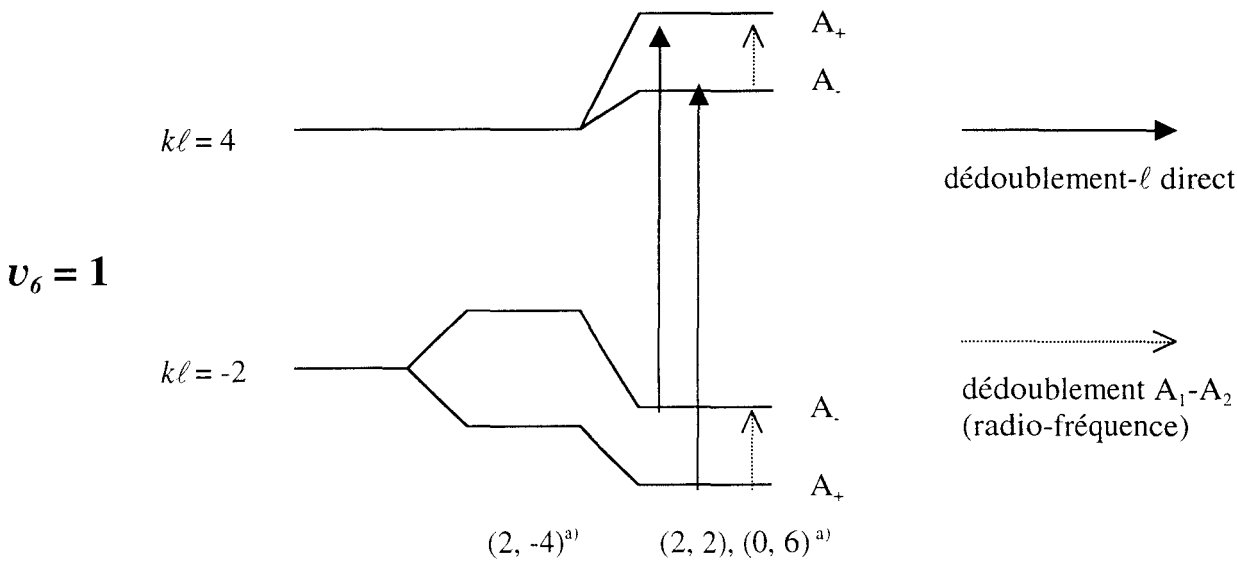
$$B_v = B_e - \sum_r \alpha_r^B (v_r + \frac{d_r}{2}) + \dots \quad (45)$$

où  $d_r$  est la dégénérescence du niveau de vibration, et  $\alpha$  est le terme d'interaction rotation-vibration qui dépend du champ de force anharmonique. Il est de l'ordre de quelques pour cent de la constante à l'équilibre. Pour corriger ces constantes des effets anharmoniques, il faut étudier tous les états fondamentaux de vibration. C'est souvent long et difficile. Donc fréquemment ces termes anharmoniques sont négligés et les constantes de forces harmonique obtenues sont biaisées. Ainsi pour obtenir un champ de force harmonique précis, il faut aussi calculer le champ de force anharmonique...

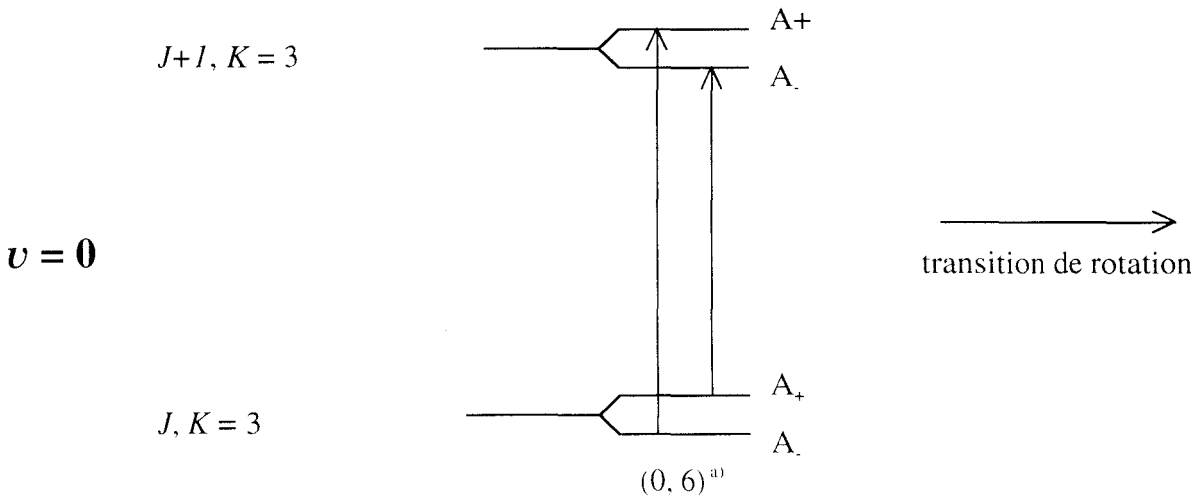
Comme nous venons de le voir le calcul d'un champ de force anharmonique expérimental devient très rapidement difficile pour des molécules de plus de trois atomes, et la détermination précise du champ de force harmonique nécessite aussi la connaissance de la partie anharmonique.

Le développement des méthodes de calcul *ab initio* a permis aux champs de force de devenir l'une des applications les plus fructueuses de la chimie quantique, car il est possible d'obtenir des champs de force *ab initio* très précis avec des temps de calcul raisonnables.

**Figure 4 :** Schéma des niveaux d'énergie  $(K-\ell) = 3$  pour une toupie symétrique  $C_{3v}$



<sup>a)</sup> principales interactions  $(\Delta\ell, \Delta k)$  intervenant sur la position des niveaux d'énergie



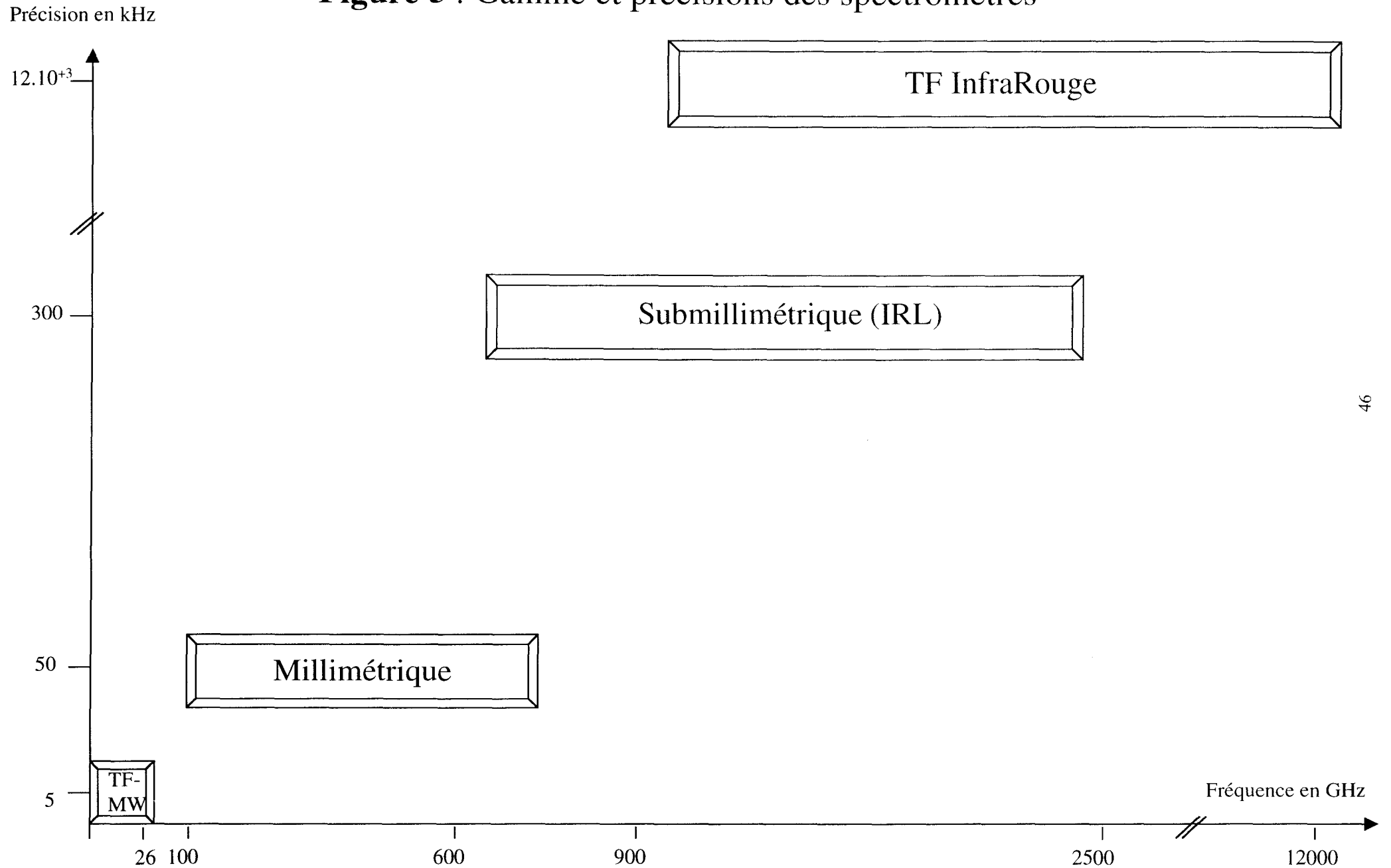
Nous avons adopté la convention suivante pour la symétrie des niveaux [97Pra] :

- J pair :  $A_+$  est  $A_1$  et  $A_-$  est  $A_2$
- J impair :  $A_+$  est  $A_2$  et  $A_-$  est  $A_1$

**Tableau 5** : Les différents types de transitions mesurées pour le trifluorosilane avec chaque spectromètre

| Spectromètre                                                 | molécule étudiée                                        | type de transitions mesurées                                              | paramètres déterminés                       | précision                   |
|--------------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------------------------|---------------------------------------------|-----------------------------|
| Micro-onde à Transformée de Fourier-2D (RF)-(Kiel-Allemagne) | • $\nu_6 = 1$                                           | "interdites" $\Delta(K - \ell) = 3$                                       | $f_{42}, h_3$                               | 30 kHz                      |
| Micro-onde à Transformée de Fourier-1D (Kiel-Allemagne)      | • $\nu_6 = 1$                                           | dédoublément- $\ell$ direct<br>$\Delta J = 0; \Delta K = \Delta \ell = 2$ | $f_{22}, C_6, \tau$                         | 5 kHz                       |
| Millimétrique et submillimétrique (Lille)                    | • $\nu=0,$<br>• $\nu_2, \nu_3, \nu_4, \nu_5, \nu_6 = 1$ | rotation $\Delta J = 1, \Delta(K - \ell) = 0$                             | $C\zeta$ , distorsion quartique et sextique | 50 kHz                      |
| InfraRouge Lointain à bandes latérales (Lille)               | • $\nu_6 = 1$<br>• $\nu = 0$                            | rotation $\Delta J = 1, \Delta(K - \ell) = 0$<br>doublets $K = 3$         | distorsion sextique<br>$h_3$                | 200 kHz                     |
| InfraRouge à Transformée de Fourier (Wuppertal-Allemagne)    | • $\nu_2, \nu_3, \nu_4, \nu_5, \nu_6 = 1$               | rovibration $\Delta J = 0, \pm 1; \Delta(K - \ell) = 0$                   | $C_0, D_K, H_K$                             | $4.10^{-4} \text{ cm}^{-1}$ |

**Figure 5 : Gamme et précisions des spectromètres**



## Structures et champ de force *ab initio*

Les calculs *ab initio* ont des applications assez larges : ils permettent de calculer la plupart des propriétés moléculaires telles que les structures géométriques, les champs de force moléculaires. On peut connaître quel est le conformère le plus stable d'une molécule, ils peuvent aussi fournir les moments dipolaires électriques, les énergies d'ionisation, les affinités électroniques... [96Bot], [96For].

L'obtention par les méthodes *ab initio* de structures à l'équilibre est très intéressante, car le calcul précis d'une structure expérimentale à l'équilibre est assez difficile. Pour obtenir les moments d'inertie à l'équilibre  $I_e$ , il faut étudier tous les états de vibration fondamentaux de la molécule. Cela est souvent difficile car les états peuvent être en interaction, les constantes obtenues sont alors perturbées. Les méthodes de "déperturbation" sont difficiles et ne donnent pas toujours des résultats fiables. Dans la plupart des cas, on doit se contenter de structures approchées plus ou moins sophistiquées [97Dem]. Souvent on doit étudier plusieurs isotopes afin d'avoir un nombre suffisant de moments d'inertie pour déterminer tous les paramètres structuraux. Par contre l'utilisation de méthodes perfectionnées et de bases étendues rend les calculs *ab initio* de plus en plus précis. Ils atteignent dans les cas favorables les précisions expérimentales souhaitées pour les structures géométriques : 0.001 Å pour les longueurs de liaison et 0.1° pour les angles. Nous verrons dans quelles conditions cela est réalisable.

Le calcul des champs de force *ab initio* est un domaine qui se développe beaucoup, car il est maintenant possible d'obtenir avec ces calculs théoriques des résultats fiables. On peut en déduire des paramètres difficiles à obtenir expérimentalement, on peut citer par exemple les constantes de distorsion centrifuge  $D_K$  et  $H_K$  d'une toupie symétrique.

Enfin, il se développe depuis quelques années de nombreuses interactions entre théorie et expérience. Lorsque l'on débute l'étude d'une nouvelle molécule, il est possible d'obtenir des constantes de rotation précises à quelques pour cent grâce à un calcul de quelques minutes. Ces constantes pourront être utilisées pour une première prévision des spectres. Une autre application est le recalibrage de la plupart des champs de force *ab initio* à l'aide de résultats expérimentaux afin d'obtenir une meilleure précision [83Pul].

## I) Méthodes et bases

Les calculs *ab initio* consistent en la résolution de l'équation de Schrödinger sans autre constantes que la vitesse de la lumière, la constante de Planck et les charge et masse de l'électron. Il est évident que des hypothèses simplificatrices sont nécessaires, la résolution exacte de l'équation n'étant possible que pour des cas très limités. Ces hypothèses concernent la prise en compte de la corrélation électronique : c'est la **méthode** de calcul. La deuxième caractéristique d'un calcul est la **base** utilisée qui est le reflet du confinement électronique. Donc lorsque l'on augmente la taille de la base, les électrons peuvent se déplacer plus librement. Le calcul est alors de meilleure qualité.

### 1) La méthode Hartree-Fock

Dans les différentes méthodes que nous avons utilisées les simplifications ne portent pas sur l'Hamiltonien mais sur la fonction d'onde. Ainsi nous n'aborderons pas les méthodes mono-électroniques et de potentiel de cœur effectif. Ce dernier cas est surtout utilisé pour les atomes lourds (3<sup>ème</sup> ligne et plus: à partir de l'atome K), et permet de limiter le problème aux seuls électrons de valence.

La fonction d'onde employée est un produit de fonctions mono-électroniques. Néanmoins un terme d'interaction électronique qui la prend en compte de façon moyenne est présent dans l'Hamiltonien. Ainsi chaque électron se déplace dans un champ moyen créé par les autres électrons [89Riv]. La fonction Hartree-Fock (noté par la suite HF) pour N électrons s'exprime sous la forme d'un déterminant de Slater. Pour déterminer ces fonctions mono-électroniques, on utilise le principe variationnel selon lequel la meilleure fonction d'onde est celle qui minimise l'énergie du système. La résolution du système d'équations qui en résulte se fait de manière itérative. Pour plus de détails on peut consulter le livre de Szabo et Ostlund [89Sza].

On peut constater que dans la fonction d'onde rien n'empêche deux électrons de spin opposés d'être à la même position, car aucune répulsion n'existe entre les électrons. Cela ne peut en revanche pas être le cas de deux électrons de même spin à cause du principe d'exclusion de Pauli. Cette méthode fournit des résultats dotés d'erreurs systématiques : longueurs de liaison trop courtes, fréquences de vibrations trop élevées, mais qui peuvent parfois sembler très bons grâce à une compensation des erreurs, il convient donc d'analyser les résultats au cas par cas. La méthode Hartree-Fock n'est maintenant principalement utilisée

que pour les macro-systèmes, pour lesquels le recours à des méthodes plus sophistiquées réclamerait des temps de calcul trop importants.

Il est nécessaire d'avoir recours à des méthodes prenant mieux en compte la corrélation électronique. Ce sont les méthodes post-Hartree-Fock, comme les méthodes perturbatives de Møller-Plesset [34Mø], et les méthodes Clusters Couplés [94Bar].

## 2) Méthodes Post Hartree-Fock :

Le principe est le suivant : on effectue un calcul avec la méthode HF, puis on utilise des méthodes plus perfectionnées pour estimer l'énergie de corrélation électronique. Les fonctions d'onde de départ sont celles obtenues par la méthode HF, puis on ajoute des excitations aux orbitales HF. On obtient alors des déterminants excités. On note  $i, j, \dots$  les orbitales occupées ; et  $a, b, \dots$  les orbitales virtuelles.

$\Phi^{HF}$  : référence

$\Phi_{i \rightarrow a}$  : mono excité, on prend un électron de l'orbitale  $i$  que l'on place dans l'orbitale virtuelle  $a$

$\Phi_{j \rightarrow b}^{i \rightarrow a}$  : di-excité

La qualité de l'énergie de corrélation obtenue dépend du nombre d'excitations qui sont prises en compte, ainsi que la manière dont elles sont traitées.

### a) Traitement perturbatif

Les méthodes de Møller-Plesset (noté par la suite MP) [34Mø], sont basées sur la théorie des perturbations. On suppose que l'on peut séparer l'Hamiltonien en deux parties :

$$H = H_0 + \lambda V \quad (46)$$

avec  $H_0$  dont on connaît les valeurs et vecteurs propres :  $\psi_0$  qui sont les fonctions propres de Hartree-Fock, et  $V$  qui est un terme correctif. L'énergie obtenue à l'ordre zéro et à l'ordre un par la méthode des perturbations est définie comme celle calculée au niveau Hartree-Fock :  $E^{HF} = E^0 + E^1$ . L'énergie de corrélation est déduite des ordres de perturbation suivants et donne son nom à la méthode : à l'ordre 2 : MP2 qui fait intervenir des déterminants di-excités, et ainsi de suite MP3, MP4... Les temps de calcul augmentent très rapidement avec l'ordre du développement.

## b) Méthode des Clusters Couplés

Pour cette méthode [94Bar], la fonction d'onde est définie comme suit :

$$\Phi^{cc} = e^T \Phi^{HF} \quad (47)$$

T peut contenir différents ordres d'excitation et s'exprime d'une manière générale :

$$T = T_1 + T_2 + \dots \quad (48)$$

$$\text{avec } T_n = \frac{1}{n!} \sum t_{ij\dots}^{ab\dots} \Phi_{ij\dots}^{ab\dots}$$

Ce sont ces coefficients d'excitation  $t_{ij}$  qu'il faut déterminer. Les méthodes que nous avons utilisées contiennent les ordres d'excitation suivants : CCSD [95Bar] et CCSD(T) [89Rag], qui sont : dans le premier cas Clusters Couplés avec simple et double excitations, et pour le deuxième cas, un traitement perturbatif de l'excitation triple est ajouté. La contribution la plus importante de l'énergie de corrélation provient de la triple excitation, mais sa prise en compte augmente considérablement les temps de calcul. Halkier et coll. [97Hal] ont montré que si on se limite à un traitement perturbatif de cette triple excitation, les résultats ne variaient que très peu. La méthode des Cluster Couplés est pour l'instant la méthode fournissant les meilleurs résultats aussi bien pour les déterminations de géométrie que pour les calculs de champs de force. Mais l'inconvénient majeur de cette méthode de calcul CCSD(T) est le temps de calcul très élevé qui est proportionnel à la puissance sept du nombre d'orbitales.

## 3) Bases

La deuxième composante du niveau d'un calcul *ab initio* est le choix de la base qui est la description des orbitales moléculaires, le temps de calcul augmentant très rapidement avec la taille de la base. On suppose que dans une molécule, lorsque l'on reste au voisinage des atomes, les orbitales sont assez proches de celles des atomes. Les bases sont donc constituées des combinaisons des orbitales atomiques centrées sur les différents atomes. Au début des calculs *ab initio* ces bases étaient représentées par des orbitales de Slater, puis on a utilisé des fonctions gaussiennes appelées "primitives" qui ont l'avantage de simplifier le calcul des intégrales électroniques :

$$\chi_{x^n y^m z^l}^{\text{Gaussienne}} = N(n, m, l, \alpha) x^n y^m z^l \exp(-\alpha r^2) \quad (49)$$

avec  $n+m+l$  qui vaut 0, 1, 2, ... suivant le type d'orbital s, p, d ...

Il faut plusieurs fonctions gaussiennes pour représenter une orbitale de Slater, mais le nombre de fonctions gaussiennes peut être diminué par l'utilisation de combinaisons linéaires de primitives appelées orbitales contractées :

$$\psi_p = \sum_{\lambda=1}^{N_{prim}} \omega_{\lambda}^p \chi_{\lambda}(\alpha_{\lambda}) \quad (50)$$

les coefficients  $\omega_{\lambda}^p$  et les exposants  $\alpha_{\lambda}$  sont optimisés par des calculs atomiques. Le mieux pour rendre compte de la qualité d'une base est de donner le nombre de primitives et de contractées pour chaque orbitales.

Les bases pour l'instant les plus utilisées sont celles de Dunning [89Dun] notées cc-pVnZ (correlation-consistent and polarized, valence n-zeta). Elles font partie des bases dites étendues pour lesquelles les orbitales sont décrites par plusieurs fonctions contractées : ceci permet de changer la taille de l'orbitale décrite, mais pas sa forme. Pour changer la forme, la solution est d'ajouter aux bases des orbitales avec des moments angulaires supérieurs à ce qui est nécessaire pour l'état fondamental de chaque atome : ce sont les fonctions de polarisation. Ces fonctions de polarisation prennent en compte les déplacements électroniques dus à la présence des charges créées par les autres atomes qui constituent la molécule, car la base centrée sur l'atome n'est alors plus suffisante.

La valeur de n est : D (double), T (triple), Q (quadruple), 5 (quintuple) et correspond au nombre d'orbitales de polarisation qui est rajouté. Les bases de Dunning ont l'avantage d'inclure des fonctions de polarisation qui sont suffisantes pour les atomes de la première ligne (de Li à Ne).

Nous avons aussi utilisé les bases augmentées : aug-cc-pVnZ [93Woo] qui contiennent des fonctions diffuses supplémentaires. Les fonctions diffuses sont des fonctions de taille beaucoup plus grandes que les fonctions de polarisation précédentes, elles permettent aux orbitales d'avoir une occupation spatiale plus large. Ces fonctions diffuses sont importantes dans le cas où les électrons sont loin du noyau, ce qui est le cas des atomes électronégatifs (F, N, O pour la première ligne).

## II) Calcul de structures *ab initio*

Nous abordons ici la détermination *ab initio* de structures moléculaires. Il est désormais possible d'effectuer des calculs de haut niveau, grâce à l'évolution très rapide des ressources informatiques. Les programmes disponibles intègrent les nouvelles méthodes de calcul et supportent des bases très étendues. Les résultats sont donc beaucoup plus précis.

Les calculs *ab initio* se présentent comme une bonne solution pour l'obtention d'une structure à l'équilibre fiable. Il existe plusieurs techniques de calculs différentes : nous verrons tout d'abord celle qui ne fait intervenir aucune donnée expérimentale qui consiste avec une méthode adéquate à augmenter la taille de la base jusqu'à ce que le résultat ne varie plus. C'est le seul moyen de s'assurer que le calcul ait bien convergé. Nous verrons que pour les angles, la convergence est atteinte plus rapidement que pour les distances. Ceci devient difficilement applicable lorsque le nombre d'atomes et le nombre d'électrons augmentent. De ce fait, on a souvent recours à la technique de "calibration", qui consiste à comparer, pour une liaison donnée, les calculs et les résultats expérimentaux. La différence entre les valeurs expérimentales et *ab initio* est appelé écart (offset). Il faut un niveau de calcul suffisant pour que l'écart soit constant pour un type de liaison donné. L'écart ainsi déduit peut être appliqué à d'autres molécules dont on ignore la structure. Cette méthode nécessite un échantillon significatif de molécules et évidemment des structures expérimentales précises pour que l'écart déduit soit fiable. On remarquera que la méthode est semi-empirique car elle se base sur des données expérimentales, et n'est donc plus strictement théorique comme la méthode de convergence. Enfin une troisième méthode consiste à calculer les moments d'inertie à l'équilibre à l'aide des moments d'inertie expérimentaux et des corrections harmoniques et anharmoniques provenant des champs de force *ab initio*, cette méthode sera abordée dans la partie suivante.

### 1) Effets des méthodes et bases sur la structure

Nous allons discuter de l'influence des méthodes et bases sur la qualité du calcul, mais ceci n'est pas limité aux calculs de structure. Le problème est le suivant : il n'est pas possible de prendre une base de taille infinie et de faire le calcul, les temps de calculs et les tailles de mémoire informatique seraient eux aussi infinis. De plus on ne peut estimer la précision d'un résultat avec un seul calcul, il est préférable d'observer les variations existantes avec une base de taille supérieure. La meilleure solution est de prendre une méthode fiable puis d'augmenter la taille de la base jusqu'à atteindre la convergence : cela signifie que les changements ne doivent pas être significatifs entre deux calculs successifs. Ceci nécessite de ne pas négliger certains phénomènes comme la corrélation entre les électrons de cœur et de valence, ainsi que l'électronégativité de certains atomes. L'objectif ici est d'estimer l'influence des approximations sur la fonction d'onde et les bases afin d'obtenir un résultat précis avec les moyens les mieux adaptés.

### a) La corrélation électronique due à la méthode de calcul

Comme nous l'avons vu dans le descriptif des méthodes, lorsque l'on utilise la méthode Hartree-Fock, on néglige la corrélation électronique. Les méthodes les plus utilisées pour la prendre en compte sont les méthodes perturbatives et les méthodes des cluster couplés. Les méthodes "fonctionnelle de densité" (notées DFT) sont aussi parfois utilisées [93Bec], elles ont l'avantage de ne demander qu'assez peu de mémoire et nécessitent des temps de calcul relativement faibles [96For], mais les résultats que nous avons obtenus avec cette méthode sont sensiblement moins fiables qu'avec MP2 [99Mar4] : les écarts obtenus entre calculs et expérience ainsi que la dispersion des valeurs sont beaucoup plus importantes pour la méthode B3LYP (qui est la fonctionnelle la plus précise) que pour MP2. Cette méthode très économique est principalement utilisée pour de grosses molécules.

Il convient de noter qu'il existe deux types de calculs : celui où les électrons de cœur sont gelés (dit "frozen core"), ainsi seuls les électrons de valence sont pris en compte, et le cas où tous les électrons sont corrélés. Les calculs en cœur gelé sont plus rapides mais ils négligent la corrélation entre les électrons de cœur et ceux de valence.

Pour établir une hiérarchie parmi les méthodes Hartree-Fock, Møller-Plesset et Coupled-Cluster, on se réfère à la plus récente étude systématique des différentes méthodes [97Hel], effectuée sur un échantillon de 19 molécules constituées d'atomes de la 1<sup>ère</sup> ligne avec des types de liaisons variées. Il est important de comparer ces méthodes avec une base suffisamment grande pour que les effets dus au confinement électronique n'interviennent pas : une compensation des erreurs pourrait biaiser les résultats. On en a la preuve dans le Tableau 6 : si l'on regarde les résultats pour la plus petite base (cc-pVDZ), MP2 et CCSD semblent donner des résultats meilleurs que CCSD(T)! Il faut donc prendre les résultats obtenus avec la base quadruple-zéta, afin de n'avoir que les effets dûs aux méthodes. Voici ce que l'on peut en déduire : il s'avère indispensable de ne pas négliger la corrélation électronique, car pour la méthode HF les résultats divergent avec l'augmentation de la base. La méthode qui fournit les meilleurs résultats, c'est à dire les plus proches des structures expérimentales, est CCSD(T), les résultats sont plus fiables que MP4 à temps de calcul équivalent. Mais ces temps de calcul sont très élevés : proportionnel à la puissance sept de la taille de la base. Il est aussi très intéressant de noter que MP2 semble être meilleure que MP3 et CCSD : l'erreur moyenne des écarts entre calcul et valeurs expérimentales n'est que de 0.54 pm alors qu'elle est de 1.30 pm et 0.89 pm respectivement pour MP3 et CCSD. La

méthode MP2 se présente donc comme une très bonne alternative aux calculs CCSD(T) car le temps de calcul est quant à lui proportionnel à la puissance cinq du nombre d'orbitales.

**Tableau 6** : Erreur moyenne des valeurs absolues des écarts entre valeurs expérimentales et *ab initio* pour différentes bases et méthodes

|         | Temps de calcul | cc-PVDZ            | cc-PVTZ | cc-PVQZ |
|---------|-----------------|--------------------|---------|---------|
| HF      | $\sim n^4$      | 2.11 <sup>a)</sup> | 2.80    | 2.91    |
| MP2     | $\sim n^5$      | 1.29               | 0.58    | 0.54    |
| MP3     | $\sim n^6$      | 0.88               | 1.16    | 1.30    |
| MP4     | $\sim n^7$      | 1.77               | 0.51    | 0.41    |
| CCSD    | $\sim n^6$      | 1.09               | 0.72    | 0.89    |
| CCSD(T) | $\sim n^7$      | 1.59               | 0.23    | 0.22    |

a) calculs tous électrons corrélés, les différences des longueurs de liaison sont en pm

**b) Influence de la taille de la base**

Il est déjà possible d’observer les effets de la taille de la base sur les longueurs de liaison avec le Tableau 6. Pour continuer avec les longueurs et angles de liaison, voyons quelques autres exemples dans le Tableau 7. Ces calculs sont tous au niveau CCSD(T), donc seule la taille de la base est en cause pour la qualité du calcul. Si l’on exclut la liaison C-H pour laquelle il semble que l’on ait convergé avec la base cc-pVTZ, le recours à la base quadruple-zéta semble indispensable, même si on ne se limite qu’aux atomes de la 1<sup>ère</sup> ligne. On peut de plus noter que deux critères semblent intervenir sur la rapidité de convergence du calcul : tout d’abord le type de liaison considéré ce qui semble assez logique. Mais pour une liaison donnée cela dépend aussi du nombre d’électrons qui composent cette molécule, c’est à dire des autres atomes qui composent la molécule. Si la convergence n'est pas atteinte avec la base quadruple zéta, il faut avoir recours à une base quintuple-zéta ce qui demande des temps de calcul considérables avec la méthode CCSD(T). A titre d’exemple un calcul CCSD(T)/cc-pVQZ sur CH<sub>3</sub>F avec une station de travail très récente (Silicon Graphics bi-processeur, 590Mo de mémoire vive, 24Go de disque dur) nécessite plus d'une semaine, alors qu’il n’y a que cinq atomes et tous de la 1<sup>ère</sup> ligne. Ceci illustre bien la difficulté de cette méthode de convergence. En ce qui concerne les atomes de la 2<sup>ème</sup> ligne la convergence est encore plus lente : nous verrons dans la partie suivante qu’il est nécessaire d’ajouter des fonctions de polarisation pour améliorer la convergence [98Mar]. Pour les angles qui apparaissent à la fin

**Tableau 7** : Exemple de convergence pour différentes liaisons et angles

| molécule                                         | liaison | exp    | réf.     | pVDZ   | pVTZ   | pVQZ   | pV5Z   | ref        | r( $\infty$ ) <sup>a)</sup> | r( $\infty$ ) <sup>b)</sup> | r(n+1) <sup>c)</sup> | r( $\infty$ ) <sup>d)</sup> |
|--------------------------------------------------|---------|--------|----------|--------|--------|--------|--------|------------|-----------------------------|-----------------------------|----------------------|-----------------------------|
| BH <sub>2</sub> F                                | B-H     | 1.1891 | [94Osw]  | 1.2085 | 1.1930 | 1.1922 |        | ce travail | 1.1922                      | 1.1922                      | 1.1922               | 1.1922                      |
| CH <sub>2</sub> (X <sup>3</sup> B <sub>1</sub> ) | C-H     | 1.0753 | [90Jen]  | 1.0955 | 1.0783 | 1.0771 |        | ce travail | 1.0771                      | 1.0770                      | 1.0770               | 1.0769                      |
| HC≡CH                                            | C-H     | 1.0625 | [93Bra]  | 1.0789 | 1.0637 | 1.0633 |        | [97Pet]    | 1.0633                      | 1.0633                      | 1.0633               | *                           |
| H <sub>2</sub> CO                                | C-H     | 1.1005 | [74Dun]  | 1.1199 | 1.1033 | 1.1022 |        | [95Mar]    | 1.1021                      | 1.1021                      | 1.1021               | 1.1004                      |
| HCF                                              | C-H     | 1.1300 | [81Suz]  | 1.1406 | 1.1153 | 1.1175 |        | ce travail | *                           | *                           | *                    | *                           |
| OCHF <sup>e)</sup>                               | C-H     | 1.0900 | [99Mar3] | 1.1072 | 1.0865 | 1.0889 |        | ce travail | *                           | *                           | *                    | *                           |
| HNO                                              | N-H     | 1.0630 | [86Hir]  | 1.0720 | 1.0554 | 1.0535 |        | ce travail | 1.0533                      | 1.0533                      | 1.0533               | 1.0528                      |
| HNCO <sup>e)</sup>                               | N-H     | 1.0030 | [93Eas]  | 1.0173 | 1.0026 | 1.0018 |        | ce travail | 1.0018                      | 1.0018                      | 1.0018               | 1.0018                      |
| HNO <sup>f)</sup>                                | N-O     | 1.2060 | [86Hir]  | 1.2196 | 1.2144 | 1.2107 |        | ce travail | *                           | *                           | 1.2081               | 1.2099                      |
| HNO <sup>f)</sup>                                | N-O     | 1.2060 | [86Hir]  | 1.2196 | 1.2144 | 1.2107 | 1.2099 | ce travail | 1.2095                      | 1.2095                      | 1.2080               | 1.2084                      |
| CO <sup>f)</sup>                                 | C-O     | 1.1283 | [79Hub]  | 1.1446 | 1.1357 | 1.1314 |        | [97Pet2]   | 1.1313                      | 1.1313                      | 1.1293               | 1.1288                      |
| CO <sup>f)</sup>                                 | C-O     | 1.1283 | [79Hub]  | 1.1446 | 1.1357 | 1.1314 | 1.1307 | [97Pet2]   | 1.1306                      | 1.1306                      | 1.1305               | 1.1299                      |
| H <sub>2</sub> CO                                | C=O     | 1.2033 | [74Dun]  | 1.2156 | 1.2096 | 1.2066 |        | [95Mar]    | 1.2036                      | 1.2036                      | 1.2051               | 1.2048                      |
| HNCO <sup>e)</sup>                               | C=O     | 1.1634 | [93Eas]  | 1.1777 | 1.1668 | 1.1640 |        | ce travail | 1.1630                      | 1.1630                      | 1.1633               | 1.1625                      |
| HC≡CH <sup>f)</sup>                              | C≡C     | 1.2020 | [93Bra]  | 1.2290 | 1.2100 | 1.2065 |        | [97Pet]    | 1.2057                      | 1.2057                      | 1.2059               | 1.2048                      |
| HC≡CH <sup>f)</sup>                              | C≡C     | 1.2020 | [93Bra]  | 1.2290 | 1.2100 | 1.2065 | 1.2056 | [97Pet]    | 1.2053                      | 1.2053                      | 1.2054               | 1.2050                      |
| H <sub>2</sub> C=C=C                             | C=C     | 1.3280 | [99Gau]  | 1.3500 | 1.3270 | 1.3310 |        | ce travail | *                           | *                           | *                    | *                           |
| H <sub>2</sub> C=C=C                             | C=C     | 1.2870 | [99Gau]  | 1.3150 | 1.2960 | 1.2910 |        | ce travail | 1.2892                      | 1.2892                      | 1.2897               | 1.2883                      |
| HCF                                              | C-F     | 1.3050 | [81Suz]  | 1.3210 | 1.3070 | 1.3052 |        | ce travail | 1.3049                      | 1.3049                      | 1.3050               | 1.3045                      |
| ClCN                                             | C-Cl    | 1.6290 | [98Dem2] | 1.6604 | 1.6437 | 1.6384 |        | ce travail | 1.6359                      | 1.6360                      | 1.6367               | 1.6354                      |
| HCP <sup>b)</sup>                                | C≡P     | 1.5399 | [98Dem2] | 1.5717 | 1.5540 | 1.5473 |        | [98Dem2]   | 1.5432                      | 1.5432                      | 1.5448               | 1.5434                      |
| HCP <sup>b)</sup>                                | C≡P     | 1.5399 | [98Dem2] | 1.5717 | 1.5540 | 1.5473 |        | [98Dem]    | 1.5432                      | 1.5432                      | 1.5448               | 1.5434                      |

| molécule                       | liaison | exp    |          | pvdz    | pvtz   | pvqz   | pv5z | ref        | $r(\infty)^a)$ | $r(\infty)^b)$ | $r(n+1)^c)$ | $r(\infty)^d)$ |
|--------------------------------|---------|--------|----------|---------|--------|--------|------|------------|----------------|----------------|-------------|----------------|
| HNO <sup>e)</sup>              | <HNO    | 109.09 | [86Hir]  | 107.68  | 108.03 | 108.09 |      | ce travail | 108.10         | 108.10         | 108.10      | 108.12         |
| H <sub>2</sub> C=C=C           | <CCH    | 121.20 | [99Gau]  | 121.39  | 121.30 | 121.30 |      | ce travail | 121.30         | 121.30         | 121.30      | 121.30         |
| F <sub>2</sub> O <sup>e)</sup> | <FOF    | 103.07 | [66Mor]  | 103.009 | 103.17 | 103.10 |      | ce travail | *              | *              | *           | *              |
| F <sub>2</sub> S <sup>e)</sup> | <FSF    | 98.05  | [79End]  | 98.61   | 98.26  | 98.06  |      | ce travail | 97.79          | 97.79          | 98.06       | 97.94          |
| CF <sub>2</sub>                | <FCF    | 104.86 | [99Mar3] | 104.62  | 105.03 | 104.94 |      | ce travail | *              | *              | *           | *              |
| HO <sup>e)</sup>               | <HOF    | 97.72  | [88Hal]  | 96.75   | 97.62  | 97.85  |      | ce travail | 97.93          | 97.93          | 97.85       | 97.98          |
| OCHF <sup>e)</sup>             | <OCH    | 127.72 | [99Mar3] | 127.56  | 127.48 | 127.61 |      | ce travail | *              | *              | *           | *              |
| OCHF <sup>e)</sup>             | <OCF    | 122.71 | [99Mar3] | 123.12  | 122.97 | 122.82 |      | ce travail | 122.82         | 122.82         | 122.82      | 122.72         |

- Valeurs en Å pour les liaisons et en degrés pour les angles
- les formules d'extrapolation a), b), c) d) sont respectivement celles des équations : (51), (52), (53), (54)
- Les calculs sont dans l'approximation coeur gelé sauf <sup>e)</sup> où tous les électrons sont corrélés
- <sup>f)</sup> calcul des extrapolations a base infinie avec et sans la base cc-pV5Z
- \* est placée lorsque la progression n'est pas monotone ou lorsque la solution mathématique est aberrante

du Tableau 7, la convergence est en général plus rapide que dans le cas des longueurs de liaison. Il est donc possible d’obtenir de bonnes précisions sur les angles avec des moyens plus modestes que pour les longueurs de liaison.

Comme on peut le voir, l’inconvénient majeur de ces bases est leur convergence assez lente. Plusieurs auteurs ont cherché des formules d’extrapolation qui permettent de simuler une base infinie. Ces formules sont de plusieurs types : exponentielles, géométriques. Voici les formules que nous avons pu recenser :

$$a) \ r(n) = r(\infty) + BC^n \mid C \mid < 1 \qquad [96\text{Mar}] \qquad (51)$$

$$b) \ r(n) = r(\infty) + Be^{-Cn} \qquad [93\text{Dun}] \qquad (52)$$

$$c) \ \Delta r(n) = \frac{-a}{b^{n-1}} \qquad [89\text{Dun}] \qquad (53)$$

$$d) \ r(n) = r(\infty) + Be^{-(n-1)} + Ce^{-(n-1)^2} \qquad [94\text{Dun}] \qquad (54)$$

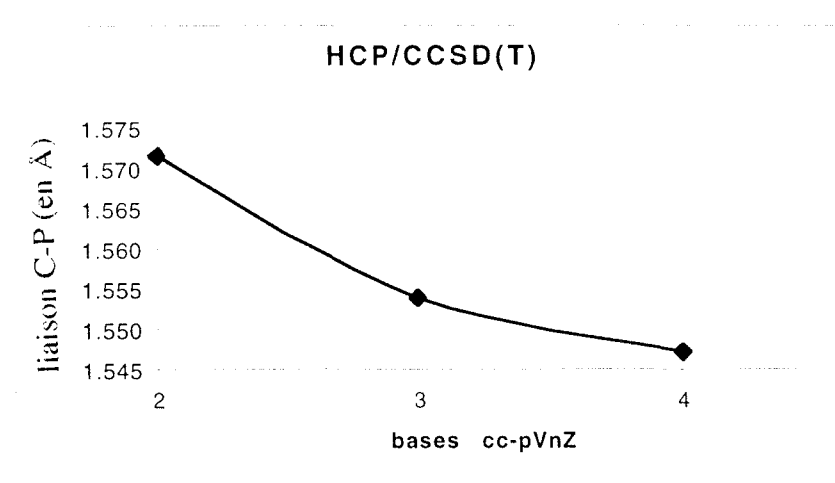
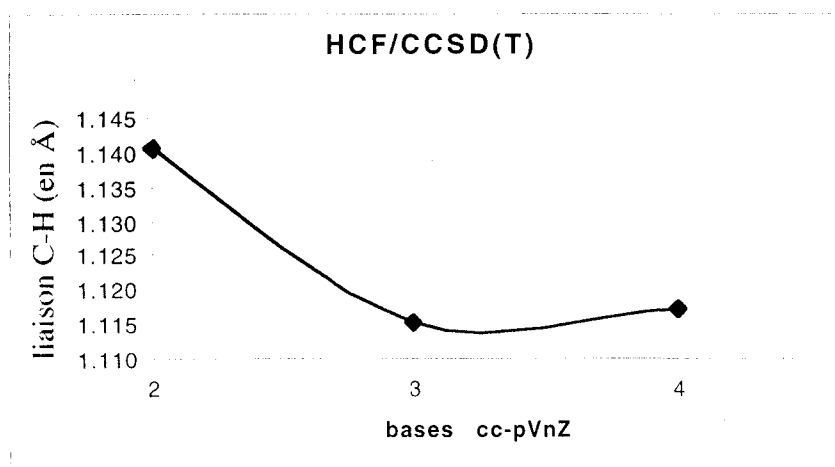
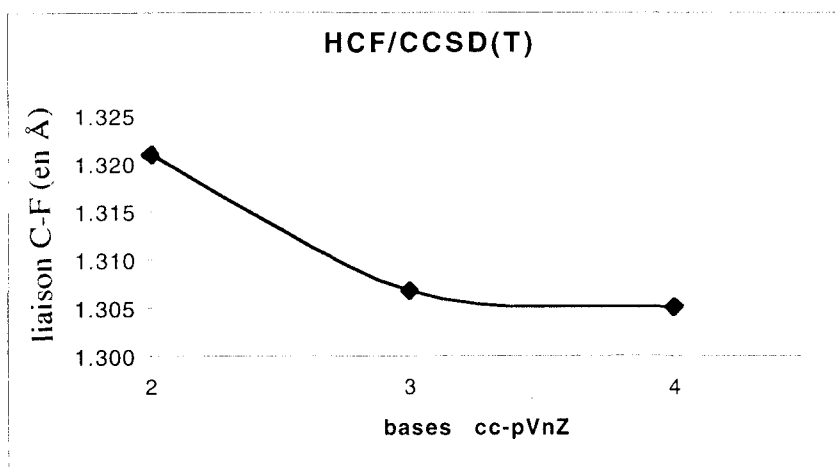
avec  $n = 2$  pour cc-pVDZ,  $n = 3$  pour cc-pVTZ,...

Ces formules sont toutes empiriques, et se basent sur une évolution monotone des longueurs et angles de liaisons avec l’augmentation de la taille de la base : elles doivent donc être utilisées avec prudence. Il faut tout d’abord s’assurer que les variations pour les différentes bases ne présentent pas d’oscillations, car dans ce cas ces formules sont inutilisables : même si une solution mathématique existe, elle n’a aucune signification. Ce sont les cas pour lesquels on a placé des étoiles dans le Tableau 7. De plus il est nécessaire de ne pas être trop loin de la convergence pour utiliser ces formules : la différence de résultats entre les deux dernières bases utilisées doit être assez faible. En d’autres termes, on risque de ne pas converger vers la bonne solution avec ces formules si les résultats utilisés sont trop loin de cette base infinie. La seule solution pour être totalement sûr que l’extrapolation à base infinie est correcte serait de faire le calcul pour la base suivante...

Nous présentons dans le Tableau 7, quelques applications utilisant ces différentes formules afin de tester leur équivalence. Les deux premières formules fournissent exactement les mêmes résultats car elles sont similaires : on peut donc utiliser l’une ou l’autre. La troisième formule en revanche n’extrapole pas à une base infinie mais à la base suivante à l’aide d’une série géométrique. Lorsque les formules sont utilisées dans des conditions correctes, les résultats obtenus sont comparables avec les différentes formules.

C’est aussi un moyen de vérifier les bonnes conditions d’extrapolation, car si les résultats ne sont pas en accord c’est souvent parce que l’on est trop loin de la convergence

**Figure 6 :** Illustrations de quelques évolutions avec l'augmentation de la taille de la base



pour les utiliser. On peut le vérifier avec  $\text{H}_2\text{CCC}$ , où la longueur de liaison varie de 0.005 Å entre les bases cc-pVTZ et cc-pVQZ, ce qui est assez élevé. Les différentes extrapolations donnent des résultats distants de 0.001 Å.

Quelques schémas (Figure 6) illustrent les cas où il paraît judicieux de faire appel à ces formules d'extrapolation, ainsi que ceux où le résultat de l'extrapolation n'aurait aucun sens. Dans le premier cas (la liaison C-F dans HCF) l'évolution est bien monotone, et la variation entre les bases triple et quadruple-zéta est faible. On peut voir que l'on est assez proche de la convergence : on peut donc extrapoler à base infinie. Ce n'est pas possible pour les deux liaisons suivantes : la progression présente des oscillations pour la liaison C-H (dans HCF) . Dans le cas de  $\text{C}\equiv\text{P}$  (dans HCP) l'écart est trop important entre les deux dernières bases pour que l'extrapolation donne des résultats précis. Ceci s'explique par le fait que P est un atome de la 2<sup>ème</sup> ligne : nous allons voir que l'ajout de fonctions de polarisation supplémentaires résout ce problème.

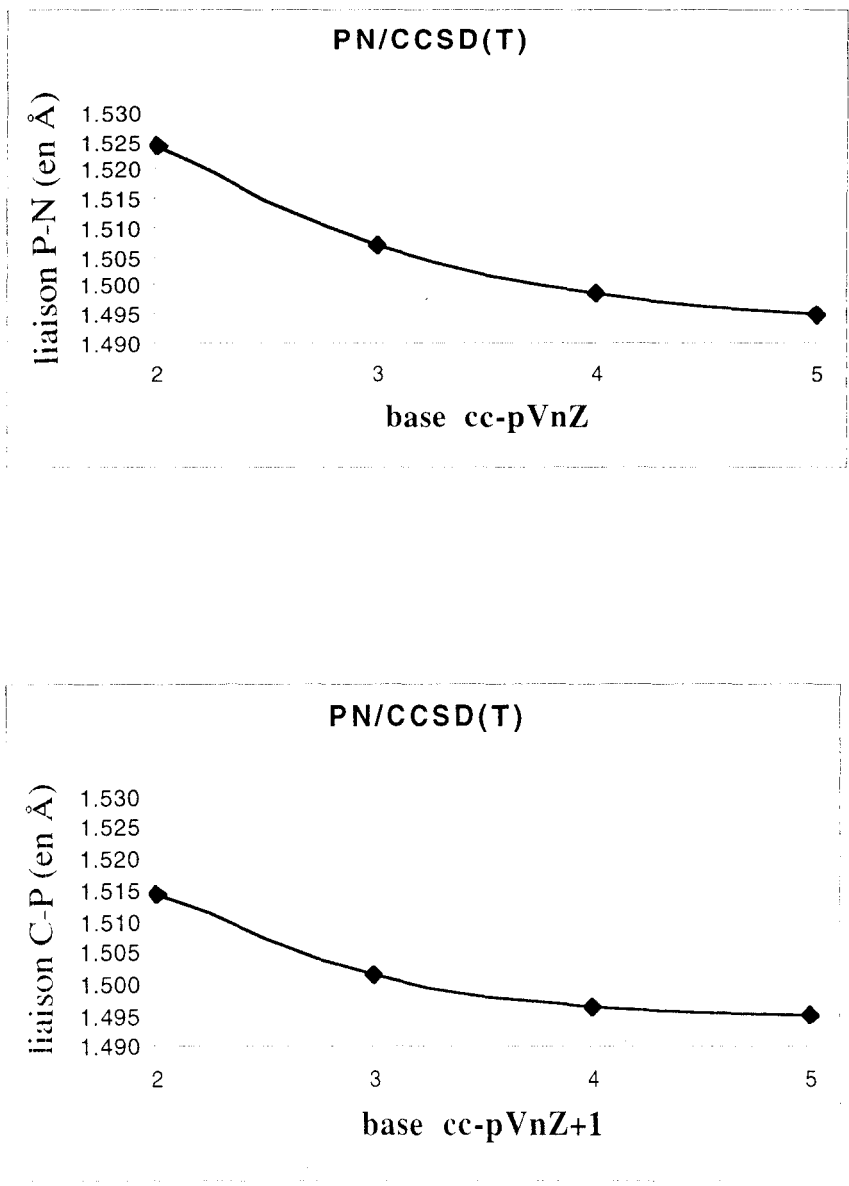
### c) Les atomes de la 2<sup>ème</sup> ligne

Comme nous l'avons remarqué dans le Tableau 7 et sur la Figure 6, la convergence est souvent plus lente en ce qui concerne les atomes de la 2<sup>ème</sup> ligne. Il semble que les fonctions de polarisation présentes dans les bases de Dunning conviennent bien aux atomes de la 1<sup>ère</sup> ligne, mais elles sont en revanche insuffisantes pour les atomes des lignes suivantes. Martin dans une étude récente [98Mar] a montré que le simple ajout d'une fonction de polarisation d avec le plus grand exposant de la base cc-pV5Z sur les bases cc-pVTZ et cc-pVQZ permettait d'obtenir pour la 2<sup>ème</sup> ligne des convergences similaires à celles de la 1<sup>ère</sup> avec les bases classiques cc-pVnZ. Ces nouvelles bases sont notées cc-pVnZ+1. Par leur définition on remarque que  $\text{cc-pV5Z}+1=\text{cc-pV5Z}$ .

Les intérêts de ces bases avec une fonction de polarisation supplémentaire sont les suivants : tout d'abord la rapidité de convergence des résultats est très nettement améliorée. Prenons dans le tableau 8 le cas de  $\text{P}_2$ , entre la base cc-pVQZ et cc-pV5Z la variation de la longueur de liaison est de 0.0052 Å, alors qu'elle n'est plus que de 0.0026 Å entre cc-pVQZ+1 et cc-pV5Z.

Si l'on extrapole à base infinie, avec les bases cc-pVnZ et cc-pVnZ+1, on peut voir que les résultats sont significativement différents :  $r(\infty)_N = 1.8958 \text{ Å}$  et  $r(\infty)_{N+1} = 1.8991 \text{ Å}$ . Ceci illustre bien le danger une nouvelle fois d'extrapoler à base infinie lorsque les variations entre les deux dernières bases sont importantes.

**Figure 7 :** Amélioration de la convergence pour les atomes de la 2<sup>ème</sup> ligne avec les bases cc-pVnZ+1



**Tableau 8** : Evolution de la convergence avec l'ajout d'une fonction de polarisation pour les atomes de la 2<sup>ème</sup> ligne.

|                             | P <sub>2</sub> | PN     | Cl <sub>2</sub> | réf.       |
|-----------------------------|----------------|--------|-----------------|------------|
| exp.                        | 1.8934         | 1.4909 | 1.9870          |            |
| cc-pVDZ                     | 1.9373         | 1.5245 | 2.0544          | ce travail |
| cc-pVTZ <sup>b)</sup>       | 1.9159         | 1.5070 | 2.0178          | [98Mar]    |
| cc-pVQZ                     | 1.9052         | 1.4987 | 2.0030          | [98Mar]    |
| cc-pV5Z                     | 1.9002         | 1.4951 | 1.9936          | [98Mar]    |
| r( $\infty$ ) <sup>a)</sup> | 1.8958         | 1.4923 | 1.9769          | [98Mar]    |
| cc-pVDZ+1                   | 1.9257         | 1.5142 | 2.0358          | ce travail |
| cc-pVTZ+1                   | 1.9096         | 1.5013 | 2.0088          | [98Mar]    |
| cc-pVQZ+1                   | 1.9025         | 1.4964 | 1.9972          | [98Mar]    |
| r( $\infty$ ) <sup>a)</sup> | 1.8991         | 1.4945 | 1.9919          | [98Mar]    |

De plus il semble évident que les bases cc-pVQZ ne sont plus suffisantes pour ces atomes de la 2<sup>ème</sup> ligne, car l'on est assez loin de la convergence (Tableau 8). Mais l'utilisation de la base quintuple zéta nécessite des temps de calculs très élevés. La base cc-pVQZ+1 apparaît donc comme une bonne alternative, car on est relativement proche de la convergence, et les temps de calcul sont très similaires à ceux de la base cc-pVQZ.

#### d) L'effet des fonctions diffuses

Il existe certaines molécules pour lesquelles les résultats oscillent lors de l'augmentation de la taille de la base. Ceci a déjà été observé sur plusieurs molécules : CH<sub>3</sub>F [97Dem], et nous l'avons nous-mêmes noté pour OCHF et HCF [99Mar3]. Cela semble être dû à la forte électronégativité de l'atome de Fluor. Mais cela n'est pas systématique, ainsi si la progression des résultats est monotone avec l'augmentation de la taille de la base, cela ne signifie pas que les fonctions diffuses n'auront aucun effet. Dans ce cas il faut utiliser les bases aug-cc-pVnZ [92Ken] qui contiennent des fonctions diffuses supplémentaires. Comme l'ont vérifié Martin et Dunning [94Mar], [97Pet], il ne sert à rien de mettre des fonctions diffuses sur tous les atomes de la molécule. Cela alourdit sensiblement le calcul, et ces fonctions diffuses n'ont une influence que pour les atomes électronégatifs. Ces bases augmentées sont des bases très importantes et leur utilisation nécessite des temps de calcul très élevés, mais il n'est pas possible d'estimer l'effet des fonctions diffuses lorsque l'on est

trop loin de la convergence, au niveau cc-pVTZ par exemple, car l'effet est alors très largement surestimé [98Mar]. Il est nécessaire d'utiliser la base aug-cc-pVQZ pour une prise en compte correcte de ces effets [94Mar]. De plus, la correction de ces fonctions diffuses ne dépend pas que de la liaison considérée, mais aussi de la polarité de la molécule, donc des autres atomes présents dans la molécule. De ce fait, il faut la calculer dans chaque cas. Plusieurs auteurs ont mis en évidence la convergence des effets de ces bases augmentées lorsque l'on accroît la taille de la base, ce que l'on peut vérifier dans le Tableau 9. On peut se demander si l'influence des fonctions diffuses deviendrait négligeable avec une base ayant une occupation spatiale suffisante, telle qu'une base sextuple zéta. Pour fournir une réponse sûre, il faudrait une étude systématique sur différents types de liaison pour un nombre significatif de molécules.

**Tableau 9** : Calculs des corrections dues aux fonctions diffuses avec les méthodes CCSD(T) et MP2

| molécule          | liaison | réf      | CCSD(T) |         |         | MP2     |
|-------------------|---------|----------|---------|---------|---------|---------|
|                   |         |          | cc-pVDZ | cc-pVTZ | cc-pVQZ | cc-pVQZ |
| HF                | H-F     | [94Mar]  |         |         | 0.0015  | 0.0012  |
| CH <sub>3</sub> F | C-F     | [98Dem]  | 0.0246  | 0.0079  | 0.0031  | 0.0031  |
| CO                | C≡O     | [97Pet]  | 0.0027  | 0.0003  | 0.0004  | 0.0006  |
| HCF               | C≡F     | [99Mar]  |         |         | 0.0015  | 0.0020  |
| NH <sub>3</sub>   | N-H     | [95Mar2] | -0.0035 | 0.0006  | 0.0003  | 0.0004  |
| NH <sub>3</sub>   | <HNH    | [95Mar2] | 2.38    | 0.74    | 0.34    | 0.40    |
| HCF               | <HCF    | [99Mar4] |         |         | -0.09   | -0.09   |
| CH <sub>3</sub> F | <HCH    | [99Mar4] |         |         | 0.19    | 0.19    |

la différence( aug-cc-pVnZ)-(cc-pVnz) en Å pour les distances et en degrés pour les angles

Les calculs au niveau CCSD(T) deviennent rapidement très longs même si on utilise les bases augmentées uniquement sur les atomes électro-négatifs. Il serait très intéressant de pouvoir considérer ces effets comme une correction à apporter au calcul au niveau CCSD(T)/cc-pVQZ, cette correction serait calculée avec une méthode moins coûteuse. Nous avons fait des essais sur plusieurs molécules avec la méthode MP2. On peut voir dans le Tableau 9 ces résultats pour plusieurs liaisons différentes qui nous montrent que la correction calculée au niveau MP2 fournit des résultats assez précis.

Nous considérons donc cette correction, due aux fonctions diffuses et calculée au niveau MP2, comme additive à des calculs faits en CCSD(T). Ceci a déjà été appliqué par Demaison et coll.[98Dem] pour CH<sub>3</sub>F, et nous l'avons utilisé pour la détermination de plusieurs structures à l'équilibre [99Mar3].

**e) La corrélation électronique cœur-valence**

Plusieurs auteurs ont mis en évidence que lorsqu'un calcul avait convergé, il restait un écart systématique avec des valeurs expérimentales précises. On peut d'ailleurs l'observer dans le tableau 7. Ceci est dû à la corrélation électronique entre les électrons de cœur et de valence qui est négligée lorsque l'on fait les calculs dans l'approximation du cœur gelé. La plupart des calculs *ab initio* sont faits dans cette approximation car les calculs sont plus rapides avec les électrons de cœur gelé, mais surtout parce qu'il est possible de définir les propriétés moléculaires avec les seuls électrons de valence.

**Tableau 10 :** Valeurs de la corrélation électronique de cœur valence pour différentes liaisons

|                   |      | cc-pCVTZ             | cc-pCVQZ | Martin-Taylor | cc-pVQZ | réf.       |
|-------------------|------|----------------------|----------|---------------|---------|------------|
| CH <sub>4</sub>   | C-H  | 0.0013 <sup>a)</sup> | 0.0015   | 0.0015        |         | [97Pet]    |
| CH <sub>3</sub> F | C-H  | 0.0012               | 0.0014   |               |         | [98Dem]    |
| H <sub>2</sub> CO | C-H  | 0.0011               |          | 0.0013        |         | [95Mar]    |
| H <sub>2</sub> CO | C-O  | 0.0014               |          | 0.0022        |         | [95Mar]    |
| CO                | C-O  | 0.0017               | 0.0022   | 0.0024        |         | [97Pet]    |
| CH <sub>3</sub> F | C-F  | 0.0018               | 0.0021   |               |         | [98Dem]    |
| HNO               | N-H  |                      | 0.0013   |               | 0.0025  | ce travail |
| HNO               | N-O  |                      | 0.0020   |               | 0.0025  | ce travail |
| HNO               | <HNO |                      | -0.070   |               | -0.082  | ce travail |

<sup>a)</sup> C'est la différence r(frozen-core)-r(all electron) en Å pour les longueurs et en degré pour les angles

Les bases classiques de Dunning cc-pVnZ surestiment la corrélation cœur-valence, c'est ce que l'on peut observer pour HNO. Il est nécessaire d'utiliser des bases spécialement développées pour ce cas, ce sont les bases cc-pCVnZ (correlation-consistent polarized Core Valence n-Zeta) de Dunning [95Woo] ou les bases de Martin-Taylor [94Mar]. Les meilleurs résultats sont obtenus avec des calculs où tous les électrons sont corrélés en utilisant les bases cc-pCVnZ. Mais ont un nombre d'orbitales très important, les calculs avec ces bases sont longs et nécessitent beaucoup de mémoire. elles sont de plus récentes. Il existe donc peu

d'études systématiques à leur sujet. En général on suppose en première approximation que cette corrélation est constante pour une liaison donnée, on calcule sa valeur avec la base cc-pCVQZ pour une liaison dans une molécule simple, puis on la considère comme une correction additive que l'on applique à des autres molécules plus complexes.

Dans le Tableau 10 on peut voir que la corrélation varie relativement peu pour une liaison donnée, mais elle dépend fortement du nombre d'électrons, donc du type de liaison considéré. On remarque aussi que pour les angles la contribution de cette corrélation est assez faible.

Les bases cc-pCVQZ et celles de Martin-Taylor donnent des résultats très voisins, mais comme l'avait déjà montré Martin [95Mar], la base cc-pCVTZ ne recouvre qu'environ 75% de cette corrélation.

### f) Applications

La méthode de convergence nécessite donc de prendre en compte toutes les corrections abordées si l'on veut atteindre les précisions expérimentales. On peut noter les travaux les plus récents sur CH<sub>3</sub>F [98Dem], NH<sub>3</sub> [ 95Mar].

Ces exemples montrent bien l'efficacité d'une telle méthode, mais son domaine d'application reste restreint à des molécules constituées de quelques atomes et relativement légers (jusqu'à la 2<sup>ème</sup> ligne). La méthode qui reste la plus utilisée est la méthode de calibration.

**Tableau 10** : Exemple d'application de la méthode de convergence

|                   |                  | cc-pVQZ | cc-PV(Q.5)Z <sup>a</sup> | cœur-val <sup>b</sup> | aug <sup>c</sup> | estimateur <sup>d</sup> | exp    |
|-------------------|------------------|---------|--------------------------|-----------------------|------------------|-------------------------|--------|
| CH <sub>3</sub> F | r <sub>C-F</sub> | 1.3824  | 1.3835                   | -0.0021               | 0.0013           | 1.3827                  | 1.3827 |
| NH <sub>3</sub>   | r <sub>N-H</sub> | 1.0124  |                          | -0.0012               | 0.0004           | 1.0116                  | 1.0116 |

a) cc-pVQZ pour H et cc-pV5Z pour C, F  
b) r(all electron)-r(frozen-core) au niveau CCSD(T)/cc-PCVQZ  
c) r(aug-cc-pVQZ)-r(cc-pVQZ) au niveau CCSD(T)  
d) estimateur = r(cc-pVQZ) + correction (cœur-val) + correction (aug)

### 2) Calibration

Cette méthode consiste à établir une correction pour un type de liaison donné entre des calculs *ab initio* de niveau “modeste” et des structures expérimentales précises. Cette correction peut alors s'appliquer à des liaisons de même type dont on ignore la longueur. Il

faut que la dispersion de la correction pour les différentes molécules soit constante : les écarts ( $r_{calc}-r_{exp}$ ) doivent être systématiques et non pas aléatoires. Pour le vérifier on peut utiliser divers tests statistiques : l'écart type des résidus entre le calcul et l'expérience, la médiane...

La méthode et la base à utiliser dépendent de la liaison en question. Par exemple, des études précédentes sur la liaison C-H ont montré que l'on obtenait des résultats très corrects à l'aide de calculs MP2/6-31G\*\* [94Dem]. On peut trouver d'autres exemples de l'application de la calibration pour la liaison suivante : CO[96Dem]. Plus récemment des essais de méthodes et bases ont été faits par Demaison et coll. [98Dem2] sur les liaisons C≡C, CF, et CCl. Cette étude montre que la méthode CCSD(T) avec la base cc-pVTZ permet d'obtenir un écart beaucoup plus précis que les méthodes MP2 et B3LYP avec la base 6-311++G(3df, 2pd), ceci illustre bien la difficulté du choix du niveau de calcul pour que la méthode de calibration soit fiable.

**Tableau 11** : Ecart entre les calculs au niveau CCSD(T) et les valeurs expérimentales pour la liaison C-F

|                | pVTZ <sup>a)</sup> | pVQZ+diff <sup>b)</sup> |
|----------------|--------------------|-------------------------|
| moyenne        | -0.0050            | -0.0001                 |
| médiane        | -0.0044            | -0.0001                 |
| écart type     | 0.0023             | 0.0007                  |
| nbre molécules | 9                  | 8                       |

<sup>a)</sup> calculs en cœur gelé  
<sup>b)</sup> calculs tous électrons corrélés. Les effets des fonctions diffuses sont estimés au niveau MP2

Nous avons complété l'étude pour la liaison C-F par des calculs au niveau CCSD(T) avec les bases cc-pVQZ et en tenant compte des fonctions diffuses ( la correction étant estimée au niveau MP2). Les résultats sont dans le tableau 8 qui est extrait de l'article consacré à la liaison C-F [99Mar]. Comme nous l'avions déjà vu, les fonctions diffuses ont un effet important sur l'atome de fluor. Leur prise en compte permet de réduire très sensiblement la dispersion des différences entre valeurs expérimentales et calculées : l'écart-type est diminué d'un facteur trois, et permet donc d'obtenir un écart plus fiable. Le fait que l'écart soit quasi nul ne signifie pas que le calcul ait convergé, mais ceci est dû à une compensation des erreurs entre la corrélation de cœur valence qui n'est pas calculée et l'insuffisance de la taille de la base.

## Conclusion

Les deux méthodes précédentes sont très intéressantes, mais leur utilisation est compliquée et longue. Pour la première méthode, il faut bien sûr atteindre la convergence, ce qui nécessite l'utilisation de bases très étendues. Quant à la méthode de calibration, on doit utiliser un niveau de calcul qui fournisse un écart constant et avoir aussi des structures expérimentales fiables. Ces méthodes de détermination directe de structures restent donc assez difficiles à utiliser.

Il est souvent plus fiable d'utiliser un champ de force anharmonique pour déterminer une structure fiable, car on peut obtenir des constantes cubiques avec une bonne précision sans avoir recours à des méthodes et des bases trop importantes.

## III) Détermination *ab initio* du champ de force

Le développement des techniques *ab initio* a permis de développer les calculs théoriques des champs de force harmonique et anharmonique qui fournissent des résultats fiables. La précision de ces champs de force permet de donner des fréquences de vibration à quelques  $\text{cm}^{-1}$  près, et les constantes spectroscopiques avec une précision meilleure que 10%. Une application très intéressante des champs de force est la détermination de structures à l'équilibre. Cette méthode d'abord appliquée par Mills [72Mil] a ensuite été utilisée intensivement par Botschwina et coll. [91Bot].

Souvent il est nécessaire de recalibrer les champ de force *ab initio* à l'aide de données expérimentales. Le principe est de corriger les constantes de force *ab initio* en comparant certains paramètres spectroscopiques déduits du champ de force *ab initio* avec ceux obtenus expérimentalement. Cette méthode a été proposée par Pulay et al. [83Pul]. Nous ne développerons pas ici cette technique, car nous n'avons pas eu à l'utiliser dans le cas du trifluorosilane

### 1) Précision du champ de force

La précision d'un champ de force *ab initio* dépend du niveau de calcul. Mais d'autres paramètres peuvent aussi avoir une influence sur la qualité. On s'intéressera donc au choix de la structure de référence avec laquelle le champ de force est calculé, et aussi au système de coordonnées choisi pour les constantes de force.

### **a) Les systèmes de coordonnées**

Le choix d'un système de coordonnées pour le champ de force ainsi que le passage de l'un à l'autre est un exercice délicat. Il n'y a pas de système unique de coordonnées. Les trois les plus utilisés sont les suivants : cartésiennes, internes et normales, ils ont chacun leurs avantages. Les coordonnées cartésiennes et internes ont l'avantage de fournir un champ de force qui ne dépend pas de la masse et qui est ainsi isotopiquement invariant, ce qui n'est pas le cas des coordonnées normales. Les coordonnées internes assurent une convergence rapide du développement en série du potentiel. Enfin ces coordonnées internes ont une signification physique relativement claire car elles définissent les variations des longueurs et angles de liaison autour de l'équilibre. Mais c'est avec les coordonnées normales que les modes de vibration sont le plus simplement définis, et c'est avec ce système de coordonnées que sont exprimés les paramètres spectroscopiques.

Il est possible de passer d'un système à l'autre à l'aide de relations tensorielles non linéaires que l'on peut trouver dans [82Pap], mais le problème réside justement dans la non-linéarité de ces équations. Ainsi si on ne veut pas de perte de précision lors du changement de coordonnées, il est mieux d'avoir le champ de force à un ordre supérieur. Par exemple pour garder de bonnes constantes cubiques lors de la transformation, il est préférable de disposer des constantes quartiques.

### **b) La géométrie de référence**

La solution naturelle consiste à prendre la géométrie de la molécule au même niveau de calcul que celui employé pour le champ de force. La forme du développement du champ de force est la plus simple, car la dérivée première du potentiel est nulle. Il faut un niveau de calcul qui soit suffisant afin d'être proche de la structure à l'équilibre, dans le cas contraire les constantes de force peuvent être biaisées. L'alternative est de prendre une géométrie expérimentale plus précise lorsqu'elle existe ou une géométrie issue d'un niveau de calcul plus élevé. Ceci améliore la précision des constantes de force, mais cela n'est pas sans conséquences, puisque des termes supplémentaires apparaissent dans le développement, qui sont dûs au décalage de la géométrie de référence. L'estimation de ces termes est assez délicate, des approximations sont nécessaires pour se ramener au développement habituel qui permet le calcul des constantes spectroscopiques.

Ainsi la solution la plus employée reste l'évaluation du champ de force avec une géométrie issue des mêmes méthodes et bases.

### c) Dérivées analytiques ou techniques numériques

Les dérivées analytiques de l'énergie pour les ordres 2, 3 et 4 existent dans les différents programmes pour la méthode Hartree-Fock. Mais pour les méthodes plus sophistiquées, elles n'utilisent que les dérivées secondes pour la méthode MP2 dans le programme Gaussian94, et pour les méthodes Clusters Couplés dans ACES2. Une étude sur un calcul *ab initio* des constantes de force pour la molécule HCN au niveau HF avec une base double-zéta [98Csá], a montré que les constantes de force obtenues à partir des dérivées analytiques à l'ordre un, deux et trois avaient des différences bien inférieures au pour cent. L'ordre des dérivées analytiques intervient essentiellement sur les temps de calculs, et n'est pas un facteur d'erreur significatif. Quand les dérivées ne sont pas calculées analytiquement, il faut les évaluer numériquement. Cela présente plusieurs désavantages essentiellement "informatiques" : Les temps de calculs sont plus longs et il est nécessaire d'avoir des espaces disques beaucoup plus importants pour "stocker" les intégrales électroniques.

## 2) Application

Nous allons aborder les deux applications que nous avons utilisées : la détermination d'une structure semi-empirique, et l'utilisation de paramètres calculés *ab initio* dans les ajustements des données expérimentales.

### a) Structure combinée expérimentale et *ab initio*

La spectroscopie de rotation est la méthode expérimentale qui fournit les constantes de rotation les plus précises. Avec les calculs *ab initio*, les constantes de force anharmoniques obtenues sont plus précises que les géométries et champ de force harmonique. En effet, dans les termes d'ordre élevé du potentiel, la contribution de l'interaction noyau-noyau ( $V_{nn}$ ) devient plus importante que le terme électronique. Ce terme  $V_{nn}$  (eq. 2) peut être calculé exactement si l'on connaît la position des noyaux, donc sa valeur est plus précise avec une bonne géométrie que la partie électronique  $E_e$  qui n'est que plus ou moins bien estimée selon le niveau de calcul. Les termes d'interaction rovibration avec un bon niveau de calcul sont obtenus avec des erreurs inférieures à dix pour cent. Ainsi l'utilisation combinée des données expérimentales et *ab initio* fournit des moments d'inertie à l'équilibre plus fiable que ne le donnerait chaque technique séparément.

## **b) Utilisation des paramètres *ab initio***

Les constantes de force obtenues par des méthodes *ab initio* nous permettent aussi de calculer des paramètres qui n'ont pu être déterminés expérimentalement. On peut citer par exemple les constantes de distorsion  $D_K$  et  $H_K$  de l'état fondamental d'une toupie symétrique. Habituellement dans les ajustements des constantes expérimentales les paramètres sont fixés à zéro, ou dans l'étude d'états excités aux valeurs des paramètres dans l'état fondamental de vibration.

La meilleure solution est de les contraindre à leurs valeurs *ab initio*, qui sont plus fiables. La valeur à laquelle est fixée un paramètre non déterminable n'est pas sans conséquence sur la valeur finale des autres paramètres, car lors d'un ajustement par moindres carrés des paramètres, les corrélations entre les paramètres ne sont jamais nulles. Il est donc important de fixer les paramètres à une valeur aussi proche que possible de la réalité.



2 ème Partie :

Résultats



# Détermination de structures géométriques à l'équilibre par les méthodes *ab initio*

## I) Etude de la liaison C-F

Les structures des molécules contenant des atomes de fluor sont très difficiles à obtenir expérimentalement, car il n'y a qu'un seul isotope stable. Les méthodes *ab initio* se présentent donc comme une solution intéressante. Mais très peu d'études précises existent au sujet de cette liaison, car l'atome de fluor est très électronégatif, et nécessite donc l'utilisation de bases très étendues.

La molécule de OCHF a été étudiée de nombreuses fois aussi bien expérimentalement que théoriquement, mais les structures obtenues sont assez peu précises. Nous avons recalculé une structure à l'équilibre *ab initio* à l'aide de méthodes prenant en compte la corrélation électronique (CCSD(T) et MP2) et avec des bases étendues. Afin d'estimer la précision des résultats, nous avons comparé les moments d'inertie *ab initio* avec ceux calculés à partir des données expérimentales. Puis nous avons appliqué cette méthode pour recalculer des structures plus précises des molécules suivantes : CF<sub>2</sub>, CH<sub>2</sub>F<sub>2</sub>, CHF.

Nous avons montré sur quelques distances et angles de liaison variés que l'effet des fonctions diffuses pouvait être calculé avec une bonne précision au niveau MP2.

Les calculs de structures ont été fait au niveau CCSD(T) avec une base cc-pVQZ à laquelle nous avons ajouté la correction des fonctions diffuses. Ces calculs permettent d'obtenir la liaison C-F avec un écart de -0.0001Å par rapport à des valeurs précises (expérimentales ou calculées), la dispersion étant de 0.0007Å.

## II) Calculs *ab initio* des angles de liaison

Il est possible d'utiliser les angles de liaison calculés *ab initio* comme données complémentaires pour les calculs de structures expérimentales, dans les cas où il n'y a pas assez de moments d'inertie disponibles pour déterminer toutes les distances et angles de liaisons de la molécule. Il est nécessaire pour cela de connaître les précisions des angles calculés.

Il existe peu d'études systématiques sur les angles de liaison avec les méthodes les plus perfectionnées. Nous avons testé les 3 méthodes suivantes : B3LYP, MP2 et CCSD(T) en utilisant les bases de Dunning cc-pVnZ sur un échantillon de 29 molécules (35 angles). Les niveaux de calcul nécessaires peuvent être moins sophistiqués que pour les distances pour obtenir une bonne fiabilité, c'est ce que nous avons voulu vérifier. Nous avons été amené à redéterminer des structures plus précises des deux molécules HNO et H<sub>2</sub>O<sub>2</sub>, car nous avons obtenu des écarts importants par rapport aux valeurs expérimentales disponibles. Nous voulions savoir si ces écarts étaient dus à notre méthode de calcul où à la structure existante, la structure de ces molécules très flexibles étant difficile à obtenir.

Pour comparer les niveaux de calcul, on observe les écarts entre nos calculs et des valeurs expérimentales fiables. Les résultats les plus précis sont obtenus avec la méthode CCSD(T) : la valeur moyenne des écarts est de 0.07° alors qu'elle est de 0.22° avec la méthode MP2. Dans les deux cas on utilise la base cc-pVQZ, et les effets des fonctions diffuses sont estimés au niveau MP2.

Sans la prise en compte des fonctions diffuses, les écarts sont de 0.14° pour la méthode CCSD(T), ceci confirme la nécessité d'utiliser des fonctions diffuses pour les atomes électronégatifs. La méthode B3LYP donne des résultats environ deux fois moins précis que MP2, les écarts étant respectivement de 0.48° et 0.25°.

The Equilibrium C-F Bond Length and The  
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# Equilibrium C–F Bond Length and the Structure of Formyl Fluoride, Difluorocarbene, Monofluoromethylene, and Difluoromethane

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Highly correlated ab initio calculations with large basis sets are reported for formyl fluoride, OCHF; difluorocarbene, CF<sub>2</sub>; monofluoromethylene, CHF, and difluoromethane, CH<sub>2</sub>F<sub>2</sub>. Based on CCSD(T)/cc-pVQZ results (including a correction for the effect of diffuse functions on fluorine and oxygen), equilibrium structures are derived. These structures are compared to experimental results, when available, and to those of similar molecules; and their accuracy is discussed.

## Introduction

The determination of the experimental structure of a fluorine derivative is a difficult problem because there is only one stable isotope for fluorine, making studies of isotopic species impossible. In fact, very few accurate structures of such molecules have been determined so far. Furthermore, in some cases, the derived geometry is obviously inaccurate. The calculation of a reliable ab initio structure is further complicated by the fact that fluorine is a highly electronegative atom which requires very large basis sets and highly correlated methods. However, this problem is now tractable, at least for small molecules. Inconsistencies in the structure of formyl fluoride, O=CHF, prompted us to try to determine an accurate structure for this molecule. During the course of this work, we found it useful to redetermine the structure of a few simple fluorocarbons in order to check the accuracy and the capability of the method used and to extend our knowledge of the C–F bond.

Many studies, both experimental and theoretical, have already been devoted to formyl fluoride because it is a small polyatomic molecule (4 atoms belonging to the first row of the periodic classification) and a fluorine substituted formaldehyde. Particularly, its reactivity has been studied in great detail (see for instance ref 1 and references therein). This prompted several theoretical studies of the potential energy surface.<sup>1–3</sup> These investigations pointed out a great uncertainty in the geometric structure of this molecule. The structure of formyl fluoride has indeed been determined by electron diffraction<sup>4</sup> but the resulting parameters are rather imprecise (for instance there is an uncertainty of 4° for the  $\angle(\text{OCH})$  angle and 0.020 Å for the CH bond length); furthermore this structure is an  $r_g$  structure which is significantly different from the equilibrium structure.

The rotational spectrum of formyl fluoride has been studied in some detail leading to the determination of several effective structures ( $r_o$ ).<sup>5–7</sup> But, again, these structures are inaccurate because they are calculated from the uncorrected ground-state

rotational constants even though vibration–rotation effects are expected to be large for a molecule with such large rotational constants. Furthermore, no isotopic substitution is possible for fluorine and the carbon and hydrogen atoms are close to the *b*-principal axis. In conclusion, the coordinates of F, C, and H are not expected to be accurate. However the high resolution infrared spectra of all fundamental bands of OCHF were recently studied. First, Wong et al.<sup>8</sup> measured the  $\nu_2$  band using a combination of laser Stark and Fourier transform spectroscopies. Later, the same group analyzed the five remaining fundamental bands which were recorded with a Fourier transform spectrometer.<sup>9</sup> Thus, in principle, the equilibrium rotational constants of the parent species are available. But, as the molecule is planar, the three moments of inertia are not independent, and these experiments only give us two independent data points to determine five structural parameters.

However it is now well established that the equilibrium structure of a simple molecule can be accurately determined with high-level coupled cluster methods and large basis sets.<sup>10–15</sup> The goal of the present paper is to determine an ab initio structure for formyl fluoride and to try to estimate its accuracy. Whereas our prime interest was the determination of an accurate structure for formyl fluoride, we also calculated the structure of a few other simple fluorocarbons whose equilibrium structure is not yet firmly established: dicarbene, monofluoromethylene, and difluoromethane.

The transient species dicarbene (or difluoromethylene), CF<sub>2</sub> has been the subject of many studies (see refs 16–21, and references therein) because it is an important intermediate in fluorine chemistry (particularly in the dissociation of fluorocarbons) and it is one of the most stable gas-phase carbenes. Its electronic ground state is  $\tilde{X}(^1A_1)$ . The effective ( $r_o$ ) structure was determined quite early<sup>16</sup> and an accurate average ( $r_z$ ) structure was calculated in 1973.<sup>17</sup> Since that time, accurate ground-state rotational constants have been obtained from millimeterwave spectroscopy<sup>18</sup> and the rotational constants of the three excited fundamental vibrational states have been determined either by high-resolution Fourier transform spec-

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troscopy<sup>19</sup> or by infrared diode laser spectroscopy.<sup>20</sup> Thus, there is enough experimental information available to determine an equilibrium ( $r_e$ ) structure, but, surprisingly, this does not seem to have been done. Many theoretical investigations have been reported for CF<sub>2</sub> (ref 21 and references therein). A paper particularly relevant to our work is that of Cameron et al.<sup>21</sup> where the geometry and harmonic force field have been calculated ab initio using the complete active space SCF method and Dunning's correlation-consistent polarized triple- $\zeta$  cc-pVTZ basis set.

Monofluoromethylene, HCF, has also received much attention from a spectroscopic point of view. But, as it is less stable and less symmetric ( $C_s$  instead of  $C_{2v}$ ) than CF<sub>2</sub>, there is not enough experimental information to determine an equilibrium structure and only an  $r_0$  structure was obtained from the ground state rotational constants of CHF and CDF.<sup>22</sup> This structure, involving the substitution of hydrogen by deuterium, is not expected to be accurate.<sup>23</sup> Many ab initio calculations have been carried out on HCF. One of the most recent reports a CCSD(T)/6-311+G\*\* structure.<sup>24</sup>

Many spectroscopic studies have also been devoted to difluoromethane, CH<sub>2</sub>F<sub>2</sub>. Accurate ground-state rotational constants have been determined by millimeterwave spectroscopy.<sup>25</sup> The microwave spectra of several excited states have been analyzed by Hirota<sup>26</sup> who deduced a cubic force field and an approximate  $r_e$  structure.<sup>27</sup> The infrared spectrum has also been analyzed in great detail, particularly to assign submillimeter emissions.<sup>28</sup> Many ab initio calculations have also been dedicated to CH<sub>2</sub>F<sub>2</sub>. Particularly relevant to this work, a MP2/6-31G\*\* quartic force field was recently calculated.<sup>29</sup> This study showed a rather large discrepancy between the ab initio structure and the experimental  $r_e$  structure of Hirota:<sup>27</sup> 0.0067 Å for the CH bond, 0.0154 Å for the CF bond, and 0.9° for the  $\angle$ (HCH) angle. These deviations are much too large and justify a new study.

### Computational Details

The calculations with all electrons correlated were performed with the ACES II program<sup>30</sup> whereas for the frozen core approximation the Gaussian 94 program<sup>31</sup> was used.

To obtain good accuracy (i.e., about 0.001 Å for bond lengths and 0.2° for angles) it is sufficient to use the coupled-cluster theory with single and double excitations<sup>32</sup> augmented by a perturbational estimate of triple excitation effects: CCSD(T).<sup>33</sup> A higher level of theory in which the triple excitations are included exactly does not bring much gain in accuracy<sup>34</sup> which is fortunate because such a method is computationally demanding. On the other hand, very large basis sets of at least quadruple- $\zeta$  quality are required, particularly in the case of a fluorine compound as was recently shown on methyl fluoride, CH<sub>3</sub>F.<sup>35</sup> The well-known Dunning's correlation-consistent polarized valence basis sets labeled cc-pVnZ (with  $n = D, T, Q$ ) were employed.<sup>36</sup>

The calculations have been carried out with all electrons correlated. In principle, to correctly calculate the core correlation, it is necessary to use a core-valence cc-pCVnZ basis set<sup>37,38</sup> because the valence cc-pVnZ basis sets overestimate the core-correlation effect. This is important only for distances because the effect of core-correlation is almost negligible for angles. Furthermore this effect of core-correlation is almost constant for a given bond and can be corrected, if necessary, if it has already been rigorously calculated on a structurally similar molecule. This is lucky because the calculations are much easier with the cc-pVQZ basis set than with the huge cc-pCVQZ basis

**TABLE 1: Influence of Diffuse Functions on the ab initio Structure: Comparison of the CCSD(T) and MP2 Methods (Distances in Å and Angles in Degrees)<sup>a</sup>**

|                   |                      | CCSD(T) |        |        | MP2    |        |        |
|-------------------|----------------------|---------|--------|--------|--------|--------|--------|
|                   |                      | AUG     | N      | diff.  | AUG    | N      | diff.  |
| CO                | $r(\text{CO})$       | 1.1318  | 1.1314 | 0.0004 | 1.1352 | 1.1346 | 0.0006 |
| HF                | $r(\text{HF})$       | 0.9177  | 0.9162 | 0.0015 | 0.9186 | 0.9174 | 0.0012 |
| NH <sub>3</sub>   | $r(\text{NH})$       | 1.0128  | 1.0124 | 0.0004 | 1.0101 | 1.0098 | 0.0003 |
| H <sub>2</sub> O  | $r(\text{OH})$       | 0.9589  | 0.9579 | 0.0011 | 0.9588 | 0.9577 | 0.0011 |
| CH <sub>3</sub> F | $r(\text{CF})$       | 1.3855  | 1.3824 | 0.0031 | 1.3854 | 1.3820 | 0.0034 |
| CHF               | $r(\text{CF})$       | 1.3067  | 1.3052 | 0.0015 | 1.3062 | 1.3042 | 0.0020 |
| NH <sub>3</sub>   | $\angle(\text{HNN})$ | 106.52  | 106.18 | 0.34   | 106.87 | 106.47 | 0.40   |
| H <sub>2</sub> O  | $\angle(\text{HOH})$ | 104.36  | 104.12 | 0.24   | 104.26 | 104.02 | 0.24   |
| CH <sub>3</sub> F | $\angle(\text{HCH})$ | 110.22  | 110.03 | 0.19   | 110.22 | 110.03 | 0.19   |
| CHF               | $\angle(\text{CHF})$ | 102.33  | 102.42 | -0.09  | 102.24 | 102.32 | -0.09  |
| FNO               | $\angle(\text{FNO})$ | 109.86  | 110.16 | -0.30  | 110.15 | 110.43 | -0.28  |

<sup>a</sup> The cc-pVQZ basis set was used: AUG = aug-cc-pVQZ; N = cc-pVQZ.

**TABLE 2: Computed Equilibrium Geometry of OCHF (Distances in Å and Angles in Degrees)<sup>a</sup>**

|                         | $r(\text{C=O})$ | $r(\text{C-H})$ | $r(\text{C-F})$ | $\angle(\text{OCH})$ | $\angle(\text{OCF})$ |
|-------------------------|-----------------|-----------------|-----------------|----------------------|----------------------|
| CCSD(T)/cc-pVDZ (ae)    | 1.1901          | 1.1072          | 1.3486          | 127.562              | 123.116              |
| CCSD(T)/cc-pVTZ (ae)    | 1.1806          | 1.0865          | 1.3372          | 127.476              | 122.972              |
| CCSD(T)/cc-pVQZ (ae)    | 1.1779          | 1.0890          | 1.3368          | 127.605              | 122.823              |
| MP2/cc-pVDZ (ae)        | 1.1903          | 1.1042          | 1.3494          | 127.800              | 123.228              |
| MP2/pVDZ (ae)+aug(F,O)  | 1.1931          | 1.1015          | 1.3706          | 128.578              | 122.763              |
| MP2/cc-pVTZ (ae)        | 1.1812          | 1.0848          | 1.3393          | 127.720              | 123.087              |
| MP2/pVTZ (ae)+aug(F,O)  | 1.1815          | 1.0867          | 1.3433          | 128.037              | 122.849              |
| MP2/cc-pVQZ (ae)        | 1.1789          | 1.0867          | 1.3392          | 127.846              | 122.943              |
| MP2/cc-pVQZ (fc)        | 1.1811          | 1.0891          | 1.3425          | 127.926              | 122.920              |
| MP2/pVQZ (fc)+aug(F,O)  | 1.1816          | 1.0892          | 1.3445          | 128.049              | 122.815              |
| best estimate, see text | 1.1773          | 1.0900          | 1.3385          | 127.719              | 122.710              |

<sup>a</sup> ae = all electrons correlated, fc = frozen core approximation.

set. Furthermore, the cc-pVQZ basis set with all electrons correlated gives results which are closer to the equilibrium values than does the frozen core approximation.<sup>12,34</sup> Finally, the overestimation of the core-correlation is small and it is important to point out that the CCSD(T)/cc-pVQZ method with all electrons correlated gives bond lengths between first row atoms that lie within 0.002 Å of experimental values, the error being almost systematic for a given bond.<sup>12,34</sup>

As the molecules investigated contain highly electronegative atoms, F and O, the aug-cc-pVnZ basis sets on F and O were also used.<sup>39</sup> The combination of an aug-cc-pVnZ basis set on F and of a cc-pVnZ basis set on the other atoms is denoted as: cc-pVnZ + aug(F). To estimate the correction due to the diffuse functions, in most cases (i.e., when single reference methods are adequate) it is enough to use the second-order Møller–Plesset perturbation theory (MP2).<sup>40</sup> This significantly reduces the complexity (time and memory) of the calculations whereas it gives a correction nearly identical to the CCSD(T) method. Table 1 shows the results for a few molecules for which the calculations were made with both the CCSD(T) and MP2 methods. It appears that the correction due to diffuse functions can be accurately calculated at the MP2 level for bond lengths as well as bond angles. The quadruple- $\zeta$  basis set results alone are given because the aug-cc-pVTZ basis set is biased toward the diffuse functions and the description of long-distance effects whereas the problem disappears with the aug-cc-pVQZ basis set.<sup>41</sup>

### Results and Discussion

**Formyl Fluoride. Results.** The results of the ab initio calculations are gathered in Table 2. Improvement of the basis set often leads to a decrease in the computed bond lengths. This

## Equilibrium Bond Lengths of C–F Compounds

J. Phys. Chem. A C

trend is observed for the C=O and C–F bonds which are shortened by 0.0122 and 0.0118 Å, respectively (going from  $n = D$  to  $n = Q$ ). The situation for the C–H bond is different: going from  $n = D$  to  $n = T$ , there is indeed a shortening by 0.0207 Å but, going from  $n = T$  to  $n = Q$  causes a lengthening by 0.0025 Å. The variation of the  $\angle(\text{OCH})$  angle is erratic, paralleling the variation of the CH bond length. This angle only decreases by  $0.09^\circ$  from D to T but increases by  $0.13^\circ$  from T to Q. But taking into account the correction due to the diffuse functions allows us to obtain a monotonic variation. An extrapolation to infinite basis size was made using the following empirical exponential function

$$\theta(n) = \theta_\infty + be^{-cn} \quad (1)$$

where  $n$  is an index associated with each basis set,  $2 = \text{DZ}$ ,  $3 = \text{TZ}$ ,  $4 = \text{QZ}$ . The parameters  $\theta_\infty$ ,  $b$ , and  $c$  are determined from a nonlinear least-squares fit. The fit gives  $\angle(\text{OCH}) = 127.719^\circ$ , to be compared with the CCSD(T)/cc-pVQZ+aug-(O,F) value,  $127.728^\circ$ . The difference is almost negligible, hence the proposed best estimate:  $127.72^\circ$ . Basis set enlargements cause a monotonic decrease of the  $\angle(\text{OCF})$  angle. Going from T to Q, there is still a change of  $0.15^\circ$  indicating that the equilibrium  $\angle(\text{OCF})$  angle is probably slightly smaller than the cc-pVQZ value,  $122.823^\circ$ . If the effect of the diffuse functions on O and F is taken into account, the value is  $122.718^\circ$ . This is probably near the equilibrium value but it is difficult to estimate the accuracy. This situation is paradoxical because there is a large documented evidence which shows that ab initio angles are quite close to the equilibrium values. Thus, in principle, no correction is necessary. But, in the case of OCHF, it is obvious that the basis set limit is not fully attained. However, when the effect of diffuse functions is taken into account, the variation of  $\angle(\text{OCF})$  is no longer monotonic with basis set enlargement. On the other hand, the variation of the  $\angle(\text{HCF})$  angle is monotonic (taking into account the effect of diffuse functions) and an extrapolation to infinite basis size gives  $109.57^\circ$ . Thus, we find  $\angle(\text{OCF}) = 122.71^\circ$ . This value is very close to the CCSD(T)/cc-pVQZ+aug-(O,F) value but the extrapolation is purely empirical and there is no assurance that it will give the exact solution. If the difference between the extrapolated value and the cc-pVQZ+aug-(O,F) value is used to estimate the accuracy of the angles, it seems to be better than  $0.1^\circ$ . If we also take into account the small effect of the core correlation (which was calculated at the MP2/cc-pVQZ level (Table 2), the final accuracy is still better than  $0.2^\circ$ .

At the CCSD(T)/cc-pVQZ level (all electrons correlated), the discrepancy from experimental bond lengths is only 0.0011 Å on average although the basis set limit is not reached and the core correlation is not properly taken into account.<sup>34</sup> It is still possible to improve the accuracy of the calculated distances by estimating the possible remaining errors with the help of structurally similar molecules whose equilibrium structures are accurately known. It is enough to calculate the structure of these molecules at the same level of theory. It is indeed well established that the error ( $\delta r = r[\text{exp.}] - r[\text{CCSD(T)/cc-pVnZ}]$  with  $n = T, Q$ ) is almost constant for a given bond<sup>15</sup> and can thus be used as an offset to correct the ab initio values. The C–F bond length is however a conspicuous exception to this rule, at least at first sight. Table 3 reports the equilibrium and ab initio CCSD(T)/cc-pVTZ bond lengths for a few molecules whose structures are accurately known. If methyl fluoride were not in the table, the offset would indeed be almost constant. Using the larger cc-pVQZ basis set reduces the discrepancy only slightly. But, the abnormal behavior of CH<sub>3</sub>F may be rational-

TABLE 3: Comparison of the Experimental and ab initio  $r(\text{C–F})$  Bond Lengths (in Å)

| molecule          | exp.   | ref       | CCSD(T)/cc-pVTZ |         | CCSD(T)/cc-pVQZ |         |
|-------------------|--------|-----------|-----------------|---------|-----------------|---------|
|                   |        |           | calc.           | e. – c. | calc.           | e. – c. |
| CH <sub>3</sub> F | 1.3826 | 35        | 1.3816          | 0.0010  | 1.3824          | 0.0002  |
| CHF <sub>3</sub>  | 1.3284 | 52        | 1.3336          | –0.0052 |                 |         |
| HC≡CF             | 1.2768 | 53        | 1.2818          | –0.0050 | 1.2791          | –0.0023 |
| FC≡N              | 1.2641 | 54        | 1.2701          | –0.0060 | 1.2669          | –0.0028 |
| FCO <sup>+</sup>  | 1.2014 | 55        | 1.2058          | –0.0044 |                 |         |
| FCH <sub>2</sub>  | 1.3050 | 22        | 1.3107          | –0.0057 |                 |         |
| FC≡CF             | 1.2835 | 56        | 1.2886          | –0.0051 | 1.2859          | –0.0024 |
| CF <sub>4</sub>   | 1.3151 | 57        | 1.3192          | –0.0041 |                 |         |
| CF <sub>2</sub>   | 1.2975 | this work | 1.3024          | –0.0050 |                 |         |
| median            |        |           |                 | –0.0050 |                 | –0.0023 |
| mean              |        |           |                 | –0.0044 |                 | –0.0018 |
| $\sigma^a$        |        |           |                 | 0.0023  |                 | 0.0014  |

<sup>a</sup> All calculations were made with the frozen core approximation. <sup>b</sup>  $r_0$  value. <sup>c</sup> Standard deviation.

TABLE 4: Comparison of the Experimental and ab initio CCSD(T)/cc-pVQZ<sup>a</sup>  $r(\text{C–F})$  Bond Lengths (in Å) with the Effect of the Diffuse Functions on F Taken into Account

|                                | exp.   | ref. | calc.  | e. – c. <sup>b</sup> | aug. corr. <sup>c</sup> | e. – c. <sup>d</sup> |
|--------------------------------|--------|------|--------|----------------------|-------------------------|----------------------|
| HC≡CF                          | 1.2768 | 53   | 1.2762 | 0.0006               | 0.0010                  | –0.0004              |
| FC≡N                           | 1.2641 | 54   | 1.2639 | 0.0002               | 0.0006                  | –0.0004              |
| FC≡CF                          | 1.2835 | 56   | 1.2831 | 0.0004               | 0.0005                  | –0.0001              |
| CH <sub>3</sub> F              | 1.3826 | 35   | 1.3792 | 0.0034               | 0.0031                  | 0.0003               |
| HCF                            | 1.3062 | e    | 1.3052 | 0.0010               | 0.0011                  | –0.0001              |
| CF <sub>2</sub>                | 1.2975 | e    | 1.2963 | 0.0011               | 0.0010                  | 0.0002               |
| CH <sub>2</sub> F <sub>2</sub> | 1.3529 | e    | 1.3511 | 0.0018               | 0.0019                  | –0.0001              |
| OCHF                           | 1.3385 | e    | 1.3368 | 0.0017               | 0.0020                  | –0.0003              |
| median                         |        |      |        | 0.0011               |                         | –0.0001              |
| mean                           |        |      |        | 0.0013               |                         | –0.0001              |
| range                          |        |      |        | 0.0032               |                         | 0.0007               |
| $\sigma$                       |        |      |        | 0.0010               |                         | 0.0003               |

<sup>a</sup> All electrons correlated. <sup>b</sup> residuals: Exp. – CCSD(T)/cc-pVQZ. <sup>c</sup> Correction due to the diffuse functions: aug-cc-pVQZ – cc-pVQZ at the MP2 level. <sup>d</sup> Residuals with the effect of the diffuse functions taken into account. <sup>e</sup> This work.

ized by using an aug-cc-pVQZ basis set on the highly electronegative F atom (and the standard cc-pVQZ basis set on the remaining atoms). It is observed that the effect of diffuse functions on the C–F bond length is about 0.001 Å, at the quadruple- $\zeta$  level for most of the molecules of Table 3 except for CH<sub>3</sub>F where it is three times as large: 0.0031 Å. When this effect is properly taken into account, the offset becomes extremely small:  $-0.0001$  Å (mean value) and almost constant, the range of variation of residuals being four times smaller, see Table 4. This is particularly important for OCHF because the effect of diffuse functions on the C–F bond is 0.002 Å, i.e., similar to that of CH<sub>3</sub>F. Neglecting this correction would lead to a systematic error of about 0.002 Å. This negligible offset is an interesting example of compensation of errors. At the quadruple- $\zeta$  level, the basis set convergence is not yet fully achieved, the overestimation of the C–F bond length being slightly less than 0.001 Å. We checked on CH<sub>3</sub>F and HC≡CF that correlating all the electrons with the valence cc-pVQZ basis set overestimates the (negative) core-correlation effect by 0.001 Å. Thus, these two errors nearly compensate for each other. This is not completely satisfactory but it is no more empirical than the extrapolation to infinite basis size which is not always suitable.

The effect of diffuse functions on the C=O bond is not negligible either but much smaller than in formaldehyde: 0.0005 Å instead of 0.0012 Å. The offset values for the C=O and C–H bonds are estimated from formaldehyde and are given in Table

TABLE 5: Determination of the Offsets for the ab initio Structure (Distances in Å and Angles in Degrees)

| molecule          | ref. | parameter            | exp.    | ab initio <sup>a</sup> | aug corr. <sup>b</sup> | total corr. <sup>c</sup> |
|-------------------|------|----------------------|---------|------------------------|------------------------|--------------------------|
| H <sub>2</sub> CO | 58   | $r(\text{C=O})$      | 1.2030  | 1.2042                 | 0.0012                 | -0.0024                  |
|                   |      | $r(\text{C-H})$      | 1.1006  | 1.0996                 | -0.0002                | 0.0013                   |
|                   |      | $\angle(\text{OCH})$ | 121.648 | 121.778                | -0.092                 | -0.038                   |
| CO <sub>2</sub>   | 62   | $r(\text{C=O})$      | 1.1600  | 1.1601                 | 0.0006                 | -0.0007                  |
| CO                | 63   | $r(\text{C=O})$      | 1.1282  | 1.1289                 | 0.0004                 | -0.0011                  |
| CH <sub>3</sub> F | 35   | $r(\text{C-H})$      | 1.0872  | 1.0863                 | -0.0001                | 0.0010                   |

<sup>a</sup> CCSD(T)/cc-pVQZ, all electrons correlated. <sup>b</sup> Correction due to the diffuse functions: aug-cc-pVQZ - cc-pVQZ at the MP2 level. <sup>c</sup> Total correction: exp. - (ab initio + aug. corr.) = offset.

5. Correcting the CCSD(T)/cc-pVQZ+aug(F, O) value gives  $r(\text{C=O})$  equal to 1.1760 Å. However, if the offsets are derived from either CO or from CO<sub>2</sub>, slightly different results are obtained, the maximal difference however being smaller than 0.002 Å and the derived distance always being smaller than 1.178 Å. It may be argued that this small discrepancy is not surprising because bonding is extremely different in these three molecules and this indicates that the method used is only approximate for the C=O bond. However, Botschwina<sup>42</sup> performed a CCSD(T)/cc-pCVQZ calculation with all electrons correlated and proposes 1.2043 Å for the equilibrium value of  $r(\text{C=O})$  instead of our value of 1.20296 Å.<sup>58</sup> If we adopt the value of Botschwina, the discrepancy disappears and gives our preferred value for  $r(\text{C=O})$  in OCHF, 1.1773 Å, this last solution being in much better agreement with the experimental equilibrium moments of inertia, see below. This slight discrepancy would justify a systematic study of the C=O bond.

**Discussion.** To estimate the accuracy of the results, the moments of inertia were calculated from the ab initio structure with offset correction (last line of Table 2) and compared to the experimental equilibrium values. The ground-state rotational constants and the experimental rotation-vibration interaction constants  $\alpha_i^g$  ( $g = a, b, c$  and  $i = 1, \dots, 6$ ) are given in Table 6. The experimental rotational constants were also corrected for a small centrifugal distortion contribution<sup>43</sup> and for electronic contribution. This correction is due to the fact that the distribution of electrons contributes to the moments of inertia because an atom in a molecule is not a mass point and the center of mass of the electrons in an atom generally does not coincide with the position of the nucleus. The electronic contribution is related to the molecular  $g$ -factor by the relation<sup>43</sup>

$$B_{\text{corr}}^{\alpha} = \frac{B_{\text{exp}}^{\alpha}}{1 + \frac{m}{M_p} g_{\alpha\alpha}} \quad (2)$$

where  $g_{\alpha\alpha}$  is expressed in units of the nuclear magneton,  $m$  is the electron mass,  $M_p$  the proton mass, and  $\alpha = a, b, c$ . The  $g$ -factor has been obtained experimentally from the analysis of the Zeeman effect on the rotational spectrum.<sup>44</sup> The comparison of experimental and calculated moments of inertia shows that the ab initio structure is rather accurate. Furthermore, the equilibrium experimental inertial defect,  $\Delta_e$  is equal to  $-0.0043$  (2)  $\text{uÅ}^2$  although much smaller than the ground-state inertial defect,  $\Delta_0$  which equals  $+0.09215 \text{ uÅ}^2$ , and  $\Delta_e$  is significantly different from zero indicating that there is still a small systematic error in the experimental vibration-rotation interaction constants. This is not surprising because it is well established that, for a polyatomic molecule, it is extremely difficult to obtain reliable rotational constants from experimental data alone.<sup>45</sup> This is particularly true for OCHF where several excited vibrational states interact. For instance, the sextic constants of the  $\nu_1$  state

are very different from the ground state constants, indicating the possible existence of an interaction which is not taken into account. Nevertheless, it might be worth noting that a slightly longer C=O or C-F bond would give better agreement with experimental rotational constants.

There is another way to check the accuracy of some parameters. There is an empirical correlation between the  $r_e$ -(C-H) distance and the isolated C-H bond stretching frequencies.<sup>23,46</sup> Using a value for  $\nu(\text{C-H})$  of  $2981.2408 \text{ cm}^{-1}$ , we obtain an  $r_e(\text{C-H})$  value of  $1.087 \text{ Å}$ .<sup>9</sup> This value is slightly lower than our derived equilibrium value but, as said above, it is not obvious that the  $\nu_1$  state is well isolated. Furthermore, ab initio calculations using very different basis sets (from 6-31G\* to cc-pVQZ) and different methods (MP2 and CCSD(T)) all give the same value after offset correction, attesting the accuracy of the C-H bond length.

The  $r_z(\text{C-F})$  value has been determined by Huisman et al.<sup>4</sup> by combining electron diffraction and rotational spectroscopy results. This  $r_z$  value can be converted into an approximate  $r_e$  value either using an empirical correlation<sup>47</sup> or the well-known formula of Kuchitsu<sup>48</sup>

$$r_z = r_e + \frac{3}{2}au^2 - K \quad (3)$$

In this formula  $u^2$  is the mean square amplitude for the bond concerned, and  $K$  the mean square perpendicular amplitude correction, both calculated from the harmonic force field, while  $a$  is the Morse anharmonicity parameter. This  $a$  parameter is generally assumed to be equal to the corresponding parameter for the diatomic molecule. The value of  $a$  for the C-F bond is  $2.357 \text{ Å}^{-1}$ .<sup>49</sup> Both methods give  $r_e(\text{C-F}) = 1.339$  (2) Å in extremely good agreement with our value. But it could be quite by chance because, on the other hand, for the C=O bond, using eq 3, we should have  $r_z - r_e \approx 0.003 \text{ Å}$  whereas we find  $0.009 \text{ Å}$ .<sup>50</sup> However, calculations with smaller basis sets and the MP2 method give results which are fully consistent with our CCSD(T)/cc-pVQZ calculation.<sup>50</sup> Furthermore, if we compare in Table 7 the variation of the  $r(\text{C=O})$  bond length in the two series  $\text{OCH}_n\text{X}_{2-n}$  (with  $\text{X} = \text{F}, \text{Cl}$  and  $n = 0, 1, 2$ ), we see that  $r(\text{C=O})$  in OCHF should be significantly lower than  $1.182 \text{ Å}$ , confirming the validity of our calculated structure.

In conclusion our calculated structure should be fairly reliable although estimating its accuracy is extremely difficult.

**Diffuorocarbene and Monofluoromethylene.** Another way to strengthen the reliability of our method is to apply it to other molecules. CF<sub>2</sub> is very favorable because it is possible to obtain an accurate  $r_e$  structure using only experimental information. The equilibrium rotational constants were determined using the rotation-vibration interaction constants listed in Table 8. The equilibrium inertial defect,  $\Delta_e$ , is only  $-0.0048 \text{ uÅ}^2$  whereas the corresponding ground-state value,  $\Delta_0$ , is  $0.1032 \text{ uÅ}^2$ . This relatively small value for  $\Delta_e$  indicates that the equilibrium rotational constants are not far from their true value as was the case for OCHF. Using  $A_e$  and  $B_e$  to calculate the structure, we find  $r_e(\text{C-F}) = 1.2975 \text{ Å}$  and  $\angle_e(\text{FCF})$  of  $104.81^\circ$ . It is difficult to estimate the accuracy of this structure precisely because the errors due to the method (neglecting anharmonic resonances, neglecting magnetic correction, approximation of the Coriolis resonances, ...) are usually at least 1 order of magnitude larger than the statistical standard deviations of the rotational constants. However, it is possible to assess the accuracy of this structure indirectly because a highly reliable  $r_z$  structure is available.<sup>17</sup> For the bond angle, we should have  $\angle_e(\text{FCF}) \approx \angle_z(\text{FCF}) = 104.78(2)^\circ$ . For the bond distance, it is necessary to use eq 3 to

1 equilibrium

Equilibrium Bond Lengths of C–F Compounds

J. Phys. Chem. A E

TABLE 6: Experimental Rotational Constants and Vibrational Corrections for Formyl Fluoride (in cm<sup>-1</sup>)

| <i>g</i>                                     | <i>A</i>          | <i>B</i>          | <i>C</i>          | ref |
|----------------------------------------------|-------------------|-------------------|-------------------|-----|
| <i>B<sub>x</sub></i> ( <i>ν</i> = 0)         | 3.040 655 50(73)  | 0.392 280 004(88) | 0.346 795 677(79) | 8   |
| <i>α</i> <sub>1</sub>                        | 0.016 954 6(59)   | 0.000 076 9(13)   | 0.000 343 88(76)  | 9   |
| <i>α</i> <sub>2</sub>                        | 0.013 109 6(20)   | 0.001 462 86(44)  | 0.001 257 01(46)  | 8   |
| <i>α</i> <sub>3</sub>                        | 0.012 163 2(25)   | −0.001 671 46(56) | 0.000 311 09(44)  | 9   |
| <i>α</i> <sub>4</sub>                        | 0.008 084(39)     | 0.002 957 78(48)  | 0.002 471 29(13)  | 9   |
| <i>α</i> <sub>5</sub>                        | −0.023 065 23(97) | 0.000 441 94(14)  | 0.001 037 10(13)  | 9   |
| <i>α</i> <sub>6</sub>                        | 0.008 830(39)     | 0.001 123 12(53)  | −0.000 115 91(45) | 9   |
| magn. <sup>a</sup>                           | −0.000 014 1      | −0.000 002 6      | −0.000 001 2      |     |
| cd <sup>b</sup>                              | −0.000 001 7      | −0.000 005 5      | 0.000 006 3       |     |
| <i>B<sub>x</sub></i> ( <i>ν</i> = <i>e</i> ) | 3.059 396(28)     | 0.394 486 7(12)   | 0.349 461 3(11)   |     |
| <i>I<sub>e</sub></i> (exp) <sup>c</sup>      | 5.510 117(50)     | 42.733 08(13)     | 48.238 90(14)     |     |
| <i>I<sub>e</sub></i> (calc) <sup>c</sup>     | 5.4958            | 42.7203           | 48.2161           |     |
| <i>e</i> − <i>c</i> <sup>c</sup>             | 0.0143            | 0.0128            | 0.0228            |     |
| <i>e</i> − <i>c</i> (%)                      | 0.26%             | 0.03%             | 0.05%             |     |

<sup>a</sup> Magnetic correction, see text. <sup>b</sup> Centrifugal distortion correction, see text. <sup>c</sup> In uÅ<sup>2</sup>.

TABLE 7: Structures of OCHF and Related Molecules (Distances in Å and Angles in Degrees)

| molecule        | O=CH <sub>2</sub>    | O=CHF                |                      |                      | O=CF <sub>2</sub>    | O=CHCl               | O=CCl <sub>2</sub>   |
|-----------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| reference       | 58                   | 7                    | 4                    | this work            | 59                   | 60                   | 61                   |
| structure       | <i>r<sub>e</sub></i> | <i>r<sub>0</sub></i> | <i>r<sub>z</sub></i> | <i>r<sub>e</sub></i> | <i>r<sub>e</sub></i> | <i>r<sub>e</sub></i> | <i>r<sub>e</sub></i> |
| <i>r</i> (C=O)  | 1.202 96             | 1.181 (5)            | 1.186 (1)            | 1.1773               | 1.170 (2)            | 1.182                | 1.176 (2)            |
| <i>r</i> (C–H)  | 1.100 64             | 1.095 (8)            | 1.096 (4)            | 1.0900               |                      | 1.090                |                      |
| <i>r</i> (C–F)  |                      | 1.338 (5)            | 1.345 (1)            | 1.3385               | 1.311 (2)            |                      |                      |
| <i>r</i> (C–Cl) |                      |                      |                      |                      |                      | 1.765                | 1.738 (2)            |
| ∠(OCH)          | 121.648              | 127.3 (30)           | 130 (1)              | 127.72               |                      | 126.49               |                      |
| ∠(OCF)          |                      | 122.8 (5)            | 122.3 (1)            | 122.71               | 126.2 (4)            |                      |                      |
| ∠(OCCl)         |                      |                      |                      |                      |                      | 123.07               | 124.11(12)           |

TABLE 8: Experimental Rotational Constants and Vibrational Corrections for CF<sub>2</sub> (in MHz)

| <i>g</i>                                    | <i>A</i>         | <i>B</i>         | <i>C</i>         | ref. |
|---------------------------------------------|------------------|------------------|------------------|------|
| <i>B<sub>x</sub></i> ( <i>ν</i> = 0)        | 88 355.0879 (61) | 12 507.7303 (12) | 10 932.2216 (12) | 18   |
| <i>α</i> <sub>1</sub>                       | −278.28 (19)     | 67.926 (90)      | 58.443 (33)      | 19   |
| <i>α</i> <sub>2</sub>                       | −787.30 (24)     | 32.134 (18)      | 48.113 (18)      | 20   |
| <i>α</i> <sub>3</sub>                       | 1265.76 (16)     | 53.344 (90)      | 65.420 (15)      | 19   |
| <i>A<sub>e</sub></i>                        | 88 455.18 (35)   | 12 584.43 (13)   | 11 018.209 (40)  |      |
| <i>I<sub>e</sub></i> (exp.) <sup>a</sup>    | 5.713 391 (22)   | 40.159 06 (41)   | 45.867 62 (17)   |      |
| <i>I<sub>e</sub></i> (calc.) <sup>a,b</sup> | 5.705 52         | 40.1668          | 45.8723          |      |
| <i>I</i> ( <i>e</i> − <i>c</i> ) %          | 0.14             | −0.02            | −0.01            |      |

<sup>a</sup> In μÅ<sup>2</sup>. <sup>b</sup> Calculated with the best theoretical estimate from Table 9.

TABLE 9: Computed Equilibrium Geometry of CF<sub>2</sub> (Distances in Å and Angles in Degrees)<sup>a</sup>

|                         | <i>r</i> (C–F) | ∠(FCF)  |
|-------------------------|----------------|---------|
| CCSD(T)/cc-pVDZ (ae)    | 1.3140         | 104.617 |
| CCSD(T)/cc-pVTZ (ae)    | 1.2985         | 105.032 |
| CCSD(T)/cc-pVQZ (ae)    | 1.2963         | 104.939 |
| MP2/cc-pVDZ (fc)        | 1.3101         | 104.708 |
| MP2/pVDZ (fc)+aug(F)    | 1.3245         | 103.793 |
| MP2/cc-pVTZ (fc)        | 1.2993         | 104.966 |
| MP2/pVTZ(fc)+aug(F)     | 1.3022         | 104.708 |
| MP2/cc-pVQZ (fc)        | 1.2969         | 104.945 |
| MP2/pVQZ (fc)+aug(F)    | 1.2979         | 104.854 |
| best estimate, see text | 1.2972         | 104.858 |

<sup>a</sup> ae = all electrons correlated, fc = frozen core approximation.

correct the *r<sub>z</sub>* value. This gives a value of *r<sub>e</sub>*(C–F) of 1.297(2) Å. These values are in perfect agreement with the experimental *r<sub>e</sub>* structure.

The results of the ab initio calculations on CF<sub>2</sub> are given in Table 9. The CCSD(T)/cc-pVQZ values corrected for the effect of diffuse functions on F gives: *r<sub>e</sub>*(C–F) = 1.2972 Å and ∠<sub>*e*</sub>(FCF) = 104.85°, in perfect agreement with the experimental values. If we extrapolate the angles using eq 1, we get ∠<sub>*e*</sub>(FCF) = 104.858°. This confirms the accuracy of the CCSD(T)/cc-pVQZ ab initio calculations, provided the effect of the diffuse

TABLE 10: Computed Equilibrium Geometry of CHF (Distances in Å and Angles in Degrees)<sup>a</sup>

|                              | <i>r</i> (C–H) | <i>r</i> (C–F) | ∠(HCF)  |
|------------------------------|----------------|----------------|---------|
| CCSD(T)/cc-pVDZ (ae)         | 1.1406         | 1.3210         | 101.867 |
| CCSD(T)/cc-pVTZ (ae)         | 1.1153         | 1.3070         | 102.444 |
| CCSD(T)/cc-pVQZ (ae)         | 1.1175         | 1.3052         | 102.420 |
| CCSD(T)/cc-pVDZ(ae)+aug(C,F) | 1.1364         | 1.3392         | 101.428 |
| CCSD(T)/cc-pVTZ(ae)+aug(C,F) | 1.1164         | 1.3081         | 102.378 |
| CCSD(T)/cc-pVQZ(ae)+aug(C,F) | 1.1176         | 1.3063         | 102.407 |
| best estimate, see text      | 1.116          | 1.306          | 102.41  |

<sup>a</sup> ae = all electrons correlated, fc = frozen core approximation.

functions on fluorine is taken into account. It may however be noted that this effect is small in the particular case of CF<sub>2</sub>.

It is also interesting to compare the experimental equilibrium moments of inertia with those calculated from the ab initio structure, see Table 8. It appears that the moments of inertia are quite sensitive to small structural changes and that the difference *I*(exp) − *I*(calc) is much greater than the uncertainty of *I*(exp) as was also the case for OCHF. The main source of error comes from the experimental determination of the vibrational correction because it is extremely difficult to obtain unperturbed rotational constants for excited states which are in interaction (which is rather common). Furthermore, in the case of CF<sub>2</sub>, the magnetic correction could not be taken into account because the molecular *g*-factor is not known.

This success prompts us to try to calculate the structure of the structurally similar molecule CHF for which no *r<sub>e</sub>* structure is known. The results of the ab initio computations are in Table 10. One may note that the angle has almost the same value at the cc-pVTZ and cc-pVQZ levels indicating that convergence is almost achieved. Taking into account the small effect of the diffuse functions, one finds: ∠<sub>*e*</sub>(HCF) = 102.41°, to be compared with the effective value, ∠<sub>*0*</sub>(HCF) = 104.1(5)°. <sup>22</sup> Our result is also in good agreement with the previous ab initio calculation made at the CCSD(T)/6-311+G\*\* level, 102.0°. <sup>24</sup> Our calculation should be more accurate because a much larger

**TABLE 11: Equilibrium Geometry of CH<sub>2</sub>F<sub>2</sub> (Distances in Å and Angles in Degrees)<sup>a</sup>**

|                                      | $r(\text{C-H})$ | $r(\text{C-F})$ | $\angle(\text{HCH})$ | $\angle(\text{FCF})$ |
|--------------------------------------|-----------------|-----------------|----------------------|----------------------|
| CCSD(T)/cc-pVDZ (ae)                 | 1.1042          | 1.3603          | 112.264              | 108.886              |
| CCSD(T)/cc-pVTZ (ae)                 | 1.0854          | 1.3518          | 112.864              | 108.666              |
| CCSD(T)/cc-pVQZ (ae)                 | 1.0861          | 1.3511          | 113.088              | 108.503              |
| MP2/cc-pVDZ (fc)                     | 1.1012          | 1.3598          | 112.392              | 108.960              |
| MP2/pVDZ (fc ← aug(F))               | 1.0985          | 1.3779          | 114.495              | 108.049              |
| MP2/cc-pVTZ (fc)                     | 1.0865          | 1.3454          | 113.028              | 108.713              |
| MP2/pVTZ (fc ← aug(F))               | 1.0863          | 1.3592          | 113.722              | 108.337              |
| MP2/cc-pVQZ (fc)                     | 1.0853          | 1.3541          | 113.312              | 108.561              |
| MP2/pVQZ (fc ← aug(F))               | 1.0854          | 1.3560          | 113.577              | 108.408              |
| best estimate, see text              | 1.0872          | 1.3529          | 113.283              | 108.364              |
| experimental, set I <sup>b</sup>     | 1.087 (3)       | 1.3514 (5)      | 113.1 (3)            | 108.43 (6)           |
| experimental, set III <sup>b,c</sup> | 1.084 (3)       | 1.3508 (5)      | 112.8 (3)            | 108.49 (6)           |

<sup>a</sup> ae = all electrons correlated, fc = frozen core approximation.<sup>b</sup> Reference 27. <sup>c</sup> Preferred value; see reference 27.

basis set has been used. The extrapolation (with diffuse functions included) at infinite basis size gives 102.41°, whereas the value is 102.42° when the diffuse functions are neglected.

For the C–F bond length, the CCSD(T)/cc-pVQZ+aug(C, F) value is 1.3063 Å, slightly larger than the experimental  $r_o$  value, 1.305(2) Å, although the difference lies within the experimental uncertainty. It may be noted that, for the CF bond length, basis set convergence is perhaps not fully achieved at the cc-pVQZ level. At infinite basis size, the length should be slightly smaller, assuming a monotonic variation. Furthermore, since the influence of the diffuse functions decreases as the basis size increases, this should further decrease the bond length. To solve this problem, we have calculated the structure of CHF at the CCSD(T) level using the cc-pVnZ+aug(C, F) basis sets with  $n = \text{D, T, Q}$ . The extrapolation to infinite basis size using eq 1 gives  $r(\text{C-F}) = 1.3061$  Å whereas the same extrapolation, neglecting the diffuse functions, gives 1.3040 Å. This is in rather good agreement with our previous result and confirms the importance of diffuse functions in this particular case. The nonextrapolated value is preferred because the overestimation of the bond length at the quadruple- $\zeta$  level is 0.001 Å, which is fully compensated by the (negative) overestimation of the core-correlation (see discussion on OCHF). The CCSD(T)/cc-pVQZ  $r(\text{C-H})$  bond length is about 0.001 Å shorter than the true equilibrium bond length, see Table 5. Thus, in principle, the equilibrium C–H bond length, should be  $r_e(\text{C-H})$ , 1.116 Å. But, as the bonding in CHF is very different from the other hydrocarbons, it is not possible to affirm that the offset is still valid for CHF and the true equilibrium value could be slightly different.

**Diffuoromethane.** To complete the series of simple fluorine compounds, the structure of difluoromethane was also calculated. The results are given in Table 11 together with the previous experimental  $r_e$  structure of Hirota.<sup>27</sup> The variation of angles with the size of the basis set is monotonic; thus it is possible to extrapolate them to infinite basis size using eq 1. This gives an angle  $\angle(\text{HCH})$  of 113.28° and an angle  $\angle(\text{FCF})$  of 108.36° whereas, if the effect of the diffuse functions on F is neglected, one finds that  $\angle(\text{HCH})$  equals 113.22° and  $\angle(\text{FCF})$  equals 108.10°. In conclusion, as expected, the effect of the diffuse functions significantly broadens the angle  $\angle(\text{FCF})$  but has almost no effect on the angle  $\angle(\text{HCH})$ . The computed value for  $\angle(\text{HCH})$  is slightly larger than the preferred experimental value (set III), 112.8(3)°. The computed value of the  $r(\text{C-F})$  bond length, after correction (see Table 4), 1.3529 Å is also larger than the preferred experimental value, 1.3508 (5) Å. Likewise, the computed value of the  $r(\text{C-H})$  bond length, after correction (see Table 4), 1.0872 Å, is also larger than the

preferred experimental value, 1.084 (3), although the large uncertainty does not allow us to draw any firm conclusion for this bond length. In conclusion, it seems that the experimental  $r_e$  structure calculated using the simple valence cubic force field (set I) is more accurate than the one obtained from the advanced force field (set III). To check that point, we have calculated the equilibrium rotational constants using the experimental ground-state constants and the rovibrational corrections calculated at the MP2/6-31G\*\* level.<sup>29</sup> This gives (in MHz)  $A_e = 49707$ ,  $B_e = 10669$ , and  $C_e = 9321$ , in excellent agreement with the values obtained from the computed structure:  $A_e = 49709$ ;  $B_e = 10664$ ; and  $C_e = 9319$ . This indicates that the ab initio force field is likely to be more accurate than the experimental one which is not surprising because it is known that ab initio methods are able to furnish with good accuracy cubic and quartic force constants.<sup>51</sup> This is further strengthened by the fact that our C–H bond length is in perfect agreement with the value estimated either from the isolated  $\nu(\text{C-H})$  stretching frequency or from the MP2/6-31G\*\* calculation.<sup>23</sup>

Finally, it may be noted that  $r(\text{C-F})$  is much smaller in CH<sub>2</sub>F<sub>2</sub> than in CH<sub>3</sub>F, see Table 4. This supports the well-documented observation that the C–F bond length decreases with increasing substitution. On the other hand, the variation of the C–H bond length from CH<sub>3</sub>F to CH<sub>2</sub>F<sub>2</sub> is negligible.

## Conclusions

The equilibrium geometries of a few simple fluorine compounds (formyl fluoride, difluorocarbene, monofluoromethylene, and difluoromethane) have been computed using the coupled cluster correlation method with basis sets up to quadruple- $\zeta$  quality. The effects of diffuse functions on the electronegative atoms have been included. It is found that the CCSD(T)/cc-pVQZ+aug(F) method with all electrons correlated nicely reproduces the experimental equilibrium C–F bond length with a standard deviation of 0.0003 Å. The ab initio C–H bond length, calculated at the same level of theory, is 0.001 Å too short. The lack of monotonic convergence which was observed for some parameters with basis set enlargement might be due to an artifact of the cc-pVnZ basis sets (this behavior is observed with all electrons correlated as well as with the frozen core approximation). The use of the appropriate cc-pCvNz basis sets might overcome this difficulty.

The theoretical predictions of bond lengths and bond angles are in good agreement with the available experimental data. However, a small discrepancy (0.0014 Å) is found for the C=O bond length in formaldehyde. This would justify a similar systematic study of the C=O bond.

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*Ab initio* and equilibrium bond angles.

Structure of HNO and H<sub>2</sub>O<sub>2</sub>

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# Ab initio and equilibrium bond angles. Structures of HNO and H<sub>2</sub>O<sub>2</sub><sup>1</sup>.

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## Abstract

The possibility of calculating accurate *ab initio* bond angles is examined using a sample of 29 molecules (35 independent angles) containing only first row atoms and whose equilibrium structures are known. Three different correlated methods are compared: MP2, CCSD(T), and DFT using the hybrid functional B3LYP. The convergence of Dunning's correlation consistent polarized valence basis sets, cc-pVnZ is also studied. It is found that the CCSD(T) method is consistently the most accurate, the DFT/B3LYP being slightly less reliable than MP2. It is shown that when convergence of the basis set is achieved (which is dependent on the kind of bonding) and when the effect of diffuse functions on electronegative atoms is taken into account, a high accuracy may be obtained: 0.03° for the median of absolute deviations or 0.07° for the mean absolute deviation. It does not exclude the possibility that the *ab initio* method may fail in some particular case, for instance when a large amplitude motion is involved. The MP2/cc-pVQZ method gives a mean absolute deviation of 0.22° to be compared with the 0.07° of the CCSD(T) method. To obtain these results, it was necessary to reanalyze the structure of a few molecules, particularly, a new and more accurate structure is proposed for nitroxyl, HNO and hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>.

**Keywords:** Structure, Angle, Ab initio

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<sup>1</sup> Dedicated to Professor Heinz-Dieter Rudolph on the occasion of his 75th birthday.

## Introduction

There is a large documented body of evidence which indicates that *ab initio* methods can calculate bond angles with an accuracy of a few tenths of a degree. However, whereas there are many recent review papers on *ab initio* bond lengths [1-5], there are almost no systematic studies of *ab initio* bond angles. Hehre *et al.* [6], in their book published in 1986, make a very thorough comparison between *ab initio* and experimental bond angles for a wide range of molecular types. But most calculations were made at the Hartree-Fock (HF) level and with a very small basis set. Furthermore, the comparison was made with molecules for which an accurate experimental structure was not always known. Indeed, although average ( $\theta_z$ ), or even effective ( $\theta_o$ ) and substitution ( $\theta_s$ ) angles are often a good approximation to the equilibrium value, large discrepancies are not uncommon [7]. For instance, Ref. [8] reports  $\angle(\text{CCH})$  angles involving the H atom to the substituted center ranging from 121.5°-129.1° for vinyl alcohol 120.9°-130.8° and vinyl fluoride [8]. The conclusion of Hehre *et al.* was that the mean absolute error between experimental and theoretical angles with the 6-31G\* basis set at the HF level is about 1.5°. They also noted that differences among the 6-31G\*, 6-31G\*\*, and 6-311G\*\* results are generally quite small. Finally, they found that, taking electron correlation into account by second-order Møller-Plesset perturbation theory (MP2) gives values which may differ by 1-2° from the HF results. Recently, Lee and Scuseria [1] analyzed the accuracy of the coupled-cluster method with single and double excitations augmented by a perturbational estimate of the effects of the connected triple excitations [CCSD(T)] with the hierarchical correlation-consistent polarized valence n-zeta basis sets (cc-pVnZ) of Dunning *et al.* [9], but their sample was limited to six molecules which may be a little small to draw reliable conclusions. Feller and Peterson [4] studied the Gaussian-2 (G2) collection of molecules and estimated the complete basis set limits for a large number of properties including the geometry but concluded that there were insufficient bond angles to obtain meaningful statistics. Bauschlicher [10, 11] also studied the same sample of G2 molecules using different density functional methods (DFT). For this set of 26 bond angles and two dihedral angles, the best results were found using the hybrid functional B3LYP (Becke's three parameter functional employing the

Lee, Yang, and Parr correlation function) [12] and the 6-311+G(3df, 2p) basis set: average absolute error of  $0.61^\circ$  and a maximum error of  $1.85^\circ$ . But, here again, the comparison is made with molecules for which an accurate experimental structure is not always known, as noticed by Feller and Peterson [4].

Quite recently, in continuation of a work on the  $\angle(\text{HCC})$  angle [13], Bouddou [14] made a systematic comparison of the HF and MP2 methods, as well as the density functional method with hybrid functional B3LYP. Four different basis sets were used : 6-31G\*, 6-31G\*\*, 6-311G\*\*, and 6-311+G\*\*. His sample comprised 40 angles from 35 molecules. He found that the MP2 method was significantly better than the HF method, the B3LYP method giving comparable results to MP2. The standard deviation (estimated from the median of the absolute deviations, see Eq. 1 below) was only  $0.5^\circ$  with the MP2 method but with a range (largest positive deviation + smallest negative deviation) of  $3.4^\circ$ . He also found that the results are apparently not very sensitive to the basis set used and that the largest deviations were generally found for molecules with relatively heavy atoms (Cl, P, S) or with electronegative atoms (F, N, O). He suspected that in some cases the discrepancy could be due to an inaccurate experimental structure. But, for the remaining cases, he could not decide whether the poor results were due to the inadequacy of the MP2 method or to an inadequate basis set. Finally, in a few cases, he found large differences between the MP2 and B3LYP results but he did not comment on them.

This lack of precise information is a pity because it is well established that it is often difficult to obtain a complete structure using only experimental information. Indeed, when more than one isotopic species is required to determine all the structural parameters, the least-squares fit is usually ill-conditioned [7]. Therefore the inclusion of additional data, e. .g. from *ab initio* calculations may help to obtain a complete and accurate structure. The *ab initio* bond lengths are generally affected by an error more or less systematic and, therefore, cannot be directly used. On the other hand, *ab initio* angles are good candidates as additional data. However, to use the technique of mixed fit which makes use of all available data, it is necessary to weight these data, i.e. to know their accuracy. The goal of this work is to try to estimate the accuracy that may be achieved with the CCSD(T) and the

MP2 methods using the cc-pVnZ basis sets for different types of bond angles. This comparison will be limited to closed-shell molecules containing first row atoms although most of the conclusions remain valid for second row atoms provided appropriate basis sets are used. This point is briefly discussed below. Finally, the performance of the B3LYP method will be compared to that of the CCSD(T) and the MP2 methods.

## Computational details

The calculations with all electrons correlated were performed with the ACES II program system [15] whereas for the frozen core approximation either the Gaussian 94 [16] or MOLPRO96 [17, 18] programs were used.

Numerous studies have shown that while HF calculations yield reasonable geometries, their accuracy is significantly worse than that of most experimental structures. For this reason two correlated methods were used : MP2 [19] and CCSD(T) [20]. The CCSD(T) method is known to yield results close to the exact  $n$ -particle solution within the given basis set [1] while the MP2 geometries remain remarkably accurate although much less expensive than the CCSD(T) ones [3]. The well-known Dunning's consistent polarized valence basis sets labelled cc-pVnZ (with  $n = D, T, Q$ ) were employed [9]. As some molecules contain highly electronegative atoms, F, N or O, the aug-ccpVnZ basis sets on these electronegative atoms were also used [21]. For instance, the combination of an aug-cc-pVnZ basis set on F and of a cc-pVnZ basis set on the other atoms is denoted as : cc-pVnZ + aug(F). To estimate the correction due to the diffuse functions, it is often enough to use the MP2 method [22-23]. This significantly reduces the complexity (time and memory) of the calculations whereas it gives a correction nearly identical to the CCSD(T) method. It is important to use the quadruple zeta basis set because the aug-cc-pVTZ basis set is biased towards the diffuse functions and the description of long-distance effects whereas the problem disappears with the aug-cc-pVQZ basis set [24].

Most geometries were optimized with a gradient convergence criterion of  $1.5 \times 10^{-5}$  au corresponding to the "tight" criterion defined by Gaussian-94.

## Origin of the equilibrium angles

In order to be able to make a meaningful comparison with the *ab initio* results, it is necessary to have accurate values for the equilibrium angles. We have used true experimental equilibrium angles  $\theta_e$  which are usually rather accurate as well as average angles  $\theta_z$  which are generally a good approximation of the true equilibrium value [7], albeit with a lesser precision. Empirical values (mainly  $\theta_m^p$ ) were retained only where their accuracy could be checked using independent methods (*ab initio* calculations, empirical correlations, etc.). Effective  $\theta_o$  as well as substitution  $\theta_s$  values were not used. Finally, when no reliable experimental value was available, the published *ab initio* value was only used when it was calculated at the CCSD(T) level and when the basis set convergence was carefully checked.

## Results

At the limit of infinite basis size, it is widely recognized that the CCSD(T) method generally gives very accurate results. The problem is that large basis sets can be used only with very small molecules, for instance  $\text{CH}_2$  whose structure was calculated with the core-valence cc-pCVnZ basis sets ( $n = 2, 3, 4, 5$ ), all electrons being correlated [25]. The first point to discuss is the need to take exact account of the core-correlation because, if it could be neglected (or estimated with the smaller valence cc-pVnZ basis sets), it would significantly reduce the complexity of the calculations. The second point is the gain of accuracy with enlargement of basis size. For most molecules considered in this work, the calculations were made only up to the quadruple zeta level, but, in a few particular cases, cc-pV5Z results are also available. When it seems that convergence is not achieved at the quadruple zeta level, the possibility to extrapolate to infinite basis size will be discussed. The accuracy of the MP2 method is next compared to that of the CCSD(T) method. And, finally, the structure of a few molecules which show large discrepancies is critically analyzed.

### Core-correlation

The first problem to assess is that of core-correlation. It is well known that this effect is not negligible for bond distances [26] but not much is known for bond angles. There are different ways to estimate this effect. To carry out a calculation with all electrons correlated, it has been recommended to use either the Martin-Taylor (MT) basis sets or the core-valence cc-pCVnZ basis sets [25, 26, 27]. The reason is that, for bond lengths, the valence cc-pVnZ basis sets overestimate the core-correlation effects. But, again, not much is known for the bond angles. Finally, it must be noted that the cc-pCVTZ basis set does not retrieve all the core-correlation and that the larger cc-pCVQZ basis set has to be used. In Table 1 we compare the core-correlation calculated rigorously with either the Martin-Taylor basis sets or the cc-pCVQZ basis set and approximately with the standard cc-pVQZ basis set.

It may be noted that the effect of the core-correlation is quite small (generally smaller than  $0.2^\circ$ ) and that its approximate calculation with the cc-pVQZ basis set is very close to the more accurate one, although usually slightly larger. It also appears that the effect of core-correlation is most important for molecules which are light and non-rigid. In conclusion, there is no need to use the huge cc-pCVQZ basis set, except for very precise calculations.

### Analysis of the results

The calculated and experimental values are given in Table 2. If  $\theta^{\text{exp.}}$  is the experimental angle and  $\theta^{\text{calc.}}$  the corresponding calculated value, the residuals may be defined by :  $e_i = \theta_i^{\text{exp.}} - \theta_i^{\text{calc.}}$ . In principle the mean error  $\bar{e}$  and its standard deviation tell us whether the residuals are random or not and what is the accuracy of the method. But the mean absolute error (mae)  $\bar{e}_{\text{abs}} = \frac{1}{n} \sum_{i=1}^n |e_i|$  is a better indicator of the magnitude of the errors and is given in Table 3 along with the largest residual. Finally, the median of absolute residuals is also given. It permits one to obtain a robust estimate of the standard deviation, i.e. an estimate which is not sensitive to a few outliers (contrary to the "normal" standard deviation) [28]:

$$s = 1.4826 \cdot \text{med}(|e_i|) \quad (1)$$

Tables 2 and 3 show that, at the CCSD(T) level, extending the basis set from cc-pVDZ to cc-pVTZ dramatically reduces the error, the mae dropping from  $0.94^\circ$  to  $0.30^\circ$ . A further extension to the cc-pVQZ basis set has a much less marked effect, the new mae being  $0.19^\circ$ . MP2, although less accurate than CCSD(T) is nevertheless reasonably accurate for most molecules, the mae at the QZ level being  $0.32^\circ$ , to be compared with  $0.19^\circ$  at the CCSD(T) level, but the median error is significantly larger at the MP2 level,  $0.25^\circ$  instead of  $0.14^\circ$  indicating that, in some cases, the MP2 method is not reliable. The mae of the difference CCSD(T)/cc-pVQZ - MP2/cc-pVQZ is  $0.19^\circ$  (median  $0.15^\circ$ ). The largest difference is found for the  $\angle(\text{HCH})$  angle in *c*-CH<sub>2</sub>O<sub>2</sub> ( $0.80^\circ$ ), the next largest differences being for the HNCO,  $\angle(\text{HNC})$  angle ( $0.61^\circ$ ) and  $\angle(\text{NCO})$  angle ( $0.42^\circ$ ).

On the other hand it is interesting to note that the change from CCSD(T)/cc-pVTZ to CCSD(T)/cc-pVQZ is almost identical to the corresponding change calculated at the MP2 level, the mean absolute difference being only  $0.07^\circ$  (and the median  $0.03^\circ$ ). In other words, the CCSD(T)/cc-pVQZ value may be often calculated more economically using the following equation:

$$\theta[\text{CCSD(T)/cc-pVQZ}] = \theta[\text{CCSD(T)/cc-pVTZ}] + \theta[\text{MP2/cc-pVQZ}] - \theta[\text{MP2/cc-pVTZ}] \quad (2)$$

This may be interesting for a large molecule for which the CCSD(T)/cc-pVQZ method is too expensive. The largest differences are found for CH<sub>2</sub> ( $0.32^\circ$ ), the HNC angle in HNCO ( $0.27^\circ$ ), the HCH angle in *c*-CH<sub>2</sub>O<sub>2</sub> ( $0.20^\circ$ ) and the torsional HOOH angle in H<sub>2</sub>O<sub>2</sub> ( $0.27^\circ$ ). For only one of these molecules is the  $T_1$  diagnostic which determines whether a single-reference-based electron correlation procedure is appropriate [29] not very small: 0.018 for HNCO. But, for most of the molecules, the origin of this discrepancy is more likely due to the large amplitude motion of the hydrogen and the resulting large anharmonicity effects.

Another interesting result is that for an  $\angle(\text{HCH})$  (or  $\angle(\text{HCC})$ ) angle in a hydrocarbon, the basis set convergence seems to be achieved at the triple zeta level.

There are several molecules which show large residuals; most of them have at least one electronegative atom (N, O, F). In this case, the addition of diffuse functions should improve the accuracy. Their effect was calculated at the MP2 level because it was previously shown that

differences due to the addition of diffuse functions at this level are transferable to CCSD(T) [23]. The diffuse functions significantly reduce the deviations, the mae dropping from 0.19° to 0.15°, and more interestingly, the median dropping from 0.14° to 0.05°. The difference between these two diagnostics indicates that the diffuse functions have indeed a significant effect but that there are still a few large deviations from a different origin. It is worth noting that the effect of the diffuse functions is quite small for F<sub>2</sub>O and NF<sub>3</sub> although all the atoms are electronegative. It may be explained by the fact that the polarities of the bonds are quite small.

Even with the effect of the diffuse functions taken into account, a few residuals remain important. For these molecules, basis set convergence might not be achieved at the QZ level. The rate of convergence is indeed not the same for the different molecules as may be verified by analyzing the change from cc-pVTZ to cc-pVQZ which is large for these molecules. This rate may also be roughly predicted by using the change from cc-pVDZ to cc-pVTZ because there is a rather good correlation with the change from cc-pVTZ to cc-pVQZ (linear correlation coefficient,  $\rho = 0.84$ ). Inspection of Table 2 shows that the convergence is particularly slow for HNCO (angle HNC), *trans*-N<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub>. It is worth noting that all these angles have an H involved in a large amplitude motion subject to a highly anharmonic potential. For the molecules with large deviations, the best solution would be to use the larger cc-pV5Z basis set, as was done for CH<sub>2</sub> [25], H<sub>2</sub>O [24], CH<sub>3</sub>F [22], H<sub>2</sub>C=CH<sub>2</sub> and H<sub>2</sub>CC [2] as well as a few other molecules. But this is extremely expensive and it is much easier to try to extrapolate to infinite basis size. Bond angles are indeed often found to converge with approximate exponential behavior [3] but inspection of Table 2 shows that there are many exceptions to the monotonic variation of the calculated value with the size of the basis set, particularly when a polar bond is present. This is for instance the case for most fluorine compounds shown in Table 2. In this case, the first thing to try is to add diffuse functions on the electronegative atom. But, this is obviously not always sufficient. The lack of monotonic convergence which is observed for some parameters with basis set enlargement might be due to an artefact of the cc-pVnZ basis sets (this behaviour is observed with all electrons correlated as well as with the frozen core approximation). The use of the cc-pCVnZ basis sets with all

electrons correlated might overcome this difficulty. To check that point, we have performed calculations on CHF with the cc-pVnZ and cc-pCVnZ basis sets, all electrons being correlated. The results are reported in Table 4. It seems indeed to solve the problem and, when the convergence is monotonic, an extrapolation to infinite basis size may be tried using the following empirical exponential function

$$\theta(n) = \theta_{\infty} + be^{-cn} \quad (3)$$

where  $n$  is an index associated with each basis set, 2 = DZ, 3 = TZ, 4 = QZ. The parameters  $\theta_{\infty}$ ,  $b$ , and  $c$  are determined from a nonlinear least-squares fit. Alternatively, a geometric extrapolation  $A + B/C^n$  [30] may also be tried. Inspection of Table 5 where the VQZ and V5Z values are reported for a few molecules seems to indicate that basis set convergence is almost achieved at the QZ level except for the lightest molecules. To check whether an extrapolation is necessary, the discrepancy will now be discussed case by case when it is larger than  $0.2^\circ$  (except for  $\text{CH}_3\text{CN}$  where it is known that the experimental value is not precise).

### 1. HNC angle in HNCO

The last published value is  $\angle(\text{HNC}) = 123.34(20)^\circ$  [31] but it is not a true experimental equilibrium value because it was calculated with experimental ground state rotational constants and with  $\alpha$ -constants derived from an *ab initio* cubic force field. There is also a  $\theta_z$  value,  $124.0(1)^\circ$  [32] which is significantly different.

The value at the CCSD(T) level extrapolated to infinite basis set and neglecting the diffuse functions is  $123.66^\circ$  to be compared to the cc-pVQZ value of  $123.61^\circ$ . Thus convergence is almost achieved. The role of diffuse functions (on N and O) seems to be small too,  $0.10^\circ$  at the QZ level, the extrapolation to infinite basis size giving  $123.87^\circ$ . The provisional conclusion is that the experiment-based equilibrium value of the angle should be revised, its best value probably being close to  $123.7^\circ$ . A likely explanation is that this molecule is extremely non-rigid with an unusually large  $A$  rotational constant, so the usual method where the ground state rotational constants are simply corrected for the effect of the  $\alpha$ -constants might not be sufficiently accurate. For the

$\angle(\text{NCO})$  angle, the extrapolation gives  $172.38^\circ$  or  $172.44^\circ$  (without diffuse functions) indicating that convergence is achieved at the QZ level.

## 2. *c*-CH<sub>2</sub>O<sub>2</sub>

The published equilibrium value for the HCH angle is  $117.03(20)^\circ$  [33], the extrapolated infinite basis set value  $116.76^\circ$  and the QZ value  $116.74^\circ$ . Here again convergence is achieved and the role of diffuse functions (on O) is negligible,  $-0.034^\circ$ . The difference exp. - calc. =  $0.29^\circ$  is only slightly larger than the stated uncertainty of  $0.2^\circ$ . It may be noted that the magnetic correction to the rotational constants was not taken into account for the structure determination. Although it is difficult to estimate its order of magnitude, it could explain the difference. On the other hand, the large difference between the CCSD(T) and MP2 calculations should remind us that this molecule is a challenge for *ab initio* methods [33].

## 3. HOF

The published equilibrium value,  $97.54(50)^\circ$  [34] is simply not very precise. The extrapolated infinite basis set value is  $97.94^\circ$  (without diffuse functions) or  $98.00^\circ$  (with diffuse functions), to be compared with the CCSD(T)/aug-cc-pVQZ value of  $98.0^\circ$ . Here again there is no need for extrapolation and the apparently large difference between the equilibrium and *ab initio* values is due to the fact that the experimental value is not precise, its estimated standard deviation being  $0.5^\circ$ .

## 4. NF<sub>3</sub>

Here the CCSD(T)/cc-pVQZ result is missing but, according to the MP2 calculations and Eq. (2), its value should be close to  $101.95^\circ$  to be compared with the experimental equilibrium value  $102.31(3)^\circ$  [35]. Convergence is achieved and the effect of the diffuse functions is negligible. The accuracy of the experimental value is likely too optimistic because this structure was determined from the  $B_e$  of two isotopic species, not from the  $B_e$  and  $C_e$  of one species, which should be much more accurate. Furthermore the effect of a small Fermi resonance between  $\nu_1$  and

$2\nu_4$  was neglected; its effect on the rotational constants is about 0.16 MHz. Finally, the magnetic correction was also neglected although it is rather large for this molecule, about 0.35 MHz for the  $B$  rotational constant [36]. These two effects are sufficient to explain the difference. The axial rotational constant was recently determined for the  $\nu_4 = 1$  excited state,  $C_4 = 5829.25(270)$  MHz [37]. Using the *ab initio* vibration-rotation interaction constants [38], the equilibrium axial constant is calculated to be :  $C_e = 5898$  MHz. This allows us to determine a more accurate experimental structure. The final result depends slightly on the weighting of the experimental constants, but, in all cases, the  $\angle_e(\text{FNF})$  angle is found to be between  $101.92^\circ$  and  $101.95^\circ$  in perfect agreement with the *ab initio* prediction.

## 5. HNO

There are two experimental values, one from Hirota,  $109.09(24)^\circ$  [39]; and a much older one from Dalby,  $108.43^\circ$  [40]. The accuracy of both of these values is questionable because in both cases doubtful approximations had to be made. There is also a previous *ab initio* determination at the CCSD(T)/cc-pVQZ level [41]. But it seems that convergence is not yet achieved at the cc-pVQZ level. In addition to the cc-pVnZ basis sets, we also used a mixed basis set composed of cc-pV5Z at all nonhydrogen atoms and cc-pVQZ at H which is denoted as cc-pV(5,Q)Z. Such a basis set has been shown to lead to little loss in accuracy compared to the full cc-pV5Z set at all atoms [21] while reducing the computation times significantly. Furthermore, in view of the high electronegativity of oxygen, the aug-cc-pVQZ and aug-cc-pV5Z basis sets for O were also used. Due to the large size of the cc-pV(5,Q)Z + aug(O) basis set, geometry optimization was only performed at the MP2 level. Finally, in order to estimate the core and core-valence correlation effects, the correlation consistent polarized core-valence quadruple-zeta (cc-pCVQZ) basis set was also employed. The results of the calculations are collected in Table 6. It is worth noting that improvement of the basis set does not lead to a monotonic variation of the bond angle  $\angle(\text{HNO})$  or for the distance  $r(\text{NH})$ , even when the effect of the diffuse functions is taken into account. In other words, extrapolation to infinite basis size using the double, triple and quadruple basis sets might not lead to the correct

result. The effect of diffuse functions on O is negligible at the aug-cc-pV5Z level. Correlating all electrons instead of only the valence electrons at the cc-pCVQZ level of theory shortens the NH and NO bonds by 0.0013 Å and 0.0020 Å respectively, whereas the bond angle is only slightly affected (increase by 0.07°). Using the cc-pVQZ basis set instead of the cc-pCVQZ one, exaggerates the decrease of the NH bond by 0.0011 Å, whereas the exaggeration is only 0.0008 Å for NO and 0.027° for the angle. To obtain the equilibrium structure, it is possible to correct the CCSD(T)/cc-pV(5,Q)Z (frozen core) structure from the effects of core correlation and diffuse functions. The result is in extremely good agreement with the CCSD(T)/cc-pVQZ + aug(N,O) (all electrons correlated) if we take into account the fact that this basis set exaggerates the core correlation effects for the NH bond length. It might be argued that diffuse functions on the O atom are not enough, and that it would be better to put diffuse functions on the N atom too. But their combined effect is less than 0.1° at the cc-pVQZ level and is thus probably almost negligible at the cc-pV(5,Q)Z level.

## 6. $H_2O_2$

There have been several attempts to determine the structure of hydrogen peroxide, experimentally [42] as well as theoretically [43, 44]. The calculated values given in Table 2 show that in this particular case basis set convergence is not achieved and the effect of the diffuse functions is also not negligible. For these reasons the previous *ab initio* values are probably not accurate enough. To determine the equilibrium structure of this molecule, we have used the same procedure as for HNO. The results are collected in Table 7. Here again, it is worth noting that the variation of the parameters is not monotonic upon basis set enlargement making the extrapolation to infinite basis size difficult to use. Upon augmenting cc-pV(5,Q)Z to cc-pV(5,Q)Z + aug(O) the dihedral angle (HOOH) is decreased by 0.188° whereas the other parameters are hardly affected. Taking the core correlation into account, this dihedral angle is increased by 0.128° whereas the effect is slightly smaller for the bond angle  $\angle(\text{HOO})$  (0.09°). The best estimate of the equilibrium structure, taking all the discussed corrections into account, and calculated in two different ways, is given at the bottom of Table 7. The core correlation was calculated only at the MP2 level (with the cc-pCVQZ basis set) but the results are slightly larger than those found at the CCSD(T)/cc-pCVTZ

level [44], indicating that they are likely to be reliable. The large effect of the core correlation on the  $\angle(\text{HOOH})$  dihedral angle has to be noted.

## 7. $\text{O}_3$

The values for ozone are given for the sake of completeness because all its atoms belong to the first row but this molecule is a textbook multireference example and connected quadruple excitations are needed for quantitative calculations [45]. It is interesting to note that the MP2 values are accidentally better than the CCSD(T) ones although the accuracy of both methods is reasonable.

## Conclusion

With the corrections described above, the mae drops to  $0.09^\circ$  at the CCSD(T)/aug-cc-pVQZ level, the two largest deviations being only  $0.36^\circ$  for the  $\angle(\text{HOOH})$  in  $\text{H}_2\text{O}_2$  and  $0.32^\circ$  for the  $\angle(\text{HCH})$  angle in  $c\text{-CH}_2\text{O}_2$ , the median of absolute residuals  $0.04^\circ$ , and the standard deviation of the residuals,  $0.16^\circ$ . The large difference between the last two diagnostics indicates that there are still a few outliers. It is not possible to exclude the possibility that the *ab initio* method remains inaccurate in some particular cases, for instance when a large amplitude motion is involved. But more likely, it demonstrates that the accuracy of the accepted  $r_e$  values is often not much more accurate than about  $0.2^\circ$ . The conclusion is that the CCSD(T)/cc-pVQZ method, when carefully used (test of convergence, influence of the diffuse functions when a polar bond is present, estimation of the core-correlation effects), allows us to determine a bond angle with an accuracy better than  $0.2^\circ$ . When core-correlation effects are neglected, the uncertainty might be slightly larger.

## Molecules with second row atoms

The previous conclusions remain -at least qualitatively valid for molecules with one (or more) second-row atom. For instance, the structure of  $\text{PH}_3$  was calculated at the CCSD(T)/cc-pVnZ level,  $n = 2, 3, 4, 5$ ; see Table 8 [46]. There are several interesting conclusions :

i) the effect of core-correlation is extremely small in this particular case

ii) the basis set convergence is good compared to that of  $\text{NH}_3$ ; this is another manifestation of the influence of the large amplitude motions which are less important in  $\text{PH}_3$ .

iii) the experimental equilibrium angle is in perfect agreement with the calculated one.

Likewise, it is easier to calculate an accurate structure for  $\text{H}_2\text{S}$  than for  $\text{H}_2\text{O}$ . The experimental equilibrium value is  $\angle(\text{HSH}) = 92.331^\circ$  [47] whereas the CCSD(T)/cc-pVQZ value is  $92.349^\circ$  and the corresponding cc-pVTZ value  $92.303^\circ$  indicating that convergence is achieved [48]. Taking into account the effect of the diffuse functions (at the aug-cc-pVQZ level) increases the angle by  $0.02^\circ$  and enlarging the basis set from cc-pVQZ to cc-pV5Z increases the angle by  $0.04^\circ$ . Both corrections may be safely neglected.

But, in some cases, the situation is more difficult because it has often been found that for second-row atoms, the convergence of the cc-pVnZ basis sets is slow. This is partly due to the fact that the  $3d$  orbitals may participate to the bonding. The convergence can be improved by adding an extra hard  $d$  function [49], as was shown for  $\text{HOCl}$  [50],  $\text{H}_2\text{SiO}$  [51], and  $\text{SO}_2$  [52] for instance. It is worth noting that  $\text{HOCl}$  combines three difficulties: i) one second row atom (Cl) ii) one electronegative atom (O) iii) a large amplitude motion of the hydrogen. Thus it is not surprising that very large basis sets are required.  $\text{SO}_2$  combines two difficulties: the  $\text{SO}$  bond is very polar requiring diffuse functions on the O atom, it is also hypervalent because the  $s(3d)$  orbital is part of the valence shell which explains the usefulness of high-exponent  $d$  and  $f$  inner polarization functions. As for  $\text{H}_2\text{SiO}$ , it is a polar molecule which requires the use of diffuse functions. There is furthermore a rather large core-correlation effect which decreases the  $\angle(\text{HSiH})$  angle by  $0.11^\circ$ .

Another problem that has to be considered is that the MP2 method might be less reliable for heavy atoms (in other words, the convergence of the perturbation method is slower) and a more sophisticated method like CCSD should perhaps be used. But there is not yet any systematic study of this problem.

To end this section, we will discuss the structure of sulfur difluoride,  $\text{SF}_2$ , because it is a typical example of the problems we may meet. The experimental structure of this  $C_{2v}$  triatomic molecule is accurately known. There is first a  $r_z$  structure [53] which gives

$\angle_z(\text{FSF}) = 98.197(11)^\circ$ . Later, the rotational spectra of all the fundamental vibrational states were analyzed and  $r_e$  structure was derived,  $\angle_e(\text{FSF}) = 98.048(13)^\circ$  [54]. It might already be noted that these two structures, although highly precise, are not compatible. The structure was calculated at the CCSD(T) and MP2 levels and the results are reported in Table 9.  $\text{F}_2\text{S}$  is isoelectronic to  $\text{F}_2\text{O}$  but there are two important differences: i) the F-S bond is much more polar than the F-O bond, ii) S has  $d$  electrons. The consequences, as seen in Table 9, is that the diffuse functions on F have a large effect and that the convergence is not achieved at the cc-pVQZ level. It is also important to note the large differences between the CCSD(T) and the MP2 results although the  $T_1$  diagnostic is only 0.014. For instance, for the angle the difference is as large as  $0.43^\circ$ . But, fortunately, the effects of the diffuse functions and of the extra hard  $d$  function are nearly additive and can be calculated at the MP2 level. This allows us to calculate the structure at the MP2/cc-pV5Z + aug(F) level to correct the CCSD(T)/cc-pVQZ+1 structure. The effect of the core correlation was only approximately taken into account by using the cc-pVQZ basis set. For the angle, this is negligible but the estimated bond length might be a little bit too short (by about  $0.001 \text{ \AA}$ ).

## DFT methods

During the past few years density functional theory (DFT) has become a popular approach to chemical problems because it includes some of the effects of electron correlation much less expensively (less memory and less disk space) than traditional correlated methods [10, 55]. Furthermore analytic derivatives are available at the DFT level. There are many different variants of the density functional. One of the most successful is the Becke-style hybrid B3LYP functional (Becke's three parameters exchange functional (B3) [12], as slightly modified by Stephens *et al.* [56] in combination with the Lee-Yang-Parr (LYP) functional [57]). It has the reputation of giving results that are comparable to MP2 (or better) [10, 11]. We have carried out geometry optimizations for the same sample of molecules as above using the B3LYP method as implemented in GAUSSIAN 94 [16] with the 6-311++G(3df, 2pd), cc-pVTZ and cc-pVQZ basis sets. The results are summarized in Table 3. At first sight the B3LYP method is comparable to the MP2 method, the

maximal deviation, the mean absolute deviation and the median of absolute deviations being comparable to the results found with the MP2 method. But a closer inspection of the residuals indicate that MP2 and B3LYP behave rather differently. Indeed the B3LYP method gives rather poor results for  $\angle(\text{HCH})$  or  $\angle(\text{HCC})$  angles (deviations up to  $1^\circ$ ) whereas the MP2 method is remarkably accurate. The same behavior is found for a few other molecules like HOF, ONF,  $\text{F}_2\text{O}$ , etc. On the other hand, when the MP2 method behaves poorly, the B3LYP method may give satisfactory results, as for instance in dioxirane and cyclopropenylidene. This seems to be the main advantage of the DFT methods.

## Conclusions

To successfully calculate an accurate angle, the following points have to be considered:

- i) the electron correlation has to be taken into account, if possible at the CCSD(T) level. If a lower level method is used, it is important to try to ensure that it is adequate (for instance by comparing the results of different levels of calculation, by using the  $T_1$  diagnostic [29], ...).
- ii) it is necessary to check the basis set convergence
- iii) when polar bonds are present, it is important to check the effect of diffuse functions on the electronegative atom(s).
- iv) for very accurate calculations, it is also useful to check the effect of the core-correlation which may be as large as a few tenths of a degree in some cases.

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Table 1. Effect of the core-correlation (angle with core-correlation minus angle without core-correlation) for some bond angles calculated with different basis sets at the CCSD(T) level.

| Molecule                         | Angle | MT <sup>a</sup> | cc-pCVQZ | cc-pVQZ |
|----------------------------------|-------|-----------------|----------|---------|
| H <sub>2</sub> O                 | HOH   | 0.12            |          | 0.13    |
| NH <sub>3</sub>                  | HNH   | 0.17            |          | 0.18    |
| H <sub>2</sub> CO                | HCH   | -0.04           |          |         |
| N <sub>2</sub> H <sub>2</sub>    | HNN   | 0.12            |          | 0.15    |
| CH <sub>2</sub> $\tilde{a}^1A_1$ | HCH   |                 | 0.13     | 0.22    |
| CH <sub>3</sub> F                | HCF   |                 | 0.03     | 0.05    |
| HNO                              |       |                 | 0.07     | 0.08    |
| BH <sub>2</sub> F                | HBH   |                 |          | -0.11   |
| H <sub>2</sub> O <sub>2</sub>    | OOH   |                 | 0.09     | 0.09    |
|                                  | HOOH  |                 | 0.13     | -0.02   |

<sup>a</sup> Martin-Taylor basis set, see text.

Table 2. Experimental and *ab initio* angles (in degrees).

| Molecule                         | angle | exp.        | ref. b | CCSD(T) a |        |          | MP2 a  |        |        |        |
|----------------------------------|-------|-------------|--------|-----------|--------|----------|--------|--------|--------|--------|
|                                  |       |             |        | VDZ       | VTZ    | VQZ      | VDZ    | VTZ    | VQZ    | AVQZ   |
| BH <sub>2</sub> F                | HBH   | 124.45 (10) | 58 fc  | 124.54    | 124.14 | 124.29   | 124.53 | 124.17 | 124.31 | 124.40 |
| CF <sub>2</sub>                  | FCF   | 104.86 (2)  | 23 ae  | 104.62    | 105.03 | 104.94   | 104.71 | 104.97 | 104.94 | 104.85 |
| HCF                              | HCF   | 102.41      | 23 ae  | 101.87    | 102.44 | 102.42   | 101.94 | 102.28 | 102.27 | 102.25 |
| OCHF                             | OCH   | 127.719     | 23 ae  | 127.56    | 127.48 | 127.61   | 127.82 | 127.77 | 127.93 | 128.05 |
| OCHF                             | OCF   | 122.71      | 23 ae  | 123.12    | 122.97 | 122.82   | 123.23 | 123.08 | 122.92 | 122.82 |
| HNCO                             | HNC   | 123.34 (20) | 31 ae  | 119.28    | 123.17 | 123.61   | 120.60 | 123.51 | 124.22 | 124.41 |
| HNCO                             | NCO   | 172.32 (20) | 31 ae  | 171.86    | 172.27 | 172.39   | 171.45 | 171.80 | 171.97 | 171.93 |
| CH <sub>2</sub> 1A               | HCH   | 102.23      | 59 ae  | 100.59    | 102.16 | 102.12   | 100.85 | 101.81 | 102.09 | 102.24 |
| CH <sub>2</sub> F <sub>2</sub>   | HCH   | 113.28 (30) | 23 ae  | 112.26    | 112.86 | 113.09   | 112.39 | 113.03 | 113.31 | 113.58 |
| CH <sub>2</sub> F <sub>2</sub>   | FCF   | 108.36 (6)  | 23 ae  | 108.89    | 108.67 | 108.50   | 108.96 | 108.71 | 108.56 | 108.41 |
| H <sub>2</sub> CO                | HCH   | 116.704     | 60 ae  | 115.21    | 116.18 | 116.44   | 115.20 | 116.15 | 116.44 | 116.64 |
| c-CH <sub>2</sub> O <sub>2</sub> | HCH   | 117.03 (20) | 33 ae  | 115.53    | 116.62 | 116.74   | 115.98 | 116.02 | 115.94 | 115.91 |
| c-CH <sub>2</sub> O <sub>2</sub> | OCO   | 66.25       | 33 ae  | 66.99     | 66.25  | 66.2     | 66.29  | 65.81  | 65.85  | 65.82  |
| CH <sub>3</sub> F                | HCH   | 110.24 (4)  | 22 fc  | 109.44    | 109.79 | 110.03   | 109.40 | 109.79 | 110.03 | 110.22 |
| H <sub>2</sub> C=C=O             | HCH   | 121.78 (1)  | 61 fc  | 121.83    | 121.85 | 121.90   | 122.05 | 122.05 | 122.10 |        |
| CH <sub>3</sub> CN               | HCH   | 108.8 (3)   | 62 fc  | 109.09    | 109.10 | 109.14 c | 108.93 | 108.96 | 109.00 | 109.00 |
| H <sub>2</sub> C=CH <sub>2</sub> | HCH   | 117.12 (3)  | 63 ae  | 117.00    | 117.20 | 117.10   | 117.24 | 117.42 | 117.32 |        |
| CH <sub>3</sub> CH <sub>3</sub>  | HCH   | 107.7 (1)   | 64 fc  | 107.68    | 107.69 | 107.68   | 107.62 | 107.66 | 107.67 |        |
| H <sub>2</sub> C=C=C             | HCH   | 117.6 (1)   | 65 ae  | 117.22    | 117.40 | 117.40   | 117.11 | 117.29 | 117.37 |        |
| c-C <sub>3</sub> H <sub>2</sub>  | HCC   | 148.0       | 66 fc  | 148.49    | 147.95 | 147.87   | 148.34 | 147.84 | 147.75 | 147.74 |
| c-C <sub>3</sub> H <sub>2</sub>  | CCC   | 55.4        | 66 fc  | 55.18     | 55.43  | 55.5     | 55.48  | 55.72  | 55.82  | 55.86  |
| H <sub>2</sub> CCCH <sub>2</sub> | HCH   | 118.2 (5)   | 67 fc  | 118.06    | 118.21 | 118.24   | 118.30 | 118.43 | 118.46 |        |
| CH <sub>3</sub> CCH              | HCH   | 108.42      | 68 fc  | 108.30    | 108.35 | 108.50 c | 108.19 | 108.10 | 108.26 |        |
| c-C <sub>3</sub> H <sub>6</sub>  | HCH   | 114.97      | 69 ae  | 114.68    | 114.89 | 114.81   | 114.87 | 114.99 | 115.06 |        |
| HOF                              | HOF   | 97.54 (50)  | 34 ae  | 96.75     | 97.62  | 97.8     | 97.16  | 97.81  | 98.00  | 98.15  |
| ONF                              | ONF   | 109.922 (7) | 70 fc  | 110.21    | 110.17 | 110.06   | 110.60 | 110.42 | 110.28 | 110.18 |
| F <sub>2</sub> O                 | OFO   | 103.07 (5)  | 71 ae  | 103.01    | 103.17 | 103.10   | 103.06 | 103.16 | 103.06 | 103.01 |
| NF <sub>3</sub>                  | FNF   | 102.37 (3)  | 35 ae  | 101.93    | 101.98 | 101.95 c | 102.01 | 101.98 | 101.95 | 101.88 |
| HNO                              | HNO   | 109.09 (24) | 39 ae  | 107.68    | 108.03 | 108.09   | 107.31 | 107.48 | 107.76 | 107.86 |
| HNNH                             | HNN   | 106.3 (2)   | 72 ae  | 105.00    | 105.91 | 106.20   | 104.71 | 105.62 | 105.91 | 106.13 |
| H <sub>2</sub> O                 | HOH   | 104.5       | 73 ae  | 101.94    | 103.73 | 104.25   | 101.93 | 103.66 | 104.15 | 104.39 |
| H <sub>2</sub> O <sub>2</sub>    | OOH   | 100         | 44 ae  | 98.86     | 99.64  | 100.00   | 98.78  | 99.32  | 99.66  | 99.81  |
| H <sub>2</sub> O <sub>2</sub>    | HOOH  | 112         | 44 ae  | 117.95    | 113.71 | 112.44   | 118.44 | 114.27 | 112.72 | 112.82 |
| NH <sub>3</sub>                  | HNH   | 106.75      | 74 ae  | 103.59    | 106.06 | 106.36   | 103.86 | 105.98 | 106.47 | 106.87 |
| O <sub>3</sub>                   | OOO   | 116.79      | 75 ae  | 116.65    | 117.01 | 117.17   | 116.65 | 116.73 | 116.81 |        |

<sup>a</sup> VnZ = cc-pVnZ. AVQZ = cc-pVQZ + aug-cc-pVQZ on the electronegative atoms.

<sup>b</sup> fc = frozen core approximation, ae = all electrons correlated.

<sup>c</sup> Calculated with Eq. (2), see text.

Table 3. Analysis of the residuals (in degrees).

| Method             | residual            | with experimental angles of table 2 |               |               |                | with improved angles, see text |               |               |                |
|--------------------|---------------------|-------------------------------------|---------------|---------------|----------------|--------------------------------|---------------|---------------|----------------|
|                    |                     | <i>e</i> -VDZ                       | <i>e</i> -VTZ | <i>e</i> -VQZ | <i>e</i> -AVQZ | <i>e</i> -VDZ                  | <i>e</i> -VTZ | <i>e</i> -VQZ | <i>e</i> -AVQZ |
| CCSD(T)            | largest             | -5.95                               | -1.71         | 1.00          | 0.90           | -5.05                          | -0.81         | 0.46          | 0.36           |
|                    | mean <sup>a</sup>   | 0.94                                | 0.30          | 0.19          | 0.15           | 0.90                           | 0.25          | 0.14          | 0.07           |
|                    | median <sup>a</sup> | 0.47                                | 0.22          | 0.14          | 0.05           | 0.49                           | 0.20          | 0.12          | 0.03           |
| MP2                | max                 | -6.44                               | -2.27         | 1.33          | 1.23           | -5.54                          | -1.37         | 1.09          | 1.12           |
|                    | mean <sup>a</sup>   | 0.89                                | 0.44          | 0.32          | 0.29           | 0.86                           | 0.38          | 0.25          | 0.22           |
|                    | median              | 0.47                                | 0.32          | 0.25          | 0.20           | 0.49                           | 0.31          | 0.21          | 0.16           |
| B3LYP <sup>b</sup> | largest             | -2.37                               | -1.96         | -2.36         |                | -2.01                          | -1.57         | -2.00         |                |
|                    | mean <sup>a</sup>   | 0.56                                | 0.58          | 0.56          |                | 0.50                           | 0.49          | 0.48          |                |
|                    | median <sup>a</sup> | 0.42                                | 0.42          | 0.39          |                | 0.31                           | 0.36          | 0.36          |                |

<sup>a</sup> For the absolute values of the residuals.

<sup>b</sup> With the B3LYP method, the 6-311++G(3df,2pd) basis set was used instead of the cc-pVDZ one.

Table 4 . Comparison of the cc-pVnZ and cc-pCVnZ basis sets at the CCSD(T) level for the  $\angle(\text{HCF})$  angle (in degrees) in HCF, all electrons being correlated.

| $n$      | pVnZ    | VnZ + aug(C, F) | CVnZ    | CVnZ + aug(C, F) |
|----------|---------|-----------------|---------|------------------|
| D        | 101.867 | 101.428         | 101.876 | 101.437          |
| T        | 102.444 | 102.378         | 102.328 | 102.262          |
| Q        | 102.420 | 102.407         | 102.393 | 102.380          |
| $\infty$ |         |                 | 102.404 | 102.400          |

Table 5 . Comparison of the cc-pVQZ and cc-pV5Z basis sets at the CCSD(T) level.

| Molecule                                    | Angle | cc-pVQZ             | cc-pV5Z             | Ref. |
|---------------------------------------------|-------|---------------------|---------------------|------|
| CH <sub>2</sub> <sup>1</sup> A <sub>1</sub> | HCH   | 101.90 <sup>a</sup> | 102.01 <sup>a</sup> | [25] |
| H <sub>2</sub> O                            | HOH   | 104.12              | 104.39              | [24] |
| H <sub>2</sub> C=CH <sub>2</sub>            | HCH   | 117.15              | 117.16              | [2]  |
| H <sub>2</sub> CC                           | HCH   | 119.95              | 120.00              | [2]  |
| CH <sub>3</sub> F                           | HCH   | 110.03              | 110.16              | [22] |
| O <sub>3</sub>                              | OOO   | 117.1               | 117.1               | [45] |
| H <sub>2</sub> SiO                          | HSiO  | 124.10              | 124.06              | [76] |
| PH <sub>3</sub>                             | HPH   | 93.48               | 93.46               | [46] |

<sup>a</sup> cc-pCVnZ basis sets.

Table 6. Structure of HNO (distances in Å and angles in degrees).

| Method                           | Basis <sup>a</sup>      | <i>r</i> (NH) | <i>r</i> (NO) | ∠(HNO)    |
|----------------------------------|-------------------------|---------------|---------------|-----------|
| CCSD(T)                          | cc-pV(5,Q)Z (fc)        | 1.0539        | 1.2099        | 108.092   |
|                                  | cc-pVQZ (fc)            | 1.0535        | 1.2107        | 108.010   |
|                                  | cc-pVTZ (fc)            | 1.0554        | 1.2144        | 107.860   |
|                                  | cc-pVDZ (fc)            | 1.0720        | 1.2196        | 107.656   |
|                                  | aug-cc-pVTZ (fc)        | 1.0556        | 1.2152        | 108.012   |
|                                  | aug-cc-pVDZ (fc)        | 1.0655        | 1.2259        | 107.708   |
|                                  | cc-pVQZ+aug(N,O) (ae)   | 1.0514        | 1.2083        | 108.188   |
|                                  | cc-pVQZ (ae)            | 1.0510        | 1.2082        | 108.094   |
|                                  | cc-pVTZ (ae)            | 1.0523        | 1.2103        | 108.026   |
|                                  | cc-pVDZ (ae)            | 1.0710        | 1.2191        | 107.682   |
|                                  | cc-pCVQZ (fc)           | 1.0537        | 1.2105        | 108.014   |
|                                  | cc-pCVQZ (ae)           | 1.0524        | 1.2085        | 108.085   |
|                                  | cc-pCVTZ (ae)           | 1.0542        | 1.2118        | 107.934   |
|                                  | cc-pCVDZ (ae)           | 1.0710        | 1.2184        | 107.692   |
| MP2                              | cc-pV(5,Q)Z+aug(O) (fc) | 1.0495        | 1.2170        | 107.765   |
|                                  | cc-pV(5,Q)Z (fc)        | 1.0494        | 1.2168        | 107.758   |
|                                  | aug-cc-pVQZ (fc)        | 1.0492        | 1.2178        | 107.763   |
|                                  | cc-pVQZ+aug(O) (fc)     | 1.0490        | 1.2180        | 107.677   |
|                                  | cc-pVQZ (fc)            | 1.0488        | 1.2175        | 107.661   |
| best estimate <sup>b</sup>       |                         | 1.0527        | 1.2080        | 108.169   |
| <i>r<sub>e</sub></i> (Ref. [39]) |                         | 1.063 (3)     | 1.206 (3)     | 109.1 (2) |

<sup>a</sup> fc = frozen core approximation, ae = all electrons correlated.

<sup>b</sup> CCSD(T)/cc-pV(5,Q)Z (fc) + diffuse corr. + core corr. with  
diffuse corr. = MP2/cc-pV(5,Q)Z+aug(O) - MP2/cc-pV(5,Q)Z  
core corr. = CCSD(T)/cc-pCVQZ (ae) - CCSD(T)/cc-pCVQZ (fc)

Table 7. Structure of H<sub>2</sub>O<sub>2</sub> (distances in Å and angles in degrees).

| method                        | basis               | $r(\text{OO})$ | $r(\text{OH})$ | $\angle(\text{HOO})$ | $\angle(\text{HOOH})$ |
|-------------------------------|---------------------|----------------|----------------|----------------------|-----------------------|
| CCSD(T)                       | cc-pVDZ (fc)        | 1.4699         | 0.9714         | 98.850               | 117.950               |
|                               | cc-pVTZ (fc)        | 1.4579         | 0.9640         | 99.550               | 113.900               |
|                               | cc-pVQZ (fc)        | 1.4525         | 0.9627         | 99.910               | 112.460               |
|                               | cc-pVQZ (ae)        | 1.4495         | 0.9610         | 100.000              | 112.440               |
|                               | cc-pV(5,Q)Z (fc)    | 1.4510         | 0.9635         | 100.043              | 112.834               |
|                               | cc-pVQZ+aug(O)      | 1.4531         | 0.9638         | 100.062              | 112.531               |
|                               | (fc)                |                |                |                      |                       |
| MP2                           | cc-pVTZ (fc)        | 1.4505         | 0.9644         | 99.321               | 114.267               |
|                               | cc-pVQZ (fc)        | 1.4464         | 0.9631         | 99.658               | 112.723               |
|                               | cc-pV(5,Q)Z (fc)    | 1.4455         | 0.9642         | 99.769               | 113.232               |
|                               | aug-cc-pVDZ (fc)    | 1.4702         | 0.9716         | 99.144               | 112.922               |
|                               | aug-cc-pVTZ (fc)    | 1.4539         | 0.9670         | 99.593               | 112.993               |
|                               | aug-cc-pVQZ (fc)    | 1.4470         | 0.9642         | 99.809               | 112.818               |
|                               | aug-cc-p(5,Q)Z (fc) | 1.4458         | 0.9646         | 99.835               | 113.044               |
|                               | cc-pCVQZ (ae)       | 1.4435         | 0.9623         | 99.757               | 112.989               |
|                               | cc-pCVQZ (fc)       | 1.4462         | 0.9632         | 99.664               | 112.861               |
| best estimate I <sup>b</sup>  |                     | 1.4492         | 0.9632         | 100.182              | 112.885               |
| best estimate II <sup>c</sup> |                     | 1.4492         | 0.9633         | 100.180              | 112.909               |

<sup>a</sup> fc = frozen core approximation, ae = all electrons correlated.

<sup>b</sup> CCSD(T)/cc-pVQZ+aug(O) (fc) +corr. I + core corr. with  
corr. I = MP2/aug-cc-p(5,Q)Z (fc) - MP2/aug-cc-pVQZ (fc)  
core corr. = MP2/cc-pCVQZ (ae) - MP2/cc-pCVQZ (fc)

<sup>c</sup> CCSD(T)/cc-pVQZ (fc) +corr. II + core corr. with  
corr. II = MP2/aug-cc-p(5,Q)Z (fc) - MP2/cc-pVQZ (fc).

Table 8 .  $\angle(\text{HPH})$  angle (in degrees) in  $\text{PH}_3$  <sup>a</sup>.

|         |    | cc-pVDZ | cc-pVTZ | cc-pVQZ | cc-pV5Z |
|---------|----|---------|---------|---------|---------|
| CCSD(T) | fc | 93.373  | 93.51   | 93.55   | 93.56   |
| CCSD(T) | ae | 93.370  | 93.31   | 93.48   | 93.46   |
| MP2     | fc |         | 93.64   | 93.69   | 93.71   |

<sup>a</sup> The experimental value is 93.45(9)° [46].

Table 9. Structure of  $\text{F}_2\text{S}$  (distances in Å and angles in degrees).

| Method                     | Basis     | without diffuse functions |                      | with aug(F)     |                      |
|----------------------------|-----------|---------------------------|----------------------|-----------------|----------------------|
|                            |           | $r(\text{S-F})$           | $\angle(\text{FSF})$ | $r(\text{S-F})$ | $\angle(\text{FSF})$ |
| CCSD(T) <sup>a</sup>       | cc-pVDZ   | 1.6482                    | 98.6124              | 1.6471          | 97.8734              |
|                            | cc-pVTZ   | 1.6032                    | 98.2603              | 1.6089          | 97.6429              |
|                            | cc-pVQZ   | 1.5959                    | 98.0752              | 1.5974          | 97.8124              |
|                            | cc-pVTZ+1 | 1.5953                    | 98.4165              | 1.6006          | 97.7918              |
|                            | cc-pVQZ+1 | 1.5924                    | 98.1643              | 1.5936          | 97.9109              |
| CCSD(T) <sup>b</sup>       | cc-pVQZ   | 1.5937                    | 98.0639              |                 |                      |
| MP2 <sup>a</sup>           | cc-pVQZ   | 1.5951                    | 98.5062              | 1.5960          | 98.2783              |
|                            | cc-pVQZ+1 | 1.5916                    | 98.6009              |                 |                      |
|                            | cc-pV5Z   | 1.5900                    | 98.4873              | 1.5904          | 98.3929              |
| best estimate <sup>c</sup> |           | 1.589                     | 97.95                |                 |                      |
| $r_z$ Ref. [53]            |           | 1.59208 (8)               | 98.197 (11)          |                 |                      |
| $r_e$ Ref. [54]            |           | 1.58745 (12)              | 98.048 (13)          |                 |                      |

<sup>a</sup> Frozen core approximation

<sup>b</sup> all electrons correlated.

<sup>c</sup> CCSD(T)/cc-pVQZ+1 +corr. I + core corr. with  
corr.I = MP2/cc-pV5Z + aug(F) - MP2/cc-pVQZ+1  
core corr. = CCSD(T)/cc-pVQZ (ae) - CCSD(T)/cc-pVQZ (fc).



# Analyse des états de vibration du trifluorosilane

Le but de cette étude est double :

- tester la possibilité de déterminer *ab initio* un champ de force anharmonique fiable pour une telle molécule
- vérifier la théorie des réductions

Pour réaliser cet objectif il suffit de déterminer des paramètres spectroscopiques précis et de les comparer à ceux calculés avec le champ de force *ab initio*.

Nous avons analysé les différentes bandes de vibration pour déterminer avec précision les différents paramètres spectroscopiques. De nouvelles mesures haute résolution ont été faites avec les spectromètres présents des universités de Kiel, Lille, et Wuppertal.

A notre demande, Thiel et Breidung (Zurich) ont calculé un champ de force anharmonique *ab initio*. Il existait déjà un champ de force expérimental déterminé par Hoy et coll. [73Hoy]. Mais compte tenu du manque de données, seules six constantes cubiques (sur un total de 38) avaient pu être déterminées.

## I) Présentation de la molécule

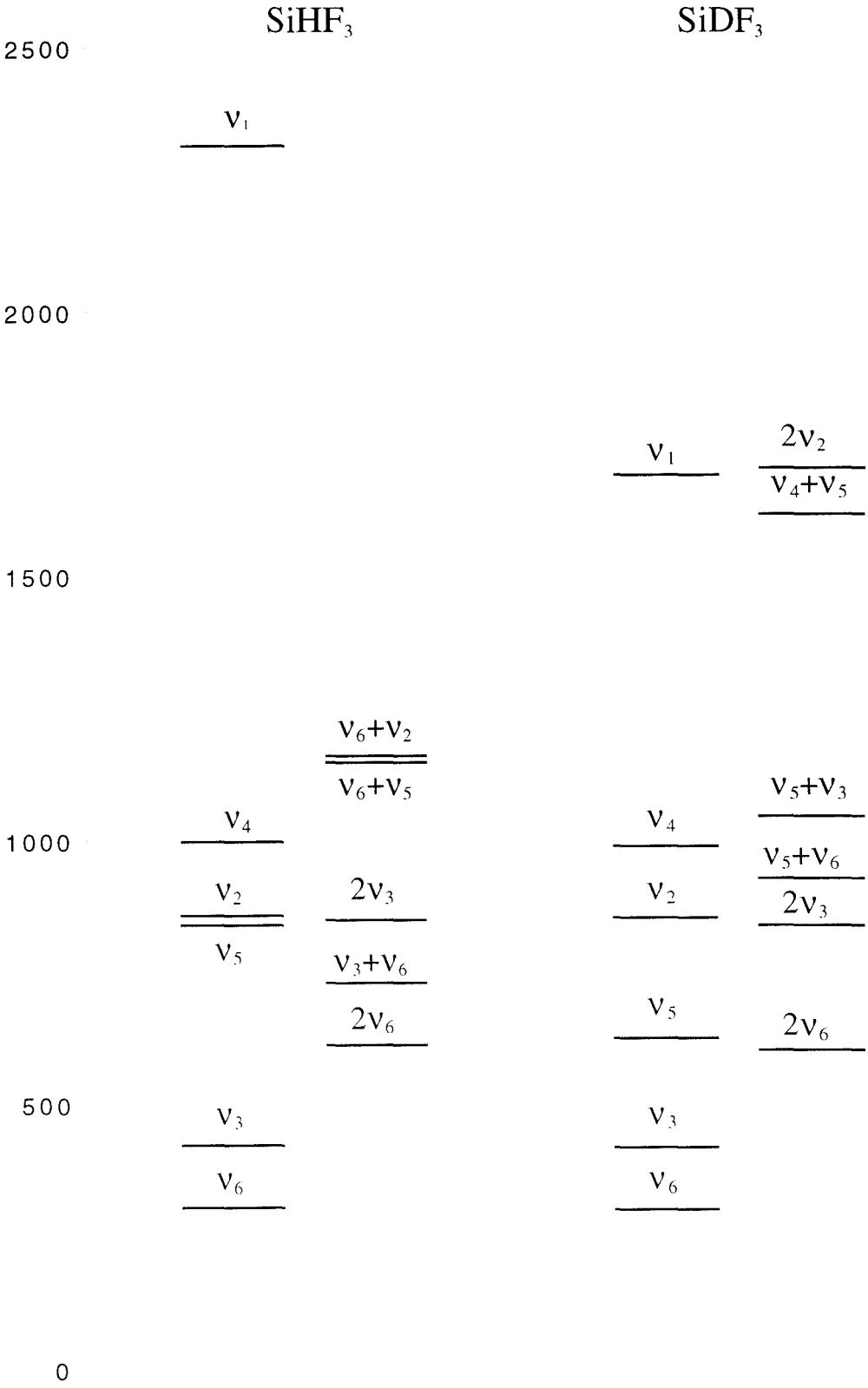
SiHF<sub>3</sub> est une molécule pentatomique de symétrie C<sub>3v</sub>, il y a donc neuf modes de vibration fondamentaux : trois modes non dégénérés ( $\nu_1, \nu_2, \nu_3$ ) et les trois modes dégénérés ( $\nu_4, \nu_5, \nu_6$ ). L'état de vibration le plus bas  $\nu_6$  est dégénéré, comme c'est souvent le cas pour une toupie C<sub>3v</sub>. Il est aussi très bien isolé, l'état le plus proche étant à plus de 100 cm<sup>-1</sup>.

**Tableau 10 :** Fréquences de vibration fondamentale du trifluorosilane

|                |         | SiHF <sub>3</sub> | intensité <sup>a)</sup> | SiDF <sub>3</sub> | intensité |                              |
|----------------|---------|-------------------|-------------------------|-------------------|-----------|------------------------------|
| A <sub>1</sub> | $\nu_1$ | 2316.9            | 0.0015                  | 1689.6            | 0.04      | allongement SiH              |
| A <sub>1</sub> | $\nu_2$ | 856               | 1.63                    | 854               | 1.69      | allongement SiF <sub>3</sub> |
| A <sub>1</sub> | $\nu_3$ | 425               | 13.00                   | 422               | 13.19     | « umbrella »                 |
| E              | $\nu_4$ | 998               | 0.83                    | 994.3             | 0.86      | allongement SiF <sub>3</sub> |
| E              | $\nu_5$ | 844               | 1.74                    | 627.2             | 4.91      | « rock » SiH                 |
| E              | $\nu_6$ | 305.5             | 23.02                   | 302.3             | 23.35     | déformation SiF <sub>3</sub> |

<sup>a)</sup> population relative des niveaux par rapport à ceux de l'état fondamental à 300K

**Figure 8 :** Niveaux d'énergie de vibration en  $\text{cm}^{-1}$



Nous avons vu dans le chapitre 2 que l'analyse de mesures provenant de plusieurs domaines spectraux fournissaient les paramètres les plus fiables. Nous avons entrepris d'utiliser en plus des spectres millimétriques les spectres infrarouge haute résolution et les spectres microondes à transformée de Fourier (Kiel). Tous les spectres infrarouges ont été enregistrés à l'université de Wuppertal, les identifications de ces spectres ont ensuite été effectuées à Wuppertal mais aussi à Lille et à Prague.

Les états de vibration dégénérés sont ceux dont l'analyse fournit le plus de renseignements, ce sont donc principalement pour ces états que nous avons fait une analyse complète

Nous avons débuté l'analyse des bandes de vibration dans la gamme millimétrique de 150 à 490 GHz. Les cinq états les plus bas en énergie sont observables en spectroscopie de rotation à température ambiante car ils sont à moins de  $1000\text{ cm}^{-1}$ . Pour la première prévision, nous avons utilisé les paramètres obtenus par Hoy et coll. Sauf pour  $v_4 = 1$ , pour lequel une étude plus récente existe le domaine infrarouge.

Le spectre de rotation que nous avons obtenu est assez dense, car en plus des états de vibration fondamentaux, les bandes chaudes et de combinaison sont encore assez intenses pour qu'on puisse les observer. Il y a aussi les isotopes  $^{29}\text{Si}$  et  $^{30}\text{Si}$  présents à respectivement cinq et trois pour cent en abondance naturelle, ainsi que les états excités de ces isotopomères. Nous n'avons donc pas pu identifier toutes les transitions présentes dans le spectre, nous nous sommes limités aux bandes fondamentales de vibration et aux espèces isotopiques dans leur état fondamental.

Le moment dipolaire est de 1.26 D, les transitions de l'état fondamental sont intenses et l'identification a pu être effectuée sans problème. Le spectre présentait bien les alternances d'intensité fournies par la statistique de spin nucléaire : les transitions pour les  $K$  multiples de trois (lorsqu'elles ne sont pas dédoublées) ont une intensité double des autres valeurs de  $K$ .

L'analyse des états  $v_4 = 1$  et  $v_6 = 1$  ainsi que celle de l'état fondamental sont détaillées dans les trois articles qui suivent cette partie.

## II) Analyse des spectres

### 1) Etats non dégénérés

Les spectres des états non dégénérés sont très semblables à celui de l'état fondamental, l'analyse des spectres de rotation a été assez simple pour  $v_2 = 1$  et  $v_3 = 1$ . Les résultats obtenus sont rassemblés dans le tableau 10.

$$v_1 = 1 :$$

Nous n'avons pas pu faire l'analyse de cet état dans le domaine millimétrique, car les transitions sont trop faibles. Des transitions ont pu être observées dans la zone concernée, mais il n'a pas été possible de faire une identification certaine, malgré l'étude des spectres infrarouge par Mkadmi et Bürger à Wuppertal.

$$v_2 = 1 :$$

Cet état est en interaction de Fermi avec  $v_3 = 2$ . Cette interaction produit un déplacement global des niveaux d'énergie, l'analyse du spectre n'est pas plus compliquée, mais les paramètres spectroscopiques obtenus sont affectés par cette interaction. Pour comparer les paramètres avec ceux du champ de force il faut les déperturber, pour cela il est nécessaire aussi d'étudier l'état  $v_3 = 2$ , mais nous n'avons pas pu faire une analyse satisfaisante de cet état.

Nous voulions surtout éliminer du spectre les raies correspondant à l'état  $v_2 = 1$ , pour permettre une identification plus facile de  $v_4 = 1$ , car les spectres de ces deux états sont mélangés.

$$v_3 = 1 :$$

L'identification a été relativement facile, il n'y a aucune interaction et les transitions sont assez intenses : 13 % de l'état fondamental. Mais comme pour  $v_2$  et  $v_4$ , les spectres de  $v_3$  et  $v_6$  sont très proches. De plus les transitions ont des intensités assez voisines, il était donc indispensable d'analyser l'état  $v_3$  pour pouvoir faire une identification correcte de l'état  $v_6$ .

**Tableau 10 :** Les paramètres spectroscopiques en MHz pour les états  $v_2$  et  $v_3$

|                 | SiDF <sub>3</sub> |                | SiHF <sub>3</sub> |                 |
|-----------------|-------------------|----------------|-------------------|-----------------|
|                 | $v_2$             | $v_3$          | $v_2$             | $v_3$           |
| $B$             | 6875.72132 (49)   | 6894.63831(49) | 7192.68982 (62)   | 7212.53209 (33) |
| $D_J * 10^3$    | 6.19650 (82)      | 6.32451 (84)   | 7.2536 (10)       | 7.54802 (69)    |
| $D_{JK} * 10^3$ | -9.9414 (17)      | -9.8883 (16)   | -12.3295 (21)     | -12.4600 (21)   |
| $H_J * 10^6$    | 0.02874 (39)      | 0.01518 (39)   | 0.04255 (53)      | 0.02263 (38)    |
| $H_{JK} * 10^6$ | -0.07829 (94)     | -0.06036 (87)  | -0.1077 (12)      | -0.0849 (11)    |
| $H_{KJ} * 10^6$ | 0.0858 (10)       | 0.07657 (94)   | 0.11460 (98)      | 0.108 (10)      |
| $\sigma$ (kHz)  | 32                | 31             | 38                | 24              |
| transitions     | 74                | 74             | 118               | 66              |

Pour les états non dégénérés  $\nu_2$  et  $\nu_3$ , Bürger et Mkadmi à Wuppertal ont débuté l'analyse des bandes de vibration dans le domaine infra-rouge à partir de nos données millimétriques. Le but est d'obtenir des données supplémentaires sur les interactions qui existent pour ces états.

## 2) L'état dégénéré $\nu_5 = 1$ :

L'identification de cet état a été un exercice assez délicat, aussi bien pour  $\text{SiHF}_3$  que pour  $\text{SiDF}_3$ .

\*  **$\text{SiDF}_3$** : La constante de rotation de cet état excité étant très voisine de celle de l'état fondamental, les deux spectres sont donc mélangés. Les transitions qui correspondent à  $\nu_5 = 1$  sont beaucoup moins intenses que celles de l'état fondamental, la plupart des transitions n'ont donc pu être observées : il n'a pas été possible d'identifier cet état à partir des seules données millimétriques.

Pracna (Prague) a analysé le spectre infrarouge, puis à partir de ces données nous avons pu faire une prévision qui nous a permis d'identifier certaines transitions dans le spectre millimétrique. Cet état fait l'objet d'une publication soumise au *Journal of Molecular Spectroscopy*.

Bien qu'il y ait une interaction avec l'état  $\nu_6 = 2$ , l'état  $\nu_5 = 1$  a pu être traité comme un état isolé.

\*  **$\text{SiHF}_3$** : sur la figure 6 qui représente les niveaux d'énergie de vibration, on peut voir qu'il y a trois états en interaction :  $\nu_5$ ,  $\nu_2$  et  $2\nu_3$ . Nous avons débuter d'identification de cet état ( $\nu_5 = 1$ ) avec le spectre millimétriques, mais il n'est pas possible d'obtenir un résultat correct en le considérant comme un état isolé, alors qu'il a été possible de le faire pour  $\nu_2 = 1$ . La solution pour compléter l'analyse de  $\nu_5 = 1$  serait de traiter ces trois états dans un ajustement global.

## 3) Les états de vibration dégénérées $\nu_4$ et $\nu_6 = 1$

En plus de  $\nu_4 = 1$  et  $\nu_6 = 1$ , nous présentons les résultats sur l'état fondamental de vibration pour l'espèce mère  $^{28}\text{SiHF}_3$ , ainsi que pour les deux isotopes  $^{29}\text{Si}$  et  $^{30}\text{Si}$ .

Nous nous sommes plus particulièrement intéressés aux états  $\nu_6 = 1$  et  $\nu_4 = 1$  pour les deux raisons suivantes :

- Pour  $v_4 = 1$ , bien qu'il soit relativement haut en énergie (994  $\text{cm}^{-1}$ ), il a été possible de le considérer comme un état isolé. Nous avons donc utilisé la théorie des états dégénérés et isolés présentée dans le premier chapitre.
- En ce qui concerne  $v_6 = 1$ , c'est un état très bien isolé, les paramètres expérimentaux ne devraient donc pas être perturbés par une interaction avec un autre état. Ces paramètres seront très importants pour la comparaison avec ceux issus du champ de force *ab initio*. C'est pour cet état que nous avons pu rassembler un maximum de données expérimentales, et donc déterminer le plus de paramètres spectroscopiques.

Pour les deux états  $v_6 = 1$  et  $v_4 = 1$ , les spectres infrarouges ont été enregistrés à l'université de Wuppertal, mais l'identification a été faite à Lille. En ce qui concerne  $v_6 = 1$  de  $\text{SiDF}_3$ , nous avons enregistré et analysé les transitions de dédoublement  $\ell$ -directes à l'université de Kiel. Pour  $\text{SiHF}_3$ , les mesures ont été faites par Gnida à Kiel.

Des mesures de ce type ne sont pas possibles pour l'état  $v_4 = 1$  qui est trop haut en énergie : les transitions ne sont pas assez intenses pour être observées.

Pour  $v_6 = 1$ , nous avons pour la première fois vérifié expérimentalement la réduction QD proposée par Harder. Cette réduction QD qui est aussi adaptée pour une toupie quasi-sphérique a permis d'obtenir des résultats équivalents aux deux autres réductions Q et D.

Avec les données expérimentales dont nous disposons, nous avons dû utiliser des termes d'ordre supérieur dans l'hamiltonien. Il faut alors appliquer une contrainte sur un des paramètres :  $\tau_J, \tau_{JK}, \tau_K, f_K^{22}$ , de plus nous avons pu confirmer expérimentalement les relations théoriques liant ces paramètres dans les trois réductions proposées par Watson [98Wat] et Harder [99Har].

# Analysis of Rotational and Rovibrational Spectra of SiDF<sub>3</sub> in the Ground and $\nu_4 = 1$ Excited States

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## Analysis of Rotational and Rovibrational Spectra of SiDF<sub>3</sub> in the Ground and $\nu_4 = 1$ Excited States

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This paper presents the analysis of the spectra of SiDF<sub>3</sub> in its vibrational ground and  $\nu_4 = 1$  states. The pure rotational spectrum of the ground state was measured up to 903 GHz ( $J'' = 65$ ). Rotational, quartic, and sextic centrifugal distortion constants were accurately determined. Furthermore the parameter  $|h_3| = 7.64(11) \times 10^{-4}$  Hz was derived from the observation of  $A_1$ - $A_2$  splittings of six  $K = 3$  lines. The assignment of the  $\nu_4 = 1$  spectrum was performed by combining 140 pure rotational frequencies and more than 2300 rovibrational transitions. Among them, because of the strong ( $\pm 2, \mp 4$ ) interaction, there are more than 90  $A_1$ - $A_2$  resolved split transitions between the ( $l = 0, k = \pm 3$ ) ground state levels and the ( $l = \pm 2, k = \mp 1$ )  $\nu_4 = 1$  levels. Although the  $\nu_4$  band is located at about  $994.3 \text{ cm}^{-1}$ , the energies of the other fundamental bands are at a distance of more than  $140 \text{ cm}^{-1}$ . The assumption of the isolated character of the state was confirmed by the small differences between the  $\nu_4 = 1$  state and the ground state parameters and by the possibility of using the  $D$  and  $Q$  reduction schemes proposed by E. I. Lobodenko, O. N. Sulakshina, V. I. Perevalov, and V. I. Tyuterev [*J. Mol. Spectrosc.* **126**, 159-170 (1987)]. © 1999 Academic Press

### 1. INTRODUCTION

Only a few papers have dealt with the rotation-vibration spectroscopy of trifluorosilane-*d*, SiDF<sub>3</sub>. Heath *et al.* observed the  $J = 2 \leftarrow 1$ ,  $3 \leftarrow 2$ , and  $4 \leftarrow 3$  rotational transitions at 27, 41, and 55 GHz of <sup>28</sup>SiDF<sub>3</sub>, <sup>29</sup>SiDF<sub>3</sub>, and <sup>30</sup>SiDF<sub>3</sub> in their vibrational ground state ( $l$ ). They derived the rotational constant  $B_0$  and a  $r_0$  structure. The second and more recent work in the centimeter-wave range was performed by Hoy *et al.* (2). They measured the  $J = 2 \leftarrow 1$  transitions in the ground state and five of the six fundamental excited vibrational states. They also refined the harmonic and cubic force fields using their new experimental data and infrared studies reported by Newman *et al.* (3) and Bürger *et al.* (4). This latter work was devoted to the assignment of the medium-resolution ( $0.3 \text{ cm}^{-1}$ ) spectra of all the fundamental vibrations with the assistance of band contours analyses. Harada *et al.* made the only high-resolution infrared analysis of the perpendicular  $\nu_4$  (SiF<sub>3</sub> antisymmetric stretching) band centered near  $994.3 \text{ cm}^{-1}$  using CO<sub>2</sub> laser Stark spectroscopy (5). By applying an electric field they were able to study the effects of the intravibrational  $l$ -type ( $\Delta l = \pm 2$ ,  $\Delta k = \mp 1$ ) resonance strengthened by a small value of  $C_4 - B_4 + 2C_4^2 = 1.7 \text{ GHz}$ . The axial rotational constant in the vibrational ground state,  $C_0$ , was determined with the help of several perturbation-induced rovibrational transitions. Finally, a precise value of the dipole moment of SiDF<sub>3</sub>,  $\mu = 1.35719(17) \text{ D}$ , was obtained.

The principal aim of the present work is to complete and improve the knowledge of the spectroscopic properties of

SiDF<sub>3</sub> by new investigations of all vibrational bands. We present in this paper the analysis of the ground and the  $\nu_4 = 1$  excited states. For both states the set of experimental data was extended to the millimeter range. A lot of new rovibrational infrared transitions in the excited state was observed too. The  $\nu_4$  band (see Fig. 1) looks like an isolated one, the energy of the closest fundamental band being  $140 \text{ cm}^{-1}$  lower. Furthermore, the band centers of the closest combination states,  $\nu_3 = \nu_5 = 1$  and  $\nu_5 = \nu_6 = 1$ , are more than  $55 \text{ cm}^{-1}$  away from the  $\nu_4$  band. Owing to this isolated character we expect that the data can be fitted using the reduction schemes proposed by Lobodenko *et al.* (6) and verified by many examples: CF<sub>3</sub>CCH,  $\nu_{10} = 1$  (7); D<sub>3</sub>GeH,  $\nu_5 = 1$  (8); CF<sub>3</sub>Cl,  $\nu_6 = 1$  (9); AsF<sub>3</sub>,  $\nu_4 = 1$  (10); CF<sub>3</sub>CN,  $\nu_8 = 1$  (11); CDF<sub>3</sub>,  $\nu_6 = 1$  (12). Finally, like the parent species SiHF<sub>3</sub> of which several far-infrared (FIR) emissions can be pumped (13), SiDF<sub>3</sub> may be a good candidate for generating FIR laser radiation as the  $\nu_4 = 1$  state lies in the range of pumping CO<sub>2</sub> laser emissions. The accurate knowledge of the position of the  $\nu_4 = 1$  energy levels will help in the assignment of the probable far-infrared laser emissions.

### 2. EXPERIMENTAL DETAILS

#### 2.1. Synthesis of SiDF<sub>3</sub>

Deuterated trichlorosilane (SiDCl<sub>3</sub>, made from Si and DCl) was converted into trifluorosilane (SiDF<sub>3</sub>) by reaction with antimony trifluoride (SbF<sub>3</sub>) at room temperature. For this purpose SiDCl<sub>3</sub> was condensed into a bulb coated with freshly

MARGULÈS ET AL.

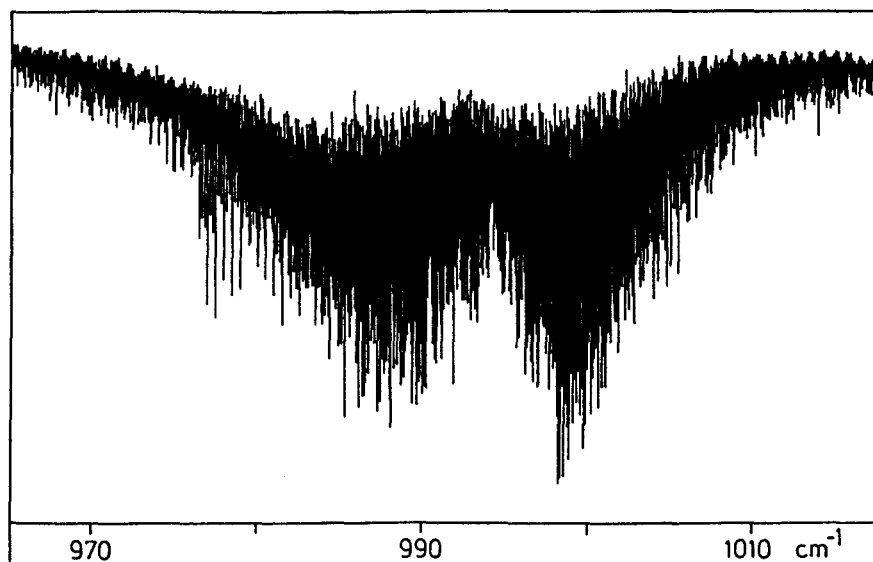


FIG. 1. Overview of the FTIR spectrum of the  $\nu_4$  band of  $\text{SiDF}_3$ .

sublimed antimony trifluoride and cooled to liquid-nitrogen temperature. As was found earlier,  $\text{SiF}_4$  was the main impurity formed by fluorination of  $\text{SiCl}_4$ . Moreover, traces of  $\text{SiH}_2\text{F}_2$  were present.

## 2.2. Rotational Spectrum

The pure rotational spectrum was observed from 150 to 900 GHz. The lower part of this range (150–315 GHz) was studied using harmonics of klystrons or a Gunn diode and superheterodyne detection (14). French Thomson-CSF and Russian Istok backward-wave oscillators (BWO) were employed be-

tween 450 and 590 GHz. The detector was a helium-cooled InSb bolometer. The accuracy of the measurements is about 50 kHz for isolated lines.

The measurements between 645 and 900 GHz were performed using a newly stabilized far-infrared (FIR) spectrometer. The principle of this experiment consists of producing sidebands in the FIR region by mixing a FIR laser radiation with the radiation emitted by a synthesizer operating in the range 2–18 GHz. These sidebands with a tunability of 32 GHz serve as a source for the spectrometer (15).

All the experiments based on the use of a FIR laser are

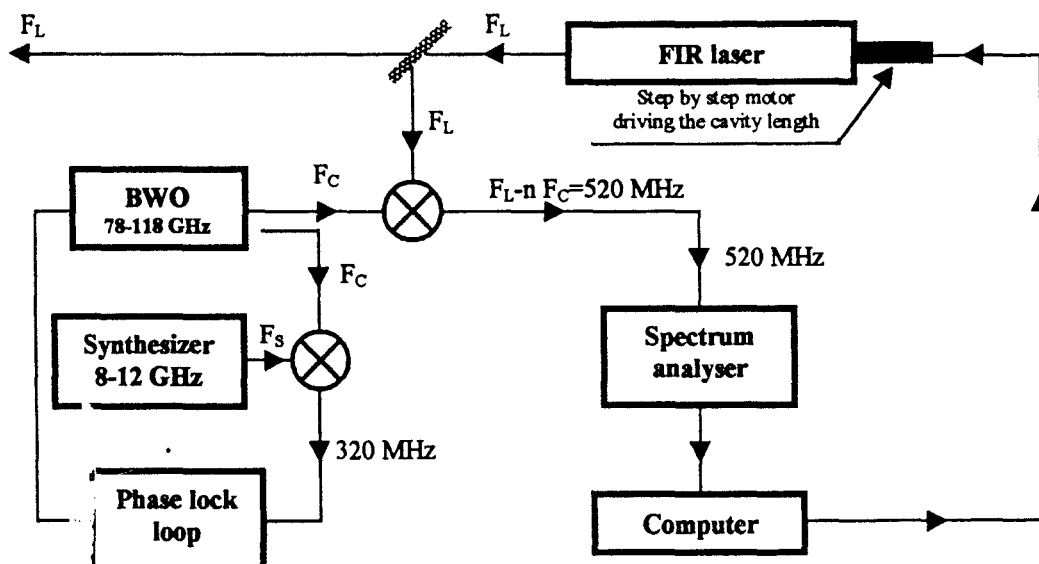


FIG. 2. Scheme of the experimental setup used to stabilize the FIR laser.

1

GROUND AND  $\nu_4 = 1$  ROVIBRATIONAL SPECTRA OF SiDF<sub>3</sub>

TABLE 1  
New Experimental Frequencies of Pure Rotational Transitions in the Vibrational Ground State of <sup>28</sup>SiDF<sub>3</sub>

| J  | K  | Obs.       | O.-C. | Unc. | J  | K  | Obs.       | O.-C. | Unc. | J  | K  | Obs.       | O.-C. | Unc. |
|----|----|------------|-------|------|----|----|------------|-------|------|----|----|------------|-------|------|
| 10 | 0  | 151548.643 | 113   | 150  | 22 | 14 | 316725.924 | 18    | 50   | 41 | 3  | 576908.151 | 57    | 50   |
| 10 | 1  | 151548.643 | -106  | 150  | 22 | 15 | 316739.120 | -44   | 50   | 41 | 18 | 577166.247 | 7     | 50   |
| 10 | 2  | 151549.401 | -5    | 50   | 22 | 16 | 316753.377 | 37    | 50   | 41 | 24 | 577374.166 | 3     | 50   |
| 10 | 3  | 151550.500 | -2    | 50   | 22 | 17 | 316768.464 | 26    | 50   | 42 | 0  | 590544.330 | 15    | 50   |
| 10 | 4  | 151552.032 | -2    | 50   | 22 | 18 | 316784.501 | 41    | 50   | 42 | 1  | 590545.171 | 18    | 50   |
| 10 | 5  | 151553.999 | -7    | 50   | 22 | 19 | 316801.388 | -19   | 50   | 42 | -3 | 590551.171 | -12   | 50   |
| 10 | 6  | 151556.390 | -26   | 50   | 22 | 20 | 316819.345 | 65    | 50   | 42 | 3  | 590552.182 | -347  | 500  |
| 10 | 7  | 151559.222 | -42   | 50   | 22 | 21 | 316838.123 | 41    | 50   | 46 | 0  | 645056.058 | 339   | 500  |
| 10 | 8  | 151562.544 | -8    | 50   | 22 | 22 | 316857.790 | -24   | 50   | 46 | 2  | 645059.282 | -84   | 300  |
| 10 | 9  | 151566.282 | 3     | 50   | 32 | 0  | 453838.443 | 322   | 500  | 46 | 3  | 645064.796 | -178  | 300  |
| 10 | 10 | 151570.458 | 12    | 50   | 32 | 2  | 453840.742 | 24    | 50   | 46 | -3 | 645062.680 | -195  | 300  |
| 16 | 0  | 234138.935 | -11   | 50   | 32 | 3  | 453843.965 | -178  | 250  | 46 | 4  | 645070.005 | -302  | 300  |
| 16 | 1  | 234139.269 | -15   | 50   | 32 | -3 | 453843.965 | 180   | 250  | 46 | 15 | 645261.399 | 189   | 300  |
| 16 | 2  | 234140.285 | -12   | 50   | 32 | 4  | 453848.533 | 24    | 50   | 46 | 21 | 645459.177 | 3     | 300  |
| 16 | 3  | 234141.982 | -11   | 50   | 32 | 5  | 453854.389 | 36    | 50   | 46 | 27 | 645723.926 | -253  | 300  |
| 16 | 4  | 234144.353 | 2     | 50   | 32 | 6  | 453861.520 | 23    | 50   | 46 | 30 | 645881.998 | -98   | 300  |
| 16 | 5  | 234147.414 | 23    | 50   | 32 | 15 | 453984.407 | -31   | 50   | 46 | 33 | 646057.544 | 415   | 300  |
| 16 | 6  | 234151.130 | 22    | 50   | 32 | 21 | 454125.370 | -17   | 50   | 63 | 0  | 875381.644 | 3     | 300  |
| 16 | 7  | 234155.523 | 21    | 50   | 32 | 24 | 454213.697 | -25   | 50   | 63 | 1  | 875383.394 | 539   | 500  |
| 16 | 8  | 234160.576 | 4     | 50   | 32 | 27 | 454314.059 | -1    | 50   | 63 | 2  | 875386.501 | 4     | 300  |
| 16 | 9  | 234166.319 | -1    | 50   | 32 | 30 | 454426.535 | 50    | 50   | 63 | 3  | 875397.454 | -9    | 300  |
| 16 | 10 | 234172.745 | -2    | 50   | 32 | 31 | 454466.887 | 25    | 50   | 63 | -3 | 875387.914 | 293   | 300  |
| 16 | 11 | 234179.831 | -20   | 50   | 32 | 32 | 454508.232 | 37    | 50   | 63 | 4  | 875401.138 | 129   | 300  |
| 16 | 12 | 234187.627 | -8    | 50   | 33 | 0  | 467533.455 | 14    | 150  | 63 | 5  | 875411.972 | 45    | 300  |
| 16 | 13 | 234196.100 | 1     | 50   | 33 | 1  | 467534.008 | -102  | 150  | 63 | 6  | 875425.311 | 48    | 300  |
| 16 | 14 | 234205.284 | 40    | 50   | 33 | 2  | 467536.043 | -71   | 50   | 63 | 7  | 875440.792 | -241  | 300  |
| 16 | 15 | 234215.118 | 47    | 50   | 33 | 3  | 467539.414 | -250  | 500  | 63 | 8  | 875459.304 | 76    | 300  |
| 16 | 16 | 234225.615 | 35    | 50   | 33 | -3 | 467539.414 | 165   | 500  | 63 | 9  | 875479.581 | -272  | 300  |
| 22 | 0  | 316636.422 | -54   | 50   | 33 | 12 | 467629.727 | -53   | 50   | 63 | 10 | 875502.533 | -381  | 300  |
| 22 | 1  | 316636.927 | -4    | 50   | 33 | 18 | 467750.464 | -48   | 50   | 65 | 0  | 902315.740 | -60   | 300  |
| 22 | 2  | 316638.285 | -13   | 50   | 33 | 21 | 467829.148 | -19   | 50   | 65 | 1  | 902317.052 | 5     | 300  |
| 22 | 3  | 316640.580 | -26   | 50   | 33 | 24 | 467920.102 | -1    | 50   | 65 | 2  | 902321.065 | 271   | 500  |
| 22 | 4  | 316643.789 | 23    | 50   | 33 | 27 | 468023.386 | -10   | 50   | 65 | 3  | 902332.330 | -411  | 300  |
| 22 | 5  | 316647.900 | 32    | 50   | 33 | 30 | 468139.079 | -53   | 50   | 65 | -3 | 902321.065 | -196  | 300  |
| 22 | 6  | 316652.902 | 20    | 50   | 33 | 33 | 468267.359 | -49   | 50   | 65 | 4  | 902335.482 | -215  | 300  |
| 22 | 7  | 316658.818 | 10    | 50   | 38 | 0  | 535930.555 | -34   | 100  | 65 | 6  | 902360.598 | -29   | 300  |
| 22 | 8  | 316665.633 | -15   | 50   | 38 | 1  | 535931.397 | 45    | 100  | 65 | 9  | 902416.922 | 187   | 300  |
| 22 | 9  | 316673.373 | -29   | 50   | 38 | -3 | 535936.993 | -52   | 50   | 65 | 12 | 902495.392 | 43    | 300  |
| 22 | 10 | 316682.021 | -49   | 50   | 38 | 3  | 535937.924 | 54    | 50   | 65 | 15 | 902596.830 | 288   | 300  |
| 22 | 11 | 316691.577 | -77   | 50   | 41 | 0  | 576900.128 | 6     | 100  | 65 | 18 | 902720.469 | 66    | 300  |
| 22 | 12 | 316702.185 | 30    | 50   | 41 | 1  | 576900.985 | 44    | 100  | 65 | 21 | 902867.248 | 206   | 300  |
| 22 | 13 | 316713.620 | 48    | 50   | 41 | -3 | 576906.906 | 8     | 50   |    |    |            |       |      |

biased by the laser frequency uncertainty. Even if the knowledge of the laser frequency is very precise, there is always a laser cavity length shift, limiting the spectrometer frequency accuracy from 500 kHz to 1 MHz (16). After demonstrating the feasibility (17), we built a frequency stabilization of the FIR laser to enhance the frequency accuracy (Fig. 2). Part of the laser output power is used to generate a beat around 520 MHz with the radiation from a BWO in the range 78–118 GHz, phase locked on a 8–12 GHz synthesizer. The beat frequency is measured by a spectrum analyzer and sent via a GPIB bus to the computer which drives the stepping motor of the laser

cavity. The FIR laser frequency is then controlled by tuning the cavity length.

For the present study, the following emissions of CH<sub>2</sub>CHF were used: 634.2220 GHz pumped by the 10P20 CO<sub>2</sub> line; 889.3414 GHz pumped by the 10P38 line. The accuracy of the measurements was about 300 kHz.

2.3. Fourier Transform Infrared Spectrum

The  $\nu_4$  band appeared with high intensity in the infrared spectrum recorded between 750 and 1400 cm<sup>-1</sup> with a Bruker

MARGULÈS ET AL.

TABLE 2  
Molecular Constants of <sup>28</sup>SiDF<sub>3</sub>, <sup>29</sup>SiDF<sub>3</sub>, and <sup>30</sup>SiDF<sub>3</sub> in the Vibrational Ground State

|                        |        | <sup>28</sup> SiDF <sub>3</sub> | <sup>29</sup> SiDF <sub>3</sub> | <sup>30</sup> SiDF <sub>3</sub> |
|------------------------|--------|---------------------------------|---------------------------------|---------------------------------|
| <i>B</i>               | (MHz)  | 6890.10533(23)                  | 6880.20882 (33)                 | 6870.57843 (34)                 |
| <i>D<sub>J</sub></i>   | (kHz)  | 6.34921 (12)                    | 6.31453 (55)                    | 6.27910 (57)                    |
| <i>D<sub>JK</sub></i>  | (kHz)  | - 9.9689 (10)                   | - 9.9067 (10)                   | - 9.8433 (11)                   |
| <i>H<sub>J</sub></i>   | (Hz)   | 0.016418 (18)                   | 0.01694 (25)                    | 0.01653 (26)                    |
| <i>H<sub>JK</sub></i>  | (Hz)   | - 0.06119 (28)                  | - 0.06230 (56)                  | - 0.06176 56)                   |
| <i>H<sub>KJ</sub></i>  | (Hz)   | 0.07724 (75)                    | 0.07806 (94)                    | 0.07664 (65)                    |
| <i>h<sub>3</sub></i>   | ( mHz) | 0.764 (11)                      |                                 |                                 |
| <i>C</i>               | (MHz)  | 4133.55 <sup>a)</sup>           |                                 |                                 |
| <i>D<sub>K</sub></i>   | (kHz)  | 4.55 <sup>b)</sup>              |                                 |                                 |
| <i>H<sub>K</sub></i>   | (Hz)   | 0 <sup>c)</sup>                 |                                 |                                 |
| No. lines              |        | 126                             | 81                              | 82                              |
| <i>J<sub>max</sub></i> |        | 65                              | 33                              | 33                              |
| σ (MM) <sup>d)</sup>   | (kHz)  | 33                              | 20                              | 21                              |
| σ (FIR) <sup>d)</sup>  | (kHz)  | 212                             |                                 |                                 |

<sup>a)</sup> Constrained to the experimental value of reference (5)  
<sup>b)</sup> Constrained to the value calculated from the harmonic force field (2)  
<sup>c)</sup> Constrained value  
<sup>d)</sup> Standard deviation of the fit . In the first column the standard deviation is given for millimeter data set (MM) and for the far infrared data set (FIR).

120 HR Fourier transform spectrometer. A Globar source, a KBr beam splitter, and a MCT 800 detector were used. The pressure was 0.3 mbar in a 280-mm long cell. The resolution of  $2.3 \times 10^{-3} \text{ cm}^{-1}$  corresponded to a maximum optical path difference of 435 cm in the interferometer. The calibration was done using residuals water lines in the range 1336–1380  $\text{cm}^{-1}$ . The precision of the wavenumbers is estimated to be  $4 \times 10^{-4} \text{ cm}^{-1}$  for well-resolved and symmetric lines, and their accuracy is better than  $1 \times 10^{-3} \text{ cm}^{-1}$ .

3. THEORY

The separation between the  $\nu_4$  band (994.3  $\text{cm}^{-1}$ ) and the closest fundamental band  $\nu_2$  (850.1  $\text{cm}^{-1}$ ) is about 140  $\text{cm}^{-1}$ . The combination states,  $\nu_3 = \nu_5 = 1$  (1050.5  $\text{cm}^{-1}$ ) and  $\nu_5 = \nu_6 = 1$  (931.5  $\text{cm}^{-1}$ ), may perturb the  $\nu_4 = 1$  state. Interactions may be anharmonic or, e.g., of Coriolis type. Since, however, the band centers are more than 55  $\text{cm}^{-1}$  apart from that of  $\nu_4$ , no crossings of levels that can interact by  $\Delta k - \Delta l = 0$  mechanisms are expected in view of the smallness of *B* and *C*. Possible resonance effects will be global and absorbed by the effective spectroscopic parameters. As a consequence, we re-

garded the  $\nu_4 = 1$  state as an isolated one. The diagonal elements of the energy matrix in the rotational quantum numbers *J*, *k*, and *l* are written as:

$$\begin{aligned} E = & \nu_0 + BJ(J+1) + (A-B)k^2 - D_JJ^2(J+1)^2 \\ & - D_{JK}J(J+1)k^2 - D_Kk^4 + H_JJ^3(J+1)^3 \\ & + H_{JK}J^2(J+1)^2k^2 + H_{KJ}J(J+1)k^4 + H_Kk^6 \\ & - 2(A\zeta)kl + \eta_JJ(J+1)kl \\ & + \eta_Kk^3l + \tau_{JJ}J^2(J+1)^2kl \\ & + \tau_{JK}J(J+1)k^3l + \tau_{KK}k^5l + \dots \end{aligned} \tag{1}$$

This expression can be used for the vibrational ground state by setting  $\nu_0$  and *l* to zero.

The off-diagonal terms must obey the general selection rule  $\Delta(k-l) = \pm 3n$ ,  $n = 0, 1, \dots$ . We included the *l*-type ( $\Delta l = \pm 2$ ,  $\Delta k = \pm 2$ ), ( $\pm 2, \mp 1$ ), and ( $\pm 2, \mp 4$ ) interactions whose expressions in the energy matrix are

GROUND AND  $\nu_4 = 1$  ROVIBRATIONAL SPECTRA OF SiDF<sub>3</sub>

TABLE 3  
Summary of the Main Characteristics of the Data Sets Used for the Analysis of <sup>28</sup>SiDF<sub>3</sub> in the  $\nu_4 = 1$  State

| Origin of the data                         | Ref.      | No. Data | <i>J</i> values <sup>a)</sup> | <i>kl</i> values <sup>a)</sup> | Uncertainty                           | St. Dev. Q Red.                       | St. Dev. D Red.                       |
|--------------------------------------------|-----------|----------|-------------------------------|--------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| <i>Rotational spectrum</i>                 |           |          |                               |                                |                                       |                                       |                                       |
| Microwave transitions                      | 2         | 3        | 2                             | -1 / +1                        | 200 kHz                               | 117 kHz                               | 117 kHz                               |
| Millimeter transitions                     | This work | 137      | 11 - 39                       | -29 / +31                      | 50 kHz                                | 54 kHz <sup>b)</sup>                  | 49 kHz                                |
| <i>Roivibrational spectrum</i>             |           |          |                               |                                |                                       |                                       |                                       |
| Laser Stark transitions                    | 5         | 109      | 2 - 24                        | -14 / +13                      | 1.6 10 <sup>-4</sup> cm <sup>-1</sup> | 7.9 10 <sup>-5</sup> cm <sup>-1</sup> | 7.9 10 <sup>-5</sup> cm <sup>-1</sup> |
| Forbidden transitions                      | 5         | 14       | 2 - 8                         | -2 / 0                         | 1.6 10 <sup>-4</sup> cm <sup>-1</sup> | 7.8 10 <sup>-5</sup> cm <sup>-1</sup> | 7.7 10 <sup>-5</sup> cm <sup>-1</sup> |
| FTIR transitions <sup>c)</sup>             | This work | 2009     | 2 - 64                        | -49 / +49                      | 4 10 <sup>-4</sup> cm <sup>-1</sup>   | 3.1 10 <sup>-4</sup> cm <sup>-1</sup> | 3.1 10 <sup>-4</sup> cm <sup>-1</sup> |
| A <sub>1</sub> - A <sub>2</sub> splittings | This work | 187      | 22 - 64                       | -2                             | 4 10 <sup>-4</sup> cm <sup>-1</sup>   | 3.6 10 <sup>-4</sup> cm <sup>-1</sup> | 3.4 10 <sup>-4</sup> cm <sup>-1</sup> |

<sup>a)</sup> Quantum numbers related to the upper level.  
<sup>b)</sup> Fit performed with the *r* constants constrained to zero. See text.  
<sup>c)</sup> Set of transitions in the <sup>R</sup>R, <sup>R</sup>P, <sup>R</sup>Q, <sup>P</sup>R, <sup>P</sup>P and <sup>P</sup>Q branches.

$\langle \nu_4 = 1^{\pm 1}; J, k \pm 2 | \mathbf{H}_{22} + \mathbf{H}_{24} + \mathbf{H}_{26} | \nu_4 = 1^{\mp 1}; J, k \rangle$   
 $= 2\{q_{22} + q_{22}'J(J+1) + q_{22}''J^2(J+1)^2\}F_2^{\pm}(J, k)$  [2]

$\langle \nu_4 = 1^{\mp 1}; J, k \pm 1 | \mathbf{H}_{22} + \mathbf{H}_{24} | \nu_4 = 1^{\pm 1}; J, k \rangle$   
 $= 2\{[q_{12} + q_{12}'J(J+1)](2k \pm 1)\}F_1^{\pm}(J, k)$  [3]

$\langle \nu_4 = 1^{\mp 1}; J, k \pm 4 | \mathbf{H}_{24} + \mathbf{H}_{26} | \nu_4 = 1^{\pm 1}; J, k \rangle$   
 $= 2\{f_{42} + f_{42}'J(J+1) + f_{42}''J^2(J+1)^2\}F_4^{\pm}(J, k)$ , [4]

respectively, and the *k*-type (0, ±3) and (0, ±6) interactions expressed by

$\langle \nu_4 = 1^{\pm 1}; J, k \pm 3 | \mathbf{H}_{23} + \mathbf{H}_{25} | \nu_4 = 1^{\mp 1}; J, k \rangle$   
 $= l\{d + d'J(J+1)\}F_3^{\pm}(J, k)$  [5]

$\langle \nu_4 = 1^{\pm 1}; J, k \pm 6 | \mathbf{H}_{06} | \nu_4 = 1^{\mp 1}; J, k \rangle$   
 $= \{h_3 + h_{3J}J(J+1)\}F_6^{\pm}(J, k)$ , [6]

respectively. In Eq. [2], *q*<sub>22</sub> is smaller by a factor (−4) than the parameter defined by Cartwright and Mills (18) and used for the analysis reported in Ref. (5). *F*<sub>*n*</sub><sup>±</sup>(*J*, *k*) in the above relations is defined by

$F_n^{\pm}(J, k) = \prod_{i=1}^n [J(J+1) - (k \pm i \mp 1)(k \pm i)]^{1/2}$ . [7]

The program SIMFIT (19) was used to perform the fits of the

ground and the  $\nu_4 = 1$  excited state transitions and the determination of the molecular parameters.

4. RESULTS

4.1. Ground State

The ground state rotational spectrum of the <sup>28</sup>Si, <sup>29</sup>Si, and <sup>30</sup>Si isotopomers of SiDF<sub>3</sub> was analyzed. For the last two we observed transitions up to 467 GHz (*J* = 34 ← 33). The *K* = 3 lines should be split because of the nonvanishing off-diagonal matrix element  $\langle k | \mathbf{H} | k \pm 6 \rangle$  whose contribution is given by Eq. [6]. However, no splitting was observed for these isotopomers.

The ground state of <sup>28</sup>SiDF<sub>3</sub> was studied up to 903 GHz (*J* = 66 ← 65). The *K* = 3 lines were found split for *J* > 38. The parameter  $|h_3| = 7.64(11) \times 10^{-4}$  Hz is relatively well determined from the measurements of six doublets. Its sign cannot be determined from the analysis of the ground state spectrum. The higher order term *h*<sub>3*J*</sub> gave a better representation of the effect of the interaction, but its value was only twice its standard deviation. So *h*<sub>3*J*</sub> was constrained to zero.

Measurements reported in Ref. (2) were also included in the fits with an assumed uncertainty of 100 kHz.

The new frequencies and the parameters for the three isotopomers are reported in Tables 1 and 2, respectively. The order of magnitude and the signs of the constants are in agreement with previous studies of oblate top molecules like CDF<sub>3</sub> for instance (20).

TABLE 4  
 New Experimental Frequencies (in MHz) of Pure Rotational Transitions in the  $\nu_4 = 1$  State of SiDF<sub>3</sub>

| J  | K  | $\ell$ | Obs.       | O.-C. <sup>a)</sup> | O.-C. <sup>b)</sup> | Unc. <sup>c)</sup> | J  | K  | $\ell$ | Obs.       | O.-C. <sup>a)</sup> | O.-C. <sup>b)</sup> | Unc. <sup>c)</sup> | J  | K  | $\ell$ | Obs.       | O.-C. <sup>a)</sup> | O.-C. <sup>b)</sup> | Unc. <sup>c)</sup> |
|----|----|--------|------------|---------------------|---------------------|--------------------|----|----|--------|------------|---------------------|---------------------|--------------------|----|----|--------|------------|---------------------|---------------------|--------------------|
| 10 | 1  | 1      | 151356.264 | -6                  | -31                 | 50                 | 16 | 15 | 1      | 233689.313 | 88                  | 39                  | 50                 | 32 | 1  | 1      | 453231.357 | 76                  | 34                  | 50                 |
| 10 | -1 | -1     | 151068.486 | 35                  | 60                  | 50                 | 16 | 16 | 1      | 233699.748 | 44                  | -10                 | 50                 | 32 | 2  | 1      | 452588.290 | 29                  | 13                  | 50                 |
| 10 | 0  | -1     | 151223.917 | -11                 | -12                 | 50                 | 22 | 1  | 1      | 316215.804 | -86                 | -112                | 200                | 32 | 3  | 1      | 452694.974 | 32                  | 28                  | 50                 |
| 10 | 1  | -1     | 151218.663 | 109                 | 112                 | 100                | 22 | -1 | -1     | 315636.191 | 24                  | 16                  | 50                 | 32 | 4  | 1      | 452743.265 | -148                | -147                | 400                |
| 10 | -2 | 1      | 151216.688 | -82                 | -74                 | 100                | 22 | 0  | -1     | 316033.080 | -64                 | -78                 | 50                 | 32 | 5  | 1      | 452771.993 | -75                 | -69                 | 50                 |
| 10 | 2  | -1     | 151218.281 | 7                   | 15                  | 100                | 22 | -2 | 1      | 315966.882 | 4                   | 12                  | 200                | 32 | 6  | 1      | 452793.080 | -62                 | -53                 | 50                 |
| 10 | 3  | -1     | 151217.622 | -21                 | -10                 | 50                 | 22 | 2  | -1     | 315992.221 | -112                | -106                | 200                | 32 | 7  | 1      | 452810.767 | -46                 | -34                 | 50                 |
| 10 | 4  | -1     | 151218.663 | -111                | -96                 | 100                | 22 | 3  | -1     | 315963.806 | 259                 | 257                 | 300                | 32 | 10 | 1      | 452858.770 | -43                 | -28                 | 50                 |
| 10 | 5  | -1     | 151220.475 | -39                 | -20                 | 50                 | 22 | 4  | -1     | 315962.657 | -16                 | -13                 | 50                 | 32 | 16 | 1      | 452970.524 | -31                 | -27                 | 50                 |
| 10 | 6  | -1     | 151222.752 | -47                 | -24                 | 50                 | 22 | 5  | -1     | 315963.806 | -76                 | -68                 | 300                | 32 | 5  | -1     | 452897.221 | -96                 | -104                | 50                 |
| 10 | 7  | -1     | 151225.585 | -4                  | 23                  | 50                 | 22 | 6  | -1     | 315966.882 | 25                  | 37                  | 200                | 32 | 0  | -1     | 453072.720 | -130                | -113                | 50                 |
| 10 | 8  | -1     | 151228.884 | 20                  | 52                  | 50                 | 22 | 7  | -1     | 315971.381 | 71                  | 88                  | 200                | 32 | 1  | -1     | 452987.753 | -29                 | -35                 | 50                 |
| 10 | 2  | 1      | 151201.474 | -4                  | -2                  | 50                 | 22 | 8  | -1     | 315977.062 | -1                  | 21                  | 50                 | 32 | 2  | -1     | 452969.281 | 3                   | 36                  | 50                 |
| 10 | 3  | 1      | 151208.166 | 7                   | 5                   | 50                 | 22 | 10 | -1     | 315992.221 | 162                 | 196                 | 200                | 32 | 6  | -1     | 452898.394 | 29                  | 18                  | 50                 |
| 10 | 4  | 1      | 151211.455 | -8                  | -14                 | 50                 | 22 | 11 | -1     | 316001.256 | 75                  | 116                 | 100                | 32 | 8  | -1     | 452908.681 | 86                  | 70                  | 50                 |
| 10 | 5  | 1      | 151214.249 | 3                   | -6                  | 50                 | 22 | 12 | -1     | 316011.258 | -78                 | -29                 | 200                | 32 | 11 | -1     | 452939.193 | 123                 | 107                 | 50                 |
| 10 | 6  | 1      | 151217.020 | -64                 | -75                 | 100                | 22 | 13 | -1     | 316022.464 | -36                 | 22                  | 50                 | 32 | 14 | -1     | 452984.751 | 336                 | 329                 | 300                |
| 10 | 7  | 1      | 151220.187 | 19                  | 5                   | 50                 | 22 | 14 | -1     | 316034.579 | -77                 | -10                 | 50                 | 33 | -1 | -1     | 466060.953 | 2                   | -33                 | 50                 |
| 10 | 8  | 1      | 151223.608 | 26                  | 9                   | 50                 | 22 | 17 | -1     | 316076.865 | -103                | 0                   | 200                | 33 | 1  | 1      | 466917.433 | -13                 | -50                 | 50                 |
| 10 | 10 | 1      | 151231.503 | -41                 | -63                 | 100                | 22 | 20 | -1     | 316127.820 | -95                 | 54                  | 50                 | 33 | 2  | 1      | 466236.321 | 36                  | 22                  | 50                 |
| 16 | 1  | 1      | 233639.082 | -6                  | -34                 | 50                 | 22 | 2  | 1      | 315837.484 | 43                  | 43                  | 50                 | 33 | 3  | 1      | 466348.230 | -3                  | -4                  | 50                 |
| 16 | -1 | -1     | 233398.211 | 22                  | 40                  | 50                 | 22 | 3  | 1      | 315886.227 | -47                 | -53                 | 50                 | 33 | 4  | 1      | 466400.156 | -61                 | -56                 | 600                |
| 16 | 1  | -1     | 233641.499 | -2                  | -3                  | 50                 | 22 | 4  | 1      | 315905.797 | -105                | -116                | 50                 | 33 | 6  | 1      | 466453.404 | -49                 | -33                 | 50                 |
| 16 | -2 | 1      | 233633.475 | -7                  | -1                  | 100                | 22 | 5  | 1      | 315918.143 | -25                 | -39                 | 50                 | 33 | 7  | 1      | 466472.116 | -90                 | -71                 | 200                |
| 16 | 2  | -1     | 233639.706 | -106                | -101                | 100                | 22 | 6  | 1      | 315927.936 | -55                 | -71                 | 50                 | 33 | 10 | 1      | 466522.550 | -26                 | -2                  | 50                 |
| 16 | 3  | -1     | 233633.475 | -34                 | -26                 | 100                | 22 | 7  | 1      | 315937.061 | 37                  | 17                  | 50                 | 33 | 13 | 1      | 466576.170 | -24                 | -1                  | 50                 |
| 16 | 4  | -1     | 233634.133 | -77                 | -65                 | 50                 | 22 | 8  | 1      | 315946.010 | 16                  | -7                  | 50                 | 33 | 22 | 1      | 466794.719 | -22                 | -46                 | 50                 |
| 16 | 5  | -1     | 233636.127 | -2                  | 15                  | 50                 | 22 | 9  | 1      | 315955.335 | 69                  | 43                  | 50                 | 33 | 26 | 1      | 466997.768 | 75                  | -21                 | 50                 |
| 16 | 6  | -1     | 233639.075 | -19                 | 4                   | 50                 | 22 | 10 | 1      | 315965.062 | 17                  | -12                 | 50                 | 33 | 31 | 1      | 467117.399 | 18                  | -127                | 200                |
| 16 | 7  | -1     | 233642.964 | -11                 | 17                  | 50                 | 22 | 11 | 1      | 315975.465 | 12                  | -20                 | 50                 | 33 | 0  | -1     | 466750.525 | -335                | -309                | 500                |
| 16 | 8  | -1     | 233647.677 | -17                 | 17                  | 50                 | 22 | 13 | 1      | 315998.523 | 77                  | 38                  | 50                 | 33 | 1  | -1     | 466669.617 | 26                  | 15                  | 50                 |
| 16 | 11 | -1     | 233666.458 | -33                 | 21                  | 50                 | 22 | 14 | 1      | 316011.258 | 137                 | 92                  | 200                | 33 | 2  | -1     | 466835.153 | 47                  | 75                  | 50                 |
| 16 | 13 | -1     | 233682.674 | -18                 | 53                  | 50                 | 22 | 15 | 1      | 316024.562 | -61                 | -109                | 50                 | 33 | 3  | -1     | 466579.432 | -26                 | -18                 | 50                 |
| 16 | 14 | -1     | 233691.728 | -134                | -54                 | 50                 | 22 | 16 | 1      | 316039.088 | 118                 | 64                  | 200                | 33 | 4  | -1     | 466570.192 | -9                  | -10                 | 50                 |
| 16 | 16 | -1     | 233712.327 | 8                   | 109                 | 100                | 22 | 17 | 1      | 316054.447 | 268                 | 209                 | 300                | 33 | 7  | -1     | 466571.484 | 46                  | 30                  | 50                 |
| 16 | 2  | 1      | 233679.005 | 21                  | 25                  | 50                 | 22 | 19 | 1      | 316067.147 | -81                 | -152                | 200                | 33 | 8  | -1     | 466577.723 | 37                  | 18                  | 50                 |
| 16 | 3  | 1      | 233600.948 | 29                  | 25                  | 50                 | 25 | -2 | 1      | 357063.309 | 115                 | 127                 | 200                | 33 | 11 | -1     | 466808.635 | 12                  | -11                 | 50                 |
| 16 | 4  | 1      | 233610.035 | 4                   | -5                  | 50                 | 25 | 2  | -1     | 357158.997 | -2                  | 1                   | 50                 | 33 | 14 | -1     | 466655.097 | 72                  | 54                  | 50                 |
| 16 | 5  | 1      | 233616.318 | -24                 | -37                 | 50                 | 25 | 4  | 1      | 357004.332 | -47                 | -58                 | 50                 | 33 | 17 | -1     | 466715.366 | 93                  | 91                  | 50                 |
| 16 | 6  | 1      | 233621.951 | 18                  | 2                   | 50                 | 26 | -2 | 1      | 370795.112 | 39                  | 55                  | 50                 | 33 | 20 | -1     | 466789.014 | 319                 | 348                 | 400                |
| 16 | 7  | 1      | 233627.518 | 19                  | -1                  | 50                 | 26 | 2  | -1     | 370889.938 | 2                   | -8                  | 50                 | 33 | 23 | -1     | 466875.128 | 133                 | 208                 | 200                |
| 16 | 8  | 1      | 233633.475 | 134                 | 111                 | 100                | 26 | 4  | 1      | 370695.447 | -43                 | -53                 | 50                 | 33 | 26 | -1     | 466973.971 | -75                 | 69                  | 200                |
| 16 | 9  | 1      | 233639.706 | 97                  | 70                  | 100                | 27 | -2 | 1      | 384493.774 | 500                 | 518                 | 200                | 33 | 29 | -1     | 467065.427 | -391                | -154                | 200                |
| 16 | 10 | 1      | 233648.399 | 11                  | -19                 | 50                 | 27 | 4  | 1      | 384382.122 | -29                 | -38                 | 50                 | 38 | 2  | -1     | 534918.873 | 23                  | 52                  | 50                 |
| 16 | 13 | 1      | 233670.230 | 15                  | -26                 | 50                 | 28 | 4  | 1      | 398064.088 | -122                | -130                | 50                 | 38 | -2 | 1      | 534890.324 | -73                 | 14                  | 50                 |
| 16 | 14 | 1      | 233679.463 | 65                  | 20                  | 50                 | 32 | -1 | -1     | 452408.360 | 41                  | 2                   | 50                 |    |    |        |            |                     |                     |                    |

MARGULES ET AL.

<sup>a)</sup> residuals (in kHz) obtained using the Q reduction  
<sup>b)</sup> residuals (in kHz) obtained using the D reduction  
<sup>c)</sup> Experimental uncertainty (in kHz)

GROUND AND  $\nu_4 = 1$  ROVIBRATIONAL SPECTRA OF SiDF<sub>3</sub>

TABLE 5  
Molecular Parameters (in cm<sup>-1</sup>) of SiDF<sub>3</sub> in the  $\nu_4 = 1$  State

|                             | Reduction Q       | Reduction D       | Harada <i>et al.</i> <sup>a)</sup> |
|-----------------------------|-------------------|-------------------|------------------------------------|
| $\nu_4$                     | 994.3025680 (91)  | 994.3025701 (91)  | 994.302604 (16)                    |
| $B$                         | 0.2293195628 (84) | 0.2293202940 (81) | 0.22932016 (32)                    |
| $C$                         | 0.137545546 (56)  | 0.137544076 (56)  | 0.1375445 (63)                     |
| $D_J \cdot 10^6$            | 0.2114109 (92)    | 0.2113933 (76)    | 0.223 (13)                         |
| $D_{JK} \cdot 10^6$         | - 0.332370 (34)   | - 0.332274 (30)   | - 0.364 (48)                       |
| $D_K \cdot 10^6$            | 0.152407 (71)     | 0.152300 (66)     | 0.1544 (47)                        |
| $H_J \cdot 10^{12}$         | 0.5728 (38)       | 0.5638 (27)       | -                                  |
| $H_{JK} \cdot 10^{12}$      | - 2.185 (18)      | - 2.134 (14)      | -                                  |
| $H_{KJ} \cdot 10^{12}$      | 2.774 (30)        | 2.717 (26)        | -                                  |
| $H_K \cdot 10^{12}$         | 0. <sup>b)</sup>  | 0. <sup>b)</sup>  | -                                  |
| $C\zeta$                    | 0.07372255 (31)   | 0.07372289 (31)   | 0.0737263 (67)                     |
| $\eta_J \cdot 10^6$         | - 0.36774 (23)    | 1.1171 (11)       | 0.190 (90)                         |
| $\eta_K \cdot 10^6$         | 0.40621 (50)      | - 1.0792 (11)     | - 0.234 (70)                       |
| $q_{22} \cdot 10^3$         | - 0.109644 (12)   | - 0.1096668 (89)  | - 0.11018 (28)                     |
| $q_{22}^J \cdot 10^9$       | 2.228 (12)        | 0.7998 (50)       |                                    |
| $q_{22}^{JJ} \cdot 10^{15}$ | - 30.4 (44)       | 0. <sup>b)</sup>  |                                    |
| $f_a \cdot 10^9$            | 2.3254 (44)       | 0.8669 (45)       |                                    |
| $f_a^J \cdot 10^{15}$       | - 66.6 (23)       | - 24.5 (18)       |                                    |
| $d \cdot 10^6$              | 0.80045 (50)      | 0. <sup>b)</sup>  |                                    |
| $d_J \cdot 10^{12}$         | - 22.28 (48)      | 0. <sup>b)</sup>  |                                    |
| $q_{12} \cdot 10^3$         | 0. <sup>b)</sup>  | 0.101478 (36)     | 0.0632 (17)                        |

<sup>a)</sup> reference (5). The value of  $q_{22}$  has been divided by a factor (-4) for a better comparison.

<sup>b)</sup> constrained value

#### 4.2. The $\nu_4 = 1$ Excited State

The rotational spectrum, measured up to 535 GHz, was rather weak and dense. Because of many overlapping lines, the assignment could only be done once the data of Harada *et al.* (5) had been fitted and used for prediction. More than 2000 lines of the infrared spectrum between 960 and 1120 cm<sup>-1</sup> were quite easily assigned. Furthermore, because of the strong ( $\pm 2, \mp 4$ ) interaction, we could observe more than 90  $A_1-A_2$  resolved split transitions between the ( $l = 0, k = \pm 3$ ) ground state levels and the ( $l = \pm 2, k = \mp 1$ )  $\nu_4 = 1$  levels. A level crossing is to be noticed for  $J = 37$  in the upper state. Rotational frequencies given in Ref. (2) were also included with an assumed uncertainty of 200 kHz. Information about the data sets used in this work are collected in Table 3. Newly measured rotational frequencies are listed in Table 4.

The ground state parameters were fixed to the values given in Table 2.

## 5. DISCUSSION

### 5.1. Multiple Fits Analysis

For such an assumed isolated state, we used the  $Q$  and  $D$  reduction schemes (constraining to zero the  $q_{12}$  or  $d$  parameter, respectively) for checking the analysis (6). The derived parameters are listed in Table 5. One can note that the higher order terms  $\tau$  of the  $z$ -type Coriolis interaction are not listed in this table. They were constrained to zero because they are not determinable within the  $D$  reduction and not well determined within the  $Q$  one:  $\tau_{JJ} = -2.01(23) \times 10^{-12}$  cm<sup>-1</sup>;  $\tau_{JK} = 6.63(76) \times 10^{-12}$  cm<sup>-1</sup>;  $\tau_{KK} = -8.80(90) \times 10^{-12}$  cm<sup>-1</sup>.

Although the standard deviation for the millimeter data set (the only one affected by setting the  $\tau$ 's to zero) is 46 kHz instead of 54 kHz as given in Table 3, we have chosen not to consider these parameters in the fit in order to have identical sets of parameters for both reductions and because they have a small influence on the main body of the data.

- Comparison of the reductions can be done by checking:
- (1) The standard deviation: Table 3 shows that they are of the same order of magnitude for the different sets of data. It should be mentioned that the measurements have different influence depending on the used reduction as can be seen with the residuals in Table 4.
  - (2) The rotational, quartic centrifugal distortion, and  $l$ -doubling constants: They should not be affected by the transformation of the Hamiltonian leading to the reductions. Table 5 shows, for  $B$  and  $C$ , significant differences with respect to their standard deviation. But divided by the average value of the two constants, these differences are of the order of millionths of the values itself. Therefore, we can consider that the rotational constants are not affected. Table 5 also shows some differences between the other parameters mainly because they could be affected by the contribution of the  $\tau$  constants.
  - (3) Some relations demonstrating the unitary equivalence of both reductions (12). The first one links the parameters  $q_{12}^D$  and  $d^Q$  obtained by using the reductions  $D$  and  $Q$ , respectively

$$q_{12}^D = -\frac{d^Q F}{4q_{22}}, \tag{8}$$

where  $F = 2C\zeta + C - B$ . The differences between the rotational dependence of the  $z$ -type Coriolis parameters  $\eta_J$  and  $\eta_K$  for both reductions can be calculated to

$$\eta_J^D - \eta_J^Q = -(\eta_K^D - \eta_K^Q) = \frac{8(q_{12}^D)^2}{F} = \frac{F(d^Q)^2}{2q_{22}^2}. \tag{9}$$

Other relations exist for higher order terms:

$$-(\tau_J^D - \tau_J^Q) = (\tau_{JK}^D - \tau_{JK}^Q) + (\tau_K^D - \tau_K^Q) \tag{10}$$

$$f_{42}^D - f_{42}^Q = q_{22}^{J,D} - q_{22}^{J,Q} = \frac{4q_{22}(q_{12}^D)^2}{F^2} = \frac{(d^Q)^2}{4q_{22}}. \tag{11}$$

Relations [8], [9], and [11] are quite well verified as can be seen in Table 6. Relation [10] is not fulfilled with the values of the  $\tau$  constants given above. This is a further argument for regarding them only as effective parameters.

In conclusion, both reductions are equivalent, at least up to the level of approximation used in this study.

Furthermore, the differences between the  $\nu_4 = 1$  state and the ground state parameters are quite small: they do not exceed

| TABLE 6<br>Demonstration of the Unitary Equivalence<br>of the Reductions <sup>a</sup> |               |                |
|---------------------------------------------------------------------------------------|---------------|----------------|
| $q_{12}^D$                                                                            | $\times 10^3$ | 0.101478 (37)  |
| $-\frac{d^Q F}{4q_{22}}$                                                              | $\times 10^3$ | 0.101589 (67)  |
| $(\eta_J^D - \eta_J^Q)_{\text{exp.}}$                                                 | $\times 10^6$ | 1.4848 (10)    |
| $-(\eta_K^D - \eta_K^Q)_{\text{exp.}}$                                                | $\times 10^6$ | 1.4854 (12)    |
| $\frac{8(q_{12}^D)^2}{F}$                                                             | $\times 10^6$ | 1.4800 (11)    |
| $\frac{F(d^Q)^2}{2q_{22}^2}$                                                          | $\times 10^6$ | 1.4832 (20)    |
| $(f_{42}^D - f_{42}^Q)_{\text{exp.}}$                                                 | $\times 10^9$ | - 1.4585 (64)  |
| $(q_{22}^{J,D} - q_{22}^{J,Q})_{\text{exp.}}$                                         | $\times 10^9$ | - 1.4282 (130) |
| $\frac{4q_{22}(q_{12}^D)^2}{F^2}$                                                     | $\times 10^9$ | - 1.4576 (11)  |
| $\frac{(d^Q)^2}{4q_{22}}$                                                             | $\times 10^9$ | - 1.4608 (19)  |

<sup>a</sup> values in  $\text{cm}^{-1}$

0.2% for the rotational and the quartic centrifugal distortion constants. The difference is higher for the sextic centrifugal distortion constants because they likely contain the contribution of higher order parameters neglected in the analysis.

These results confirm our initial hypothesis that the  $\nu_4 = 1$  state is not perturbed and could have been treated as an isolated state.

5.2. Sign of the Parameters

The sign of the  $l$ -type  $q_{22}$  constant was determined by Harada *et al.* (5) and is confirmed by different ways in this study. A band contour simulation of the  ${}^PQ_1$ ,  ${}^RQ_0$ , and  ${}^RQ_1$  branches is presented in Fig. 3 both for  $Q$  and  $D$  reductions. It clearly shows that the set of data with  $q_{22} < 0$  reproduces well the spectrum. The set with opposite-signed  $q_{22}$  gives a completely different shape. Furthermore, for this latter set, some higher order terms like  $f_{42}^{J'}$  had to be included to get standard deviations close to the experimental uncertainties. This might be proof that the system of normal equations was probably not well conditioned with  $q_{22} > 0$ .

The determination of the sign of  $f_{42}$ ,  $d$ , and  $q_{12}$  was more ambiguous. The best reproduction of the data was obtained with the signed parameters of Table 5.

1

# GROUND AND $\nu_4 = 1$ ROVIBRATIONAL SPECTRA OF SiDF<sub>3</sub>

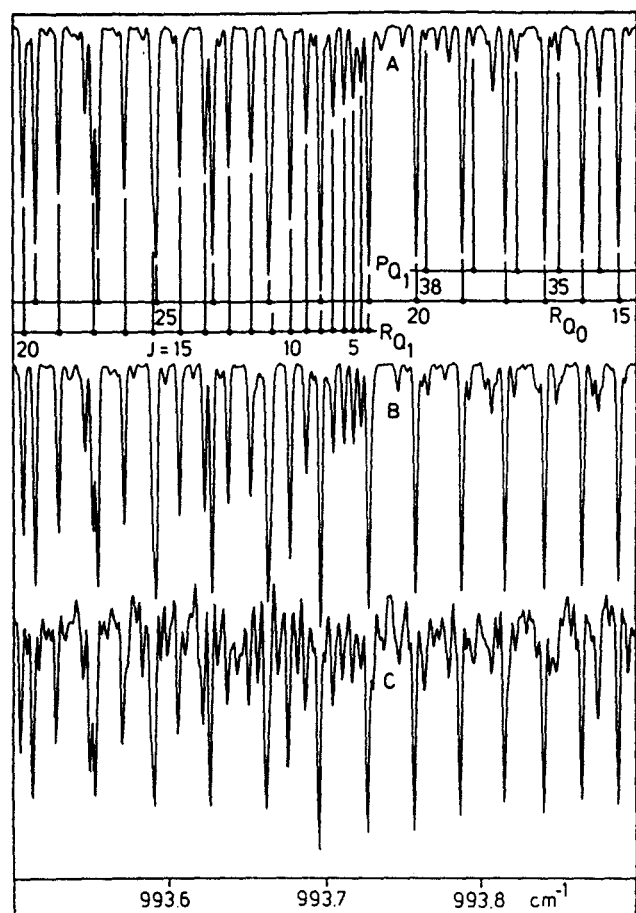


FIG. 3. Detail of the  $\nu_4$  band of  $^{28}\text{SiDF}_3$ , showing the region of the  $^{\circ}Q_1$ ,  $^{\circ}Q_0$ , and  $^{\circ}Q_1$  branches. (A) simulation employing the parameters of the  $D$  luction; (B) simulation employing the parameters of the  $Q$  reduction; (C) experimental spectrum.

## 3. Comparison with Previous Results

Inspection of Table 5 shows that our results agree well with the analysis performed by Harada *et al.* (5). Nevertheless, because of much more data, we could improve all the parameters by several orders of magnitude.

We included new constants compatible with the theory of luction for an isolated degenerate state. The interaction parameters cannot be compared. For taking into account the  $H|k \pm 3\rangle$  interaction, Harada *et al.* used a parameter  $\lambda$  (21), whose contribution in the energy matrix significantly differs from that of  $d$ . The only common parameter is  $q_{12}$  (denoted  $r_4$ , Ref. (5)) whose order of magnitude is the same for both di-

The comparison with the microwave study of Hoy *et al.* (2) is more difficult. The parameters derived from experimental observations and from the harmonic force field agree with what we found. For the other vibrational states, the results will help us to begin further analysis.

## ACKNOWLEDGMENTS

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Radio-frequency, Centimeter-wave, Millimeter-wave, and Infrared Spectra of SiDF<sub>3</sub> in the  $\nu_6 = 1$  Excited State

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# Radio-Frequency, Centimeter-Wave, Millimeter-Wave, and Infrared Spectra of SiDF<sub>3</sub> in the $\nu_6 = 1$ Excited State

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This paper deals with the first study of high-resolution radio-frequency, centimeter-wave, millimeter-wave, and infrared spectra of the deuterated isotopomer of trifluorosilane, SiDF<sub>3</sub>, in its lowest degenerate excited  $\nu_6 = 1$  state. Following the work of E. I. Lobodenko, O. N. Sulakshina, V. I. Perevalov, and V. I. Tyuterev. (*J. Mol. Spectrosc.* **126**, 159–170 (1987)) and Harder (*J. Mol. Spectrosc.* **194**, 145 (1999)), the data (18  $A_1-A_2$  transitions, 229  $I$ -type resonance transitions, 189 pure rotational transitions, and 1167 rovibrational transitions) have been fitted using three equivalent  $Q$ ,  $D$ , and  $QD$  reduction schemes enabling the fit of one of the three interaction parameters  $d$ ,  $q_{12}$ , and  $\epsilon$ , respectively, while the other two are fixed to zero. In addition to further higher order constants, either  $f_{22}^K$  or  $\tau_K$  also had to be constrained. By checking the standard deviation of each data set and the relations between parameters determined within different constraints, the six reduction schemes have been shown to be unitary equivalent. Furthermore, the axial rotational ground state constant  $C_0$  has been accurately determined. © 1999 Academic Press

## 1. INTRODUCTION

It is well established that the contact transformation of the effective Hamiltonian,  $H_{\text{transf}} = e^{-iS} H^{\text{eff}} e^{iS}$  leads to interdependences of molecular parameters through free transformation parameters. Lobodenko *et al.* transformed the rotation–vibrational Hamiltonian in an isolated degenerate state of a symmetric-top molecule of  $C_{3v}$  symmetry (1) and predicted constraints to be applied on either the rovibrational constant  $d$  or  $q_{12}$ . Many studies were performed using both the  $D$  ( $d = 0$ ) and  $Q$  ( $q_{12} = 0$ ) reductions and relations between the derived parameter sets agreed well with the theory (2–7). Harder recently proposed a third reduction ( $QD$ ) in which both  $q_{12}$  and  $d$  are constrained (8). Because high-resolution spectroscopy allows the determination of high-order terms of the Hamiltonian, Watson *et al.* showed that eight parameters must be constrained up to fifth order and accordingly proposed several constraints and discussed how they must be employed (9). Although it is not *a priori* necessary to use different schemes of reduction for reproducing the same set of experimental data, these authors nevertheless recommended the application of the multiple fit procedure to check the consistency of the data, analysis, and employed model.

We applied these recent results for the first study of high-resolution radio-frequency, centimeter-wave, millimeter-wave, and infrared spectra of the deuterated isotopomer of trifluorosilane, SiDF<sub>3</sub>, in its lowest degenerate excited  $\nu_6 = 1$  state.

To our knowledge only three papers dealt with this state. Two infrared studies were reported by Newman *et al.* (10) and Bürger *et al.*, the latter devoted to the assignment of the medium resolution ( $0.3 \text{ cm}^{-1}$ ) spectra of all the fundamental vibrations by a band contour analysis (11). The last and more recent work was performed by Hoy *et al.*, who measured the  $J = 2 \leftarrow 1$  transition in the centimeter-wave range (12). They also refined the harmonic and cubic force fields using their new experimental data and previous infrared works.

## 2. EXPERIMENTAL DETAILS

### 2.1. Synthesis of SiDF<sub>3</sub>

Deuterated trichlorosilane (SiDCl<sub>3</sub>, made from Si and DCl) was converted into trifluorosilane (SiDF<sub>3</sub>) by reaction with antimony trifluoride (SbF<sub>3</sub>) at room temperature. For this purpose SiDCl<sub>3</sub> was condensed into a bulb coated with freshly sublimed antimony trifluoride and cooled to liquid nitrogen temperature. As has been found earlier, SiF<sub>4</sub> was the main impurity formed by fluorination of SiCl<sub>4</sub>. Moreover, traces of SiH<sub>2</sub>F<sub>2</sub> were present.

### 2.2. One- and Two-Dimensional Microwave Fourier Transform Spectra

A total number of 229 direct  $I$ -type resonance transitions with the selection rules  $\Delta J = 0$ ,  $\Delta k = \Delta l = \pm 2$  ( $\Delta G =$



TABLE 1  
Experimental Frequencies (in MHz) of the Direct  $I$ -Type Transitions  
in the  $v_6 = 1$  State of SiDF<sub>3</sub>

| $J$ | $G'$ | Obs.       | $e-c^a$ | $e-c^b$ | Unc. | $J$ | $G'$ | Obs.       | $e-c^a$ | $e-c^b$ | Unc. |
|-----|------|------------|---------|---------|------|-----|------|------------|---------|---------|------|
| 22  | 3-   | 8993.8597  | 0.0     | -1.0    | 3.0  | 27  | 11   | 26496.3263 | 0.0     | -1.0    | 11.1 |
| 22  | 3+   | 8997.7412  | 1.0     | 1.0     | 0.9  | 28  | 0    | 9340.6090  | 0.0     | 0.0     | 1.2  |
| 22  | 4    | 10835.7745 | 0.0     | 0.0     | 0.9  | 28  | 1    | 9619.5084  | 0.0     | 0.0     | 1.0  |
| 22  | 5    | 12819.2278 | 1.0     | 1.0     | 1.5  | 28  | 2    | 10394.2448 | 0.0     | 1.0     | 0.7  |
| 22  | -6   | 14889.0373 | 0.0     | -1.0    | 0.5  | 28  | 3-   | 11559.7525 | 0.0     | 0.0     | 1.2  |
| 22  | 8    | 19175.4448 | -3.0    | -2.0    | 3.9  | 28  | 3+   | 11569.3007 | 0.0     | 1.0     | 1.3  |
| 22  | 9    | 21362.8397 | 2.0     | 3.0     | 3.7  | 28  | 4    | 13034.6844 | 0.0     | 0.0     | 0.6  |
| 22  | 10   | 23568.9505 | 0.0     | 3.0     | 7.8  | 28  | 5    | 14710.4852 | -1.0    | 0.0     | 2.3  |
| 22  | 11   | 25789.1147 | 4.0     | 10.0    | 12.0 | 28  | 7    | 18450.0106 | 7.0     | 7.0     | 5.1  |
| 23  | 3-   | 9341.2468  | 2.0     | 1.0     | 2.6  | 28  | 8    | 20443.0776 | 0.0     | 0.0     | 4.5  |
| 23  | 3+   | 9345.8411  | 1.0     | 0.0     | 1.5  | 28  | 9    | 22489.6697 | 0.0     | 0.0     | 2.9  |
| 23  | 4    | 11123.9131 | 0.0     | 0.0     | 0.6  | 28  | 10   | 24576.5194 | -2.0    | -3.0    | 4.9  |
| 23  | 5    | 13061.2204 | 0.0     | 0.0     | 0.9  | 29  | 0    | 10003.9686 | 0.0     | 0.0     | 1.3  |
| 23  | -6   | 15095.2740 | 0.0     | 0.0     | 0.6  | 29  | 1    | 10264.6316 | 0.0     | 0.0     | 0.9  |
| 23  | 8    | 19330.8076 | 7.0     | 8.0     | 3.6  | 29  | 2    | 10992.7727 | -1.0    | 0.0     | 0.7  |
| 23  | 9    | 21499.5261 | -8.0    | -7.0    | 24.0 | 29  | 3-   | 12098.0640 | 0.0     | 0.0     | 1.9  |
| 23  | 10   | 23690.0186 | 2.0     | 5.0     | 9.2  | 29  | 3+   | 12108.8836 | 0.0     | 0.0     | 1.6  |
| 23  | 11   | 25896.8482 | -6.0    | -2.0    | 12.1 | 29  | 4    | 13512.9479 | 0.0     | 0.0     | 1.8  |
| 24  | 2    | 8273.0321  | 0.0     | 0.0     | 0.7  | 29  | 5    | 15133.2962 | -1.0    | -1.0    | 1.0  |
| 24  | 3-   | 9720.8476  | 0.0     | 0.0     | 3.2  | 29  | 7    | 18783.2412 | 1.0     | 1.0     | 4.2  |
| 24  | 3+   | 9726.2466  | 0.0     | 0.0     | 3.6  | 29  | 8    | 20741.1336 | 0.0     | 0.0     | 4.8  |
| 24  | 4    | 11442.6959 | 1.0     | 1.0     | 0.9  | 29  | 9    | 22757.6412 | 1.0     | 0.0     | 4.2  |
| 24  | 5    | 13331.2522 | 0.0     | 0.0     | 0.8  | 29  | 10   | 24818.5819 | 1.0     | -1.0    | 5.8  |
| 24  | -6   | 15326.8338 | -6.0    | -5.0    | 5.0  | 30  | 0    | 10689.6260 | 0.0     | 0.0     | 0.8  |
| 24  | 8    | 19506.7884 | -4.0    | -3.0    | 3.0  | 30  | 1    | 10934.1008 | 0.0     | 1.0     | 0.7  |
| 24  | 10   | 23828.1633 | 1.0     | 3.0     | 8.9  | 30  | 2    | 11619.2048 | -1.0    | -1.0    | 1.0  |
| 24  | 11   | 26020.2432 | 1.0     | 4.0     | 11.2 | 30  | 3-   | 12666.9121 | 0.0     | 0.0     | 2.0  |
| 25  | 2    | 8823.8882  | 1.0     | 1.0     | 1.3  | 30  | 3+   | 12679.0866 | -1.0    | -1.0    | 2.0  |
| 25  | 3-   | 10132.6982 | -1.0    | -1.0    | 3.4  | 30  | 4    | 14023.2229 | 0.0     | 0.0     | 1.0  |
| 25  | 3+   | 10138.9930 | 0.0     | 1.0     | 1.7  | 30  | 5    | 15588.0459 | -1.0    | -1.0    | 1.8  |
| 25  | 4    | 11792.7860 | 0.0     | 1.0     | 1.1  | 30  | 7    | 19145.8618 | 3.0     | 3.0     | 4.8  |
| 25  | 5    | 13630.3837 | 0.0     | 0.0     | 1.6  | 30  | 8    | 21066.8567 | 1.0     | 1.0     | 5.1  |
| 25  | -6   | 15584.9917 | -1.0    | -1.0    | 3.6  | 30  | 9    | 23051.5384 | -1.0    | -2.0    | 3.9  |
| 25  | 8    | 19704.7651 | 3.0     | 3.0     | 3.0  | 30  | 10   | 25084.8969 | -1.0    | -3.0    | 4.1  |
| 25  | 9    | 21830.4348 | 2.0     | 2.0     | 3.3  | 31  | 0    | 11397.5044 | 0.0     | 0.0     | 0.6  |
| 25  | 10   | 23984.6512 | 2.0     | 3.0     | 7.9  | 31  | 1    | 11627.5294 | 0.0     | 0.0     | 1.0  |
| 25  | 11   | 26160.4782 | -3.0    | -1.0    | 14.6 | 31  | 2    | 12272.8807 | 0.0     | 0.0     | 1.4  |
| 26  | 0    | 8081.0481  | 0.0     | 0.0     | 0.4  | 31  | 3-   | 13265.7777 | 1.0     | 1.0     | 2.0  |
| 26  | 1    | 8406.6093  | 0.0     | 0.0     | 0.4  | 31  | 3+   | 13279.3778 | 0.0     | 1.0     | 1.6  |
| 26  | 2    | 9286.3387  | 0.0     | 0.0     | 1.3  | 31  | 4    | 14565.2633 | -1.0    | -1.0    | 0.8  |
| 26  | 3-   | 10576.6634 | 0.0     | 0.0     | 1.4  | 31  | 7    | 19538.5558 | -1.0    | -1.0    | 3.0  |
| 26  | 3+   | 10583.9456 | 0.0     | 0.0     | 1.3  | 31  | 8    | 21421.1074 | -4.0    | -5.0    | 4.8  |
| 26  | 4    | 12174.6511 | -1.0    | 0.0     | 1.0  | 31  | 9    | 23372.3401 | -2.0    | -4.0    | 4.6  |
| 26  | 5    | 13959.5099 | -1.0    | 0.0     | 0.8  | 31  | 10   | 25376.5072 | -2.0    | -4.0    | 5.6  |
| 26  | -6   | 15870.8698 | 0.0     | 0.0     | 0.5  | 32  | 0    | 12127.5212 | 1.0     | 1.0     | 1.1  |
| 26  | 8    | 19925.9957 | -1.0    | -1.0    | 4.5  | 32  | 1    | 12344.6386 | 0.0     | 0.0     | 1.5  |
| 26  | 9    | 22027.2240 | 1.0     | 1.0     | 2.1  | 32  | 2    | 12953.2534 | 0.0     | 1.0     | 1.5  |
| 26  | 10   | 24160.7232 | -4.0    | -3.0    | 9.7  | 32  | 3-   | 13894.1205 | 0.0     | -1.0    | 2.4  |
| 26  | 11   | 26318.7775 | 0.0     | 0.0     | 10.3 | 32  | 3+   | 13909.1986 | 2.0     | 1.0     | 1.6  |
| 27  | 0    | 8699.6150  | 0.0     | 0.0     | 0.6  | 32  | 4    | 15138.7486 | -1.0    | -1.0    | 1.0  |
| 27  | 1    | 8999.4157  | 0.0     | 0.0     | 0.8  | 32  | -6   | 18214.8801 | 0.0     | -1.0    | 1.8  |
| 27  | 2    | 9824.5869  | 0.0     | 0.0     | 0.8  | 32  | 7    | 19961.9144 | 6.0     | 5.0     | 6.6  |
| 27  | 3-   | 11052.4714 | 0.0     | 0.0     | 0.6  | 32  | 8    | 21804.6604 | -4.0    | -6.0    | 4.2  |
| 27  | 3+   | 11060.8395 | 1.0     | 1.0     | 0.9  | 32  | 9    | 23720.9401 | 0.0     | -2.0    | 4.5  |
| 27  | 4    | 12588.5786 | 1.0     | 1.0     | 1.1  | 32  | 10   | 25694.3799 | -5.0    | -7.0    | 7.8  |
| 27  | 5    | 14319.3574 | 0.0     | 0.0     | 0.8  | 33  | 0    | 12879.5745 | 0.0     | 0.0     | 1.4  |
| 27  | 7    | 18145.3461 | 15.0    | 15.0    | 45.0 | 33  | 1    | 13085.1968 | 0.0     | 0.0     | 0.9  |
| 27  | 8    | 20171.7240 | 5.0     | 5.0     | 4.8  | 33  | 2    | 13659.8446 | 0.0     | 0.0     | 1.5  |
| 27  | 9    | 22246.5746 | 2.0     | 2.0     | 24.2 | 33  | 3-   | 14551.4119 | 2.0     | 2.0     | 2.0  |
| 27  | 10   | 24357.6143 | -6.0    | -6.0    | 16.2 | 33  | 3+   | 14567.9726 | -6.0    | -6.0    | 3.0  |

<sup>a)</sup> obs. - calc. (in kHz) from the D reduction with  $r_K$  constrained to zero

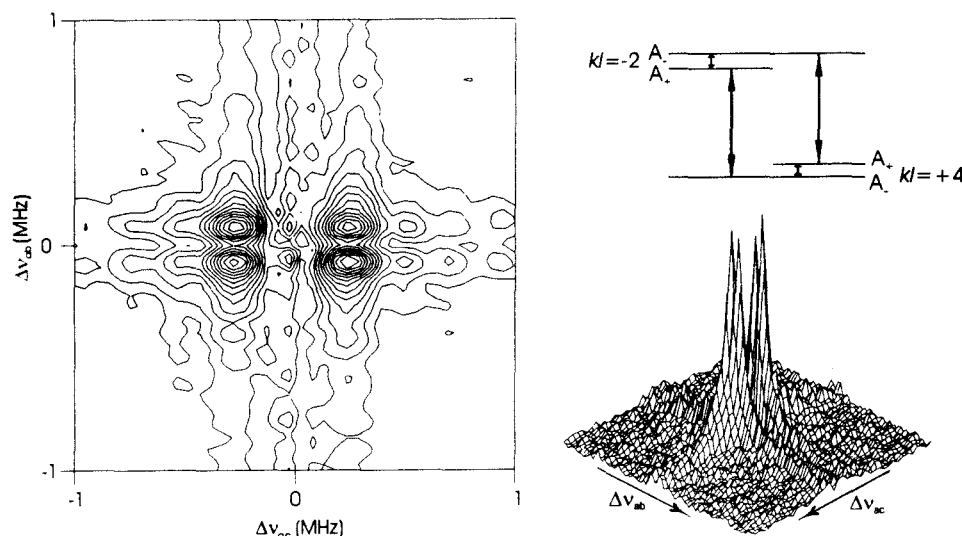
<sup>b)</sup> obs. - calc. (in kHz) from the D reduction with  $f_{22}^K$  constrained to zero

TABLE 1—Continued

| <i>J</i> | <i>G'</i> | Obs.       | <i>e</i> - <i>c</i> <sup>a</sup> | <i>e</i> - <i>c</i> <sup>b</sup> | Unc. | <i>J</i> | <i>G'</i> | Obs.       | <i>e</i> - <i>c</i> <sup>a</sup> | <i>e</i> - <i>c</i> <sup>b</sup> | Unc. |
|----------|-----------|------------|----------------------------------|----------------------------------|------|----------|-----------|------------|----------------------------------|----------------------------------|------|
| 33       | 4         | 15743.2956 | 1.0                              | 1.0                              | 2.8  | 40       | 3-        | 19938.5600 | -7.0                             | -9.0                             | 3.9  |
| 33       | -6        | 18715.2054 | -1.0                             | -2.0                             | 30.0 | 40       | 4         | 20806.3304 | 9.0                              | 7.0                              | 7.2  |
| 33       | 7         | 20416.3719 | 1.0                              | 0.0                              | 5.1  | 40       | 5         | 21871.5391 | 4.0                              | 3.0                              | 3.9  |
| 33       | 8         | 22218.1648 | -6.0                             | -7.0                             | 5.9  | 40       | -6        | 23105.9791 | -3.0                             | -3.0                             | 2.5  |
| 33       | 10        | 26039.4188 | -4.0                             | -6.0                             | 7.6  | 40       | 7         | 24484.5962 | 0.0                              | 1.0                              | 4.2  |
| 34       | 0         | 13653.5502 | -1.0                             | -1.0                             | 1.7  | 40       | 8         | 25984.6100 | 4.0                              | 8.0                              | 12.9 |
| 34       | 1         | 13849.0034 | 0.0                              | 0.0                              | 0.9  | 41       | 0         | 19663.5265 | 2.0                              | 1.0                              | 4.2  |
| 34       | 2         | 14392.2223 | -1.0                             | 0.0                              | 3.1  | 41       | 1         | 19832.8502 | 0.0                              | 1.0                              | 3.6  |
| 34       | 3-        | 15237.1154 | 0.0                              | 0.0                              | 3.1  | 41       | 2         | 20211.6171 | 4.0                              | 4.0                              | 3.6  |
| 34       | 3+        | 15255.1462 | 0.0                              | 0.0                              | 2.0  | 41       | 3-        | 20792.2467 | -1.0                             | -2.0                             | 5.4  |
| 34       | -6        | 19247.4869 | 0.0                              | -1.0                             | 1.8  | 41       | 3+        | 20804.0764 | -1.0                             | -3.0                             | 7.8  |
| 34       | 7         | 20902.2875 | 5.0                              | 4.0                              | 3.6  | 41       | 5         | 22666.6643 | 3.0                              | 1.0                              | 14.2 |
| 34       | 9         | 24504.6244 | 1.0                              | 0.0                              | 2.6  | 41       | -6        | 23857.4924 | -2.0                             | -2.0                             | 2.6  |
| 34       | 10        | 26412.4371 | -2.0                             | -3.0                             | 8.6  | 41       | 7         | 25192.1250 | 0.0                              | 2.0                              | 3.3  |
| 35       | 0         | 14449.3082 | 0.0                              | 0.0                              | 1.3  | 42       | 1         | 20776.9850 | 5.0                              | 6.0                              | 6.3  |
| 35       | 1         | 14635.8763 | 0.0                              | 0.0                              | 0.8  | 42       | 2         | 21138.4778 | 7.0                              | 7.0                              | 6.0  |
| 35       | 2         | 15149.9954 | 0.0                              | 0.0                              | 0.7  | 42       | 3-        | 21688.4847 | 10.0                             | 8.0                              | 5.0  |
| 35       | 5         | 18341.2071 | 0.0                              | -1.0                             | 4.9  | 42       | 3+        | 21688.6019 | -2.0                             | -3.0                             | 5.0  |
| 35       | -6        | 19811.7069 | 1.0                              | 0.0                              | 1.5  | 42       | 4         | 22505.7371 | 3.0                              | 2.0                              | 4.4  |
| 35       | 7         | 21419.8875 | 13.0                             | 12.0                             | 5.5  | 42       | 5         | 23490.4434 | 4.0                              | 3.0                              | 7.9  |
| 35       | 8         | 23137.1315 | 6.0                              | 5.0                              | 5.4  | 42       | -6        | 24639.0513 | -1.0                             | 0.0                              | 2.8  |
| 35       | 9         | 24941.0212 | 0.0                              | -1.0                             | 2.2  | 42       | 7         | 25930.6466 | -2.0                             | 2.0                              | 5.6  |
| 36       | 0         | 15266.6656 | 1.0                              | 1.0                              | 2.6  | 43       | 0         | 21538.9410 | 7.0                              | 5.0                              | 39.0 |
| 36       | 1         | 15445.6494 | -2.0                             | -2.0                             | 1.2  | 43       | 1         | 21743.0179 | 1.0                              | 1.0                              | 3.4  |
| 36       | 2         | 15932.8033 | 0.0                              | 0.0                              | 2.5  | 43       | 2         | 22088.4833 | 0.0                              | 0.0                              | 3.5  |
| 36       | 5         | 18986.4727 | 2.0                              | 1.0                              | 4.8  | 43       | 3-        | 22584.6021 | -2.0                             | -4.0                             | 4.5  |
| 36       | -6        | 20407.7661 | 3.0                              | 1.0                              | 1.8  | 43       | 3+        | 22609.5446 | 7.0                              | 6.0                              | 4.0  |
| 36       | 7         | 21969.2819 | 3.0                              | 2.0                              | 3.3  | 43       | 4         | 23395.2611 | 7.0                              | 6.0                              | 8.1  |
| 36       | 8         | 23643.3580 | 2.0                              | 1.0                              | 4.6  | 43       | -6        | 25450.2452 | -5.0                             | -3.0                             | 2.3  |
| 36       | 9         | 25407.8398 | 0.0                              | 0.0                              | 1.7  | 44       | 0         | 22468.9487 | 6.0                              | 4.0                              | 5.0  |
| 37       | 4         | 18463.1292 | 4.0                              | 2.0                              | 6.0  | 44       | 1         | 22730.8202 | 3.0                              | 4.0                              | 7.3  |
| 37       | 5         | 19662.5488 | 3.0                              | 1.0                              | 3.0  | 44       | 2         | 23061.4398 | -3.0                             | -3.0                             | 7.6  |
| 37       | -6        | 21035.4822 | -2.0                             | -3.0                             | 2.4  | 44       | 3+        | 23471.9236 | 3.0                              | 1.0                              | 9.4  |
| 37       | 7         | 22550.5373 | 4.0                              | 3.0                              | 4.9  | 44       | 3-        | 23554.7483 | 22.0                             | 21.0                             | 15.0 |
| 37       | 9         | 25905.4962 | 1.0                              | 2.0                              | 2.5  | 44       | 4         | 24310.7268 | -2.0                             | -2.0                             | 4.6  |
| 38       | 3-        | 18254.1929 | 51.0                             | 50.0                             | 87.0 | 44       | 5         | 25222.1603 | 0.0                              | 1.0                              | 3.2  |
| 38       | 3+        | 18275.5960 | 16.0                             | 15.0                             | 6.9  | 44       | -6        | 26290.6485 | -24.0                            | -20.0                            | 10.3 |
| 38       | 4         | 19216.1071 | -2.0                             | -3.0                             | 3.9  | 45       | 1         | 23740.2179 | -8.0                             | -7.0                             | 7.2  |
| 38       | 7         | 23163.5929 | 0.0                              | 0.0                              | 3.5  | 45       | 2         | 24057.1477 | -2.0                             | -1.0                             | 4.5  |
| 38       | 8         | 24750.5421 | 2.0                              | 3.0                              | 5.6  | 45       | 3-        | 24272.6128 | 8.0                              | 6.0                              | 3.9  |
| 38       | 9         | 26434.3145 | 0.0                              | 4.0                              | 4.1  | 45       | 3+        | 24523.8868 | 21.0                             | 20.0                             | 6.7  |
| 39       | 1         | 18010.8625 | -8.0                             | -7.0                             | 45.0 | 45       | 4         | 25251.7179 | -5.0                             | -4.0                             | 3.7  |
| 39       | 2         | 18428.2500 | -1.0                             | -1.0                             | 5.7  | 45       | 5         | 26129.2203 | -1.0                             | 1.0                              | 7.0  |
| 39       | 3-        | 19074.6470 | 1.0                              | 0.0                              | 4.5  | 46       | 1         | 24771.0670 | -6.0                             | -4.0                             | 5.4  |
| 39       | 3+        | 19095.1504 | 3.0                              | 1.0                              | 5.4  | 46       | 0         | 25074.6621 | 10.0                             | 8.0                              | 4.4  |
| 39       | 4         | 19997.3355 | 3.0                              | 1.0                              | 4.2  | 46       | 2         | 25075.4038 | -6.0                             | -5.0                             | 4.0  |
| 39       | 5         | 21105.5153 | 5.0                              | 4.0                              | 4.5  | 46       | 3+        | 25516.6700 | 5.0                              | 4.0                              | 4.3  |
| 39       | -6        | 22384.9058 | 1.0                              | 0.0                              | 1.8  | 46       | 3-        | 26000.6635 | 2.0                              | 1.0                              | 18.1 |
| 39       | 7         | 23808.3439 | 3.0                              | 3.0                              | 5.2  | 46       | 4         | 26217.7983 | -6.0                             | -5.0                             | 6.3  |
| 39       | 8         | 25351.7095 | 1.0                              | 3.0                              | 4.1  | 47       | 1         | 25823.1632 | -6.0                             | -4.0                             | 5.0  |
| 40       | 1         | 18910.7728 | 5.0                              | 5.0                              | 4.2  | 47       | 0         | 25953.3203 | 6.0                              | 2.0                              | 6.8  |
| 40       | 2         | 19308.1238 | -5.0                             | -5.0                             | 3.6  | 47       | 2         | 26116.0282 | -7.0                             | -5.0                             | 9.4  |
| 40       | 3+        | 19920.8123 | 4.0                              | 3.0                              | 3.9  |          |           |            |                                  |                                  |      |

$\Delta|k - l| = 0$ ) could be observed in the ranges of 4.5–15 and 18–26 GHz using Fourier transform microwave spectrometers with rectangular (13 and references therein) and circular waveguides (14) as sample cells. The measurements were made at room temperature and the pressure in the cells was about 2 mTorr. The transition frequencies and their experimental error (three times the standard deviation) was determined from a least-squares fit of the time-domain data.

Because of the small value of  $|C_6 - B_6 - (C\zeta)_6|$ , these transitions are quite strong in the centimeter-wave range and several bands for different  $G = |k - l|$  values have been assigned. First, the  $G = 0$  transitions for  $J = 26$ –30 were assigned giving preliminary values of the  $l$ -type doubling parameters  $q_{22}$  and  $f'_{22}$ . Then measurements were performed for  $G = 0$ –11 and  $J$  up to 46. The  $kl = -2$  and  $+4$  ( $G = 3$ ) levels are split into two  $A_1$ – $A_2$  sublevels because of  $l$ -type

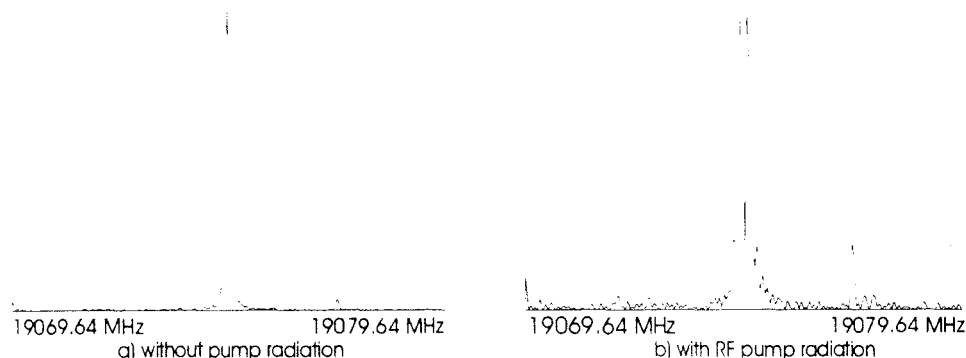


**FIG. 1.** Contour and stacked plot of the 2D spectrum in which for  $G = 3$ , two direct  $l$ -type transitions and two  $A_1$ – $A_2$  splittings have been observed simultaneously for  $J = 42$ .  $\Delta\nu_{ab}$  is the off-resonance of the direct  $l$ -type resonance transitions from the microwave-frequency  $\nu_{MW} = 21\,688.532$  MHz.  $\Delta\nu_{sc} = \nu_{sc} - (\nu_{MW} + \nu_{RF})$  refers to the off-resonance of the (dipole forbidden) double quantum transition from the sum of the microwave- and the radio-frequency  $\nu_{RF} = 29.7$  MHz.

$[(\Delta l = \pm 2, \Delta k = \pm 2), (\pm 2, \mp 1) \text{ and } (\pm 2, \mp 4)]$  and  $k$ -type  $[(0, \pm 3) \text{ and } (0, \pm 6)]$  interactions. Forty-four transitions with  $kl = -2 \leftarrow +4$  have been measured.

Furthermore, 17 transitions between these  $A_1$ – $A_2$  sublevels have been observed for  $J = 38$ – $46$  in the radio-frequency range (4–437 MHz) using the technique of two-dimensional radio-frequency–microwave double resonance Fourier transform (2D-(RF)MWFT) spectroscopy (13, 15). In the 2D experiment, a microwave pulse is followed by two radio-frequency pulses with adjustable evolution time between them; 128 1D experiments are performed with different evolution times to obtain a  $128 \times 1024$  data set from which the transition frequencies are derived from a least-squares fit. The  $G = 3$  states, as investigated in the present work, form a four level system and the allowed transitions between these levels form a

closed loop. To measure the  $A_1$ – $A_2$  splittings in the radio-frequency range, the experiment is normally performed with one of the two possible  $G = 3$  transitions,  $kl = -2$ ,  $A_+ \leftarrow kl = +4$ ,  $A_-$  ( $G = 3^-$ ; for  $J$  even,  $A_+$  is  $A_1$  and  $A_-$  is  $A_2$ , while for  $J$  odd,  $A_+$  is  $A_2$  and  $A_-$  is  $A_1$ ; see (7)), in the microwave range and the radio-frequency transition to be investigated. For  $J = 42$ , both microwave transitions and thus both radio-frequency transitions have nearly the same frequencies. For this, in one experiment all four transitions could be measured and four peaks appear in the 2D spectrum as shown in Fig. 1. The fit of this data set did not converge reasonably and the transition frequencies have been determined from the Fourier transformation. For a closed-loop four-level system, in which each microwave transition is progressively and regressively connected to a radio-frequency transition (see Fig. 1),



**FIG. 2.** (a) The  $J = 38$ ,  $kl = -2$ ,  $A_+ \leftarrow kl = +4$ ,  $A_-$  transition in a single resonance experiment (microwave-frequency 10 074.64 MHz). (b) Same transition with the connected  $kl = -2$ ,  $A_1$ – $A_2$  splitting pumped with a continuous radio-frequency radiation of 588 kHz and 200 mW power. Maximum amplitude was approximately 20% compared to (a).

TABLE 2

Experimental Frequencies (in MHz) of Radio-Frequency Transitions between  $A_1$ - $A_2$  Components of the  $G = 3$  Levels and of Perturbation-Allowed Transitions in the  $\nu_6 = 1$  State of SiDF<sub>3</sub>

| $J$                                      | $(k, \ell)' \leftarrow (k, \ell)''$ | Obs.      | $o - c^a$ | $o - c^b$ | Unc. |
|------------------------------------------|-------------------------------------|-----------|-----------|-----------|------|
| <b><math>A_1 - A_2</math> splittings</b> |                                     |           |           |           |      |
| 38                                       | -2, 1 $\leftarrow$ 2, -1            | 4.143     | 48        | 48        | 20   |
| 38                                       | -4, -1 $\leftarrow$ 4, 1            | 17.337    | -6        | -6        | 12   |
| 39                                       | -2, 1 $\leftarrow$ 2, -1            | 0.588     | 5         | 5         | 12   |
| 39                                       | -4, -1 $\leftarrow$ 4, 1            | 19.925    | 7         | 6         | 9    |
| 40                                       | -2, 1 $\leftarrow$ 2, -1            | 5.015     | -1        | -1        | 14   |
| 40                                       | -4, -1 $\leftarrow$ 4, 1            | 22.768    | -7        | -7        | 11   |
| 41                                       | -2, 1 $\leftarrow$ 2, -1            | 14.091    | -11       | -11       | 13   |
| 41                                       | -4, -1 $\leftarrow$ 4, 1            | 25.926    | -6        | -7        | 14   |
| 42                                       | -2, 1 $\leftarrow$ 2, -1            | 29.540    | -3        | -2        | 50   |
| 42                                       | -4, -1 $\leftarrow$ 4, 1            | 29.360    | -54       | -54       | 50   |
| 43                                       | -2, 1 $\leftarrow$ 2, -1            | 58.177    | 3         | 3         | 15   |
| 43                                       | -4, -1 $\leftarrow$ 4, 1            | 33.277    | 36        | 36        | 16   |
| 44                                       | -2, 1 $\leftarrow$ 2, -1            | 120.257   | 11        | 12        | 8    |
| 44                                       | -4, -1 $\leftarrow$ 4, 1            | 37.445    | 5         | 5         | 7    |
| 45                                       | -2, 1 $\leftarrow$ 2, -1            | 293.281   | -13       | -13       | 9    |
| 45                                       | -4, -1 $\leftarrow$ 4, 1            | 42.040    | 6         | 6         | 6    |
| 46                                       | -2, 1 $\leftarrow$ 2, -1            | 436.956   | 11        | 11        | 11   |
| 46                                       | -4, -1 $\leftarrow$ 4, 1            | 47.039    | -12       | -12       | 13   |
| <b>Perturbation allowed transitions</b>  |                                     |           |           |           |      |
| 45                                       | -1, -1 $\leftarrow$ 4, 1            | 25514.118 | 0         | 1         | 5    |
| 45                                       | 1, 1 $\leftarrow$ -2, 1             | 24550.950 | -11       | -10       | 5    |
| 46                                       | -1, -1 $\leftarrow$ 4, 1            | 24759.919 | 4         | 5         | 5    |
| 46                                       | 1, 1 $\leftarrow$ -2, 1             | 23833.895 | -11       | -11       | 5    |

<sup>a)</sup> obs. - calc. (in kHz) from the D reduction with  $\tau_K$  constrained to zero  
<sup>b)</sup> obs. - calc. (in kHz) from the D reduction with  $f_{22}^K$  constrained to zero

the four peaks in the 2D spectrum should form a perfect rectangle perpendicular to the  $ab, ac$  axes system as defined in Ref. (15). This is fulfilled as shown in the contour plot of the 2D spectrum in Fig. 1. For  $J = 38$ , due to strong resonances, the  $A_1$ - $A_2$  splitting with  $kl = -2$  is accidentally small ( $<1$  MHz) and it was not possible to apply 2D-(RF)MWFT spectroscopy. We therefore made use of the observation of coherence splittings by means of MW-RF double resonance (16). In this experiment, the microwave transition is split due to the pumping of a radio-frequency transition during the measuring time. A symmetric splitting is only obtained if the rf is resonant (17). The coherence splitting observed in this case is displayed in Fig. 2. The assumed error of the determined transition frequency of 588 kHz is only 12 kHz and thus this method can be very suitable for measurements in the kHz range.

Finally four "perturbation-allowed" transition frequencies obeying the selection rule  $\Delta G = \pm 3$  could be measured thanks to a local resonance of the  $kl = 1$  and  $-2$  levels with  $A_-$  symmetry for  $J = 45$  and 46.

The direct  $l$ -resonance transition frequencies are listed in Table 1. The other frequencies are given in Table 2.

2.3. Rotational Spectrum

The pure rotational spectrum has been observed from 150 to 645 GHz. The lower part of this range (150-315 GHz) was studied using the second, third, and fourth harmonic of a Gunn diode. French Thomson-CSF and Russian Istok backward-waves oscillators were employed between 450 and 590 GHz. For the whole range, the detector was a helium-cooled InSb bolometer. The accuracy of the new measurements is about 50 kHz for isolated lines.

$J = 47 \leftarrow 46$  transitions at about 645 GHz were measured using a newly stabilized far-infrared spectrometer (18). The following emission of CH<sub>2</sub>CHF was used: 634.2220 GHz pumped by the 10P20 CO<sub>2</sub> line. The accuracy of the measurements was about 300 kHz. The new rotational transition frequencies are listed in Table 3.

2.3. FTIR Spectrum

The  $\nu_6$  band appears in the infrared spectrum to be recorded between 210 and 360 cm<sup>-1</sup> with a Bruker 120 HR Fourier transform spectrometer. A Globar source, a 6- $\mu$ m Mylar beam-splitter and a helium-cooled Si bolometer were used. The pressure was 6.9 mbar in a 280-mm long cell equipped with CsBr windows. The resolution of  $6.0 \times 10^{-3}$  cm<sup>-1</sup> corresponded to a maximum optical path difference of 165 cm; 224 scans were coadded. The calibration was done using residual H<sub>2</sub>O lines (19). Assigned were 1167 transitions between 281 and 323 cm<sup>-1</sup>. Because the spectrum is dense, the accuracy of the wavenumbers was fixed to  $8 \times 10^{-4}$  cm<sup>-1</sup>.

The spectrum consists of a dense and intense  $Q$ -branch region extending from ca. 301-304 cm<sup>-1</sup>, with unresolved features, but with well-resolved lines in the wings which are mostly  $^pP$  and  $^rR$  transitions occurring to lower and higher wavenumbers from the  $Q$  branch region, respectively. This  $Q$ -branch region is illustrated in Fig. 3, lower trace C, together with two simulations with (wrong) positive sign of the  $l$ -type resonance  $q_{22}$  (trace A) and with (correct) negative sign of  $q_{22}$  (trace B) (see Section 4.1 for the discussion of the sign). As is evident from traces B and C, the unresolved  $^rQ_k$  branches are much stronger than the (almost invisible)  $^pQ$  branches and they exhibit pronounced strong-weak-weak intensity alternation. The prominence of these  $^rQ$  branches is due to the fact that they form bandheads at high wavenumbers with the exception of  $^rQ_0$ , which is uniformly degraded to a small wavenumber. The almost absent  $^pQ$  branches are much weaker for two reasons. First, their individual  $J$  lines are very weak because of the intensity perturbation caused by the interplay of the different perturbations (above all the  $l(2, 2)$  resonance) and second, they are widely spaced, degrading uniformly to high wavenumber rather than forming a prominent bandhead as  $J$  increases.

TABLE 3  
Experimental Frequencies (in MHz) of the Rotational  $\Delta J = 1$  Transitions  
in the  $\nu_6 = 1$  State of SiDF<sub>3</sub>

| <i>J</i> | <i>k</i> | <i>l</i> | Obs.       | e-c <sup>a</sup> | e-c <sup>b</sup> | Unc. | <i>J</i> | <i>k</i> | <i>l</i> | Obs.       | e-c <sup>a</sup> | e-c <sup>b</sup> | Unc. |
|----------|----------|----------|------------|------------------|------------------|------|----------|----------|----------|------------|------------------|------------------|------|
| 10       | -1       | -1       | 151529.554 | 16               | 15               | 50   | 22       | -1       | -1       | 316597.323 | 48               | 46               | 50   |
| 10       | 1        | 1        | 151783.559 | 26               | 25               | 50   | 22       | 0        | -1       | 317109.029 | 23               | 21               | 50   |
| 10       | 0        | -1       | 151722.418 | 5                | 4                | 50   | 22       | 1        | -1       | 317072.324 | -14              | -16              | 50   |
| 10       | 1        | -1       | 151693.662 | 17               | 17               | 50   | 22       | -2       | 1        | 317039.620 | 9                | 7                | 50   |
| 10       | 2        | -1       | 151682.612 | 15               | 14               | 200  | 22       | 3        | -1       | 317012.803 | 4                | 2                | 50   |
| 10       | 3        | -1       | 151677.685 | 39               | 39               | 200  | 22       | 4        | -1       | 316993.877 | 4                | 3                | 50   |
| 10       | 4        | -1       | 151675.595 | 109              | 109              | 200  | 22       | 5        | -1       | 316981.109 | 49               | 48               | 50   |
| 10       | 5        | -1       | 151674.989 | -9               | -9               | 50   | 22       | 6        | -1       | 316973.004 | 51               | 51               | 50   |
| 10       | 6        | -1       | 151675.595 | -71              | -71              | 200  | 22       | 7        | -1       | 316968.465 | -48              | -48              | 100  |
| 10       | 8        | -1       | 151679.508 | -23              | -23              | 50   | 22       | 8        | -1       | 316967.021 | 5                | 5                | 100  |
| 10       | 9        | -1       | 151682.612 | 122              | 122              | 200  | 22       | 9        | -1       | 316967.986 | 31               | 32               | 100  |
| 10       | 10       | -1       | 151685.995 | -52              | -51              | 50   | 22       | 10       | -1       | 316971.002 | 29               | 30               | 50   |
| 10       | 2        | 1        | 151591.117 | 13               | 12               | 50   | 22       | 11       | -1       | 316975.853 | 41               | 42               | 50   |
| 10       | 3        | 1        | 151621.168 | -22              | -23              | 50   | 22       | 12       | -1       | 316982.315 | 29               | 30               | 50   |
| 10       | 4        | 1        | 151634.446 | 34               | 33               | 50   | 22       | 13       | -1       | 316990.252 | -3               | -2               | 50   |
| 10       | 5        | 1        | 151642.508 | 6                | 5                | 50   | 22       | 14       | -1       | 316999.582 | -30              | -30              | 50   |
| 10       | 6        | 1        | 151648.606 | -39              | -40              | 50   | 22       | 15       | -1       | 317010.296 | 18               | 17               | 50   |
| 10       | 7        | 1        | 151653.972 | -29              | -30              | 50   | 22       | 16       | -1       | 317022.161 | -28              | -30              | 50   |
| 10       | 8        | 1        | 151659.057 | -30              | -31              | 50   | 22       | 17       | -1       | 317035.291 | -4               | -7               | 50   |
| 10       | 9        | 1        | 151664.127 | -41              | -41              | 250  | 22       | 18       | -1       | 317049.549 | -7               | -12              | 50   |
| 10       | 10       | 1        | 151669.337 | -55              | -55              | 250  | 22       | 19       | -1       | 317064.939 | -2               | -10              | 50   |
| 16       | -1       | -1       | 234109.731 | -7               | -8               | 50   | 22       | 20       | -1       | 317081.462 | 38               | 27               | 50   |
| 16       | 1        | 1        | 234501.447 | 3                | 2                | 50   | 22       | 21       | -1       | 317099.003 | 18               | 3                | 50   |
| 16       | 0        | -1       | 234467.005 | 12               | 11               | 50   | 22       | 22       | -1       | 317117.678 | 73               | 53               | 50   |
| 16       | 1        | -1       | 234421.163 | -14              | -15              | 50   | 22       | 2        | 1        | 316616.100 | -22              | -24              | 50   |
| 16       | 2        | -1       | 234392.555 | 135              | 134              | 200  | 22       | 3        | 1        | 316652.665 | -34              | -36              | 100  |
| 16       | 3        | -1       | 234375.757 | -41              | -42              | 50   | 22       | 4        | 1        | 316691.662 | 151              | 149              | 200  |
| 16       | 4        | -1       | 234366.042 | 20               | 19               | 50   | 22       | 5        | 1        | 316724.681 | 21               | 19               | 50   |
| 16       | 5        | -1       | 234360.585 | -8               | -8               | 50   | 22       | 6        | 1        | 316751.899 | 19               | 18               | 50   |
| 16       | 6        | -1       | 234358.116 | -2               | -2               | 50   | 22       | 7        | 1        | 316774.830 | 6                | 5                | 50   |
| 16       | 7        | -1       | 234357.819 | 3                | 3                | 50   | 22       | 8        | 1        | 316794.896 | -9               | -9               | 50   |
| 16       | 8        | -1       | 234359.171 | -51              | -50              | 50   | 22       | 9        | 1        | 316813.184 | 23               | 23               | 50   |
| 16       | 9        | -1       | 234362.032 | -11              | -11              | 50   | 22       | 10       | 1        | 316830.325 | 6                | 6                | 50   |
| 16       | 10       | -1       | 234366.042 | -47              | -46              | 50   | 22       | 13       | 1        | 316879.592 | -4               | 0                | 50   |
| 16       | 11       | -1       | 234371.200 | -29              | -28              | 50   | 22       | 14       | 1        | 316896.204 | 24               | 28               | 50   |
| 16       | 12       | -1       | 234377.315 | -56              | -56              | 50   | 22       | 15       | 1        | 316913.109 | -15              | -9               | 50   |
| 16       | 13       | -1       | 234384.435 | -14              | -15              | 50   | 22       | 16       | 1        | 316930.531 | -3               | 3                | 50   |
| 16       | 14       | -1       | 234392.555 | 140              | 139              | 200  | 22       | 17       | 1        | 316948.412 | -82              | -75              | 100  |
| 16       | 15       | -1       | 234401.232 | 0                | -2               | 50   | 22       | 18       | 1        | 316967.021 | -50              | -41              | 50   |
| 16       | 16       | -1       | 234410.907 | 36               | 33               | 50   | 22       | 19       | 1        | 316986.308 | -7               | 3                | 50   |
| 16       | 2        | 1        | 234144.929 | 12               | 11               | 50   | 22       | 20       | 1        | 317006.301 | 31               | 43               | 50   |
| 16       | 3        | 1        | 234192.649 | -1               | -2               | 50   | 22       | 21       | 1        | 317026.932 | -37              | -24              | 100  |
| 16       | 4        | 1        | 234224.741 | 23               | 22               | 50   | 22       | 22       | 1        | 317048.457 | 14               | 30               | 50   |
| 16       | 5        | 1        | 234246.272 | 1                | -1               | 50   | 32       | 1        | 1        | 454535.637 | 7                | 4                | 50   |
| 16       | 6        | 1        | 234262.207 | 16               | 15               | 50   | 32       | -1       | -1       | 453783.595 | 19               | 17               | 50   |
| 16       | 7        | 1        | 234275.153 | 24               | 23               | 50   | 32       | 0        | -1       | 454530.121 | 18               | 15               | 50   |
| 16       | 8        | 1        | 234286.455 | -24              | -25              | 50   | 32       | 1        | -1       | 454515.009 | -14              | -16              | 50   |
| 16       | 9        | 1        | 234297.039 | 15               | 15               | 50   | 32       | 2        | -1       | 454493.761 | 134              | 132              | 200  |
| 16       | 10       | 1        | 234307.215 | -14              | -13              | 50   | 32       | 3        | -1       | 454471.740 | 9                | 7                | 50   |
| 16       | 11       | 1        | 234317.349 | -38              | -37              | 50   | 32       | 4        | -1       | 454450.798 | -6               | -7               | 50   |
| 16       | 13       | 1        | 234338.311 | 38               | 41               | 50   | 32       | 5        | -1       | 454432.779 | -6               | -7               | 100  |
| 16       | 14       | 1        | 234349.226 | 1                | 5                | 50   | 32       | 6        | -1       | 454418.358 | -29              | -30              | 50   |
| 16       | 15       | 1        | 234360.604 | -11              | -6               | 50   | 32       | 7        | -1       | 454407.813 | 58               | 58               | 50   |
| 16       | 16       | 1        | 234372.496 | 2                | 8                | 50   | 32       | 8        | -1       | 454400.719 | -38              | -37              | 50   |
| 22       | 1        | 1        | 317125.613 | 11               | 9                | 50   | 32       | 11       | -1       | 454399.047 | -36              | -32              | 50   |

<sup>a</sup> obs. - calc. (in kHz) from the D reduction with  $\tau_K$  constrained to zero

<sup>b</sup> obs. - calc. (in kHz) from the D reduction with  $\int_{22}^K$  constrained to zero

### 3. THEORY

The diagonal elements of the Hamiltonian matrix in the rotational quantum numbers *J*, *k*, and *l* are written as

$$\begin{aligned}
 E = & \nu_0 + BJ(J+1) + (A-B)k^2 - D_JJ^2(J+1)^2 \\
 & - D_{JK}J(J+1)k^2 - D_Kk^4 + H_JJ^3(J+1)^3 \\
 & + H_{JK}J^2(J+1)^2k^2 + H_{KJ}J(J+1)k^4 + H_Kk^6
 \end{aligned}$$

TABLE 3—Continued

| $J$ | $k$ | $\ell$ | Obs.       | e-c <sup>a</sup> | e-c <sup>b</sup> | Unc. | $J$ | $k$ | $\ell$ | Obs.       | e-c <sup>a</sup> | e-c <sup>b</sup> | Unc. |
|-----|-----|--------|------------|------------------|------------------|------|-----|-----|--------|------------|------------------|------------------|------|
| 32  | 17  | -1     | 454463.393 | -35              | -29              | 50   | 38  | 2   | -1     | 536725.814 | 4                | 2                | 50   |
| 32  | 20  | -1     | 454522.240 | -41              | -39              | 50   | 38  | -4  | -1     | 535905.362 | 56               | 54               | 50   |
| 32  | 2   | 1      | 453789.575 | 30               | 28               | 50   | 38  | 4   | 1      | 535902.747 | 16               | 15               | 50   |
| 32  | 3   | 1      | 453808.406 | -26              | -28              | 50   | 42  | 1   | 1      | 591445.909 | 29               | 29               | 50   |
| 32  | -4  | -1     | 453836.325 | -13              | -15              | 50   | 42  | 0   | -1     | 591443.892 | -36              | -37              | 50   |
| 32  | 4   | 1      | 453835.119 | 60               | 58               | 50   | 42  | 1   | -1     | 591438.326 | 12               | 12               | 50   |
| 32  | 5   | 1      | 453867.195 | 8                | 7                | 50   | 42  | -2  | 1      | 591399.590 | -12              | -12              | 50   |
| 32  | 6   | 1      | 453899.952 | -32              | -33              | 50   | 42  | 2   | -1     | 591428.247 | 13               | 13               | 50   |
| 32  | 10  | 1      | 454023.535 | -30              | -29              | 50   | 42  | 3   | -1     | 591417.468 | 109              | 109              | 50   |
| 32  | 13  | 1      | 454107.958 | -23              | -21              | 50   | 42  | 4   | -1     | 591406.505 | 37               | 38               | 50   |
| 32  | 19  | 1      | 454280.405 | -27              | -23              | 50   | 42  | 5   | -1     | 591395.449 | -17              | -15              | 50   |
| 33  | 1   | 1      | 468251.555 | -14              | -16              | 50   | 42  | 2   | 1      | 590477.882 | -9               | -10              | 50   |
| 33  | -1  | -1     | 467477.610 | 18               | 16               | 50   | 42  | 3   | 1      | 590488.297 | -4               | -5               | 50   |
| 33  | 0   | -1     | 468246.566 | -15              | -17              | 50   | 42  | -4  | -1     | 590507.325 | 25               | 24               | 50   |
| 33  | 3   | -1     | 468192.174 | 0                | -2               | 50   | 42  | 4   | 1      | 590503.607 | 134              | 134              | 250  |
| 33  | 4   | -1     | 468172.003 | 9                | 8                | 50   | 42  | 6   | 1      | 590554.483 | -4               | -4               | 50   |
| 33  | 5   | -1     | 468154.241 | -44              | -44              | 50   | 46  | 1   | 1      | 645158.515 | -287             | -284             | 300  |
| 33  | 7   | -1     | 468129.060 | -11              | -10              | 50   | 46  | 1   | 1      | 646037.346 | -118             | -117             | 300  |
| 33  | 8   | -1     | 468121.806 | 5                | 7                | 50   | 46  | -2  | 1      | 645846.413 | -1514            | -1514            | 2000 |
| 33  | 11  | -1     | 468119.319 | -21              | -17              | 50   | 46  | 2   | -1     | 646025.420 | -155             | -154             | 300  |
| 33  | 14  | -1     | 468141.463 | 1                | 7                | 50   | 46  | 3   | -1     | 646016.771 | -358             | -355             | 300  |
| 33  | 17  | -1     | 468183.778 | -40              | -33              | 50   | 46  | 4   | -1     | 646010.300 | -647             | -644             | 300  |
| 33  | 20  | -1     | 468243.682 | -18              | -13              | 50   | 46  | 5   | -1     | 646003.616 | -179             | -175             | 300  |
| 33  | 23  | -1     | 468319.448 | -18              | -22              | 50   | 46  | 6   | -1     | 645997.159 | -38              | -31              | 300  |
| 33  | 2   | 1      | 467482.872 | 97               | 95               | 200  | 46  | 7   | -1     | 645990.605 | -1243            | -1235            | 1000 |
| 33  | 3   | 1      | 467500.495 | 15               | 12               | 50   | 46  | 8   | -1     | 645987.771 | -466             | -456             | 300  |
| 33  | 4   | 1      | 467525.733 | 19               | 17               | 50   | 46  | 9   | -1     | 645986.500 | -221             | -209             | 300  |
| 33  | -4  | -1     | 467527.164 | -4               | -6               | 50   | 46  | 10  | -1     | 645987.605 | 57               | 72               | 300  |
| 33  | 5   | 1      | 467557.176 | 178              | 177              | 200  | 46  | 11  | -1     | 645990.875 | -8               | 11               | 300  |
| 33  | 6   | 1      | 467589.372 | -38              | -39              | 50   | 46  | 2   | 1      | 644984.023 | -136             | -136             | 300  |
| 33  | 7   | 1      | 467622.024 | 19               | 19               | 50   | 46  | 3   | 1      | 644991.872 | -249             | -248             | 1000 |
| 33  | 10  | 1      | 467715.304 | -6               | -5               | 50   | 46  | -4  | -1     | 645009.026 | -364             | -363             | 300  |
| 33  | 13  | 1      | 467802.860 | -90              | -87              | 50   | 46  | 4   | 1      | 645003.878 | -45              | -44              | 300  |
| 33  | 16  | 1      | 467890.403 | -43              | -40              | 50   | 46  | 5   | 1      | 645026.140 | -261             | -260             | 300  |
| 33  | 19  | 1      | 467982.214 | -24              | -21              | 50   | 46  | 6   | 1      | 645049.536 | -980             | -979             | 1000 |
| 33  | 22  | 1      | 468081.126 | -11              | -10              | 50   | 46  | 7   | 1      | 645078.514 | 265              | 267              | 300  |
| 33  | 25  | 1      | 468188.909 | 3                | 1                | 50   | 46  | 10  | 1      | 645176.945 | -17              | -16              | 300  |
| 38  | -2  | 1      | 536722.347 | 48               | 47               | 50   |     |     |        |            |                  |                  |      |

$$\begin{aligned}
 & -2(A\zeta)kl + \eta_J J(J+1)kl + \eta_K k^3 l \\
 & + \tau_J J^2(J+1)^2 kl + \tau_{JK} J(J+1)k^3 l \\
 & + \tau_K k^5 l + \sigma_J J^3(J+1)^3 kl + \sigma_{JK} J^2(J+1)^2 k^3 l \\
 & + \sigma_{KJ} J(J+1)k^5 l + \sigma_K k^7 l + \dots, \quad [1]
 \end{aligned}$$

This expression can be used for the vibrational ground state by setting  $\nu_6$  and  $l$  to zero.

The off-diagonal terms must obey the general selection rule  $\Delta(k-l) = \pm 3n$ ,  $n = 0, 1, \dots$ . We included the  $l$ -type [ $(\Delta l = \pm 2, \Delta k = \pm 2)$ ,  $(\pm 2, \mp 1)$ , and  $(\pm 2, \mp 4)$ ] and  $k$ -type [ $(0, \pm 3)$  and  $(0, \pm 6)$ ] interactions for which we have made use of higher order constraints to remove terms with the  $k$ -dependent parameters ( $f_{12}^K, \epsilon_K$ ). The expressions in the Hamiltonian matrix are

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 2 | \mathbf{H}_{22} + \mathbf{H}_{24} + \mathbf{H}_{26} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = 2\{q_{22} + f_{22}^J J(J+1) + f_{22}^{JJ} J^2(J+1)^2 \\
 + f_{22}^K k(k+1)\} F_2^{\pm}(J, k) \quad [2]
 \end{aligned}$$

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 1 | \mathbf{H}_{22} + \mathbf{H}_{24} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = 2\{q_{12} + f_{12}^J J(J+1)\} (2k \pm 1) F_1^{\pm}(J, k) \quad [3]
 \end{aligned}$$

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 4 | \mathbf{H}_{24} + \mathbf{H}_{26} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = 2\{f_{42} - f_{42}^J J(J+1)\} F_4^{\pm}(J, k) \quad [4]
 \end{aligned}$$

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 3 | \mathbf{H}_{23} + \mathbf{H}_{25} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = l_1^{\pm} d + d^J J(J+1) F_3^{\pm}(J, k) \quad [5]
 \end{aligned}$$

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 3 | \mathbf{H}_{24} + \mathbf{H}_{26} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = \{\epsilon + \epsilon^J J(J+1)\} (2k \pm 3) F_3^{\pm}(J, k) \quad [6]
 \end{aligned}$$

and

$$\begin{aligned}
 \langle \nu_6 = 1^{\pm 1}; J, k \pm 6 | \mathbf{H}_{06} | \nu_6 = 1^{\pm 1}; J, k \rangle \\
 = \{h_3 + h_3^J J(J+1)\} F_6^{\pm}(J, k), \quad [7]
 \end{aligned}$$

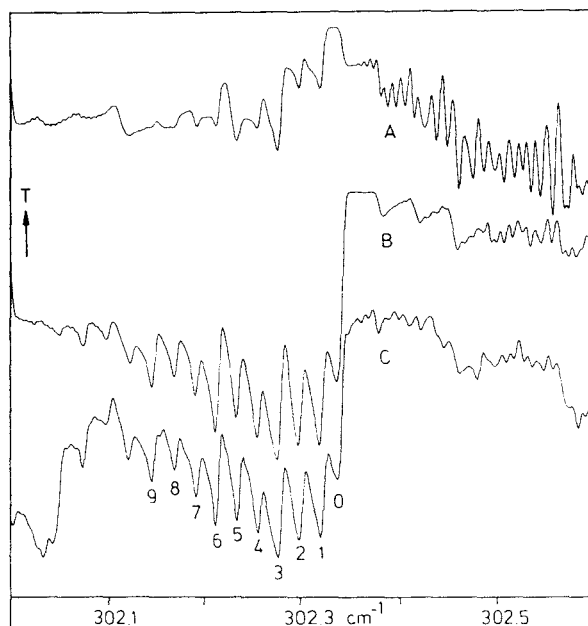


FIG. 3. Detail of the  $\nu_6$  band of  $\text{SiDF}_3$  in the region of the  $Q$  branches. A: Contour simulation, with  $q_{22}$  positive; B: Contour simulation, with  $q_{22}$  negative; C: Experimental spectrum. The  $^RQ$  branches extending to small wave-numbers are assigned by their  $K\Delta K$  values.

where

$$F_n^\pm(J, k) = \prod_{i=1}^n [J(J+1) - (k \pm i \mp 1)(k \pm i)]^{1/2}. \quad [8]$$

In Eq. [2],  $-4q_{22} = q_r^-$ , as defined by Cartwright and Mills (20).

## 4. RESULTS AND DISCUSSION

### 4.1. Value and Sign of the Parameters

The program SIMFIT (21) was used to perform the fits of the  $\nu_6 = 1$  excited state transitions and the determination of the molecular parameters. Four lines of Ref. (12) were included. The ground state parameters (except  $C_0$ , see the following discussion) were fixed to the values given in Table 4.

The fitted parameters are listed in Tables 5 and 6. For getting the best reproduction of the direct  $l$ -doubling transitions within the  $f_{22}^K = 0$  constraint, the higher order  $z$ -type Coriolis term  $\sigma_J$  was fitted. The sextic centrifugal distortion constant  $H_{KJ}$  was not determined ( $H_{KJ}/\sigma(H_{KJ}) = 1.6$ ) when the  $QD$  reduction was chosen. We had the possibility of fixing this constant either to zero or to the ground state value or to the value derived with relations [16] and [17] (see Section 4.2). While with the ground state value the standard deviation of each data set is significantly worsened, the other two solutions led to equivalent good results. To have the best consistency with

respect to the reduction theory, fits were performed using the calculated value  $H_{KJ} = -0.0554$  Hz.

The axial ground state rotational constant  $C_0$  could be fitted without including forbidden transitions between the ground and excited states. This can be explained by the resonances in the upper level whose strength depends on the difference between the interacting levels and thus on  $C_6$ . Because the interactions are strong enough in the present case and because the difference  $(C_6 - C_0)$  is fitted in the usual way instead of  $C_6$ ,  $C_0$  has been precisely determined (see Tables 5 and 6). Its accuracy is improved by two orders of magnitude when comparing with the value obtained by Harada *et al.* by  $\text{CO}_2$  laser Stark spectroscopy (22). The axial centrifugal distortion constant  $D_{K,0}$  could not be determined and was fixed to the force field calculated value.

The  $(0, \pm 6)$  resonance parameter,  $h_3$ , could be accurately determined. Its value is in good agreement with the ground state value derived from split  $K = 3$  transitions (see Table 4). The sign has been determined without ambiguity. Note that the fits were performed using the ground state  $h_{3,GS}$  parameter with the same sign as determined from the excited state. The higher order term  $h_{3J}$  is not very well determined but was necessary for the reproduction of the radio-frequency data.

No transitions in the data sets permitted the determination of the sign of the  $l$ -type parameter  $q_{22}$ . The direct  $l$ -type resonance and pure rotational transitions lead to the absolute value of  $q_{22}$ . The sign could have been obtained from the  $^RX_0$

TABLE 4  
Molecular Parameters of  $\text{SiDF}_3$  in the  
Vibrational Ground State

|            |       |               |
|------------|-------|---------------|
| $B^a$      | (MHz) | 6890.10533    |
| $C^{b,c}$  | (MHz) | 4133.55       |
| $C^{c,d}$  | (MHz) | 4133.687 (11) |
| $C^{d,e}$  | (MHz) | 4133.704 (14) |
| $D_J^a$    | (kHz) | 6.34921       |
| $D_{JK}^a$ | (kHz) | -9.9689       |
| $D_K^c$    | (kHz) | 4.55          |
| $H_J^a$    | (Hz)  | 0.016418      |
| $H_{JK}^a$ | (Hz)  | -0.06119      |
| $H_{KJ}^a$ | (Hz)  | 0.07724       |
| $H_K^a$    | (Hz)  | 0.0           |
| $ h_3 ^a$  | (mHz) | 0.764         |

<sup>a)</sup> Reference (18)

<sup>b)</sup> Reference (22)

<sup>c)</sup> This work. Average value derived within the  $\tau_K = 0$  constraint. See also Table 5.

<sup>d)</sup> This work. Average value derived within the  $f_{22}^K = 0$  constraint. See also Table 6.

<sup>e)</sup> Calculated from the harmonic force field (12)

TABLE 5  
Molecular Parameters (in MHz) of SiDF<sub>3</sub> in the  $v_6 = 1$  State with  $\tau_K$  Constrained to Zero

|                         |                  | Reduction Q      | Reduction D      | Reduction QD           |
|-------------------------|------------------|------------------|------------------|------------------------|
| $v_6$                   | cm <sup>-1</sup> | 302.288269 (42)  | 302.288294 (42)  | 302.288257 (42)        |
| $B$                     | MHz              | 6895.04201 (29)  | 6895.03826 (29)  | 6895.04198 (29)        |
| $C$                     | MHz              | 4129.6326 (14)   | 4129.6398 (14)   | 4129.63299 (90)        |
| $D_J$                   | kHz              | 6.37471 (26)     | 6.37472 (26)     | 6.37462 (26)           |
| $D_{JK}$                | kHz              | - 10.0714 (14)   | - 10.0712 (14)   | - 10.0711 (12)         |
| $D_K$                   | kHz              | 4.6907 (84)      | 4.6814 (86)      | 4.6947 (80)            |
| $H_J$                   | Hz               | 0.016983 (74)    | 0.016994 (74)    | 0.011865 (73)          |
| $H_{JK}$                | Hz               | - 0.06302 (52)   | - 0.06284 (53)   | - 0.01716 (52)         |
| $H_{KJ}$                | Hz               | 0.0713 (14)      | 0.0709 (14)      | - 0.00554 <sup>a</sup> |
| $H_K$                   | Hz               | 0.0335 (30)      | 0.0301 (31)      | 0.0710 (30)            |
| $C\zeta$                | MHz              | - 2190.2080 (13) | - 2190.2103 (13) | - 2190.20761 (82)      |
| $\eta_J$                | kHz              | - 31.4032 (27)   | - 38.9818 (28)   | - 31.4040 (24)         |
| $\eta_K$                | kHz              | 29.743 (32)      | 37.283 (33)      | 29.762 (31)            |
| $\tau_J$                | Hz               | 0.335 (17)       | 0.446 (18)       | 0.348 (17)             |
| $\tau_{JK}$             | Hz               | - 0.677 (33)     | - 0.763 (34)     | - 0.703 (32)           |
| $q_{22}$                | MHz              | - 2.8906371 (18) | - 2.8906334 (18) | - 2.8906379 (17)       |
| $f_{22}^J$              | Hz               | 18.15752 (48)    | 16.62415 (48)    | 18.15663 (47)          |
| $f_{22}^K$              | Hz               | - 31.18 (90)     | - 31.49 (93)     | - 30.57 (87)           |
| $f_{22}^{JJ}$           | mHz              | - 0.08733 (18)   | - 0.07149 (18)   | - 0.08562 (17)         |
| $f_{42}$                | Hz               | - 3.90407 (32)   | - 5.43725 (33)   | - 3.90428 (32)         |
| $f_{42}^J$              | mHz              | 0.01958 (20)     | 0.03533 (20)     | 0.02110 (20)           |
| $\epsilon_1 d^b$        | kHz              | 4.210642 (76)    | 0. <sup>a</sup>  | 0. <sup>a</sup>        |
| $\epsilon_1 d_J$        | Hz               | - 0.030951 (36)  | 0. <sup>a</sup>  | 0. <sup>a</sup>        |
| $\epsilon_1 q_{12}$     | MHz              | 0. <sup>a</sup>  | - 2.601931 (47)  | 0. <sup>a</sup>        |
| $\epsilon_1 f_{12}^J$   | Hz               | 0. <sup>a</sup>  | 23.814 (26)      | 0. <sup>a</sup>        |
| $\epsilon_1 \epsilon$   | kHz              | 0. <sup>a</sup>  | 0. <sup>a</sup>  | 2.658485 (49)          |
| $\epsilon_1 \epsilon_J$ | mHz              | 0. <sup>a</sup>  | 0. <sup>a</sup>  | - 5.027 (40)           |
| $h_3$                   | mHz              | - 0.7630 (19)    | - 0.7629 (19)    | - 3.3188 (19)          |
| $h_{3J}$                | mHz              | 0.00000851 (95)  | 0.00000851 (96)  | 0.00000895 (96)        |
| $C_0$                   | MHz              | 4133.6831 (63)   | 4133.6926 (63)   | 4133.6841 (61)         |

<sup>a</sup> Constrained value

<sup>b</sup>  $\epsilon_1 = \pm 1$  is arbitrary

transitions ( $X = P, Q, R$ ) simultaneously but the corresponding lines are not resolved in the spectrum. However, a simulation of the  $Q$  branch is shown in Fig. 3 to be in perfect agreement with the experimental spectrum (trace C) if  $q_{22} < 0$  only (trace B). Fits were thus performed with this signed value. The  $l$ -type interaction parameter  $f_{12}$  must have the same sign as  $q_{22}$  (7). Finally the sign of  $d$  and  $q_{12}$  is arbitrary. However, they should be compatible with the reduction theory: according to Eq. [9] of the next section, if  $F/q_{22} < 0$  ( $F = 2C\zeta - C - B$ ),

$d$  and  $q_{12}$  must have the same sign; the other case implies opposite signs. In the present work, both  $q_{22}$  and  $F$  are negative. Thus  $d$  has been arbitrarily chosen to be positive and  $q_{12}$  negative.

#### 4.2. Multiple Fits Analysis

Lobodenko *et al.* (1) and Harder (8) have shown the existence of three equivalent  $Q$ ,  $D$ , and  $QD$  reduction schemes

TABLE 6  
Molecular Parameters (in MHz) of SiDF<sub>3</sub> in the  $v_6 = 1$  State with  $f_{22}^K$  Constrained to Zero

|                         |                  | Reduction Q       | Reduction D       | Reduction QD           |
|-------------------------|------------------|-------------------|-------------------|------------------------|
| $v_6$                   | $\text{cm}^{-1}$ | 302.288350 (46)   | 302.288350 (45)   | 302.288351 (46)        |
| $B$                     | $\text{MHz}$     | 6895.04209 (29)   | 6895.03830 (29)   | 6895.04212 (29)        |
| $C$                     | $\text{MHz}$     | 4129.6333 (14)    | 4129.6412 (14)    | 4129.63285 (91)        |
| $D_J$                   | $\text{kHz}$     | 6.37412 (26)      | 6.37407 (26)      | 6.37411 (26)           |
| $D_{JK}$                | $\text{kHz}$     | - 10.0668 (13)    | - 10.0667 (13)    | - 10.0664 (12)         |
| $D_K$                   | $\text{kHz}$     | 4.657 (11)        | 4.657 (11)        | 4.656 (11)             |
| $H_J$                   | $\text{Hz}$      | 0.016980 (74)     | 0.016977 (73)     | 0.011871 (74)          |
| $H_{JK}$                | $\text{Hz}$      | - 0.06275 (52)    | - 0.06281 (52)    | - 0.01641 (52)         |
| $H_{KJ}$                | $\text{Hz}$      | 0.0720 (14)       | 0.0723 (14)       | - 0.00554 <sup>a</sup> |
| $H_K$                   | $\text{Hz}$      | 0.0214 (40)       | 0.0212 (40)       | 0.0576 (40)            |
| $C\zeta$                | $\text{MHz}$     | - 2190.2065 (13)  | - 2190.2081 (13)  | - 2190.20691 (83)      |
| $\eta_J$                | $\text{kHz}$     | - 31.3912 (29)    | - 38.9728 (29)    | - 31.3907 (26)         |
| $\eta_K$                | $\text{kHz}$     | 29.633 (42)       | 37.215 (43)       | 29.631 (43)            |
| $\tau_J$                | $\text{Hz}$      | - 0.2985 (16)     | - 0.1892 (16)     | - 0.2754 (16)          |
| $\tau_{JK}$             | $\text{Hz}$      | 0.5210 (62)       | 0.4415 (62)       | 0.4751 (27)            |
| $\tau_K$                | $\text{Hz}$      | - 0.519 (25)      | - 0.548 (25)      | - 0.495 (25)           |
| $\sigma_J$              | $\text{mHz}$     | 0.01137 (37)      | 0.01089 (37)      | 0.01164 (37)           |
| $q_{22}$                | $\text{MHz}$     | - 2.89069993 (31) | - 2.89069689 (31) | - 2.89070026(31)       |
| $f_{22}^J$              | $\text{Hz}$      | 18.15813 (50)     | 16.62484 (50)     | 18.15879 (50)          |
| $f_{22}^{JJ}$           | $\text{mHz}$     | - 0.08746 (19)    | - 0.07171 (19)    | - 0.08659 (19)         |
| $f_{42}$                | $\text{Hz}$      | - 3.90403 (32)    | - 5.43735 (33)    | - 3.90390 (32)         |
| $f_{42}^J$              | $\text{mHz}$     | 0.01961 (20)      | 0.03540 (20)      | 0.02061 (20)           |
| $\epsilon_1 d$          | $\text{kHz}$     | 4.210577 (76)     | 0. <sup>a</sup>   | 0. <sup>a</sup>        |
| $\epsilon_1 d_J$        | $\text{Hz}$      | - 0.030826 (36)   | 0. <sup>a</sup>   | 0. <sup>a</sup>        |
| $\epsilon_1 q_{12}$     | $\text{MHz}$     | 0. <sup>a</sup>   | - 2.602308 (45)   | 0. <sup>a</sup>        |
| $\epsilon_1 f_{12}^J$   | $\text{Hz}$      | 0. <sup>a</sup>   | 24.296 (22)       | 0. <sup>a</sup>        |
| $\epsilon_1 \epsilon$   | $\text{kHz}$     | 0. <sup>a</sup>   | 0. <sup>a</sup>   | 2.657813 (44)          |
| $\epsilon_1 \epsilon_J$ | $\text{mHz}$     | 0. <sup>a</sup>   | 0. <sup>a</sup>   | - 3.847 (21)           |
| $h_3$                   | $\text{mHz}$     | - 0.7645 (19)     | - 0.7646 (19)     | - 3.3189 (20)          |
| $h_{3J}$                | $\text{mHz}$     | 0.00000853 (95)   | 0.00000854 (95)   | 0.00000667 (96)        |
| $C_0$                   | $\text{MHz}$     | 4133.7042 (78)    | 4133.7044 (78)    | 4133.7040 (78)         |

<sup>a)</sup> Constrained value

<sup>b)</sup>  $\epsilon_1 = \pm 1$  is arbitrary

enabling the fit of one of the three interaction parameters  $d$ ,  $q_{12}$ , and  $\epsilon$  (or  $\tau_{xxx} = 4\epsilon$  in Ref. (8)), respectively, while the other two are fixed, usually to zero value. Furthermore, one of the following higher order constants,  $f_{22}^K$ ,  $\tau_J$ ,  $\tau_{JK}$ , and  $\tau_K$ , must be constrained because they depend on the transformation parameter  $w$  (9). In general, a parameter of an off-diagonal rather than a diagonal term should be constrained. Neverthe-

less, we have allowed  $f_{22}^K$  to be fitted to check if the different choices are all suitable. Although the resulting 12 possible sets of parameters are unitary equivalent, the reproduction of the data may be different with the choice of the constraints, and the determination of the parameters depends on the data available. For the given data set we could not use the constraints  $\tau_J = 0$  and  $\tau_{JK} = 0$  because the first constraint resulted in the bad

TABLE 7  
Standard Deviations of the Data Sets Used for the Analysis of SiDF<sub>3</sub> in the  $\nu_6 = 1$  State

|                            | RF<br>transitions  | MW<br>transitions | Millimeter<br>transitions | Far infrared<br>transitions | FTIR<br>transitions    |
|----------------------------|--------------------|-------------------|---------------------------|-----------------------------|------------------------|
| No. Data                   | 18                 | 229               | 168                       | 21                          | 1167                   |
| Constraints                | Standard Deviation |                   |                           |                             |                        |
|                            | (kHz)              | (kHz)             | (kHz)                     | (kHz)                       | (cm <sup>-1</sup> )    |
| $q_{12} = \varepsilon = 0$ | $\tau_K = 0$       | 12                | 1.2                       | 30                          | 298                    |
|                            | $f_{22}^K = 0$     | 12                | 1.2                       | 30                          | 297                    |
| $d = \varepsilon = 0$      | $\tau_K = 0$       | 12                | 1.2                       | 30                          | 299                    |
|                            | $f_{22}^K = 0$     | 12                | 1.2                       | 29                          | 296                    |
| $q_{12} = d = 0$           | $\tau_K = 0$       | 12                | 1.2                       | 30                          | 295                    |
|                            | $f_{22}^K = 0$     | 12                | 1.2                       | 30                          | 300                    |
| Uncertainty <sup>a)</sup>  | 12                 | 5                 | 50                        | 300                         | 8.0 x 10 <sup>-4</sup> |

<sup>a)</sup> average value of the experimental uncertainties

determination of  $\tau_{JK}$  (the Student coefficient  $\tau_{JK}/\sigma(\tau_{JK}) = 3.4$ ) and vice versa. In the other fits these two parameters are highly correlated (0.995 when  $\tau_k = 0$ ) but much better determined.

Tables 5, 6, and 7 allow a comparison between the six remaining reduction schemes, the  $Q$ ,  $D$ , and  $QD$  ones with the constraints  $\tau_K = 0$  or  $f_{22}^K = 0$ . Table 7 shows that the standard deviation of each set of data is the same whatever the constraints are. The rotational and quartic centrifugal distortion constants and  $C\zeta$  are not affected by the unitary transformation even though small differences can be noted between the parameters obtained within the  $D$  reduction and those obtained within the other two. The rotational ground state constant  $C_0$  is also reduction-independent. Its value is the same within the  $\tau_K = 0$  or  $f_{22}^K = 0$  scheme and the difference between the values of Tables 5 and 6 is lower than three times the standard deviation. The  $l$ -type resonance constant  $q_{22}$  is different in both tables because in the second scheme it contains a part of the contribution of the constrained parameter  $f_{22}^K$  due to the definition of the matrix element (7). Nevertheless the agreement is still very good.

The equivalence of the reductions and the quality of the analysis can be demonstrated with some relations linking the parameters of the reductions  $Q$  and  $D$  (9):

$$q_{12}^D = -\frac{d^Q F}{4q_{22}} \tag{9}$$

$$\eta_J^D - \eta_J^Q = -(\eta_K^D - \eta_K^Q) = \frac{8(q_{12}^D)^2}{F} = \frac{F(d^Q)^2}{2q_{22}} \tag{10}$$

$$\eta_J^Q + \eta_K^Q = \eta_J^D - \eta_K^D \tag{11}$$

$$\tau_J^Q + \tau_{JK}^Q + \tau_K^Q = \tau_J^D + \tau_{JK}^D + \tau_K^D \tag{12}$$

$$\begin{aligned} (\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q) \\ = 8P f_{12}^{JD} + 2P^2(\eta_J + \eta_K + D_{JK} + 2D_K) \end{aligned} \tag{13}$$

$$f_{42}^D - f_{42}^Q = f_{22}^{JD} - f_{22}^{JQ} = \frac{4q_{22}(q_{12}^D)^2}{F^2} = \frac{(d^Q)^2}{4q_{22}} \tag{14}$$

and

$$f_{12}^{JD} = -\frac{d^Q F}{4q_{22}} - \frac{P}{2} \left[ \eta_J^Q + D_{JK} + \frac{F}{q_{22}} (f_{22}^{JQ} + f_{42}^D) + P^2 F \right], \tag{15}$$

where  $F = 2C\zeta + C - B$  and  $P = -(d^Q/2q_{22}) = (2q_{12}^D/F)$ , and those of the reductions  $QD$  and  $D$  (8):

$$\epsilon^{QD} = d^Q \frac{(C - B)}{2C\zeta} \tag{16}$$

$$\begin{aligned} (H_J^{QD} - H_J^Q) &= -\frac{1}{9} (H_{JK}^{QD} - H_{JK}^Q) = \frac{1}{15} (H_{KJ}^{QD} - H_{KJ}^Q) \\ &= -\frac{1}{7} (H_K^{QD} - H_K^Q) = 2(h_3^{QD} - h_3^Q) = \frac{2(\epsilon^{QD})^2}{(C - B)} \end{aligned} \tag{17}$$

$$\begin{aligned} \tau_J^{QD} - \tau_J^Q &= \tau_K^{QD} - \tau_K^Q = -\frac{1}{2} (\tau_{JK}^{QD} - \tau_{JK}^Q) \\ &= -12 \left( \frac{\epsilon^{QD}}{C - B} \right)^2 C\zeta \end{aligned} \tag{18}$$

TABLE 8  
Demonstration of the Unitary Equivalence of the Parameter Sets  
of the  $Q$  and  $D$  Reductions

| Equation |                                                            | $\tau_K = 0$        | $f_{22}^K = 0$  |
|----------|------------------------------------------------------------|---------------------|-----------------|
| [9]      | $\frac{q_{12}^D}{F d^Q}$                                   | MHz - 2.601940 (47) | - 2.602306 (45) |
|          | $\frac{F d^Q}{4 q_{22}}$                                   | MHz - 2.602239 (16) | - 2.602141 (22) |
| [10]     | $\eta_J^D - \eta_J^Q$                                      | kHz - 7.5786 (38)   | - 7.5816 (41)   |
|          | $-(\eta_K^D - \eta_K^Q)$                                   | kHz - 7.540 (46)    | - 7.582 (60)    |
|          | $\frac{8 (q_{12}^D)^2}{F}$                                 | kHz - 7.57930 (27)  | - 7.58151 (26)  |
|          | $\frac{F (d^Q)^2}{2 q_{22}^2}$                             | kHz - 7.58109 (27)  | - 7.58053 (13)  |
| [11]     | $\eta_J^Q + \eta_K^Q$                                      | kHz - 1.660 (32)    | - 1.758 (42)    |
|          | $\eta_J^D + \eta_K^D$                                      | kHz - 1.699 (32)    | - 1.758 (42)    |
| [12]     | $\tau_J^Q + \tau_{JK}^Q + \tau_K^Q$                        | Hz - 0.342 (37)     | - 0.297 (26)    |
|          | $\tau_J^D + \tau_{JK}^D + \tau_K^D$                        | Hz - 0.317 (38)     | - 0.296 (26)    |
| [13]     | $(\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q)$            | Hz 0.111 (25)       | 0.138 (36)      |
|          | $((\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q))_{calc}^a$ | Hz 0.13632 (16)     | 0.13889 (15)    |
| [14]     | $f_{42}^D - f_{42}^Q$                                      | Hz - 1.53318 (46)   | - 1.53331 (46)  |
|          | $f_{22}^{J,D} - f_{22}^{J,Q}$                              | Hz - 1.53337 (68)   | - 1.53329 (71)  |
|          | $\frac{4 q_{22} (q_{12}^D)^2}{F^2}$                        | Hz - 1.532994(55)   | - 1.533472 (53) |
|          | $\frac{(d^Q)^2}{4 q_{22}}$                                 | Hz - 1.533356 (55)  | - 1.533276 (26) |
| [15]     | $f_{12}^{JD}$                                              | Hz 23.814 (26)      | 24.296 (22)     |
|          | $(f_{12}^{JD})_{calc}^b$                                   | Hz 24.161 (22)      | 24.077 (22)     |

<sup>a)</sup> Calculated according the right-hand side of Eq. [13]

<sup>b)</sup> Calculated according the right-hand side of Eq. [15]

and

$$\epsilon_J^{QD} = -\frac{d^Q D_{JK}}{2C\zeta} + \frac{(C-B)}{2C\zeta} \left[ d_J^Q + \left( \eta_J^Q + 8 \frac{q_{22}^2}{F} \right) \frac{d^Q}{2C\zeta} \right]. \quad [19]$$

Most of the relations are fulfilled within the given error limits both for the constraints  $f_{22}^K = 0$  and  $\tau_K = 0$  as can be seen in Tables 8 and 9. The largest deviation is found for  $\epsilon_J$  (Eq. [19]) for which the calculated value significantly ( $13\sigma$ )

differs from the observed one. In comparison, the relations are slightly better fulfilled for  $f_{22}^K = 0$ .

In principle, the values of all parameters except for the  $l$ -type resonance constants and the  $\tau$  constants should be independent of the choice to constrain either  $f_{22}^K$  or  $\tau_K$ . This is verified within the error limits for most of the parameters with only exceptions of  $f_{12}^J$  in reduction  $D$  and  $\epsilon_J$  in reduction  $QD$ . It is interesting to note also that the sums of the  $\eta$  constants as well as of the  $\tau$  constants are not significantly affected by the constraint on  $\tau_K$ . The differences are within the given accuracy. Again one is able to check the unitary equivalence

TABLE 9  
Demonstration of the Unitary Equivalence of the Parameter Sets  
of the  $QD$  and  $Q$  Reductions

| Equation |                                                                      |     | $\tau_K = 0$         | $f_{22}^K = 0$       |
|----------|----------------------------------------------------------------------|-----|----------------------|----------------------|
| [16]     | $\varepsilon^{QD}$                                                   | kHz | 2.658485 (49)        | 2.657813 (44)        |
|          | $d^Q \frac{(C-B)}{2C\zeta}$                                          | kHz | 2.658229 (47)        | 2.658189 (47)        |
| [17]     | $(H_J^{QD} - H_J^Q)$                                                 | mHz | - 5.118 (105)        | - 5.109 (103)        |
|          | $-\frac{1}{9}(H_{JK}^{QD} - H_{JK}^Q)$                               | mHz | - 5.096 (72)         | - 5.149 (82)         |
|          | $\frac{1}{15}(H_{KJ}^{QD} - H_{KJ}^Q)$                               | mHz | - 5.123 <sup>a</sup> | - 5.169 <sup>a</sup> |
|          | $-\frac{1}{7}(H_K^{QD} - H_K^Q)$                                     | mHz | - 5.36 (61)          | - 5.17 (72)          |
|          | $2(h_3^{QD} - h_3^Q)$                                                | mHz | - 5.1116 (56)        | - 5.1088 (56)        |
|          | $\frac{2(\varepsilon^{QD})^2}{(C-B)}$                                | mHz | - 5.11139 (19)       | - 5.10881 (17)       |
| [18]     | $\tau_J^{QD} - \tau_J^Q$                                             | Hz  | 0.013 (24)           | 0.0231 (23)          |
|          | $-\frac{1}{2}(\tau_{JK}^{QD} - \tau_{JK}^Q)$                         | Hz  | 0.013 (46)           | 0.0230 (88)          |
|          | $\tau_K^{QD} - \tau_K^Q$                                             | Hz  | 0                    | 0.024 (35)           |
|          | $-12\left(\frac{\varepsilon^{QD}}{C-B}\right)^2 C\zeta$ <sup>b</sup> | Hz  | -                    | 0.02427041 (88)      |
| [19]     | $\varepsilon_J^{QD}$                                                 | mHz | - 5.027 (40)         | - 3.847 (21)         |
|          | $(\varepsilon_J^{QD})_{calc}$ <sup>c</sup>                           | mHz | - 4.487 (23)         | - 4.411 (23)         |

<sup>a)</sup> Calculated with the constrained value of  $H_{JK}^{QD} = -0.00554$  Hz.

<sup>b)</sup> Eq. [18] is only valid when the constraint is  $f_{22}^K = 0$ .

<sup>c)</sup> Calculated according the right-hand side of Eq. [19].

between the parameter sets with  $f_{22}^K$  (indicated by a superscript  $\alpha$ ) or  $\tau_K$  (superscript  $\beta$ ) constrained to zero. With  $f_{22}^K$  as defined in Eq. [2] and the results reported in (9), one finds that  $\Delta X = X^\alpha - X^\beta$ :

$$\tau_K^\alpha = \Delta\tau_J = -\frac{1}{2} \Delta\tau_{JK} = \frac{4f_{22}^{K\beta} q_{22}}{C-B-C\zeta}, \quad [20]$$

where  $\tau_K$  is interchanged with  $\tau_J$  or  $(-\frac{1}{2})\tau_{JK}$  if these are

constrained instead of  $\tau_K$ . Also, this relation is verified with the data obtained in this work.

This study shows that the sets of parameters determined using six reduction schemes are unitary equivalent. With any of the parameter sets the experimental data are reproduced according to their accuracy and relations between the parameter sets which follow from the theory of reduction are fulfilled. Thus the derived parameters have clear physical meanings taking into account the applied constraints, and all the derived parameter sets are equally well suitable for comparison with *ab initio* or force field calcula-

tions. Nevertheless, this study demonstrates that at higher order some constraints may fail due to a shortage of data or still remaining high correlations.

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Radio-frequency, Centimeter-wave, Millimeter-wave, and Infrared Spectra of  $\text{SiHF}_3$ . Investigation of the ground,  $\nu_4 = 1$  and  $\nu_6 = 1$  Vibrational States

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Running Head : Rovibrational spectra of SiHF<sub>3</sub>

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## ABSTRACT

The present paper deals with the analysis of the microwave, millimeterwave and infrared spectra of SiHF<sub>3</sub> in its ground,  $v_6 = 1$  and  $v_4 = 1$  excited states. The former was observed up to 1055 GHz leading to the determination of one octic centrifugal distortion constant,  $L_J = -0.0000749$  (55) mHz. Furthermore the  $\langle H | k \pm 6 \rangle$  interaction term  $|h_{3,GS}| = 1.1032$  (70) mHz has been fitted from splittings of six  $K=3$  lines. The excited states have been regarded as isolated ones. This enabled fits according the Q-, D- and QD-reduction schemes proposed by Lobodenko *et al* (*J. Mol. Spectrosc.* **126**, 159-170 (1987)) and Harder (*J. Mol. Spectrosc.* 194, 145 (1999)). A multiple fit analysis was performed confirming the assumption that the excited states are not affected by intervibrational resonances. The sign of the parameters is also discussed.

## 1 - INTRODUCTION

Recently we have published results on high resolution spectra in the radiofrequency, centimeterwave, millimeterwave and infrared ranges of the deuterated isotopomer of trifluorosilane, SiDF<sub>3</sub>, in the ground and the fundamental vibrational states  $\nu_4 = 1$  (1) and  $\nu_6 = 1$  (2). The analysis of the  $\nu_5 = 1$  state of SiDF<sub>3</sub> (3) as well as the analyses of the  $\nu_1 = 1$  and  $\nu_3 = 1$  states (4) of both SiHF<sub>3</sub> and SiDF<sub>3</sub> are completed and will be presented later.

The data obtained for SiDF<sub>3</sub> in the excited degenerate states were e.g. used to test the unitary equivalence of parameter sets (5) obtained from three different reduced forms of the effective Hamiltonian which have been proposed by Lobodenko *et al.* (6) and Harder (7) for an isolated degenerate state of a symmetric-top molecule of C<sub>3v</sub> symmetry. They allowed to test recently derived relations between the parameters of the different reductions (7), (8).

With this paper we start on the investigation of the normal isotopomer and the results obtained for both isotopomers will provide additional precise molecular parameters which are quite valuable for checking the reliability of the force field which was recently calculated up to the quartic terms at the MP2 level of theory employing a basis set of polarized valence triple zeta quality (9). For this purpose,  $\nu_4$  and  $\nu_6$  are the only candidates because  $\nu_5$  is perturbed with  $\nu_2$  and  $2\nu_3$ .

Only a few papers have dealt with the rotation-vibration spectroscopy of trifluorosilane. In the most recent microwave work done in 1973, Hoy *et al.* measured the  $J = 2 \leftarrow 1$  transitions in the ground state and in five of the six fundamental excited states of SiHF<sub>3</sub> and SiDF<sub>3</sub> (10). They also refined the harmonic and cubic force fields using their experimental data as well as earlier infrared data from Newman *et al.* (11) and Bürger *et al.* (12). Finally, they also determined an equilibrium structure. Harada *et al.* measured laser Stark spectra of the  $\nu_4$  band both in SiHF<sub>3</sub> (13) and SiDF<sub>3</sub> (14).

## 2 - THEORY

The  $v_6 = 1$  (SiF<sub>3</sub> antisymmetric deformation) and  $v_4 = 1$  (SiF<sub>3</sub> antisymmetric stretching) excited states were regarded as isolated ones. The former has the lowest energy (305.46 cm<sup>-1</sup>) of all fundamentals and the separation from the nearest band,  $v_3$  (SiF<sub>3</sub> symmetric deformation), is 120 cm<sup>-1</sup>. The other excited state ( $v_4 = 999.58$  cm<sup>-1</sup>) may be perturbed by the  $v_2 = 1$  state (856 cm<sup>-1</sup>) and the combination state  $v_5 = v_6 = 1$  (1150 cm<sup>-1</sup>) only. However since the band centers are about 150 cm<sup>-1</sup> apart from that of  $v_4$ , no level crossings are expected in view of the smallness of  $B$  and  $C$ . Possible resonance effects will be global and effective Hamiltonians of isolated states are suitable.

The diagonal elements of the Hamiltonian matrix in the quantum numbers  $J$ ,  $k$  and  $\ell$  are written as

$$\begin{aligned}
 E = & v_0 + BJ(J+1) + (C-B)k^2 \\
 & - D_J J^2(J+1)^2 - D_{JK} J(J+1)k^2 - D_K k^4 \\
 & + H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 k^2 + H_{KJ} J(J+1)k^4 + H_K k^6 \\
 & - 2(C\zeta)k\ell + \eta_J J(J+1)k\ell + \eta_K k^3\ell + \tau_J J^2(J+1)^2 k\ell + \tau_{JK} J(J+1)k^3\ell + \tau_K k^5\ell \\
 & + \sigma_J J^3(J+1)^3 k\ell + \sigma_{JK} J^2(J+1)^2 k^3\ell + \sigma_{KJ} J(J+1)k^5\ell + \sigma_K k^7\ell + \dots
 \end{aligned} \tag{1}$$

This expression can be used for the vibrational ground state by setting  $\ell$  to zero.

The off-diagonal terms must obey the general selection rule  $\Delta(k-\ell) = \pm 3n$ ,  $n = 0, 1, \dots$ . We included the  $\ell$ -type ( $\Delta\ell = \pm 2$ ,  $\Delta k = \pm 2$ ),  $(\pm 2, \mp 1)$  and  $(\pm 2, \mp 4)$  and the  $k$ -type  $(0, \pm 3)$  and  $(0, \pm 6)$  interactions for which we have made use of higher order constraints (8) to remove the terms with the  $k$ -dependent parameters ( $f_{12}^\wedge, f_{22}^\wedge, f_{42}^\wedge \dots$ ) interactions. The matrix elements can be written as

$$\langle v_6 = 1^{\pm 1}; J, k \pm 2 | \mathbf{H} | v_6 = 1^{\mp 1}; J, k \rangle = 2 \{ y_{22} + f_{22}^J J(J+1) + f_{22}^{JJ} J^2(J+1)^2 \} F_2^\pm(J, k) \tag{2}$$

$$\langle v_6 = 1^{\pm 1}; J, k \pm 1 | \mathbf{H} | v_6 = 1^{\pm 1}; J, k \rangle = 2 \{ g_{12} + f_{12}^J J(J+1) \} (2k \pm 1) F_1^{\pm}(J, k) \quad [3]$$

$$\langle v_6 = 1^{\pm 1}; J, k \pm 4 | \mathbf{H} | v_6 = 1^{\pm 1}; J, k \rangle = 2 \{ f_{42} + f_{42}^J J(J+1) \} F_4^{\pm}(J, k) \quad [4]$$

$$\langle v_6 = 1^{\pm 1}; J, k \pm 3 | \mathbf{H} | v_6 = 1^{\pm 1}; J, k \rangle = \ell \{ d + d^J J(J+1) \} F_3^{\pm}(J, k) \quad [5]$$

$$\langle v_6 = 1^{\pm 1}; J, k \pm 3 | \mathbf{H} | v_6 = 1^{\pm 1}; J, k \rangle = \{ \epsilon + \epsilon^J J(J+1) \} (2k \pm 3) F_3^{\pm}(J, k) \quad [6]$$

$$\langle v_6 = 1^{\pm 1}; J, k \pm 6 | \mathbf{H} | v_6 = 1^{\pm 1}; J, k \rangle = \{ h_3 + h_{3,J} J(J+1) \} F_6^{\pm}(J, k) \quad [7]$$

where

$$F_n^{\pm}(J, k) = \sum_{i=1}^n [J(J+1) - (k \pm i \mp 1)(k \pm i)]^{1/2} \quad [8]$$

In Eq. [2],  $-4 q_{22} = q_i^+$  as defined by Cartwright and Mills (15). The explicit form of the Hamiltonian  $\mathbf{H}$  in the matrix elements in Eqs. [2-7] is given in Ref. (5) (8).

### 3 - EXPERIMENTAL DETAILS

#### 3.1 – Synthesis of $\text{SiHF}_3$

$\text{SiHF}_3$  was prepared by reacting  $\text{HSiCl}_3$  with  $\text{SbF}_3$  at room temperature. For this purpose  $\text{HSiCl}_3$  was condensed at liquid  $\text{N}_2$  temperature into a bulb, the inner surface of which had been covered with freshly sublimed  $\text{SbF}_3$ .  $\text{SiHF}_3$  was purified by fractional condensation using a standard vacuum line. The sample contained minor amounts of  $\text{SiF}_4$  and  $\text{SiH}_2\text{F}_2$  as contaminants.

#### 3.2 – One- and two-dimensional Microwave Fourier transform spectra for the $v_6=1$ state

281 direct  $\ell$ -type resonance transitions in the  $v_6 = 1$  vibrational state with the selection rules  $\Delta J = 0$ ,  $\Delta k = \Delta \ell = \pm 2$  ( $\Delta G = \Delta |k - \ell| = 0$ ) could be observed in the ranges 8 – 18 GHz and 18 – 26 GHz using Fourier transform microwave spectrometers with rectangular ((5) and

references therein) and circular waveguides (16) as cells. The measurements were made at room temperature ( $\nu > 18$  GHz)) and at 210 K ( $\nu < 18$  GHz) and the pressure in the cells was in the range from 1 to 5 mTorr. The transition frequencies and their experimental error (three times the standard deviation) were determined from a least squares fit of the time-domain data.

Because of the small value of  $|C_6 - B_6 - (C\zeta)_6|$ , these transitions are quite strong in the centimeterwave range and several bands for different  $G$  values have been assigned. The assignment was based on the parameters determined by Hoy *et al.* (10). First, the  $G = 0$  transitions for  $J = 25$  to 36 were assigned to improve the  $\ell$ -type doubling parameters  $q_{22}$  and  $f_{22}^J$ . Since the value of  $C_6 - B_6 - (C\zeta)_6$  determined by Hoy *et al.* was very inaccurate, it was necessary to make wide range scans for the assignment of the  $G = 0$  series. In Figure 1 a scan from 9013 to 9090 MHz is shown. Based on the predictions it was not possible to assign lines of this series. The successful assignment was finally found from the splitting of the  $G=3$  lines. The  $k\ell = -2$  and  $+4$  ( $G = 3$ ) levels are split into two  $A_1 - A_2$  sublevels because of  $\ell$ -type ( $\Delta\ell = \pm 2$ ,  $\Delta k = \pm 2$ ),  $(\pm 2, \mp 1)$  and  $(\pm 2, \mp 4)$  and  $k$ -type  $(0,3)$  and  $(0, \pm 6)$  interactions leading to the splittings of the  $G = 3$  lines. Two such splittings are seen on Figure 1. All together measurements were performed for  $G = 0$  to 8 and for  $J=5$  to 44. The observed  $\ell$ -type resonance transitions are in Table 1.

We have also observed 18 transitions between these  $A_1 - A_2$  sublevels for  $J = 35$  to 43 in the radiofrequency range (1.4 – 93 MHz) using the technique of two-dimensional radiofrequency-microwave double resonance Fourier transform (2D-(RF)MWFT) spectroscopy (5), (17). In the 2D-experiment, a microwave pulse is followed by two radiofrequency pulses with adjustable evolution time between them. 128 1D-experiments are performed with different evolution times to obtain a 128x1024 data set from which the transition frequencies are derived from a least squares fit. The  $G=3$  states, as investigated in the present work, form a four level system and the allowed transitions between these levels yield a closed loop. To measure the  $A_1$ - $A_2$  splittings in the radiofrequency range, the experiment is normally performed with one of the two possible  $G=3$  transitions,  $k\ell = -2$ ,  $A_+ \leftarrow k\ell = +4$ ,  $A_+$ , ( $G = 3^\pm$ ; for  $J$  even,  $A_+$  is  $A_1$  and  $A_-$  is  $A_2$ , while for  $J$  odd,  $A_+$  is  $A_2$  and  $A_-$  is  $A_1$ , see (18)) in the microwave range and the radiofrequency transition to be investigated. For  $J=42$ , both microwave transitions and thus both radiofrequency transitions have nearly the same frequencies. Nevertheless we were not able to obtain all transition frequencies in

one experiment. For  $J=38$ , due to strong resonances, the  $A_1$ - $A_2$  splitting with  $k\ell = -2$  is accidentally small (1.4 MHz). A similar situation occurred for  $\text{SiDF}_3$  for the same value of  $J$  (2). For  $\text{SiDF}_3$  the splitting was even smaller (0.6 MHz) and 2D-spectroscopy could not be applied whereas for  $\text{SiHF}_3$  the transition at 1.4 MHz could be observed by 2D-(RF)MWFT spectroscopy, the lowest frequency observed so far using this technique. These radiofrequency transitions are given in Table 2.

Furthermore 9 ‘perturbation-allowed’ transitions (listed also in Table 1) obeying the selection rule  $\Delta(k-\ell) = \pm 3$  could be measured owing to a local resonance of the  $k\ell = -1$  and  $k\ell = +2$  levels for  $J = 24$ -26 (selection rule of the transitions:  $k\ell=0 \leftarrow -1, 2 \leftarrow 3$ ) and due to a resonance of the  $A_-$  levels with  $k\ell = +1$  and  $k\ell = -2$  (selection rule:  $k\ell = +1, A_+ \leftarrow -2, A_-$ ) for  $J = 43$ -46. The perturbation-allowed transitions with the selection rule  $k\ell = 0 \leftarrow -1, 2 \leftarrow 3$  form together with the direct  $\ell$ -type resonance transitions with  $G=1$  and 2 closed loops (see Figure 2) and the consistency of the measurements can be checked with the Ritz principle. For all three values of  $J = 24$ -25, the Ritz principle is fulfilled within the given error limits.

Finally the  $J = 1 \leftarrow 0$  transition in  $\nu_6=1$  was observed and is reported in Table 4.

### 3.3 – Rotational spectrum

The pure rotational spectrum has been observed from 100 GHz up to 1055 GHz. The lower part of this range, 100–320 GHz, was recorded using the second harmonic of a 48-54 GHz klystron ( $J'=6$ ) with a superheterodyne detection (19), the second, third and fourth harmonic of a 74-80 GHz Gunn diode ( $J'=10$ -20) and a 170-270 GHz Russian Istok backward-waves oscillator ( $J'=12$ ). French Thomson-CSF were employed between 340 and 490 GHz ( $J'=23$ -31). For the range 150-490 GHz, the detector was a Helium-cooled InSb bolometer. The accuracy of the new measurements is about 50 kHz for isolated lines.

Transitions between 630 and 1055 GHz were measured using a newly stabilized far infrared spectrometer (1). The following emissions of  $\text{CH}_2\text{CHF}$  were used: 634.2220 GHz (pumped by the 10P20  $\text{CO}_2$  line), 889.3414 GHz (10P38) and 902.0004 GHz (10P6). Used emissions of  $\text{CH}_2\text{F}_2$  were: 783.4860 GHz (9P10), 1035.5527 GHz (9P4) and 1042.1504 GHz (9R34). The accuracy of the measurements was better than 300 kHz.

The assignment of the ground state rotational spectrum was straightforward thanks to its characteristic pattern and the intensity of the absorption lines ( $\mu = 1.35920$  (22) D (13)).

The pure rotational spectrum of the  $\nu_6 = 1$  vibrational state, which is mixed with the spectrum of the  $\nu_3 = 1$  state, is similar to the one of the deuterated species. Because of their different accuracy, the microwave, rotational and infrared data concerning this excited state could be fitted together only once their respective spectra had been separately assigned.

The spectrum of the  $\nu_4 = 1$  vibrational state was weak, dense and partly mixed with that of the  $\nu_2 = 1$  state. Only based on a prediction using the data of Harada *et al.* (13), a successful assignment was possible.

The observed rotational transition frequencies are listed in Tables 3-5.

### 3.4 – FTIR spectrum

High resolution IR spectra were obtained using a Bruker 120 HR interferometer and cells of 28 cm length.

For the  $\nu_6$  band the region of  $210\text{-}360\text{ cm}^{-1}$  was studied, and the interferometer was equipped with a Globar source, a  $6\text{ }\mu\text{m}$  Mylar beam and a liquid He-cooled Si bolometer. Cell windows made of polyethylene were used, and a pressure of 7 mbar adjusted. The resolution was  $0.0039\text{ cm}^{-1}$  (1/MOPD, maximum optical path difference), and trapezoidal apodization was employed. In total 126 scans were coadded, and the spectrum calibrated with  $\text{H}_2\text{O}$  lines reported in (20). A set of 1363 infrared measurements up to  $J, K_\ell = 65, 63$  in the  $^R R$  branch and 57, 50 in the  $^P P$  branch was assigned.

Two spectra in the  $750\text{-}1400\text{ cm}^{-1}$  region covering the  $\nu_4$  band were recorded. Pressures of 0.3 and 2 mbar were chosen, and the cell was outfitted with KBr windows. In total 319 and 492 scans respectively were coadded. The interferometer was equipped with a Globar source, a KBr beam splitter and a MCT 800 detector, and a  $7\text{ }\mu\text{m}$  low pass filter was used. A resolution (1/MOPD) of  $0.0026\text{ cm}^{-1}$  was adjusted, and trapezoidal apodization was employed. The 0.3 mbar spectrum was calibrated with  $\text{H}_2\text{O}$  lines in the  $1250\text{-}1350\text{ cm}^{-1}$  region taken from Ref. (21) with consideration of a systematic correction as given in (22). The 2 mbar spectrum was internally calibrated to match the 0.3 mbar spectrum which was mostly used. Almost 2400 lines

were assigned in the  $P$ ,  $Q$  and  $R$  branches up to  $J$ ,  $K\ell = 61,61$ . Furthermore because of the  $\ell$ -type  $\langle k \pm 4, \ell \mp 2 | \mathbf{H} | k, \ell \rangle$  interaction,  $^P X_J$  (3) transitions ( $X = P, Q, R$ ) should be split. This was observed in the  $\nu_4$  band from  $J = 20$  and we could assign 209 transitions up to  $J = 52$ .

The accuracy of high quality lines in all spectra is  $5 \times 10^{-4} \text{ cm}^{-1}$  (22).

## 4 - RESULTS AND DISCUSSION

The program SIMFIT (23) was used to perform the fits of the ground and the excited states transitions and the determination of the molecular parameters except for the ground state transitions of the  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopomers which were fitted to the expression of the transition frequency.

### 4.1 – Vibrational Ground State

The ground state rotational spectrum of the  $^{28}\text{Si}$ ,  $^{29}\text{Si}$  and  $^{30}\text{Si}$  isotopomers of  $\text{SiHF}_3$  was recorded and analysed. For the last two isotopomers, transitions were observed up to 460 GHz ( $J = 32 \leftarrow 31$ ). A splitting of the  $K=3$  lines due to the non-vanishing off-diagonal matrix element  $\langle k | \mathbf{H} | k \pm 6 \rangle$  given by the Eq. [7], was, as for  $\text{SiDF}_3$  (1), not observed for these isotopomers.

The ground state of  $^{28}\text{SiHF}_3$  has been studied up to 1055 GHz ( $J = 73 \leftarrow 74$ ). In the analysis of the obtained data set we have constrained the pure  $k$ -dependent parameters. The axial rotational constant  $C_0$  has been constrained to the value obtained from the analysis of the  $\nu_6 = 1$  state. Its accuracy was improved by two orders of magnitude when comparing with the value obtained by Harada *et al.* by  $\text{CO}_2$  laser Stark spectroscopy (13). The axial centrifugal distortion constants  $D_{K,0}$  and  $H_{K,0}$  were fixed to the values calculated from the force field (9). All further parameters up to fourth order could be precisely determined, even the octic centrifugal distortion constant  $L_J$  (6<sup>th</sup> order) which had to be included in order to reproduce the data according to the experimental accuracy.

The  $K = 3$  lines were found split for  $J'' > 43$ . The parameter  $|h_{3,\text{GS}}| = 1.1032 (70) \cdot 10^{-3} \text{ Hz}$  is well determined from the measurements of six doublets ( $J'' = 43, 44, 53, 54, 61$  and  $62$ ). For  $J'' = 63, 72$  and  $73$ , the components contained  $K = 1$  and  $4$  lines and could not be resolved. The sign

of  $h_{3,\text{GS}}$  can not be determined from pure rotational transition frequencies. The analysis of the  $\nu_6 = 1$  excited state was performed using the ground state  $h_{3,\text{GS}}$  parameter with the same negative sign as that determined from the excited state analysis.

The ground state parameters for the three isotopomers are reported in Table 6.

## 4.2 – Excited States

In the analysis of the upper states we have constrained the ground state parameters to the values given in Table 6, only  $C_0$  was refined in the fit of the  $\nu_6 = 1$  state. It was possible to refine it also in the fit of the  $\nu_4 = 1$  spectrum. However its accuracy was not as good and that of  $C_4$  was significantly affected. Therefore,  $C_0$  was constrained to the value obtained from the  $\nu_6 = 1$  analysis. In the upper states we made use of three reduced forms of the effective Hamiltonian, the reductions Q and D as introduced by Lobodenko *et al.* (6) and the reduction QD (7). In reduction Q, parameters of the  $\ell$ -dependent (0, 3) interaction are fitted while those of the  $k$ -dependent (0, 3) and (2, -1) interactions are constrained, in reduction D those of the (2, -1) interaction are fitted and in reduction QD those of the  $k$ -dependent (0, 3) interaction. Besides this, one of the following higher order constants,  $f_{22}^K$ ,  $\tau_J$ ,  $\tau_{JK}$  and  $\tau_K$ , must be constrained (8). In this study  $f_{22}^K$  was fixed to zero, since it is preferable to constrain an off-diagonal term. Nevertheless any of these choices lead to the same reproduction of the data as has been demonstrated for the deuterated molecule (2). Taking into account these necessary constraints, all possible parameters up to the fifth order have been determined except  $f_{12}^J$  in the D-reduction of the  $\nu_4 = 1$  state. For the  $\nu_6 = 1$  state furthermore some parameters of the sixth and seventh order have been determined with high precision (e.g. for  $f_{22}^{JJ}$  0.05 %). All parameters appear at the correct order of magnitude and correlations exceeding 0.9 are only found for a limited number of pairs of parameters and can be explained with the natural limitation in measurable values of the quantum numbers  $J$  and  $k$  for a given molecule and experimental setup. The fitted parameters of the  $\nu_6 = 1$  and  $\nu_4 = 1$  states are included in Tables 7 and 8 respectively.

Another recommended test to check the internal consistency of the data, the chosen model and the analysis, is the application of the concept of multiple fits. The use of the Q, D and QD reductions lead to three unitary equivalent parameter sets. The unitary equivalence can be checked using relations between parameters which result from the theory of reduction (8) (7).

As a first evidence for the quality of the results presented in this paper, it is observed that the rotational, quartic centrifugal distortion and  $\ell$ -doubling constants are not or only marginally affected by the used reductions. An exceptional good agreement is found for these parameters of reduction Q and QD which should not differ according to theory. An exception is the  $C$  constant determined in the reduction D which significantly differs from those in reduction Q and QD. Especially for  $v_4 = 1$ , the difference exceeds by far the given error limit. This affects also  $C\zeta$ ,  $B$  and  $q_{22}$ .

The  $\langle k | \mathbf{H} | k \pm 3 \rangle$  parameter  $\epsilon^{QD}$  is very well determined for  $v_4 = 1$ . Using Eq. [2-4] of ref. (7) and the value of the unreduced parameters presented in Ref. (9), one can calculate  $\epsilon$  within the QD reduction :  $\epsilon_{calc}^{QD} = -15.75$  kHz which is very close to the experimental value. For  $v_4 = 1$  yet, the  $h_3$  parameter could be fitted within the QD reduction whereas it was not possible within the others two :  $h_3^Q = -1.46$  (54) mHz and  $h_3^D = -3.43$  (52) mHz. By calculating  $h_3^{QD}$  in the same way than  $\epsilon_{calc}^{QD}$ , we found  $h_{3,calc}^{QD} = -81.9$  mHz close to the experimental value. This proves that  $\epsilon^{QD}$  and  $h_3^{QD}$  have a physical meaning. For  $J = 52$  (the highest  $J$  measured for the infrared transitions sensitive to  $h_3$ ), the contribution of  $h_3$  to the energy is about  $1.1 \times 10^{-3} \text{ cm}^{-1}$  for  $h_3^{QD}$  and about  $3.9 \times 10^{-4} \text{ cm}^{-1}$  for  $h_3^Q$  and  $h_3^D$ , the order of magnitude of the experimental uncertainty. This could explain the failure of our attempt to determine  $h_3$  within the Q and D reductions. Note that for  $h_3^Q$  and  $h_3^D$ , the ground state value was used because  $h_3$  should not be affected by the Q and D reductions and it has often been shown that the vibrational contribution of this parameter is negligible.

The control of the quality of the results is also possible with the following relations linking the parameters of the reductions Q and D (8) :

$$q_{12}^D = -\frac{d^U F}{4 q_{22}} \quad [9]$$

$$\eta_J^D - \eta_J^Q = -(\eta_K^D - \eta_K^Q) = \frac{8 (q_{12}^U)^2}{F} = \frac{F (d^U)^2}{2 q_{22}^2} \quad [10]$$

$$\eta_J^U + \eta_K^U = \eta_J^D + \eta_K^D \quad [11]$$

$$\tau_J^Q + \tau_{JK}^Q + \tau_K^Q = \tau_J^D + \tau_{JK}^D + \tau_K^D \quad [12]$$

$$(\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q) = 8 P f_{12}^{JD} + 2 P^2 (\eta_J + \eta_K + D_{JK} + 2 D_K) \quad [13]$$

$$f_{42}^D - f_{42}^Q = f_{22}^{JD} - f_{22}^{JQ} = \frac{4 q_{22} (q_{12}^D)^2}{F^2} = \frac{(d^Q)^2}{4 q_{22}} \quad [14]$$

where  $F = 2C\zeta + C - B$  and  $P = -\frac{d^Q}{2q_{22}} = \frac{2q_{12}^D}{F}$ , and those of the reductions QD and Q (7) :

$$\epsilon^{QD} = d^Q \frac{(C - B)}{2 C \zeta} \quad [15]$$

$$\begin{aligned} (H_J^{QD} - H_J^Q) &= -\frac{1}{9}(H_{JK}^{QD} - H_{JK}^Q) = \frac{1}{15}(H_{KJ}^{QD} - H_{KJ}^Q) = -\frac{1}{7}(H_K^{QD} - H_K^Q) \\ &= 2(h_3^{QD} - h_3^Q) = \frac{2(\epsilon^{QD})^2}{(C - B)} \end{aligned} \quad [16]$$

$$\tau_J^{QD} - \tau_J^Q = \tau_K^{QD} - \tau_K^Q = -\frac{1}{2}(\tau_{JK}^{QD} - \tau_{JK}^Q) = -12 \frac{-\epsilon^{QD}}{C - B} \sqrt[2]{C \zeta} \quad [17]$$

For both states, these relations are quite well verified as can be seen in Tables 8 and 9.

For both states, no transitions in the data sets permitted the determination of the sign of the  $\ell$ -type parameter  $q_{22}$ . The sign could have been obtained from the  ${}^R X_0$  transitions ( $X = P, Q, R$ ) simultaneously but the corresponding lines are not resolved in the spectrum. A simulation of the infrared  $\nu_6$  and  $\nu_4$  bands perfectly reproduces the spectra (figure 3) when the negative sign is given to  $q_{22}$  for both states. This negative sign used to perform the fits is also this obtained with *ab initio* calculations (9).

The sign of  $f_{42}$  can be determined from this of  $q_{22}$  and from the off-diagonal interactions involving the  $G = \pm 3$  levels in the upper state. If these interactions are not present or only have a weak effect on the  $G = \pm 3$  levels (23), one would be able to determine only the absolute value of  $f_{42}$  whose contribution in the Hamiltonian matrix is purely diagonal in that case. Fortunately in the present study of the  $\nu_6 = 1$  and  $\nu_4 = 1$  states, the  $(\pm 2, \mp 1)$  and  $(0, \pm 3)$  interactions are strong enough to perturb the  $G = \pm 3$  levels. In the former state, from the microwave measurements, we got a direct information on the A<sub>1</sub>-A<sub>2</sub> splittings and the effect of the off-diagonal interactions.

For the latter state, we could assign infrared  $(k, \ell) = (\pm 2, \mp 1) \leftarrow (\pm 3, 0)$  transitions where the upper levels are perturbed. Thus performing fits with the two signs of  $f_{42}$  should give one fit with a better standard deviation than the other. Furthermore and because the strong interactions enabled us to use the Q and D reductions, Eq. [14] must be satisfied :  $(f_{22}^{J,D} - f_{22}^{J,Q})$  being negative for both states,  $(f_{42}^D - f_{42}^Q)$  must be also negative.  $f_{42}$  was found negative for the  $\nu_6 = 1$  state, and positive for the  $\nu_4 = 1$  state.

The signs of  $d$  and  $q_{12}$  are arbitrary. However they should be compatible with the reduction theory : according to equation [9], if  $F/q_{22} < 0$  ( $F = 2C\zeta + C - B$ ),  $d$  and  $q_{12}$  must have the same sign ; the other case implies opposite signs. In the present work, for the  $\nu_6 = 1$  state, both  $q_{22}$  and  $F$  are negative. Thus  $d$  has been arbitrarily chosen to be negative and  $q_{12}$  positive, following the *ab initio* results. For the  $\nu_4 = 1$  state,  $q_{22}$  and  $F$  having opposite signs,  $d$  and  $q_{12}$  were chosen to be positive. A similar discussion can be made for  $d$  and  $\varepsilon$  whose signs depend on the value of  $(C-B)$  and  $C\zeta$  (see Eq. [15]). Because these latter and  $d$  are negative,  $\varepsilon$  must be negative too.

It is also interesting to compare the values of the ground state parameters with those of the excited states. The differences do not exceed 0.2 %, 1 % and 10 % for the rotational, quartic and sextic centrifugal distortion constants respectively. This definitively shows that the  $\nu_6 = 1$  and  $\nu_4 = 1$  excited states are not significantly affected by interactions with other vibrational states.

## 5 – ACKNOWLEDGMENTS

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## **Table Captions**

Table 1 : Experimental frequencies (in MHz) of the direct  $\ell$ -type resonance transitions in the  $\nu_6 = 1$  state of  $^{28}\text{SiHF}_3$ .

Table 2. Experimental frequencies (in MHz) of the transitions in the  $\nu_6=1$  state of  $^{28}\text{SiHF}_3$  recorded by applying 2D-(RF)MWFT spectroscopic techniques.

Table 3 : Experimental frequencies (in MHz) of the rotational  $\Delta J = 1$  transitions in the ground state of  $^{28}\text{SiHF}_3$ ,  $^{29}\text{SiHF}_3$  and  $^{30}\text{SiHF}_3$ .

Table 4 : Experimental frequencies (in MHz) of the rotational  $\Delta J = 1$  transitions in the  $\nu_6 = 1$  state of  $^{28}\text{SiHF}_3$ .

Table 5 : Experimental frequencies (in MHz) of the rotational  $\Delta J = 1$  transitions in the  $\nu_4 = 1$  state of  $^{28}\text{SiHF}_3$ .

Table 6 : Molecular constants of  $^{28}\text{SiHF}_3$ ,  $^{29}\text{SiHF}_3$  and  $^{30}\text{SiHF}_3$  in the vibrational ground state.

Table 7 : Molecular Parameters of  $^{28}\text{SiHF}_3$  in the  $\nu_6 = 1$  vibrational state.

Table 8 : Molecular Parameters of  $^{28}\text{SiHF}_3$  in the  $\nu_4 = 1$  vibrational state.

Table 9 : Demonstration of the equivalence of the parameter sets determined within the Q and D reductions.

Table 10 : Demonstration of the equivalence of the parameter sets determined within the QD and Q reductions.

## **Figure Captions**

Figure 1. Microwave spectrum of  $^{28}\text{SiHF}_3$  in the range of 9013 – 9090 MHz.

The spectrum reveals two splittings of the  $G=3$  spectral lines of the  $v_6=1$  state, one splitting of about 200 kHz for  $J=11$  [3: 9020.9 MHz, 4: 9021.1 MHz] and for  $J=12$  the separation of the components is about 400 kHz [6: 9083.9 MHz, 7: 9084.3 MHz].

The most intensive line corresponds to  $G=1$ ,  $J=25$  of  $v_6=1$  [5: 9023.2 MHz].

Furthermore, two transitions of  $v_6=2$  have been assigned: [1: 9016.1 MHz,  $G=10$ ,  $J=24$ ,  $\Delta k=2$ ] and [2: 9018.2 MHz,  $G=8$ ,  $J=22$ ,  $\Delta k=2$ ].

Figure 2. Closed loops ( $v_6=1$ ,  $^{28}\text{SiHF}_3$ , observable for  $J=24-26$ ) and Ritz' combination principle.

The direct  $\ell$ -type transitions  $\nu_{\text{MW}1,2}$  and the perturbation allowed transitions (or so-called “forbidden transitions”)  $\nu_{\text{fl},2}$  form a closed loop which allows to check the consistency of the measurements with Ritz' combination principle.

Table 1. Experimental frequencies (in MHz) of the direct  $\ell$ -type resonance transitions in the  $v_6 = 1$  state of  $\text{CH}_3\text{F}$ .

| $J$ | $k$ | $l$ | Exp.       | $e. - c.^a$ | Unc. $^b$ | $J$ | $k$ | $l$ | Exp.       | $e. - c.^a$ | Unc. $^b$ | $J$ | $k$ | $l$ | Exp.       | $e. - c.^a$ | Unc. $^b$ | $J$ | $k$ | $l$ | Exp.                   | $e. - c.^a$ | Unc. $^b$ |
|-----|-----|-----|------------|-------------|-----------|-----|-----|-----|------------|-------------|-----------|-----|-----|-----|------------|-------------|-----------|-----|-----|-----|------------------------|-------------|-----------|
| 25  | -1  | -1  | 8521.2034  | 0.1         | 0.3       | 33  | 3   | 1   | 15778.9692 | -0.5        | 0.7       | 24  | -4  | -1  | 11798.9368 | 0.0         | 0.5       | 23  | 5   | 1   | 13789.6517             | 1.0         | 1.8       |
| 26  | -1  | -1  | 9199.3502  | 0.0         | 0.4       | 34  | 3   | 1   | 16599.2906 | -0.4        | 0.9       | 24  | 4   | 1   | 11803.8398 | 0.4         | 1.3       | 24  | 5   | 1   | 14122.6345             | 0.3         | 0.6       |
| 27  | -1  | -1  | 9903.0057  | 0.2         | 0.5       | 35  | 3   | 1   | 17449.1316 | -1.0        | 5.6       | 25  | -4  | -1  | 12239.0433 | -0.1        | 0.4       | 25  | 5   | 1   | 14489.9718             | 0.2         | 0.6       |
| 28  | -1  | -1  | 10632.0968 | 0.1         | 0.5       | 5   | -4  | -1  | 8873.6156  | 14.4        | 30.0      | 25  | 4   | 1   | 12244.7508 | 0.6         | 0.6       | 26  | 5   | 1   | 14892.4617             | 0.1         | 0.5       |
| 29  | -1  | -1  | 11386.5449 | -0.5        | 0.4       | 6   | -4  | -1  | 8880.5518  | 12.6        | 30.0      | 26  | -4  | -1  | 12715.7256 | -0.2        | 0.5       | 27  | 5   | 1   | 15330.6982             | 0.4         | 1.2       |
| 30  | -1  | -1  | 12166.2655 | -0.3        | 0.4       | 7   | -4  | -1  | 8892.1967  | 25.5        | 30.0      | 26  | 4   | 1   | 12722.3186 | 0.4         | 1.0       | 28  | 5   | 1   | 15805.0799             | 0.0         | 0.6       |
| 31  | -1  | -1  | 12971.1630 | -0.3        | 0.4       | 8   | -4  | -1  | 8910.1162  | 7.7         | 12.8      | 27  | -4  | -1  | 13228.9118 | -0.3        | 1.0       | 29  | 5   | 1   | 16315.8289             | -0.3        | 2.4       |
| 32  | -1  | -1  | 13801.1318 | 0.1         | 0.9       | 8   | 4   | 1   | 8910.1752  | -5.2        | 13.9      | 27  | 4   | 1   | 13236.4722 | 1.0         | 1.9       | 30  | 5   | 1   | 16863.0057             | -1.7        | 4.9       |
| 33  | -1  | -1  | 14656.0492 | 0.3         | 1.6       | 9   | -4  | -1  | 8936.1681  | 0.2         | 7.5       | 28  | -4  | -1  | 13778.3775 | 0.0         | 1.8       | 31  | 5   | 1   | 17446.5380             | 0.4         | 4.1       |
| 34  | -1  | -1  | 15535.7695 | -1.4        | 1.8       | 9   | 4   | 1   | 8936.2821  | 1.2         | 6.8       | 28  | 4   | 1   | 13786.9812 | -0.2        | 1.9       | 7   | 6   | 1   | 14788.7404             | -3.0        | 19.8      |
| 35  | -1  | -1  | 16440.1229 | 1.2         | 3.2       | 10  | -4  | -1  | 8972.3538  | -0.7        | 5.8       | 29  | -4  | -1  | 14363.7750 | -0.8        | 0.5       | 8   | 6   | 1   | 14797.4226             | -1.7        | 13.5      |
| 36  | -1  | -1  | 17368.8733 | -3.5        | 1.5       | 10  | 4   | 1   | 8972.5213  | -2.7        | 5.8       | 29  | 4   | 1   | 14373.4966 | 0.3         | 1.0       | 9   | 6   | 1   | 14810.7634             | 0.0         | 9.4       |
| 24  | 2   | 1   | 8369.3410  | -0.5        | 0.3       | 11  | -4  | -1  | 9020.8366  | -0.7        | 4.6       | 30  | -4  | -1  | 14984.6673 | -0.6        | 1.2       | 10  | 6   | 1   | 14830.0038             | -2.5        | 11.2      |
| 25  | 2   | 1   | 9023.2643  | 0.6         | 0.5       | 11  | 4   | 1   | 9021.0819  | 0.0         | 5.4       | 30  | 4   | 1   | 14995.5645 | -1.3        | 3.9       | 11  | 6   | 1   | 14856.5248             | 1.4         | 3.3       |
| 26  | 2   | 1   | 9661.1950  | -0.2        | 0.7       | 12  | -4  | -1  | 9083.9166  | -1.1        | 2.3       | 31  | -4  | -1  | 15640.5472 | -0.6        | 2.2       | 12  | 6   | 1   | 14891.8025             | -0.2        | 2.0       |
| 27  | 2   | 1   | 10332.0866 | 0.4         | 0.4       | 12  | 4   | 1   | 9084.2591  | -0.7        | 2.5       | 31  | 4   | 1   | 15652.6703 | 4.1         | 5.5       | 13  | 6   | 1   | 14937.4399             | 0.0         | 3.2       |
| 28  | 2   | 1   | 11032.3475 | 0.0         | 0.2       | 13  | -4  | -1  | 9163.9937  | 2.4         | 3.7       | 32  | -4  | -1  | 16330.8636 | -0.7        | 4.1       | 14  | 6   | 1   | 14995.1243             | -1.7        | 6.2       |
| 29  | 2   | 1   | 11761.0340 | -0.2        | 0.4       | 13  | 4   | 1   | 9164.4526  | -4.7        | 4.0       | 32  | 4   | 1   | 16344.2175 | -2.0        | 2.2       | 15  | 6   | 1   | 15066.6300             | -3.0        | 4.7       |
| 30  | 2   | 1   | 12517.6102 | -0.3        | 0.4       | 14  | -4  | -1  | 9263.5023  | -0.1        | 3.9       | 33  | -4  | -1  | 17055.0367 | -2.6        | 2.3       | 16  | 6   | 1   | 15153.7929             | -2.7        | 1.6       |
| 31  | 2   | 1   | 13301.6740 | -1.1        | 0.6       | 14  | 4   | 1   | 9264.1238  | 0.9         | 4.5       | 33  | 4   | 1   | 17069.6071 | -0.4        | 1.8       | 17  | 6   | 1   | 15258.4905             | -1.4        | 2.4       |
| 32  | 2   | 1   | 14112.8916 | -1.5        | 0.5       | 15  | -4  | -1  | 9384.8920  | -0.9        | 2.6       | 34  | -4  | -1  | 17812.4803 | -2.4        | 2.7       | 18  | 6   | 1   | 15382.6201             | -0.2        | 1.7       |
| 33  | 2   | 1   | 14950.9707 | -0.8        | 0.9       | 15  | 4   | 1   | 9385.7039  | 0.8         | 2.4       | 34  | 4   | 1   | 17828.1831 | 2.9         | 8.2       | 19  | 6   | 1   | 15528.0761             | 0.6         | 2.7       |
| 34  | 2   | 1   | 15815.6472 | 0.1         | 0.3       | 16  | -4  | -1  | 9530.5484  | -0.1        | 1.2       | 7   | 5   | 1   | 11838.7833 | -0.7        | 7.2       | 20  | 6   | 1   | 15696.7242             | 1.1         | 6.0       |
| 35  | 2   | 1   | 16706.6768 | -2.9        | 0.8       | 16  | 4   | 1   | 9531.5885  | 0.3         | 1.2       | 8   | 5   | 1   | 11851.1204 | 4.4         | 7.2       | 21  | 6   | 1   | 15890.3711             | -2.7        | 1.9       |
| 36  | 2   | 1   | 17623.8454 | -1.5        | 2.9       | 17  | -4  | -1  | 9702.7432  | -0.3        | 1.5       | 9   | 5   | 1   | 11869.4391 | 0.9         | 3.5       | 22  | 6   | 1   | 16110.7592             | 1.5         | 3.7       |
| 20  | 3   | 1   | 8059.6546  | 0.8         | 0.3       | 17  | 4   | 1   | 9704.0580  | 0.6         | 1.2       | 10  | 5   | 1   | 11895.2897 | -0.7        | 3.0       | 23  | 6   | 1   | 16359.4987             | -2.4        | 4.6       |
| 21  | 3   | 1   | 8442.4946  | 0.7         | 0.4       | 18  | -4  | -1  | 9903.5896  | 0.0         | 1.1       | 11  | 5   | 1   | 11930.3581 | 0.0         | 2.1       | 24  | 6   | 1   | 16638.1030             | -2.2        | 4.4       |
| 22  | 3   | 1   | 8861.6165  | 0.5         | 0.4       | 18  | 4   | 1   | 9905.2282  | 0.8         | 1.6       | 12  | 5   | 1   | 11976.4571 | -0.5        | 1.5       | 25  | 6   | 1   | 16947.9265             | -1.5        | 1.6       |
| 23  | 3   | 1   | 9315.5120  | 2.1         | 2.1       | 19  | -4  | -1  | 10134.9908 | -0.1        | 0.7       | 13  | 5   | 1   | 12035.5176 | -0.9        | 1.5       | 26  | 6   | 1   | 17290.1700             | -1.4        | 1.2       |
| 24  | 3   | 1   | 9785.2929  | -0.7        | 0.6       | 19  | 4   | 1   | 10137.0084 | 0.9         | 1.0       | 14  | 5   | 1   | 12109.5620 | 0.7         | 1.2       | 11  | -7  | -1  | 17791.4208             | -0.5        | 3.9       |
| 25  | 3   | 1   | 10353.8452 | 0.7         | 0.5       | 20  | -4  | -1  | 10398.6079 | 0.1         | 0.7       | 15  | 5   | 1   | 12200.6703 | -0.4        | 0.8       | 12  | -7  | -1  | 17819.0859             | 0.1         | 7.6       |
| 26  | 3   | 1   | 10911.9292 | 0.5         | 0.4       | 20  | 4   | 1   | 10401.0638 | 0.8         | 0.7       | 16  | 5   | 1   | 12310.9657 | -0.2        | 0.7       | 24  | 1   | -1  | 8551.1667 <sup>c</sup> | -0.4        | 1.3       |
| 27  | 3   | 1   | 11508.3538 | 0.2         | 0.4       | 21  | -4  | -1  | 10695.8331 | -0.4        | 0.8       | 17  | 5   | 1   | 12442.5670 | -0.2        | 0.3       | 25  | 1   | -1  | 8551.9742 <sup>c</sup> | -4.2        | 6.8       |
| 28  | 3   | 1   | 12139.3124 | -0.1        | 0.5       | 21  | 4   | 1   | 10698.7930 | 0.8         | 2.3       | 18  | 5   | 1   | 12597.5607 | 0.2         | 1.0       | 26  | 1   | -1  | 8595.4378 <sup>c</sup> | -6.7        | 12.0      |
| 29  | 3   | 1   | 12803.5950 | -0.1        | 0.2       | 22  | -4  | -1  | 11027.7829 | 0.2         | 0.7       | 19  | 5   | 1   | 12777.9625 | 0.5         | 0.5       | 26  | 3   | 1   | 9846.1681 <sup>c</sup> | -9.9        | 12.0      |
| 30  | 3   | 1   | 13500.3738 | -0.4        | 0.6       | 22  | 4   | 1   | 11031.3151 | 0.7         | 0.7       | 20  | 5   | 1   | 12985.6829 | 0.4         | 0.9       | 25  | 3   | 1   | 9882.5597 <sup>c</sup> | 0.4         | 15.9      |
| 31  | 3   | 1   | 14228.9452 | -0.7        | 0.6       | 23  | -4  | -1  | 11395.2915 | -1.4        | 1.4       | 21  | 5   | 1   | 13222.4963 | 0.4         | 0.7       | 24  | 3   | 1   | 9967.1049 <sup>c</sup> | -14.3       | 8.7       |
| 32  | 3   | 1   | 14988.6730 | -0.4        | 1.4       | 23  | 4   | 1   | 11399.4716 | 0.2         | 0.6       | 22  | 5   | 1   | 13490.0118 | 0.5         | 1.4       | 37  | -1  | -1  | 18321.7354             | 0.8         | 0.3       |

<sup>a</sup>) residuals (in kHz) ; <sup>b</sup>) Experimental uncertainty (in kHz) ; <sup>c</sup>)  $\Delta(k-\ell) = \pm 3$  'perturbation-allowed' transitions

Table I — Continued

| <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. – c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|----------|------------|----------------------|-------------------|
| 38       | -1       | -1       | 19298.2625 | -0.4                 | 0.3               |
| 39       | -1       | -1       | 20297.7943 | 0.2                  | 0.3               |
| 40       | -1       | -1       | 21319.1985 | 0.5                  | 0.5               |
| 41       | -1       | -1       | 22360.3332 | 0.8                  | 0.5               |
| 42       | -1       | -1       | 23416.4883 | 0.2                  | 1.6               |
| 43       | -1       | -1       | 24474.9469 | -0.4                 | 0.6               |
| 44       | -1       | -1       | 25489.8396 | -0.6                 | 1.0               |
| 37       | 2        | 1        | 18566.9404 | 0.2                  | 0.2               |
| 38       | 2        | 1        | 19535.7625 | 0.3                  | 0.2               |
| 39       | 2        | 1        | 20530.1234 | -0.1                 | 0.2               |
| 40       | 2        | 1        | 21549.8407 | 0.3                  | 0.2               |
| 41       | 2        | 1        | 22594.7322 | 0.1                  | 0.2               |
| 42       | 2        | 1        | 23664.6188 | 0.3                  | 0.3               |
| 43       | 2        | 1        | 24759.3164 | -0.4                 | 0.4               |
| 44       | 2        | 1        | 25878.6377 | -0.5                 | 0.4               |
| 36       | 3        | 1        | 18328.0260 | -0.2                 | 0.3               |
| 37       | 3        | 1        | 19235.5360 | -0.2                 | 0.2               |
| 38       | 3        | 1        | 20171.2571 | -0.5                 | 0.2               |
| 39       | 3        | 1        | 21134.8123 | -0.2                 | 0.2               |
| 40       | 3        | 1        | 22125.8473 | -0.3                 | 0.3               |
| 41       | 3        | 1        | 23144.0321 | 0.5                  | 0.4               |
| 42       | 3        | 1        | 24189.0516 | -0.7                 | 0.5               |
| 43       | 3        | 1        | 25260.6145 | 0.1                  | 0.5               |
| 44       | 3        | 1        | 26358.4369 | -0.3                 | 0.6               |
| 35       | 4        | 1        | 18619.2564 | -0.6                 | 0.4               |
| 35       | -4       | -1       | 18602.6030 | -0.1                 | 0.4               |
| 36       | 4        | 1        | 19442.1187 | -0.4                 | 0.4               |
| 36       | -4       | -1       | 19424.8171 | -0.1                 | 0.3               |
| 37       | 4        | 1        | 20295.9868 | 0.2                  | 0.2               |
| 37       | -4       | -1       | 20278.5555 | 0.1                  | 0.2               |
| 38       | 4        | 1        | 21179.9700 | 0.3                  | 0.2               |
| 38       | -4       | -1       | 21163.2668 | 0.4                  | 0.2               |
| 39       | 4        | 1        | 22092.9661 | -0.3                 | 0.2               |
| 39       | -4       | -1       | 22078.4202 | 0.3                  | 0.2               |
| 40       | 4        | 1        | 23033.4376 | 0.6                  | 0.2               |

| <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. – c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|----------|------------|----------------------|-------------------|
| 40       | -4       | -1       | 23023.5074 | -0.5                 | 0.2               |
| 41       | 4        | 1        | 23998.8533 | -1.5                 | 0.7               |
| 41       | -4       | -1       | 23998.0463 | 0.9                  | 0.4               |
| 42       | 4        | 1        | 24984.1514 | 0.0                  | 0.4               |
| 42       | -4       | -1       | 25001.5707 | 0.4                  | 0.4               |
| 43       | 4        | 1        | 25976.2742 | 0.0                  | 0.4               |
| 43       | -4       | -1       | 26033.6424 | -0.5                 | 0.4               |
| 32       | 5        | 1        | 18066.2242 | -0.2                 | 0.2               |
| 33       | 5        | 1        | 18721.7752 | 0.4                  | 0.2               |
| 34       | 5        | 1        | 19412.8179 | 0.3                  | 0.2               |
| 35       | 5        | 1        | 20138.9202 | -0.5                 | 0.2               |
| 36       | 5        | 1        | 20899.6064 | 0.2                  | 0.6               |
| 37       | 5        | 1        | 21694.3640 | -0.5                 | 0.2               |
| 38       | 5        | 1        | 22522.6640 | -0.2                 | 0.2               |
| 39       | 5        | 1        | 23383.9623 | 0.4                  | 0.2               |
| 40       | 5        | 1        | 24277.7083 | -0.1                 | 0.2               |
| 41       | 5        | 1        | 25203.3532 | -0.5                 | 0.4               |
| 42       | 5        | 1        | 26160.3500 | -0.5                 | 0.4               |
| 28       | 6        | 1        | 18075.8935 | 0.4                  | 0.2               |
| 29       | 6        | 1        | 18520.9340 | 0.6                  | 0.2               |
| 30       | 6        | 1        | 19001.5222 | 0.0                  | 0.2               |
| 31       | 6        | 1        | 19518.0325 | 0.3                  | 0.2               |
| 32       | 6        | 1        | 20070.6897 | 0.2                  | 0.2               |
| 33       | 6        | 1        | 20659.5867 | 0.4                  | 0.2               |
| 34       | 6        | 1        | 21284.6959 | 0.2                  | 0.3               |
| 35       | 6        | 1        | 21945.8868 | 0.2                  | 0.2               |
| 36       | 6        | 1        | 22642.9381 | -0.4                 | 0.4               |
| 37       | 6        | 1        | 23375.5566 | 0.1                  | 0.4               |
| 38       | 6        | 1        | 24143.3843 | -0.4                 | 0.8               |
| 39       | 6        | 1        | 24946.0205 | 1.7                  | 0.4               |
| 40       | 6        | 1        | 25783.0175 | 0.4                  | 0.4               |
| 21       | -7       | -1       | 18639.9964 | 0.1                  | 0.2               |
| 22       | -7       | -1       | 18825.1841 | -0.2                 | 0.2               |
| 23       | -7       | -1       | 19035.3665 | -0.2                 | 0.2               |
| 24       | -7       | -1       | 19272.1217 | 0.1                  | 0.2               |

| <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. – c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|----------|------------|----------------------|-------------------|
| 25       | -7       | -1       | 19536.9404 | -0.1                 | 0.2               |
| 26       | -7       | -1       | 19831.2124 | 0.5                  | 0.2               |
| 27       | -7       | -1       | 20156.2069 | -0.4                 | 0.2               |
| 28       | -7       | -1       | 20513.0699 | 0.0                  | 0.2               |
| 29       | -7       | -1       | 20902.8059 | -0.2                 | 0.2               |
| 30       | -7       | -1       | 21326.2806 | -0.3                 | 0.2               |
| 31       | -7       | -1       | 21784.2158 | -0.1                 | 0.2               |
| 32       | -7       | -1       | 22277.1905 | -0.4                 | 0.3               |
| 33       | -7       | -1       | 22805.6486 | 0.5                  | 0.2               |
| 34       | -7       | -1       | 23369.8986 | -0.2                 | 0.2               |
| 35       | -7       | -1       | 23970.1313 | -0.4                 | 0.2               |
| 36       | -7       | -1       | 24606.4231 | -0.3                 | 0.2               |
| 37       | -7       | -1       | 25278.7488 | -0.4                 | 0.2               |
| 38       | -7       | -1       | 25986.9944 | -0.2                 | 0.4               |
| 39       | -7       | -1       | 26730.9666 | -0.1                 | 0.3               |
| 8        | 8        | 1        | 20697.8018 | -0.1                 | 4.2               |
| 9        | 8        | 1        | 20704.7816 | 0.1                  | 3.3               |
| 10       | 8        | 1        | 20715.7133 | -0.6                 | 9.0               |
| 11       | 8        | 1        | 20731.5929 | 0.2                  | 1.1               |
| 12       | 8        | 1        | 20753.5037 | -0.1                 | 0.5               |
| 13       | 8        | 1        | 20782.6222 | 0.8                  | 0.8               |
| 14       | 8        | 1        | 20820.2035 | 0.2                  | 0.6               |
| 15       | 8        | 1        | 20867.5835 | -1.5                 | 0.6               |
| 16       | 8        | 1        | 20926.1715 | -1.0                 | 0.3               |
| 17       | 8        | 1        | 20997.4343 | 0.3                  | 0.5               |
| 18       | 8        | 1        | 21082.8907 | 1.0                  | 0.3               |
| 19       | 8        | 1        | 21184.1008 | -0.2                 | 0.7               |
| 20       | 8        | 1        | 21302.6581 | 0.5                  | 0.4               |
| 21       | 8        | 1        | 21440.1637 | -0.1                 | 0.3               |
| 22       | 8        | 1        | 21598.2234 | -0.4                 | 0.4               |
| 23       | 8        | 1        | 21778.4254 | -1.1                 | 0.4               |
| 24       | 8        | 1        | 21982.3302 | 0.6                  | 0.2               |
| 25       | 8        | 1        | 22211.4434 | -0.3                 | 0.3               |
| 26       | 8        | 1        | 22467.2172 | -0.2                 | 0.2               |
| 27       | 8        | 1        | 22751.0236 | 0.6                  | 0.3               |

| <i>J</i> | <i>k</i> | <i>l</i> | Exp.                    | e. – c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|----------|-------------------------|----------------------|-------------------|
| 28       | 8        | 1        | 23064.1406              | -2.5                 | 0.2               |
| 29       | 8        | 1        | 23407.7592              | -0.5                 | 0.3               |
| 30       | 8        | 1        | 23782.9443              | -0.7                 | 0.3               |
| 31       | 8        | 1        | 24190.6537              | -0.2                 | 0.3               |
| 32       | 8        | 1        | 24631.7213              | 0.9                  | 0.3               |
| 33       | 8        | 1        | 25106.8554              | 1.0                  | 0.3               |
| 34       | 8        | 1        | 25616.6454              | 2.4                  | 0.8               |
| 35       | 8        | 1        | 26161.5534              | 1.6                  | 0.4               |
| 9        | 9        | 1        | 23655.1047              | -18.7                | 11.7              |
| 10       | 9        | 1        | 23663.1454              | 8.5                  | 7.5               |
| 11       | 9        | 1        | 23675.3333              | 1.6                  | 6.3               |
| 12       | 9        | 1        | 23692.6653              | 1.9                  | 1.5               |
| 13       | 9        | 1        | 23716.1672              | 0.0                  | 2.6               |
| 14       | 9        | 1        | 23746.9567              | 1.5                  | 1.6               |
| 15       | 9        | 1        | 23786.2118              | -0.1                 | 1.2               |
| 16       | 9        | 1        | 23835.1895              | -0.1                 | 0.4               |
| 17       | 9        | 1        | 23895.2021              | -0.3                 | 0.5               |
| 18       | 9        | 1        | 23967.6172              | -1.9                 | 1.4               |
| 19       | 9        | 1        | 24053.8561              | 0.8                  | 0.5               |
| 20       | 9        | 1        | 24155.3637              | -0.9                 | 0.6               |
| 21       | 9        | 1        | 24273.6279              | -0.1                 | 0.5               |
| 22       | 9        | 1        | 24410.1441              | 0.5                  | 0.4               |
| 23       | 9        | 1        | 24566.4168              | 3.0                  | 1.6               |
| 24       | 9        | 1        | 24743.9353              | 1.4                  | 0.4               |
| 25       | 9        | 1        | 24944.1778              | -0.5                 | 0.4               |
| 26       | 9        | 1        | 25168.5895              | 1.3                  | 0.4               |
| 27       | 9        | 1        | 25418.5591              | 0.6                  | 0.4               |
| 28       | 9        | 1        | 25695.4261              | 0.7                  | 0.3               |
| 29       | 9        | 1        | 26000.4549              | -0.1                 | 0.4               |
| 30       | 9        | 1        | 26334.8333              | 0.5                  | 0.4               |
| 43       | -2       | 1        | 26916.1751 <sup>c</sup> | 5.0                  | 2.2               |
| 45       | -2       | 1        | 26269.5555 <sup>c</sup> | 0.1                  | 0.6               |
| 46       | -2       | 1        | 26593.7128 <sup>c</sup> | -4.7                 | 2.8               |

<sup>a</sup>) residuals (in kHz) ; <sup>b</sup>) Experimental uncertainty (in kHz) ; <sup>c</sup>)  $\Delta(k-l) = \pm 3$  'perturbation-allowed' transitions

Table 2. Experimental frequencies (in MHz) of the transitions in the  $\nu_6=1$  state of  $^{28}\text{SiHF}_3$  recorded by applying 2D-(RF)MWFT spectroscopic techniques.

| <i>J</i> | <i>k'</i> | <i>l'</i> | ← | <i>k''</i> | <i>l''</i> | Exp.   | e. - c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|-----------|-----------|---|------------|------------|--------|----------------------|-------------------|
| 35       | -2        | 1         | ← | 2          | -1         | 5.297  | -7                   | 4                 |
| 35       | -4        | -1        | ← | 4          | 1          | 11.341 | -10                  | 6                 |
| 36       | -2        | 1         | ← | 2          | -1         | 3.956  | -16                  | 5                 |
| 36       | -4        | -1        | ← | 4          | 1          | 13.318 | -12                  | 7                 |
| 37       | -2        | 1         | ← | 2          | -1         | 1.864  | -3                   | 8                 |
| 37       | -4        | -1        | ← | 4          | 1          | 15.523 | -41                  | 12                |
| 38       | 2         | -1        | ← | -2         | 1          | 1.412  | 42                   | 9                 |
| 38       | -4        | -1        | ← | 4          | 1          | 18.046 | -27                  | 10                |
| 39       | 2         | -1        | ← | -2         | 1          | 6.329  | -6                   | 6                 |
| 39       | -4        | -1        | ← | 4          | 1          | 20.839 | -43                  | 14                |
| 40       | 2         | -1        | ← | -2         | 1          | 14.110 | 26                   | 6                 |
| 40       | -4        | -1        | ← | 4          | 1          | 23.973 | -41                  | 5                 |
| 41       | 2         | -1        | ← | -2         | 1          | 26.732 | 47                   | 36                |
| 41       | -4        | -1        | ← | 4          | 1          | 27.436 | -59                  | 36                |
| 42       | 2         | -1        | ← | -2         | 1          | 48.822 | 50                   | 13                |
| 42       | -4        | -1        | ← | 4          | 1          | 31.355 | 2                    | 12                |
| 43       | 2         | -1        | ← | -2         | 1          | 93.033 | 48                   | 13                |
| 43       | -4        | -1        | ← | 4          | 1          | 35.610 | -7                   | 10                |

<sup>a)</sup> residuals (in kHz)  
<sup>b)</sup> Experimental uncertainty (in kHz)

Table 3 : Experimental frequencies (in MHz) of the rotational  $\Delta J = 1$  transitions in the ground state of  $^{28}\text{SiHF}_3$ ,  $^{29}\text{SiHF}_3$  and  $^{30}\text{SiHF}_3$ 

| <i>J</i>             | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i>             | <i>K</i> | Exp.        | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------------------|----------|------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|----------------------|----------|-------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|
| $^{28}\text{SiHF}_3$ |          |            |                    |                   | 23       | 21       | 345833.438 | -4                 | 50                | 44       | 36       | 647428.112 | -402               | 400               | 63                   | 0        | 914831.669  | 67                 | 300               | 6        | 2        | 100730.906 | -16                | 100               |
|                      |          |            |                    |                   | 29       | 0        | 431668.546 | 27                 | 50                | 44       | 39       | 647681.558 | -9                 | 300               | 63                   | 1        | 914833.354  | 231                | 300               | 6        | 3        | 100731.754 | -40                | 100               |
|                      |          |            |                    |                   | 29       | 1        | 431669.250 | -13                | 50                | 53       | 0        | 773760.497 | -77                | 300               | 63                   | 2        | 914837.653  | -40                | 500               | 6        | 4        | 100732.977 | -36                | 100               |
| 10                   | 0        | 158536.917 | 25                 | 150               | 29       | 2        | 431671.511 | 16                 | 50                | 53       | 2        | 773765.419 | -369               | 300               | 63                   | 3        | 914852.624  | 269                | 300               | 6        | 5        | 100734.476 | -105               | 100               |
| 10                   | 1        | 158537.178 | 10                 | 150               | 29       | 3        | 431675.221 | -154               | 200               | 53       | -3       | 773769.159 | -104               | 300               | 63                   | 4        | 914855.947  | 87                 | 300               | 6        | 6        | 100736.429 | -69                | 100               |
| 10                   | 2        | 158538.005 | 10                 | 50                | 29       | 6        | 431695.350 | 39                 | 50                | 53       | 3        | 773775.586 | 255                | 300               | 63                   | 5        | 914869.401  | -146               | 300               | 10       | 0        | 158266.685 | 142                | 200               |
| 10                   | 3        | 158539.378 | 4                  | 50                | 29       | 9        | 431728.811 | -13                | 50                | 53       | 4        | 773781.556 | 142                | 300               | 63                   | 6        | 914886.370  | 114                | 500               | 10       | 2        | 158267.691 | 54                 | 100               |
| 10                   | 4        | 158541.295 | -8                 | 50                | 29       | 12       | 431775.775 | -9                 | 50                | 53       | 6        | 773807.542 | 60                 | 300               | 63                   | 9        | 914954.622  | -59                | 300               | 10       | 3        | 158269.012 | 8                  | 100               |
| 10                   | 5        | 158543.784 | -1                 | 50                | 29       | 15       | 431836.221 | -10                | 50                | 53       | 9        | 773866.529 | 363                | 300               | 63                   | 12       | 915050.167  | -377               | 400               | 10       | 4        | 158270.945 | 27                 | 100               |
| 10                   | 6        | 158546.814 | -5                 | 50                | 29       | 18       | 431910.187 | -32                | 50                | 53       | 15       | 774054.255 | 9                  | 300               | 63                   | 15       | 915173.770  | -177               | 300               | 10       | 5        | 158273.391 | 11                 | 100               |
| 10                   | 7        | 158550.393 | -13                | 50                | 29       | 21       | 431997.786 | -26                | 50                | 53       | 21       | 774336.912 | -301               | 300               | 63                   | 24       | 915710.713  | 61                 | 300               | 10       | 6        | 158276.369 | -21                | 100               |
| 10                   | 8        | 158554.523 | -22                | 50                | 29       | 24       | 432099.098 | 10                 | 50                | 53       | 27       | 774716.141 | 55                 | 300               | 63                   | 27       | 915945.321  | -276               | 300               | 10       | 7        | 158279.939 | -8                 | 100               |
| 10                   | 9        | 158559.225 | -12                | 50                | 29       | 27       | 432214.195 | 61                 | 60                | 53       | 33       | 775191.976 | -246               | 300               | 63                   | 33       | 916500.847  | 50                 | 300               | 10       | 8        | 158284.022 | -31                | 100               |
| 10                   | 10       | 158564.477 | -5                 | 50                | 29       | 29       | 432298.792 | 262                | 300               | 53       | 36       | 775467.305 | 25                 | 300               | 63                   | 39       | 917171.452  | -8                 | 300               | 10       | 9        | 158288.657 | -50                | 100               |
| 15                   | 0        | 230533.798 | 14                 | 50                | 31       | 0        | 460327.264 | 35                 | 50                | 53       | 39       | 775767.073 | -244               | 300               | 63                   | 42       | 917550.800  | -29                | 300               | 10       | 10       | 158293.825 | -86                | 100               |
| 15                   | 1        | 230534.172 | -12                | 50                | 31       | 1        | 460328.042 | 21                 | 50                | 53       | 42       | 776092.727 | 129                | 300               | 71                   | 1        | 1026909.362 | -14                | 500               | 15       | 0        | 230141.160 | 160                | 200               |
| 15                   | 2        | 230535.390 | 5                  | 50                | 31       | 2        | 460330.427 | 29                 | 50                | 54       | 0        | 787912.766 | 193                | 300               | 71                   | 2        | 1026914.081 | -392               | 300               | 15       | 2        | 230142.720 | 132                | 150               |
| 15                   | 3        | 230537.392 | -2                 | 50                | 31       | 3        | 460334.379 | -202               | 200               | 54       | 2        | 787917.970 | 94                 | 300               | 71                   | 4        | 1026934.239 | -200               | 500               | 15       | 3        | 230144.570 | -4                 | 100               |
| 15                   | 4        | 230540.190 | 1                  | 50                | 31       | 6        | 460355.769 | 9                  | 50                | 54       | 3        | 787928.026 | 205                | 500               | 72                   | 0        | 1040864.058 | -99                | 300               | 15       | 4        | 230147.430 | 77                 | 100               |
| 15                   | 5        | 230543.797 | 4                  | 50                | 31       | 9        | 460391.461 | 14                 | 50                | 54       | -3       | 787921.175 | 6                  | 300               | 72                   | 2        | 1040870.969 | -65                | 300               | 15       | 5        | 230150.970 | 42                 | 100               |
| 15                   | 6        | 230548.209 | 11                 | 50                | 31       | 12       | 460441.445 | -8                 | 50                | 54       | 15       | 788211.013 | -217               | 300               | 72                   | 3        | 1040892.930 | -193               | 300               | 15       | 6        | 230155.320 | 23                 | 100               |
| 15                   | 7        | 230553.415 | 10                 | 50                | 31       | 15       | 460505.801 | -22                | 50                | 61       | 0        | 886700.191 | 83                 | 300               | 72                   | 4        | 1040891.040 | -161               | 300               | 15       | 7        | 230160.490 | 28                 | 100               |
| 15                   | 8        | 230559.420 | 6                  | 50                | 31       | 18       | 460584.587 | -25                | 50                | 61       | 1        | 886701.752 | 165                | 300               | 72                   | 6        | 1040925.371 | 73                 | 300               | 15       | 8        | 230166.450 | 28                 | 100               |
| 15                   | 9        | 230566.234 | 7                  | 50                | 31       | 21       | 460677.858 | -31                | 50                | 61       | 2        | 886706.152 | 126                | 300               | 72                   | 9        | 1041002.083 | 52                 | 300               | 15       | 9        | 230173.130 | -50                | 100               |
| 15                   | 10       | 230573.844 | 1                  | 50                | 31       | 24       | 460785.732 | -5                 | 50                | 61       | 3        | 886719.648 | 205                | 300               | 72                   | 21       | 1041618.049 | 473                | 400               | 15       | 11       | 230189.090 | 3                  | 100               |
| 15                   | 11       | 230582.267 | 3                  | 50                | 31       | 27       | 460908.290 | 41                 | 50                | 61       | -3       | 886707.359 | 28                 | 300               | 73                   | 2        | 1054815.269 | -60                | 300               | 15       | 12       | 230198.200 | -39                | 100               |
| 15                   | 12       | 230591.492 | 3                  | 50                | 31       | 31       | 461094.754 | 158                | 250               | 61       | 4        | 886723.863 | 160                | 300               | 73                   | 3        | 1054838.264 | -197               | 300               | 15       | 13       | 230208.200 | 9                  | 100               |
| 15                   | 13       | 230601.530 | 9                  | 50                | 43       | 2        | 631754.087 | -324               | 300               | 61       | 9        | 886819.839 | 68                 | 300               | 73                   | 4        | 1054835.743 | 53                 | 300               | 15       | 14       | 230219.010 | 66                 | 100               |
| 15                   | 14       | 230612.375 | 15                 | 50                | 43       | -3       | 631758.561 | -141               | 300               | 61       | 12       | 886912.913 | -55                | 300               | 73                   | 5        | 1054851.166 | -97                | 300               | 15       | 15       | 230230.490 | -8                 | 100               |
| 15                   | 15       | 230624.027 | 19                 | 50                | 43       | 3        | 631760.827 | -52                | 300               | 61       | 15       | 887032.909 | -29                | 300               | 73                   | 6        | 1054870.202 | 15                 | 300               | 20       | 2        | 301945.620 | 0                  | 100               |
| 23                   | 0        | 345568.864 | 6                  | 50                | 43       | 6        | 631788.569 | -283               | 300               | 62       | 0        | 900771.220 | -35                | 300               | 73                   | 9        | 1054947.739 | -77                | 300               | 20       | 3        | 301948.204 | -15                | 100               |
| 23                   | 1        | 345569.443 | -13                | 50                | 43       | 9        | 631837.137 | -180               | 300               | 62       | 1        | 900772.832 | 77                 | 300               | 73                   | 15       | 1055196.768 | 346                | 300               | 20       | 4        | 301951.853 | -5                 | 100               |
| 23                   | 2        | 345571.242 | -7                 | 50                | 44       | 2        | 645993.240 | -1                 | 300               | 62       | 2        | 900777.540 | 281                | 500               | 73                   | 21       | 1055570.881 | 399                | 400               | 20       | 5        | 301956.547 | 10                 | 100               |
| 23                   | 3        | 345574.235 | -56                | 50                | 44       | -3       | 645997.423 | -95                | 300               | 62       | -3       | 900777.540 | -622               | 500               | 73                   | 24       | 1055805.577 | 599                | 600               | 20       | 6        | 301962.267 | 10                 | 100               |
| 23                   | 6        | 345590.393 | 7                  | 50                | 44       | 3        | 645999.914 | -41                | 300               | 62       | 3        | 900791.281 | -2                 | 300               | $^{29}\text{SiHF}_3$ |          |             |                    |                   | 20       | 7        | 301969.012 | -7                 | 100               |
| 23                   | 9        | 345617.315 | 2                  | 50                | 44       | 6        | 646028.291 | -131               | 300               | 62       | 9        | 900892.754 | 123                | 300               | 6                    | 0        | 100730.235  | 9                  | 200               | 20       | 8        | 301976.863 | 41                 | 100               |
| 23                   | 12       | 345655.050 | 5                  | 50                | 44       | 9        | 646077.880 | -49                | 300               | 62       | 15       | 901108.941 | 84                 | 300               | 6                    | 1        | 100730.235  | -165               | 200               | 20       | 9        | 301985.719 | 50                 | 100               |
| 23                   | 15       | 345703.609 | -5                 | 50                | 44       | 24       | 646624.948 | 21                 | 300               | 62       | 21       | 901434.217 | 33                 | 300               |                      |          |             |                    |                   | 20       | 10       | 301995.580 | 21                 | 100               |
| 23                   | 18       | 345763.064 | 2                  | 50                | 44       | 27       | 646794.928 | 27                 | 300               | 62       | 24       | 901638.013 | -104               | 300               |                      |          |             |                    |                   | 20       | 11       | 302006.488 | -7                 | 100               |

a) residuals (in kHz)

b) Experimental uncertainty (in kHz)

| <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.                            | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>K</i> | Exp.       | e.-c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|------------|--------------------|-------------------|----------|----------|---------------------------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|----------|----------|------------|--------------------|-------------------|
| 20       | 12       | 302018.519 | 43                 | 100               | 29       | 19       | 431203.254                      | -59                | 100               | 10       | 0        | 158003.924 | 212                | 200               | 20       | 12       | 301517.494 | 22                 | 100               | 29       | 9        | 430283.372 | -8                 | 50                |
| 20       | 19       | 302131.793 | 42                 | 100               | 29       | 20       | 431232.279                      | 2                  | 50                | 10       | 2        | 158005.008 | 210                | 250               | 20       | 13       | 301530.373 | -27                | 100               | 29       | 10       | 430297.327 | 17                 | 50                |
| 20       | 20       | 302152.326 | 172                | 200               | 29       | 21       | 431262.750                      | 2                  | 50                | 10       | 3        | 158006.192 | 37                 | 200               | 20       | 14       | 301544.397 | 29                 | 100               | 29       | 11       | 430312.729 | 17                 | 50                |
| 23       | 0        | 344981.338 | 39                 | 200               | 29       | 22       | 431294.728                      | 1                  | 50                | 10       | 4        | 158008.105 | 51                 | 100               | 20       | 15       | 301559.397 | 19                 | 100               | 29       | 12       | 430329.584 | -3                 | 50                |
| 23       | 1        | 344981.817 | -75                | 200               | 29       | 23       | 431328.230                      | 10                 | 50                | 10       | 5        | 158010.511 | 14                 | 100               | 20       | 16       | 301575.442 | 10                 | 100               | 29       | 13       | 430347.949 | 11                 | 50                |
| 23       | 2        | 344983.657 | -13                | 50                | 29       | 24       | 431363.231                      | 2                  | 50                | 10       | 6        | 158013.450 | -34                | 100               | 20       | 17       | 301592.740 | 209                | 250               | 29       | 14       | 430367.798 | 33                 | 50                |
| 23       | 3        | 344986.619 | -16                | 50                | 29       | 25       | 431399.763                      | 5                  | 50                | 10       | 7        | 158016.981 | -33                | 100               | 20       | 18       | 301610.669 | -8                 | 100               | 29       | 15       | 430389.045 | -26                | 50                |
| 23       | 9        | 345029.339 | -16                | 50                | 29       | 26       | 431437.804                      | -6                 | 50                | 10       | 9        | 158025.678 | -28                | 100               | 20       | 19       | 301629.880 | 8                  | 100               | 29       | 18       | 430461.882 | -6                 | 50                |
| 23       | 15       | 345114.953 | -3                 | 50                | 29       | 27       | 431477.396                      | 5                  | 50                | 15       | 0        | 229759.091 | -41                | 200               | 23       | 0        | 344410.073 | 33                 | 200               | 29       | 19       | 430489.154 | 19                 | 50                |
| 23       | 21       | 345243.753 | -3                 | 50                | 29       | 28       | 431518.497                      | -5                 | 50                | 15       | 3        | 229762.602 | -76                | 100               | 23       | 1        | 344410.560 | -69                | 200               | 29       | 20       | 430517.866 | -8                 | 50                |
| 23       | 23       | 345296.335 | -33                | 50                | 29       | 29       | 431561.155                      | 5                  | 50                | 15       | 4        | 229765.403 | -33                | 100               | 23       | 2        | 344412.361 | -32                | 50                | 29       | 21       | 430548.134 | 27                 | 50                |
| 26       | 0        | 387980.433 | 26                 | 200               | 31       | 0        | 459546.809                      | -66                | 200               | 15       | 5        | 229768.953 | -29                | 100               | 23       | 3        | 344415.316 | -19                | 50                | 29       | 22       | 430579.836 | -2                 | 50                |
| 26       | 1        | 387981.071 | -2                 | 200               | 31       | 1        | 459547.715                      | 54                 | 200               | 15       | 6        | 229773.312 | -6                 | 100               | 23       | 6        | 344431.233 | 8                  | 50                | 29       | 23       | 430613.096 | 26                 | 50                |
| 26       | 3        | 387986.390 | -8                 | 50                | 31       | 2        | 459550.026                      | 9                  | 50                | 15       | 7        | 229778.539 | 96                 | 100               | 23       | 12       | 344494.863 | 6                  | 50                | 29       | 24       | 430647.794 | -14                | 50                |
| 26       | 9        | 388034.341 | -16                | 50                | 31       | 3        | 459553.957                      | 11                 | 200               | 15       | 8        | 229784.397 | 39                 | 100               | 23       | 15       | 344542.664 | 4                  | 50                | 29       | 25       | 430684.066 | 13                 | 50                |
| 26       | 15       | 388130.467 | 12                 | 50                | 31       | 6        | 459575.167                      | 1                  | 50                | 15       | 9        | 229791.064 | 1                  | 100               | 23       | 18       | 344601.158 | -19                | 50                | 29       | 26       | 430721.886 | 76                 | 100               |
| 26       | 21       | 388275.068 | 18                 | 50                | 31       | 9        | 459610.557                      | 3                  | 50                | 15       | 10       | 229798.579 | 20                 | 100               | 23       | 21       | 344670.478 | 14                 | 50                | 29       | 27       | 430761.065 | -19                | 50                |
| 26       | 24       | 388365.698 | 2                  | 50                | 31       | 12       | 459660.144                      | -1                 | 50                | 15       | 11       | 229806.823 | -25                | 100               | 23       | 23       | 344722.886 | 217                | 200               | 31       | 0        | 458788.131 | 7                  | 200               |
| 29       | 0        | 430936.168 | 30                 | 200               | 31       | 15       | 459723.993                      | 9                  | 50                | 15       | 12       | 229815.876 | -53                | 100               | 26       | 0        | 387338.608 | 28                 | 200               | 31       | 1        | 458788.903 | 0                  | 200               |
| 29       | 1        | 430936.886 | 10                 | 200               | 31       | 18       | 459802.128                      | -4                 | 50                | 15       | 13       | 229825.738 | -66                | 100               | 26       | 1        | 387339.199 | -42                | 200               | 31       | 3        | 458795.135 | -5                 | 200               |
| 29       | 2        | 430939.096 | 6                  | 50                | 31       | 21       | 459894.660                      | -1                 | 50                | 15       | 14       | 229836.488 | 14                 | 100               | 26       | 2        | 387341.230 | 8                  | 50                | 31       | 6        | 458816.197 | 4                  | 50                |
| 29       | 3        | 430942.779 | 0                  | 50                | 31       | 24       | 460001.654                      | -4                 | 50                | 15       | 15       | 229847.967 | 27                 | 100               | 26       | 3        | 387344.522 | -2                 | 50                | 31       | 9        | 458851.302 | -2                 | 50                |
| 29       | 4        | 430947.957 | 12                 | 50                | 31       | 25       | 460040.558                      | 2                  | 50                | 20       | 0        | 301443.332 | 214                | 200               | 26       | 9        | 387392.101 | -8                 | 50                | 31       | 12       | 458900.491 | -16                | 50                |
| 29       | 5        | 430954.603 | 16                 | 50                | 31       | 26       | 460081.071                      | -6                 | 50                | 20       | 2        | 301445.087 | -93                | 100               | 26       | 15       | 387487.467 | 8                  | 50                | 31       | 15       | 458963.836 | -11                | 50                |
| 29       | 6        | 430962.688 | -19                | 50                | 31       | 27       | 460123.221                      | -3                 | 50                | 20       | 3        | 301447.750 | -9                 | 100               | 26       | 18       | 387553.135 | -16                | 50                | 31       | 18       | 459041.381 | -3                 | 50                |
| 29       | 7        | 430972.274 | -31                | 50                | 31       | 28       | 460166.997                      | -5                 | 50                | 20       | 4        | 301451.399 | 29                 | 100               | 26       | 21       | 387630.906 | -27                | 50                | 31       | 21       | 459133.000 | -191               | 200               |
| 29       | 8        | 430983.383 | 0                  | 50                | 31       | 29       | 460212.418                      | 2                  | 50                | 20       | 5        | 301456.054 | 41                 | 100               | 26       | 24       | 387720.880 | 3                  | 50                | 31       | 24       | 459239.349 | -6                 | 50                |
| 29       | 9        | 430995.953 | 12                 | 50                | 31       | 30       | 460259.474                      | 4                  | 50                | 20       | 6        | 301461.734 | 45                 | 100               | 26       | 26       | 387787.604 | -33                | 50                | 31       | 25       | 459277.949 | -1                 | 50                |
| 29       | 10       | 431009.989 | 8                  | 50                |          |          |                                 |                    |                   | 20       | 7        | 301468.362 | -36                | 100               | 29       | 0        | 430224.056 | 11                 | 200               | 31       | 26       | 459318.152 | -4                 | 50                |
| 29       | 11       | 431025.492 | -12                | 50                |          |          | <sup>29</sup> SiHF <sub>3</sub> |                    |                   | 20       | 8        | 301476.113 | -28                | 100               | 29       | 1        | 430224.748 | -29                | 200               | 31       | 27       | 459359.965 | -10                | 50                |
| 29       | 12       | 431042.513 | 1                  | 50                |          |          |                                 |                    |                   | 20       | 9        | 301484.910 | -9                 | 100               | 29       | 2        | 430226.963 | -10                | 50                | 31       | 30       | 459495.178 | 13                 | 50                |
| 29       | 15       | 431102.458 | -6                 | 50                | 1        | 0        | 28734.920                       | -18                | 100               | 20       | 10       | 301494.752 | 19                 | 100               | 29       | 3        | 430230.647 | 13                 | 50                | 31       | 31       | 459543.491 | 4                  | 50                |
| 29       | 18       | 431175.858 | 5                  | 50                | 1        | 1        | 28734.920                       | -68                | 100               | 20       | 11       | 301505.699 | 115                | 100               | 29       | 6        | 430250.409 | 3                  | 50                |          |          |            |                    |                   |

<sup>a</sup>) residuals (in kHz)<sup>b</sup>) Experimental uncertainty (in kHz)

Table 4 : Experimental frequencies (in MHz) of the rotational  $\Delta J = 1$  transitions in the  $v_6 = 1$  state of  $^{28}\text{SiHF}_3$

| 175 |          |          |          |            |                      |                   |          |          |          |            |                      |                   |          |          |          |            |                      |                   |          |          |          |            |                      |                   |
|-----|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|
|     | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> |
|     | 0        | 0        | 1        | 14429.718  | 0.9                  | 1.0               | 10       | 2        | -1       | 158713.039 | 30                   | 50                | 15       | 3        | -1       | 230812.418 | 7                    | 50                | 23       | 3        | -1       | 346069.520 | 2                    | 50                |
|     | 6        | -1       | -1       | 100905.300 | -64                  | 200               | 10       | 3        | -1       | 158708.265 | -4                   | 50                | 15       | 4        | -1       | 230804.456 | -29                  | 50                | 23       | 4        | -1       | 346047.781 | 13                   | 50                |
|     | 6        | 1        | 1        | 101089.720 | 81                   | 200               | 10       | 4        | -1       | 158706.538 | 37                   | 50                | 15       | 5        | -1       | 230800.749 | -19                  | 50                | 23       | 5        | -1       | 346033.465 | -25                  | 50                |
|     | 6        | 2        | 1        | 100978.390 | 78                   | 200               | 10       | 5        | -1       | 158706.538 | -5                   | 50                | 15       | 6        | -1       | 230799.909 | 4                    | 50                | 23       | 6        | -1       | 346024.897 | -21                  | 50                |
|     | 6        | 3        | 1        | 100988.990 | 203                  | 200               | 10       | 6        | -1       | 158707.876 | 9                    | 50                | 15       | 7        | -1       | 230801.196 | 27                   | 50                | 23       | 8        | -1       | 346020.205 | -33                  | 50                |
|     | 6        | 4        | 1        | 100993.450 | 173                  | 200               | 10       | 7        | -1       | 158710.197 | -9                   | 50                | 15       | 8        | -1       | 230804.147 | 9                    | 50                | 23       | 11       | -1       | 346034.873 | 6                    | 50                |
|     | 6        | 5        | 1        | 100996.610 | 133                  | 200               | 10       | 8        | -1       | 158713.402 | -5                   | 50                | 15       | 9        | -1       | 230808.552 | -1                   | 50                | 23       | 14       | -1       | 346068.175 | 8                    | 50                |
|     | 6        | 6        | 1        | 100999.520 | 153                  | 200               | 10       | 9        | -1       | 158717.373 | -7                   | 50                | 15       | 10       | -1       | 230814.253 | 8                    | 50                | 23       | 17       | -1       | 346116.521 | 0                    | 50                |
|     | 6        | 0        | -1       | 101017.170 | 123                  | 200               | 10       | 10       | -1       | 158722.051 | -18                  | 50                | 15       | 11       | -1       | 230821.106 | 5                    | 50                | 23       | 20       | -1       | 346178.293 | 3                    | 50                |
|     | 6        | 1        | -1       | 101007.800 | 165                  | 200               | 15       | -1       | -1       | 230540.860 | 20                   | 50                | 15       | 12       | -1       | 230829.064 | 23                   | 50                | 23       | 23       | -1       | 346252.687 | 34                   | 50                |
|     | 6        | 2        | -1       | 101004.970 | 61                   | 200               | 15       | 1        | 1        | 230960.765 | -9                   | 50                | 15       | 13       | -1       | 230838.017 | 8                    | 50                | 29       | -1       | -1       | 431683.348 | -6                   | 50                |
|     | 6        | 3        | -1       | 101004.400 | 198                  | 200               | 15       | 2        | 1        | 230593.736 | -11                  | 50                | 15       | 14       | -1       | 230847.969 | 6                    | 50                | 29       | 1        | 1        | 432463.066 | -9                   | 50                |
|     | 6        | 4        | -1       | 101004.400 | -105                 | 200               | 15       | 3        | 1        | 230649.412 | -9                   | 50                | 15       | 15       | -1       | 230858.874 | 2                    | 50                | 29       | 2        | 1        | 431695.608 | 85                   | 200               |
|     | 6        | 5        | -1       | 101005.700 | 205                  | 200               | 15       | 4        | 1        | 230681.558 | 23                   | 50                | 23       | -1       | -1       | 345579.992 | -5                   | 50                | 29       | 3        | 1        | 431727.469 | -10                  | 50                |
|     | 6        | 6        | -1       | 101007.090 | 58                   | 200               | 15       | 5        | 1        | 230702.129 | 13                   | 50                | 23       | 1        | 1        | 346206.916 | -12                  | 50                | 29       | -4       | -1       | 431769.205 | -26                  | 50                |
|     | 10       | -1       | -1       | 158541.657 | 11                   | 50                | 15       | 6        | 1        | 230717.293 | -29                  | 50                | 23       | 2        | 1        | 345625.202 | -13                  | 50                | 29       | 4        | 1        | 431768.378 | 5                    | 50                |
|     | 10       | 1        | 1        | 158830.893 | -26                  | 50                | 15       | 7        | 1        | 230729.921 | -16                  | 50                | 23       | 3        | 1        | 345649.348 | -4                   | 50                | 29       | 5        | 1        | 431811.285 | -4                   | 50                |
|     | 10       | 2        | 1        | 158618.317 | -12                  | 50                | 15       | 8        | 1        | 230741.322 | 5                    | 50                | 23       | 4        | 1        | 345696.751 | 107                  | 200               | 29       | 6        | 1        | 431851.344 | -22                  | 50                |
|     | 10       | 3        | 1        | 158650.598 | -6                   | 50                | 15       | 9        | 1        | 230752.193 | 2                    | 50                | 23       | 5        | 1        | 345736.510 | -25                  | 50                | 29       | 7        | 1        | 431888.196 | -3                   | 50                |
|     | 10       | 4        | 1        | 158664.510 | -15                  | 50                | 15       | 10       | 1        | 230762.993 | 11                   | 50                | 23       | 6        | 1        | 345769.145 | -19                  | 50                | 29       | 10       | 1        | 431983.930 | -9                   | 50                |
|     | 10       | 5        | 1        | 158673.189 | -13                  | 50                | 15       | 11       | 1        | 230773.951 | 1                    | 50                | 23       | 7        | 1        | 345796.705 | -30                  | 50                | 29       | 13       | 1        | 432070.361 | -8                   | 50                |
|     | 10       | 6        | 1        | 158680.003 | 20                   | 50                | 15       | 12       | 1        | 230785.260 | -7                   | 50                | 23       | 10       | 1        | 345864.353 | -21                  | 50                | 29       | 16       | 1        | 432158.121 | -28                  | 50                |
|     | 10       | 7        | 1        | 158686.107 | 38                   | 50                | 15       | 13       | 1        | 230797.049 | 2                    | 50                | 23       | 13       | 1        | 345925.940 | -14                  | 50                | 29       | 19       | 1        | 432252.682 | 42                   | 100               |
|     | 10       | 8        | 1        | 158691.983 | -6                   | 50                | 15       | 14       | 1        | 230809.381 | 9                    | 50                | 23       | 16       | 1        | 345990.754 | -4                   | 50                | 29       | 22       | 1        | 432356.645 | 4                    | 50                |
|     | 10       | 9        | 1        | 158697.995 | -16                  | 50                | 15       | 15       | 1        | 230822.306 | 7                    | 50                | 23       | 19       | 1        | 346062.499 | 4                    | 50                | 29       | 25       | 1        | 432471.765 | 19                   | 50                |
|     | 10       | 10       | 1        | 158704.312 | 25                   | 50                | 15       | 0        | -1       | 230908.710 | -2                   | 50                | 23       | 22       | 1        | 346142.945 | 28                   | 50                | 29       | 28       | 1        | 432599.020 | 76                   | 50                |
|     | 10       | 0        | -1       | 158754.822 | 25                   | 50                | 15       | 1        | -1       | 230855.345 | -16                  | 50                | 23       | -2       | 1        | 346100.920 | -91                  | 100               | 29       | -2       | 1        | 432390.282 | -160                 | 200               |
|     | 10       | 1        | -1       | 158724.149 | -31                  | 50                | 15       | 2        | -1       | 230827.332 | 118                  | 200               | 23       | 2        | -1       | 346100.570 | 9                    | 100               | 29       | 2        | -1       | 432390.282 | 159                  | 200               |

<sup>a)</sup> residuals (in kHz) obtained using the Q reduction

<sup>b)</sup> Experimental uncertainty (in kHz)

Table 4 — *Continued*

| <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | e. - c. <sup>a</sup> | Unc. <sup>b</sup> |
|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|----------|----------|----------|------------|----------------------|-------------------|
| 29       | 3        | -1       | 432358.455 | -13                  | 50                | 31       | 25       | 1        | 461173.349 | 149                  | 200               | 44       | 6        | 1        | 646116.200 | 672                  | 500               | 53       | 14       | -1       | 775201.140 | 241                  | 500               |
| 29       | 4        | -1       | 432331.953 | -2                   | 50                | 31       | 28       | 1        | 461309.620 | 44                   | 50                | 44       | 7        | 1        | 646153.600 | 617                  | 600               | 53       | 17       | -1       | 775278.220 | -167                 | 500               |
| 29       | 5        | -1       | 432311.645 | -29                  | 50                | 31       | -2       | 1        | 461110.504 | -58                  | 100               | 44       | -7       | -1       | 646153.600 | 618                  | 600               | 53       | 23       | -1       | 775524.990 | -139                 | 500               |
| 29       | 6        | -1       | 432297.280 | -26                  | 50                | 31       | 2        | -1       | 461110.504 | 17                   | 100               | 44       | 16       | 1        | 646560.900 | 478                  | 500               | 62       | -1       | -1       | 900808.769 | -871                 | 500               |
| 29       | 8        | -1       | 432283.570 | -57                  | 50                | 31       | 3        | -1       | 461080.631 | 0                    | 50                | 44       | 25       | 1        | 647063.900 | 229                  | 500               | 62       | 1        | 1        | 902382.242 | 265                  | 500               |
| 29       | 11       | -1       | 432292.014 | -23                  | 50                | 31       | 4        | -1       | 461054.337 | -10                  | 50                | 44       | 28       | 1        | 647261.300 | 25                   | 500               | 62       | 4        | 1        | 900831.110 | -468                 | 300               |
| 29       | 14       | -1       | 432326.348 | 5                    | 50                | 31       | 5        | -1       | 461033.321 | 0                    | 50                | 44       | 2        | -1       | 647144.200 | 159                  | 500               | 62       | 2        | 1        | 900844.618 | 586                  | 500               |
| 29       | 17       | -1       | 432381.306 | 5                    | 50                | 31       | 6        | -1       | 461017.793 | 13                   | 50                | 44       | 3        | -1       | 647130.000 | 279                  | 500               | 62       | 3        | 1        | 900844.618 | 343                  | 500               |
| 29       | 20       | -1       | 432454.260 | 8                    | 50                | 31       | 8        | -1       | 461001.645 | -21                  | 50                | 44       | 4        | -1       | 647117.200 | 177                  | 500               | 62       | 6        | 1        | 900882.161 | -84                  | 300               |
| 29       | 23       | -1       | 432543.763 | -7                   | 50                | 31       | 11       | -1       | 461007.715 | -110                 | 200               | 44       | 5        | -1       | 647104.800 | 571                  | 600               | 62       | 10       | 1        | 901024.846 | -159                 | 300               |
| 29       | 26       | -1       | 432649.055 | -1                   | 50                | 31       | 14       | -1       | 461041.965 | -6                   | 50                | 44       | 6        | -1       | 647093.000 | 12                   | 500               | 62       | 31       | 1        | 902614.693 | 275                  | 500               |
| 29       | 29       | -1       | 432769.668 | 11                   | 50                | 31       | 17       | -1       | 461098.632 | 10                   | 50                | 44       | 8        | -1       | 647078.900 | 481                  | 500               | 62       | 3        | -1       | 902354.200 | 198                  | 500               |
| 31       | -1       | -1       | 460343.547 | -8                   | 50                | 31       | 20       | -1       | 461174.804 | -40                  | 50                | 53       | 1        | 1        | 775157.390 | -299                 | 500               | 62       | 5        | -1       | 902385.042 | -233                 | 300               |
| 31       | 1        | 1        | 461173.349 | -175                 | 200               | 31       | 23       | -1       | 461269.011 | -2                   | 50                | 53       | -4       | -1       | 773828.740 | -76                  | 500               | 62       | 6        | -1       | 902393.323 | -42                  | 300               |
| 31       | 2        | 1        | 460353.364 | 6                    | 50                | 31       | 26       | -1       | 461380.191 | -9                   | 50                | 53       | 7        | 1        | 773905.500 | 40                   | 500               | 62       | 7        | -1       | 902401.345 | -138                 | 300               |
| 31       | 3        | 1        | 460381.440 | -3                   | 50                | 43       | -1       | -1       | 631886.900 | 354                  | 500               | 53       | 16       | 1        | 774340.720 | 223                  | 500               | 62       | 8        | -1       | 902411.025 | -62                  | 300               |
| 31       | -4       | -1       | 460420.175 | 4                    | 50                | 43       | 3        | 1        | 631793.800 | 624                  | 500               | 53       | 25       | 1        | 774946.080 | 378                  | 500               | 62       | 11       | -1       | 902453.289 | -13                  | 300               |
| 31       | 4        | 1        | 460418.991 | -17                  | 50                | 43       | 4        | 1        | 631813.800 | 460                  | 500               | 53       | 28       | 1        | 775184.700 | -54                  | 500               | 62       | 14       | -1       | 902520.921 | 249                  | 300               |
| 31       | 6        | 1        | 460501.688 | -2                   | 50                | 43       | 5        | 1        | 631845.100 | 112                  | 500               | 53       | -2       | 1        | 775148.400 | -123                 | 500               | 62       | 17       | -1       | 902617.237 | 154                  | 300               |
| 31       | 7        | 1        | 460540.339 | -7                   | 50                | 43       | 7        | 1        | 631917.500 | 142                  | 500               | 53       | 2        | -1       | 775151.000 | 37                   | 500               |          |          |          |            |                      |                   |
| 31       | 10       | 1        | 460644.025 | -65                  | 100               | 43       | 10       | 1        | 632043.500 | 274                  | 500               | 53       | 4        | -1       | 775138.800 | -324                 | 500               |          |          |          |            |                      |                   |
| 31       | 13       | 1        | 460738.913 | -10                  | 50                | 44       | -1       | -1       | 645211.300 | 507                  | 500               | 53       | 5        | -1       | 775136.680 | -254                 | 500               |          |          |          |            |                      |                   |
| 31       | 16       | 1        | 460834.784 | 4                    | 50                | 44       | 1        | 1        | 647164.900 | -228                 | 500               | 53       | 6        | -1       | 775134.640 | -140                 | 500               |          |          |          |            |                      |                   |
| 31       | 19       | 1        | 460937.265 | -5                   | 50                | 44       | -4       | -1       | 646056.500 | 391                  | 600               | 53       | 8        | -1       | 775134.640 | -405                 | 500               |          |          |          |            |                      |                   |
| 31       | 22       | 1        | 461049.473 | -3                   | 50                | 44       | 4        | 1        | 646051.500 | 558                  | 600               | 53       | 11       | -1       | 775154.300 | 355                  | 500               |          |          |          |            |                      |                   |

<sup>a</sup>) residuals (in kHz) obtained using the Q reduction<sup>b</sup>) Experimental uncertainty (in kHz)

| 177 | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | <i>e.</i> – <i>c.</i> <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | <i>e.</i> – <i>c.</i> <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | <i>e.</i> – <i>c.</i> <sup>a</sup> | Unc. <sup>b</sup> | <i>J</i> | <i>k</i> | <i>l</i> | Exp.       | <i>e.</i> – <i>c.</i> <sup>a</sup> | Unc. <sup>b</sup> |
|-----|----------|----------|----------|------------|------------------------------------|-------------------|----------|----------|----------|------------|------------------------------------|-------------------|----------|----------|----------|------------|------------------------------------|-------------------|----------|----------|----------|------------|------------------------------------|-------------------|
|     | 6        | -1       | -1       | 100588.539 | -11                                | 100               | 15       | 7        | -1       | 230074.460 | 37                                 | 100               | 23       | 10       | 1        | 344886.682 | -38                                | 50                | 29       | 25       | 1        | 431214.031 | -14                                | 50                |
|     | 10       | -1       | -1       | 158044.180 | -5                                 | 100               | 15       | 8        | -1       | 230080.000 | 24                                 | 100               | 23       | 13       | 1        | 344931.257 | -10                                | 50                | 31       | -1       | -1       | 458905.029 | -35                                | 50                |
|     | 10       | 4        | -1       | 158210.710 | -247                               | 200               | 15       | 12       | -1       | 230111.020 | -12                                | 100               | 23       | 16       | 1        | 344985.221 | -23                                | 50                | 31       | 1        | 1        | 459781.200 | 35                                 | 50                |
|     | 10       | 5        | -1       | 158212.940 | -134                               | 200               | 15       | 13       | -1       | 230120.970 | 46                                 | 100               | 23       | 19       | 1        | 345049.393 | -27                                | 50                | 31       | 2        | -1       | 459509.500 | -19                                | 50                |
|     | 10       | 6        | -1       | 158215.800 | -60                                | 100               | 15       | 14       | -1       | 230131.690 | 41                                 | 100               | 23       | 0        | -1       | 344965.765 | 8                                  | 200               | 31       | -2       | 1        | 459453.611 | -76                                | 50                |
|     | 10       | 7        | -1       | 158219.230 | -42                                | 100               | 15       | 2        | 1        | 230012.420 | 159                                | 100               | 23       | -2       | 1        | 344883.663 | -151                               | 500               | 31       | 3        | -1       | 459438.177 | -27                                | 200               |
|     | 10       | 8        | -1       | 158223.190 | -97                                | 100               | 15       | 3        | 1        | 230033.290 | 36                                 | 100               | 23       | 3        | -1       | 344879.281 | 51                                 | 200               | 31       | 4        | -1       | 459430.863 | 177                                | 50                |
|     | 10       | 4        | 1        | 158203.810 | 93                                 | 200               | 15       | 4        | 1        | 230042.460 | 19                                 | 100               | 23       | 5        | -1       | 344879.281 | -156                               | 200               | 31       | 5        | -1       | 459428.855 | -16                                | 50                |
|     | 10       | 5        | 1        | 158207.240 | 32                                 | 100               | 15       | 7        | 1        | 230062.050 | 145                                | 200               | 23       | 6        | -1       | 344883.265 | 72                                 | 200               | 31       | 6        | -1       | 459430.863 | -232                               | 200               |
|     | 10       | 6        | 1        | 158210.710 | -115                               | 200               | 15       | 9        | 1        | 230076.200 | 10                                 | 100               | 23       | 8        | -1       | 344896.183 | -30                                | 50                | 31       | 8        | -1       | 459444.530 | -82                                | 50                |
|     | 10       | 7        | 1        | 158214.710 | -73                                | 100               | 15       | 10       | 1        | 230084.160 | -107                               | 100               | 23       | 11       | -1       | 344927.172 | -18                                | 50                | 31       | 9        | -1       | 459455.097 | 19                                 | 50                |
|     | 10       | 8        | 1        | 158219.190 | 18                                 | 200               | 15       | 13       | 1        | 230112.620 | -175                               | 100               | 23       | 14       | -1       | 344970.394 | 21                                 | 50                | 31       | 10       | -1       | 459467.572 | -134                               | 50                |
|     | 10       | 10       | 1        | 158229.170 | -238                               | 100               | 20       | 0        | -1       | 301907.671 | -53                                | 100               | 23       | 17       | -1       | 345025.168 | 65                                 | 50                | 31       | 11       | -1       | 459482.350 | -5                                 | 50                |
|     | 12       | -1       | -1       | 186761.020 | 91                                 | 100               | 20       | 3        | -1       | 301848.579 | -98                                | 200               | 29       | -1       | -1       | 430333.983 | -16                                | 50                | 31       | 14       | -1       | 459537.609 | 9                                  | 50                |
|     | 12       | 1        | 1        | 187137.710 | 91                                 | 100               | 20       | 4        | -1       | 301848.579 | -44                                | 200               | 29       | 0        | -1       | 430978.869 | -24                                | 50                | 31       | 17       | -1       | 459608.841 | 18                                 | 200               |
|     | 12       | 0        | -1       | 186970.270 | -7                                 | 100               | 20       | 5        | -1       | 301850.728 | 36                                 | 100               | 29       | 6        | -1       | 430823.918 | 106                                | 50                | 31       | 20       | -1       | 459695.439 | 41                                 | 50                |
|     | 12       | 3        | -1       | 186957.690 | 135                                | 100               | 20       | 6        | -1       | 301854.634 | 75                                 | 100               | 29       | 7        | -1       | 430829.426 | -6                                 | 50                | 31       | 23       | -1       | 459796.924 | -129                               | 50                |
|     | 12       | 4        | -1       | 186959.050 | 143                                | 100               | 20       | 7        | -1       | 301859.979 | 15                                 | 100               | 29       | 8        | -1       | 430837.456 | 1                                  | 50                | 31       | 29       | -1       | 460044.876 | -376                               | 250               |
|     | 12       | 5        | -1       | 186961.280 | 63                                 | 100               | 20       | 8        | -1       | 301866.646 | -105                               | 100               | 29       | 9        | -1       | 430847.714 | 94                                 | 50                | 31       | 2        | 1        | 459109.873 | 44                                 | 50                |
|     | 12       | 6        | -1       | 186964.280 | -90                                | 100               | 20       | 10       | -1       | 301884.101 | -17                                | 100               | 29       | 10       | -1       | 430859.752 | -1                                 | 50                | 31       | 3        | 1        | 459222.677 | 30                                 | 50                |
|     | 12       | 7        | -1       | 186968.200 | -97                                | 100               | 20       | 11       | -1       | 301894.614 | 20                                 | 100               | 29       | 11       | -1       | 430873.719 | -21                                | 50                | 31       | 4        | 1        | 459273.349 | 57                                 | 150               |
|     | 12       | 8        | -1       | 186972.960 | 2                                  | 100               | 20       | 3        | 1        | 301783.687 | 10                                 | 100               | 29       | 12       | -1       | 430889.357 | -142                               | 50                | 31       | 5        | 1        | 459304.179 | 12                                 | 50                |
|     | 12       | 9        | -1       | 186978.300 | -29                                | 100               | 20       | 4        | 1        | 301801.537 | 4                                  | 100               | 29       | 13       | -1       | 430907.011 | 36                                 | 50                | 31       | 6        | 1        | 459327.352 | 24                                 | 50                |
|     | 12       | 2        | 1        | 186929.470 | -39                                | 100               | 20       | 7        | 1        | 301833.056 | 73                                 | 100               | 29       | 14       | -1       | 430926.145 | 21                                 | 50                | 31       | 7        | 1        | 459347.314 | 26                                 | 50                |
|     | 12       | 3        | 1        | 186941.390 | -94                                | 100               | 20       | 8        | 1        | 301842.977 | 161                                | 200               | 29       | 20       | -1       | 431074.909 | 33                                 | 50                | 31       | 8        | 1        | 459366.049 | -7                                 | 50                |
|     | 12       | 4        | 1        | 186947.220 | 25                                 | 200               | 20       | 11       | 1        | 301876.113 | -27                                | 100               | 29       | 23       | -1       | 431170.588 | 80                                 | 50                | 31       | 9        | 1        | 459384.661 | 0                                  | 50                |
|     | 12       | 6        | 1        | 186956.490 | 110                                | 200               | 20       | 12       | 1        | 301889.052 | 148                                | 200               | 29       | 4        | 1        | 430690.927 | 328                                | 250               | 31       | 11       | 1        | 459423.499 | 25                                 | 50                |
|     | 12       | 7        | 1        | 186961.280 | 28                                 | 100               | 20       | 13       | 1        | 301902.601 | 8                                  | 100               | 29       | 5        | 1        | 430717.195 | 31                                 | 50                | 31       | 13       | 1        | 459466.167 | -23                                | 50                |
|     | 12       | 8        | 1        | 186966.670 | 94                                 | 100               | 20       | 14       | 1        | 301917.198 | -41                                | 100               | 29       | 6        | 1        | 430737.391 | 11                                 | 50                | 31       | 14       | 1        | 459489.362 | -11                                | 50                |
|     | 12       | 9        | 1        | 186972.350 | -79                                | 200               | 20       | 15       | 1        | 301932.859 | -5                                 | 100               | 29       | 7        | 1        | 430755.062 | -14                                | 50                | 31       | 15       | 1        | 459513.864 | -21                                | 50                |
|     | 12       | 10       | 1        | 186978.850 | -3                                 | 200               | 23       | -1       | -1       | 344498.564 | 44                                 | 50                | 29       | 8        | 1        | 430771.954 | 10                                 | 50                | 31       | 22       | 1        | 459726.137 | -53                                | 200               |
|     | 15       | -1       | -1       | 229818.026 | -141                               | 100               | 23       | 1        | 1        | 345162.012 | -49                                | 50                | 29       | 10       | 1        | 430806.300 | 36                                 | 50                | 31       | 25       | 1        | 459840.221 | -21                                | 50                |
|     | 15       | 1        | 1        | 230279.720 | 27                                 | 100               | 23       | 2        | 1        | 344722.878 | -105                               | 50                | 29       | 11       | 1        | 430824.402 | -91                                | 200               |          |          |          |            |                                    |                   |
|     | 15       | 0        | -1       | 230088.240 | 62                                 | 100               | 23       | 3        | 1        | 344783.730 | 0                                  | 50                | 29       | 13       | 1        | 430864.028 | -47                                | 50                |          |          |          |            |                                    |                   |
|     | 15       | 2        | -1       | 230067.610 | 2                                  | 250               | 23       | 4        | 1        | 344808.706 | 11                                 | 50                | 29       | 15       | 1        | 430908.453 | -34                                | 50                |          |          |          |            |                                    |                   |
|     | 15       | 3        | -1       | 230062.780 | 49                                 | 200               | 23       | 5        | 1        | 344824.604 | 10                                 | 50                | 29       | 16       | 1        | 430932.596 | -62                                | 200               |          |          |          |            |                                    |                   |
|     | 15       | 4        | -1       | 230063.860 | 37                                 | 100               | 23       | 7        | 1        | 344849.464 | 52                                 | 200               | 29       | 17       | 1        | 430958.109 | -82                                | 50                |          |          |          |            |                                    |                   |
|     | 15       | 5        | -1       | 230066.270 | 21                                 | 100               | 23       | 8        | 1        | 344861.354 | 24                                 | 50                | 29       | 19       | 1        | 431013.421 | -30                                | 50                |          |          |          |            |                                    |                   |
|     | 15       | 6        | -1       | 230069.720 | -103                               | 100               | 23       | 9        | 1        | 344873.700 | 20                                 | 50                | 29       | 22       | 1        | 431107.313 | 194                                | 50                |          |          |          |            |                                    |                   |

<sup>a)</sup> residuals (in kHz) obtained using the Q reduction

<sup>b)</sup> Experimental uncertainty (in kHz)

Table 6. Molecular constants of  $^{28}\text{SiHF}_3$ ,  $^{29}\text{SiHF}_3$  and  $^{30}\text{SiHF}_3$  in the vibrational ground state.

|                           |       | $^{28}\text{SiHF}_3$ | $^{29}\text{SiHF}_3$ | $^{30}\text{SiHF}_3$ |
|---------------------------|-------|----------------------|----------------------|----------------------|
| $B$                       | (MHz) | 7208.05434 (23)      | 7195.7531 (44)       | 7183.7943 (60)       |
| $D_J$                     | (kHz) | 7.57428 (21)         | 7.5223 (69)          | 7.4729 (93)          |
| $D_{JK}$                  | (kHz) | - 12.55120 (10)      | - 12.450 (12)        | - 12.354 (15)        |
| $H_J$                     | (Hz)  | 0.022578 (61)        | 0.0230 (35)          | 0.0237 (46)          |
| $H_{JK}$                  | (Hz)  | - 0.08377 (11)       | - 0.0853 (73)        | - 0.0856 (97)        |
| $H_{KJ}$                  | (Hz)  | 0.1010 (57)          | 0.1069 (75)          | 0.1067 (96)          |
| $L_J$                     | (mHz) | - 0.0000749 (55)     |                      |                      |
| $ h_{3,\text{GS}} $       | (mHz) | 1.1032 (70)          |                      |                      |
| $C^{\text{a}}$            | (MHz) | 4134.73 (71)         |                      |                      |
| $C^{\text{b}}$            | (MHz) | 4134.1554 (49)       |                      |                      |
| $D_K$                     | (kHz) | 5.78 <sup>c</sup>    |                      |                      |
| $H_K$                     | (Hz)  | - 0.045 <sup>c</sup> |                      |                      |
| No.                       |       | 178                  | 104                  | 85                   |
| lines                     |       |                      |                      |                      |
| $J_{\text{max}}$          |       | 73                   | 31                   | 29                   |
| $\sigma (MM)^{\text{d}}$  | (kHz) | 22                   | 24                   | 41                   |
| $\sigma (FIR)^{\text{d}}$ | (kHz) | 179                  |                      |                      |

<sup>a)</sup> (13)

<sup>b)</sup> This work : the value is an average value of those obtained using the reductions Q, D and QD.

<sup>c)</sup> Constrained to the value calculated from the harmonic force field (9).

<sup>d)</sup> Standard deviation for the millimeter (MM) and the far infrared (FIR) data set.

Table 7 : Molecular Parameters of  $^{28}\text{SiHF}_3$  in the  $\nu_6 = 1$  state

|                 |                      | Reduction Q       | Reduction D       | Reduction QD      |
|-----------------|----------------------|-------------------|-------------------|-------------------|
| $\nu_6$         | ( $\text{cm}^{-1}$ ) | 305.455402 (29)   | 305.455403 (29)   | 305.455402 (31)   |
| $B$             | (MHz)                | 7214.87375 (26)   | 7214.87004 (26)   | 7214.87376 (28)   |
| $C$             | (MHz)                | 4130.34641 (63)   | 4130.35353 (62)   | 4130.34691 (66)   |
| $D_J$           | (kHz)                | 7.60603 (20)      | 7.60603 (20)      | 7.60598 (22)      |
| $D_{JK}$        | (kHz)                | - 12.67308 (62)   | - 12.67325 (61)   | - 12.67254 (66)   |
| $D_K$           | (kHz)                | 5.8723 (22)       | 5.8727 (22)       | 5.8719 (23)       |
| $H_J$           | (Hz)                 | 0.022227 (36)     | 0.022231 (36)     | 0.016421 (38)     |
| $H_{JK}$        | (Hz)                 | - 0.08649 (28)    | - 0.08648 (27)    | - 0.03412 (29)    |
| $H_{KJ}$        | (Hz)                 | 0.10957 (55)      | 0.10951 (54)      | 0.02211 (58)      |
| $H_K$           | (Hz)                 | - 0.04759 (54)    | - 0.04753 (53)    | - 0.00668 (57)    |
| $C\zeta$        | (MHz)                | - 2345.46886 (55) | - 2345.47104 (54) | - 2345.46837 (58) |
| $\eta_J$        | (kHz)                | - 33.8880 (12)    | - 41.3198 (12)    | - 33.8878 (13)    |
| $\eta_K$        | (kHz)                | 31.4553 (90)      | 38.8865 (88)      | 31.4556 (95)      |
| $\tau_J$        | (Hz)                 | - 0.29180 (56)    | - 0.19763 (55)    | - 0.26551 (59)    |
| $\tau_{JK}$     | (Hz)                 | 0.5006 (34)       | 0.4387 (33)       | 0.4473 (36)       |
| $\tau_K$        | (Hz)                 | - 0.1364 (57)     | - 0.1654 (56)     | - 0.1126 (60)     |
| $\sigma_J$      | (mHz)                | 0.011537 (70)     | 0.011270 (69)     | 0.011599 (73)     |
| $\sigma_{JK}$   | (mHz)                | - 0.0235 (16)     | -0.0242 (16)      | - 0.0228 (17)     |
| $q_{22}$        | (MHz)                | - 3.29296664 (13) | - 3.29296369 (12) | - 3.29296669 (13) |
| $f_{22}^J$      | (Hz)                 | 23.88951 (19)     | 22.31635 (19)     | 23.88966 (20)     |
| $f_{22}^{JJ}$   | (mHz)                | - 0.136464 (67)   | - 0.121047 (68)   | - 0.135322 (71)   |
| $f_{42}$        | (Hz)                 | - 3.57229 (12)    | - 5.14565 (13)    | - 3.57224 (13)    |
| $f_{42}^J$      | (mHz)                | 0.022825 (79)     | 0.038333 (80)     | 0.023984 (83)     |
| $d$             | (kHz)                | - 4.552390 (30)   | 0. <sup>a</sup>   | 0. <sup>a</sup>   |
| $d_J$           | (Hz)                 | 0.035253 (17)     | 0. <sup>a</sup>   | 0. <sup>a</sup>   |
| $q_{12}$        | (MHz)                | 0. <sup>a</sup>   | 2.687534 (18)     | 0. <sup>a</sup>   |
| $f_{12}^J$      | (Hz)                 | 0. <sup>a</sup>   | - 23.1929 (99)    | 0. <sup>a</sup>   |
| $\varepsilon$   | (kHz)                | 0. <sup>a</sup>   | 0. <sup>a</sup>   | - 2.993041 (21)   |
| $\varepsilon_J$ | (mHz)                | 0. <sup>a</sup>   | 0. <sup>a</sup>   | 6.191 (12)        |
| $h_3$           | (mHz)                | - 1.1800 (17)     | - 1.1773 (17)     | - 4.0891 (18)     |
| $h_{3J}$        | (mHz)                | 0.0000221 (10)    | 0.0000205 (10)    | 0.0000253 (11)    |
| $C_0$           | (MHz)                | 4134.1554 (28)    | 4134.1552 (27)    | 4134.1557 (29)    |

<sup>a</sup>) Constrained value. <sup>b</sup>) Standard deviation for radiofrequency (RF),microwave (MW), millimeter (MM) and infrared (IR) data sets

Table 7 - *Continued*

|                     |                      | Reduction Q          | Reduction D          | Reduction QD         |
|---------------------|----------------------|----------------------|----------------------|----------------------|
| $\sigma(\text{RF})$ | (kHz)                | 25                   | 24                   | 26                   |
| $\sigma(\text{MW})$ | (kHz)                | 0.6                  | 0.6                  | 0.7                  |
| $\sigma(\text{MM})$ | (kHz)                | 34                   | 33                   | 35                   |
| $\sigma(\text{IR})$ | ( $\text{cm}^{-1}$ ) | $3.7 \times 10^{-4}$ | $3.7 \times 10^{-4}$ | $3.7 \times 10^{-4}$ |

Table 8 : Molecular Parameters of  $^{28}\text{SiHF}_3$  in the  $\nu_4 = 1$  state

|                       |                     | Reduction Q           | Reduction D           | Reduction QD    | Harada <i>et al.</i> <sup>a</sup> |
|-----------------------|---------------------|-----------------------|-----------------------|-----------------|-----------------------------------|
| $\nu_4$               | (cm <sup>-1</sup> ) | 999.5810826 (96)      | 999.5810792 (96)      | 999.581079 (10) | 999.581076 (30)                   |
| $B$                   | (MHz)               | 7192.91485 (38)       | 7192.93646 (39)       | 7192.91574 (40) | 7192.9252 (64)                    |
| $C$                   | (MHz)               | 4124.9618 (15)        | 4124.9189 (15)        | 4124.9543 (16)  | 4125.48 (71)                      |
| $D_J$                 | (kHz)               | 7.56151 (33)          | 7.56154 (33)          | 7.56308 (42)    | 7.575 (26)                        |
| $D_{JK}$              | (kHz)               | - 12.54797 (92)       | - 12.54817 (92)       | - 12.5497 (21)  | - 12.62 (16)                      |
| $D_K$                 | (kHz)               | 5.7934 (16)           | 5.7937 (16)           | 5.7904 (23)     | 5.90 (24)                         |
| $H_J$                 | (Hz)                | 0.02232 (11)          | 0.02230 (11)          | - 0.13366 (37)  |                                   |
| $H_{JK}$              | (Hz)                | - 0.08437 (65)        | - 0.08420 (65)        | 1.3291 (32)     |                                   |
| $H_{KJ}$              | (Hz)                | 0.1019 (12)           | 0.1015 (12)           | - 2.2659 (50)   |                                   |
| $H_K$                 | (Hz)                | - 0.04302 (72)        | - 0.04275 (72)        | 1.0646 (22)     |                                   |
| $C\zeta$              | (MHz)               | 2445.113 (12)         | 2445.119 (12)         | 2445.112 (12)   | 2445.59 (71)                      |
| $\eta_J$              | (kHz)               | - 7.250 (13)          | 35.945 (64)           | - 7.264 (14)    | 6.8 (10)                          |
| $\eta_K$              | (kHz)               | 6.613 (37)            | - 36.595 (72)         | 6.639 (39)      | - 8.4 (16)                        |
| $\tau_J$              | (Hz)                | - 0.2010 (73)         | - 0.0953 (75)         | - 0.9669 (81)   |                                   |
| $\tau_{JK}$           | (Hz)                | 0.529 (21)            | 0.275 (21)            | 2.089 (22)      |                                   |
| $\tau_K$              | (Hz)                | - 0.307 (16)          | - 0.155 (16)          | - 1.090 (17)    |                                   |
| $q_{22}$              | (MHz)               | - 3.64704 (43)        | - 3.64855 (44)        | - 3.64765 (46)  | - 3.6273 (63)                     |
| $f_{22}^J$            | (Hz)                | 72.04 (28)            | 31.20 (26)            | 74.56 (30)      |                                   |
| $f_{42}$              | (Hz)                | 69.67 (16)            | 28.062 (81)           | 71.83 (18)      |                                   |
| $d$                   | (kHz)               | 25.128 (27)           | 0. <sup>b</sup>       | 0. <sup>b</sup> |                                   |
| $d_J$                 | (Hz)                | - 0.649 (28)          | 0. <sup>b</sup>       | 0. <sup>b</sup> |                                   |
| $q_{12}$              | (MHz)               | 0. <sup>b</sup>       | 3.1370 (22)           | 0. <sup>b</sup> | 1.779 (58)                        |
| $\varepsilon$         | (kHz)               | 0. <sup>b</sup>       | 0. <sup>b</sup>       | - 15.568 (13)   |                                   |
| $\varepsilon_J$       | (mHz)               | 0. <sup>b</sup>       | 0. <sup>b</sup>       | 47.0 (34)       |                                   |
| $h_3$                 | (mHz)               | - 1.1032 <sup>c</sup> | - 1.1032 <sup>c</sup> | - 83.36 (60)    |                                   |
| $\sigma(\text{MM})$ d | (kHz)               | 66                    | 66                    | 91              |                                   |
| $\sigma(\text{IR})$ d | (cm-1)              | 2.8 x 10-4            | 2.8 x 10-4            | 3.0 x 10-4      |                                   |

<sup>a</sup>) reference (13). The value of  $q_{22}$  has been divided by a factor (-4) for a better comparison. <sup>b</sup>) constrained value. <sup>c</sup>) constrained to the ground state value (see text). <sup>d</sup>) Standard deviation for millimeter (MM) and infrared (IR) data sets.

Table 9 : Demonstration of the unitary equivalence of the parameter sets determined within the Q and D reductions

| Equation |                                                            | $\nu_6 = 1$           | $\nu_4 = 1$   |
|----------|------------------------------------------------------------|-----------------------|---------------|
| [9]      | $q_{12}^D \text{ exp}$                                     | (MHz) 2.687534 (18)   | 3.1370 (22)   |
|          | $-\frac{F d^Q}{4 q_{22}}$                                  | (MHz) 2.687324 (18)   | 3.1389 (34)   |
| [10]     | $\eta_J^D - \eta_J^Q$                                      | (kHz) - 7.4318 (17)   | 43.195 (65)   |
|          | $-(\eta_K^D - \eta_K^Q)$                                   | (kHz) - 7.431 (13)    | 43.208 (81)   |
|          | $\frac{8 (q_{12}^D)^2}{F}$                                 | (kHz) - 7.431420 (99) | 43.202 (62)   |
|          | $\frac{F (d^Q)^2}{2 q_{22}^2}$                             | (kHz) - 7.430227 (99) | 43.252 (93)   |
| [11]     | $\eta_J^Q + \eta_K^Q$                                      | (kHz) - 2.4327 (91)   | - 0.637 (39)  |
|          | $\eta_J^D + \eta_K^D$                                      | (kHz) - 2.4333 (89)   | - 0.650 (96)  |
| [12]     | $\tau_J^Q + \tau_{JK}^Q + \tau_K^Q$                        | (Hz) 0.0724 (66)      | 0.021 (26)    |
|          | $\tau_J^D + \tau_{JK}^D + \tau_K^D$                        | (Hz) 0.0757 (65)      | 0.025 (26)    |
| [13]     | $(\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q)$            | (Hz) 0.1232 (80)      | - 0.046 (25)  |
|          | $((\tau_J^D - \tau_J^Q) - (\tau_K^D - \tau_K^Q))_{calc}^a$ | (Hz) 0.125053 (55)    | - 0.038 (12)  |
| [14]     | $f_{42}^D - f_{42}^Q$                                      | (Hz) - 1.57336 (18)   | - 41.60 (18)  |
|          | $f_{22}^{J,D} - f_{22}^{J,Q}$                              | (Hz) - 1.57316 (27)   | - 40.84 (38)  |
|          | $\frac{4 q_{22} (q_{12}^D)^2}{F^2}$                        | (Hz) - 1.573628 (21)  | - 43.235 (61) |
|          | $\frac{(d^Q)^2}{4 q_{22}}$                                 | (Hz) - 1.573376 (63)  | - 43.283 (26) |
|          |                                                            |                       |               |

<sup>a)</sup> Calculated according the right-hand side of Eq. [13]

Table 10 : Demonstration of the equivalence of the parameter sets determined within the Q and QD reductions

|        | Equation                                                                   |       | $\nu_6 = 1$     | $\nu_4 = 1$           |
|--------|----------------------------------------------------------------------------|-------|-----------------|-----------------------|
| [ 15 ] | $\varepsilon^{QD}$                                                         | (kHz) | - 2.993041 (21) | - 15.568 (13)         |
|        | $d^Q \frac{(C-B)}{2 C \zeta}$                                              | (kHz) | - 2.993426 (20) | - 15.764 (17)         |
| [ 16 ] | $(H_J^{QD} - H_J^Q)$                                                       | (mHz) | - 5.806 (52)    | - 155.98 (39)         |
|        | $-\frac{1}{9}(H_{JK}^{QD} - H_{JK}^Q)$                                     | (mHz) | - 5.819 (45)    | - 157.05 (36)         |
|        | $\frac{1}{15}(H_{KJ}^{QD} - H_{KJ}^Q)$                                     | (mHz) | - 5.831 (53)    | - 157.85 (34)         |
|        | $-\frac{1}{7}(H_K^{QD} - H_K^Q)$                                           | (mHz) | - 5.84 (11)     | - 158.23 (33)         |
|        | $2(h_3^{QD} - h_3^Q)$                                                      | (mHz) | - 5.8182 (49)   | - 164.51 <sup>a</sup> |
|        | $\frac{2(\varepsilon^{QD})^2}{(C-B)}$                                      | (mHz) | - 5.808536 (82) | - 157.99 (26)         |
| [ 17 ] | $\tau_J^{QD} - \tau_J^Q$                                                   | (Hz)  | 0.02629 (81)    | - 0.766 (11)          |
|        | $-\frac{1}{2}(\tau_{JK}^{QD} - \tau_{JK}^Q)$                               | (Hz)  | 0.0267 (25)     | - 0.780 (15)          |
|        | $\tau_K^{QD} - \tau_K^Q$                                                   | (Hz)  | 0.0238 (83)     | - 0.783 (23)          |
|        | $-12 \frac{\varepsilon^{QD}}{C-B} \sqrt{\frac{C}{B}} C \zeta$ <sup>b</sup> | (Hz)  | 0.02650080 (19) | - 0.7555 (13)         |

<sup>a)</sup>  $h_3^Q$  constrained to the ground state value ; see text.

<sup>b)</sup> Eq. [17] is only valid when the constraint is  $f_{22}^\Lambda = 0$ .

Figure 1. Microwave spectrum of  $^{28}\text{SiHF}_3$  in the range of 9013 – 9090 MHz.

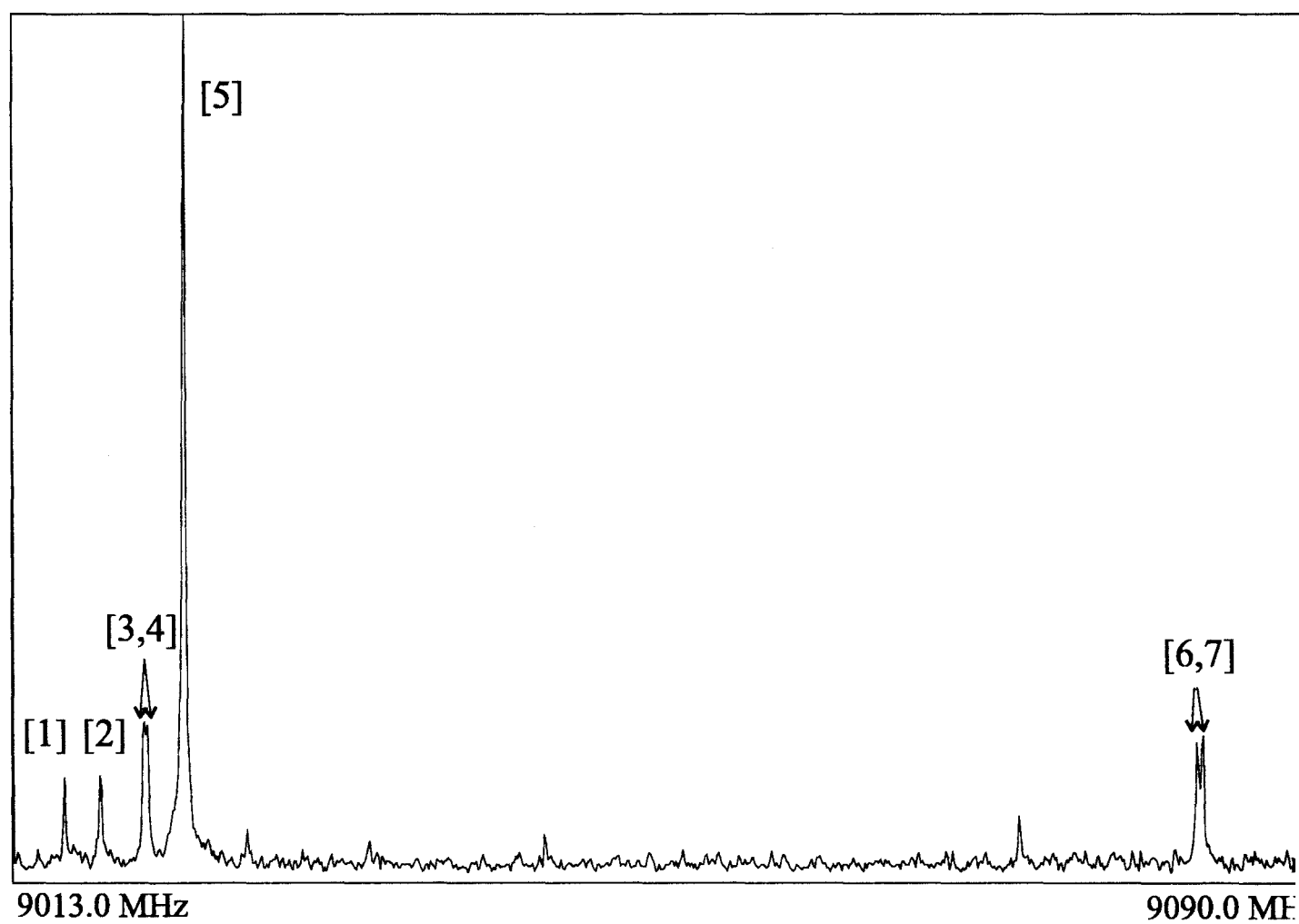
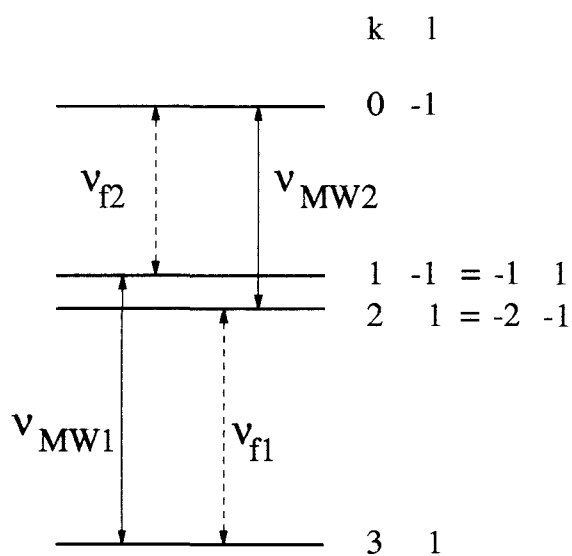


Figure 2: Closed loops ( $v_6=1$ ,  $^{28}\text{SiHF}_3$ , observable for  $J=24-26$ ) and Ritz'combination principle.



J=25 (p=0.5 Pa, T=210 K):

$$\nu_{\text{MW1}} = 10353.845(1) \text{ MHz}$$

$$\nu_{\text{MW2}} = 9023.264 (1) \text{ MHz}$$

$$\nu_{f1} = 9882.560(16) \text{ MHz}$$

$$\nu_{f2} = 8551.974(7) \text{ MHz}$$

**Ritz' combination principle:**

$$\mathbf{v}_{\text{MW1}} + \mathbf{v}_{\text{f2}} = \mathbf{v}_{\text{f1}} + \mathbf{v}_{\text{MW2}}$$

$$18905.819(8) \text{ MHz} = 18905.824(16) \text{ MHz}$$



# Calcul du champ de force et applications

## I) Déterminations des paramètres moléculaires du trifluorosilane

Nous avons plusieurs intérêts dans le calcul du champ de force *ab initio* du trifluorosilane :

- tout d'abord estimer la précision des calculs théoriques pour cette molécule relativement peu favorable du point de vue *ab initio*, car il y a un atome de la 2<sup>ème</sup> ligne (Si) et des atomes de fluor très électronégatifs, ce qui nécessite des bases très importantes.

Le champ de force est calculé au niveau MP2/cc-pVTZ+1, ce qui est relativement modeste comparativement au niveau nécessaire pour déterminer une structure précise. Nous avons comparé les constantes calculées avec celles que nous avons obtenues expérimentalement : les fréquences de vibration sont obtenues avec une erreur inférieure à 2%, et l'erreur maximale pour les constantes de distorsion est de 6.8 % pour  $H_{KL}$ .

- Le deuxième objectif de cette étude était la vérification de la théorie des réductions, car jusqu'alors les relations de passage entre les différentes réductions utilisées ont bien été vérifiées expérimentalement. Mais il restait à confirmer que les relations entre les paramètres déterminables (réduits) et ceux reliés aux constantes de force (non réduits) sont elles aussi correctes. SiHF<sub>3</sub> est une molécule adéquate pour ce test car son état de vibration le plus bas ( $v_6 = 1$ ) est très bien isolé des autres. Les paramètres réduits, pour l'état  $v_6 = 1$  de SiHF<sub>3</sub> et SiDF<sub>3</sub>, obtenus expérimentalement et calculés à partir des constantes de force présentent des écarts maximums de 6%.

- Le dernier objectif était de déduire une structure à l'équilibre fiable par la combinaison des moments d'inertie expérimentaux et des constantes d'interaction de ro-vibration obtenues à l'aide du champ de force anharmonique. Pour estimer la précision de cette structure, nous l'avons comparée avec des calculs au niveau MP2/cc-pVQZ+1. Mais pour ce niveau déjà élevé nous n'avons pas encore atteint la convergence, nous avons donc établi des offsets sur des molécules similaires : SiF<sub>2</sub> et SiH<sub>4</sub> avec ce même niveau de calcul. Nous l'avons fait à l'aide de calculs en cœur-gelé et d'autres où tous les électrons sont corrélés, pour s'assurer de la qualité des offsets.

## II) Structure à l'équilibre de SiF<sub>4</sub>

Lors de la détermination de la structure de SiHF<sub>3</sub> nous nous sommes aperçus que la structure de SiF<sub>4</sub> n'était pas fiable bien que plusieurs études aient déjà été consacrées à la détermination de la structure de cette molécule tétraédrique (symétrie T<sub>d</sub>). Il n'y a donc qu'une longueur de liaison à calculer.

Nous avons calculé une structure à partir des données expérimentales existantes en appliquant plusieurs méthodes. Puis nous avons comparé ces structures à celles obtenues à l'aide de calculs *ab initio* effectués aux niveaux CCSD(T) et MP2 avec une base quadruple zéta. Les résultats sont en bon accord et nous permettent donc de donner une nouvelle structure avec une précision de 0.001 Å.

*Ab initio* anharmonic force field, spectroscopic  
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# ***Ab initio* anharmonic force field, spectroscopic parameters and equilibrium structure of trifluorosilane**

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The quadratic, cubic and semidiagonal quartic force field of trifluorosilane has been calculated at the MP2 level of theory employing a basis set of polarized valence triple-zeta quality. This force field has been used to predict the spectroscopic constants, including the parameters specific of the double degenerate vibrational states. The calculated values are found to be in good agreement with the available experimental data, and explanations are offered for discrepancies. This confirms the accuracy of the *ab initio* force field and the validity of the theory of the reduction of the rovibrational Hamiltonian of a doubly degenerate vibrational state. The equilibrium structure has been derived from the experimental rotational constants and the *ab initio* rovibrational interaction parameters. This semiexperimental structure is in excellent agreement with the *ab initio* equilibrium geometry.

## **1. Introduction**

Rotational spectra of symmetric top molecules in excited doubly degenerate vibrational states are complicated by various interactions. In this case, the problems of different reductions of the effective Hamiltonians are extremely important and have started to be understood only recently [1]. In 1994 the concept of multiple fit has been introduced: highly precise data from different spectroscopies (Fourier transform microwave, submillimetrewave, high resolution Fourier transform infrared, laser ...) on the rovibrational transitions involving a doubly degenerate fundamental vibrational level of molecules of  $C_{3v}$  symmetry are fitted by using two different reductions of the Hamiltonian called reduced Q (all the coefficients of the '2, -1' interaction are constrained to zero, i.e.,  $q_{12} = 0$ , etc.) and reduction D (all the coefficients of the '0,  $\pm 3$ ' interaction are constrained to zero, i.e.,  $d = 0$  etc.). It appeared, in agreement with theory, that some parameters are strongly dependent on the reduction used (for instance  $\eta_J$  and  $\eta_K$ , besides  $q_{12}$  and  $d$ ). It was established that the 'true' parameters (i.e., the unreduced parameters which are expressed as a function of the force field) cannot be obtained from the experiment, but only certain combinations of them. It was also

proved that certain relations predicted from theory are satisfied by the coefficients of the Q and D reductions. Perfect agreement was obtained between theory and experiment for all the molecules studied so far. Nevertheless the fulfilment of these relations does not necessarily give confidence in the parameters determined. They could still be fitting parameters without a clear relation to the force field of the molecule. It is very desirable to check this point because if the experimental parameters were not too complicated functions of the molecular force field, they could be used advantageously to improve the accuracy of the geometry and force field of the molecule. Actually they furnish supplementary data to determine the force field and, particularly, these parameters are not affected by potential resonances provided the excited state is well isolated. This last point is extremely important because the lowest excited state of a symmetric  $C_{3v}$  molecule is usually a doubly degenerate one which furthermore is well isolated. At this point, it is important to emphasize that most molecular parameters depend not only on the harmonic part of the force field but also the anharmonic part (cubic and quartic for some parameters).

Another reason why it is desirable to determine a force field at least up to cubic terms is that a true experimental equilibrium structure is difficult to obtain for polyatomic molecules with more than three atoms,

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because the rotational constants of the vibrational ground state ( $A_0, B_0, C_0$ ) are different from those of the hypothetical vibrationless equilibrium configuration ( $A_e, B_e, C_e$ ). In principle, it is possible to obtain the equilibrium constants if the rotational constants for all the first vibrationally excited states can be determined. This has to be done for each isotopic species. This is a tedious task which is complicated further by the fact that often interactions (anharmonic resonances, Coriolis interactions, etc.) occur between these vibrational states and make their analysis more difficult. Furthermore, when all the anharmonic perturbations are not taken into account properly, inherently wrong parameters are obtained. Particularly, the correct determination of equilibrium rotational constants assumes that there is no anharmonic resonance between the vibrationally excited states. Although such resonances can be analysed and unperturbed rotational constants can be derived, often this is a time-consuming task requiring the study of many overtone and combination levels [2]. Actually, to avoid the difficult problem of analysing the anharmonic resonances, the best method is to determine first the cubic force field, which then is used to calculate the vibrational corrections. This also makes unnecessary the analysis of the excited states of rare isotopomers that are used to enlarge the body of ground state data. This method was advocated by Hoy, Mills and Strey [3] and then extensively used by Botschwina *et al.* [4, 5], who showed that it is possible to obtain reliable equilibrium rotational constants by correcting the experimental ground state rotational constants with *ab initio* vibration-rotation interaction constants ( $\alpha$  constants).

Currently, the most accurate force fields are obtained with the help of quantum chemical calculations which are able to furnish, with good accuracy, the cubic and quartic force constants [6–8]. Actually, the anharmonic force constants can be calculated to higher precision than geometries or quadratic force constants because, for the higher order force constants, the contribution of the derivatives of the nuclear-nuclear repulsion terms (which may be calculated accurately once the structure is known) becomes increasingly dominant [8]. The problem is that the accuracy of the calculated *ab initio* force field may be still sensitive to the method and the basis set used. If an equilibrium structure is determined with this method, it is important to estimate its accuracy, either directly, by determining the structure in an independent way, or indirectly, by comparing experimental parameters with those calculated from the force field.

The choice of the molecule to be studied by this method is an important factor of success. It must be simple enough to be amenable to high level *ab initio* calculations and, particularly, as many basic experi-

mental data as possible should be available. For these two reasons, the molecule of trifluorosilane, SiHF<sub>3</sub>, was chosen. Although it is not the simplest molecule from the *ab initio* point of view, it is very favourable experimentally for at least four reasons: (i) almost all the fundamental excited states are populated enough so that their rotational spectra are observable; (ii) all the vibrations are observable in the high resolution infrared spectrum; (iii) the lowest states are relatively free from perturbations so that most of the derived parameters are not significantly perturbed; and (iv) it is an oblate molecule, so that the parameters of the off-diagonal elements are easily determinable, as well as the axial rotational constant.

Actually, only a few papers have dealt with the rotation-vibration spectroscopy of trifluorosilane. In the most recent microwave work done in 1973, Hoy *et al.* measured the  $J = 2 \leftarrow 1$  transitions in the ground state and in five of the six fundamental excited states of SiHF<sub>3</sub> and SiDF<sub>3</sub>. They also refined the harmonic and cubic force fields using their experimental data together with earlier infrared data from Newman *et al.* [10] and Bürger *et al.* [11]. Finally, they also determined an equilibrium structure. Harada *et al.* measured laser Stark spectra of the  $\nu_4$  band both in SiHF<sub>3</sub> [13] and SiDF<sub>3</sub> [13]. Recently, we started to measure and analyse the spectra of all fundamental states of both SiHF<sub>3</sub> and SiDF<sub>3</sub> from microwave up to far-, mid-, and near-infrared range. The results for SiDF<sub>3</sub>  $\nu_4 = 1$  are in [14] and for  $\nu_6 = 1$  are in [15], and the analysis of the other states is largely completed.

## 2. Methods of computation

All quantum chemical calculations were carried out at the correlated level of second-order Møller-Plesset perturbation theory (MP2) [16] using the Gaussian94 program [17].

The correlation-consistent polarized valence basis sets (cc-pVXZ) [18, 19] were used throughout, supplemented as suggested recently [20] to take into account core polarization effects in the case of second-row atoms. Specifically, four different basis sets were employed: the first one (denoted as VTZ + 1) is derived from the triple-zeta cc-pVTZ basis [18, 19] by adding a single set of d functions for Si [20] whose exponent equals the highest d exponent in the corresponding cc-pV5Z basis [21]. Analogously, the second basis (VQZ + 1) is obtained from the quadruple-zeta cc-pVQZ basis set [18, 19] by adding the same set of high exponent d functions for Si [20, 21]. Furthermore, two basis sets of intermediate size were employed which are designated by the acronyms VTZ + 1(Q) and V(Q,T)Z + 1, respectively. VTZ + 1(Q) is formed from the first basis (VTZ + 1) by replacing the cc-pVTZ set at the central atom (Si)

Table 1. Computed and experimental equilibrium geometries of SiHF<sub>3</sub>.<sup>a</sup>

| Basis <sup>b</sup>            | r(SiH)       | r(SiF)       | ∠HSiF        | ∠FSiF               |
|-------------------------------|--------------|--------------|--------------|---------------------|
| VTZ + 1                       | 1.445 1      | 1.570 5      | 110.48       | 108.44              |
| VTZ + 1(Q)                    | 1.442 9      | 1.565 3      | 110.52       | 108.40              |
| V(Q, T)Z + 1                  | 1.442 5      | 1.565 1      | 110.55       | 108.37              |
| VQZ + 1                       | 1.437 6      | 1.565 0      | 110.53       | 108.39              |
| VTZ + 1(fc)                   | 1.450 2      | 1.574 8      | 110.49       | 108.43              |
| VQZ + 1(fc)                   | 1.450 7      | 1.573 7      | 110.57       | 108.35              |
| Corrected <sup>c</sup>        | 1.450 5      | 1.562 0      | 110.53       | 108.39              |
| Corrected (fc) <sup>c</sup>   | 1.450 4      | 1.563 0      | 110.57       | 108.35              |
| Exp. [9]                      | 1.446 8 (5)  | 1.562 4 (1)  | 110.64 (3)   | 108.28 <sup>d</sup> |
| Exp. (this work) <sup>e</sup> | 1.448 72 (3) | 1.562 66 (1) | 110.6884 (4) | 108.2271 (4)        |

<sup>a</sup> Bond lengths in Å, bond angles in deg.

<sup>b</sup> fc = frozen core approximation.

<sup>c</sup> See text.

<sup>d</sup> Redundant angle (not given in [9]).

<sup>e</sup> From ground state moments of inertia and vibrational corrections calculated from the force field.

by the larger cc-pVQZ one. V(Q, T)Z + 1 differs from VQZ + 1 only by the employment of cc-pVTZ at H instead of cc-pVQZ.

Spherical harmonics were used throughout. Although the chosen basis sets are not ideally suited to the description of inner-shell contributions to the electron correlation, all electrons were correlated unless otherwise noted. In those cases where the frozen core approximation was applied, the silicon 1s2s2p-like and the fluorine 1s-like core molecular orbitals were required to remain doubly occupied.

The molecular geometry of DSiHF<sub>3</sub> was optimized within the constraint of C<sub>3v</sub> point group symmetry. For the purpose of comparison, the molecular structures of SiF<sub>2</sub> (C<sub>2v</sub>) and SiH<sub>4</sub> (T<sub>d</sub>) also were optimized. Analytical energy gradients as implemented in the Gaussian94 program [17] were used throughout. The largest internal gradient components did not exceed 2 × 10<sup>-6</sup> au.

At the MP2/VTZ + 1(Q) equilibrium geometry of SiHF<sub>3</sub>, the associated harmonic force field was evaluated analytically in Cartesian coordinates [17]. The normal modes and the harmonic vibrational frequencies were obtained in the usual manner [22, 23].

For comparison with the experimental data, the cubic and quartic force fields of SiHF<sub>3</sub> are required. Therefore, the MP2/VTZ + 1(Q) cubic ( $\phi_{ijk}$ ) and semidiagonal quartic ( $\phi_{ijkk}$ ) normal coordinate force constants were determined with the use of a finite difference procedure [24] involving displacements along reduced normal coordinates (step size  $\Delta q = 0.03$ ) and the calculation of analytical second derivatives (relative precision  $\varepsilon < 10^{-7}$ ) at these displaced geometries. At the MP2/VTZ + 1(Q) equilibrium geometry of SiHF<sub>3</sub>, the Cartesian gradient components did not exceed

5 × 10<sup>-7</sup> au. The evaluation of anharmonic spectroscopic constants was based on second-order rovibrational perturbation theory [25].

The symmetry-adapted internal coordinates chosen to represent the complete cubic MP2/VTZ + 1(Q) force field of SiHF<sub>3</sub> using appropriate nonlinear transformations [26] are given in appendix A.

Table 1 shows the computed equilibrium geometries of SiHF<sub>3</sub> and compares them with the experimentally derived equilibrium structure which is so far available in the literature [9]. The enlargement of the basis set from VTZ + 1 to VQZ + 1 shortens the bond distances in SiHF<sub>3</sub> considerably when all electrons are correlated, viz. the SiH bond is contracted by as much as 0.0075 Å and the SiF bond lengths decrease by 0.0055 Å. Virtually the same effect on the SiF bond results from the replacement of the cc-pVTZ basis at the central atom by the larger cc-pVQZ basis, whereas the shortening of the SiH bond is much less pronounced in this case (0.0022 Å). Both basis sets of intermediate size (VTZ + 1(Q) and V(Q, T)Z + 1) yield molecular structures of SiHF<sub>3</sub> which are very similar. Within the frozen core approximation, the differences between VTZ + 1 and VQZ + 1 seems to be much more plausible than those found when all electrons are correlated: the SiH bond length increases by only 0.0005 Å and the SiF bond distances decrease by 0.0011 Å upon enlargement of the basis set. This finding underlines the fact that the basis sets employed are not ideally suited to correlating the core electrons, which offers an explanation for the unexpectedly large basis effects in the all-electron bond lengths (see above). The computed bond angles of a given type (HSiF or FSiF) differ by at most 0.09° for each other and are close to 110.5° (HSiF) and 108.4° (FSiF), re-

Table 2. Computed and experimental equilibrium geometries of SiF<sub>2</sub> and SiH<sub>4</sub>.<sup>a</sup>

| Molecule         | Basis <sup>b</sup> | <i>r</i> (SiH) | <i>r</i> (SiF) | ∠FSiF      |
|------------------|--------------------|----------------|----------------|------------|
| SiF <sub>2</sub> | VQZ + 1            |                | 1.5931         | 101.06     |
|                  | VQX 1 (fc)         |                | 1.6008         | 100.95     |
|                  | exp. (Ref. 27)     |                | 1.5901 (1)     | 100.77 (2) |
| SiH <sub>4</sub> | VQZ + 1            | 1.4605         |                |            |
|                  | VQZ + 1 (fc)       | 1.4737         |                |            |
|                  | exp. (Ref. 28)     | 1.4734 (10)    |                |            |

<sup>a</sup> Bond lengths in Å, bond angles in deg.<sup>b</sup> fc = frozen core approximation.

spectively. Comparing the MP2/VQZ + 1 geometrical data of SiHF<sub>3</sub> with their experimental counterparts [9], the SiH bond length is considerably underestimated (by 0.0092 Å) by the all-electron calculation and somewhat overestimated (by 0.0039 Å) if core correlation is neglected. The SiF bond lengths are slight overestimated (by 0.0026 Å) when correlating all electrons, and much too large (0.0113 Å) within the frozen core approximation. The MP2/VQZ + 1 bond angles agree with the corresponding experimental ones to within 0.11°.

The calculated bond distances in SiHF<sub>3</sub> may be improved by taking into account the errors which appear in analogous calculations for the related molecules SiF<sub>2</sub> and SiH<sub>4</sub>, where accurate experimental equilibrium geometries are known [27, 28]. For this purpose table 2 presents computed and experimental equilibrium structures for both species. It is seen that MP2/VQZ + 1 overestimates the bond distances in SiF<sub>2</sub> by as much as 0.0107 Å, if the frozen core approximation is applied, whereas the theoretical bond lengths in SiH<sub>4</sub> are fortuitously in perfect agreement with experiment. The bond angle in SiF<sub>2</sub> is overestimated by 0.18°, although it must be noted that the very small uncertainty given in [27], 0.02°, does not take into account the imperfections of the model. As for SiHF<sub>3</sub>, taking core correlation into account at the MP2/VQZ + 1 level leads to a considerable contraction of the bond lengths in SiF<sub>2</sub> (−0.0077 Å) and SiH<sub>4</sub> (−0.0132 Å), while the bond angle in SiF<sub>2</sub> changes only moderately (+0.11°). If the errors in the calculated bond lengths of these two molecules (with and without the frozen core approximation) are used to correct the corresponding data for the target molecule SiHF<sub>3</sub>, we arrive at two consistent estimates for the equilibrium distances in SiHF<sub>3</sub> (see table 1). The corrected SiH bond length is larger than the reported experimental value [9] by about 0.004 Å, and the corrected SiF bond distances deviate by less than 0.001 Å from experiment [9]. Since the calculated bond angles do not depend much on the chosen basis (see above), they remain uncorrected. Their deviation from experiment [9] is quite small (about 0.1°). The corrected MP2/VQZ + 1

Table 3. Computed<sup>a</sup> harmonic wavenumbers  $\omega_i$  (in cm<sup>−1</sup>) and anharmonicity corrections  $\omega_i - \nu_i$  (in cm<sup>−1</sup>) for <sup>28</sup>SiHF<sub>3</sub> and <sup>28</sup>SiDF<sub>3</sub>.

| Constant                          | <sup>28</sup> SiHF <sub>3</sub> | <sup>28</sup> SiDF <sub>3</sub> |
|-----------------------------------|---------------------------------|---------------------------------|
| $\omega_1$ SiH (SiD) str          | 2444.1                          | 1760.3                          |
| $\omega_2$ SiF <sub>3</sub> s-str | 867.6                           | 863.4                           |
| $\omega_3$ umbrella               | 425.5                           | 422.3                           |
| $\omega_4$ SiF <sub>3</sub> a-str | 1022.5                          | 1016.0                          |
| $\omega_5$ SiH (SiD) rock         | 867.3                           | 641.7                           |
| $\omega_6$ SiF <sub>3</sub> def   | 307.0                           | 303.8                           |
| $\omega_1 - \nu_1$                | 81.61                           | 39.16                           |
| $\omega_2 - \nu_2$                | 7.33                            | 7.39                            |
| $\omega_3 - \nu_3$                | 0.92                            | 0.95                            |
| $\omega_4 - \nu_4$                | 14.03                           | 13.72                           |
| $\omega_5 - \nu_5$                | 9.72                            | 4.79                            |
| $\omega_6 - \nu_6$                | 1.16                            | 1.14                            |

<sup>a</sup> MP2/VTZ + 1(Q).

geometries of SiHF<sub>3</sub> are used in this work to assist a new experimental determination of the equilibrium structure of this molecule (see below).

Table 3 contains the computed (MP2/VTZ + 1(Q)) harmonic vibrational wavenumbers  $\omega_i$  and the corresponding anharmonicity corrections  $\omega_i - \nu_i$ , both for <sup>28</sup>SiHF<sub>3</sub> and its deuterated isotopomer <sup>28</sup>SiDF<sub>3</sub>. The  $\omega_i - \nu_i$  values were obtained from the anharmonicity constants  $x_{ij}$  and  $g_{ij}$  (see table 4) which have been calculated using standard formulas of perturbation theory [25]. There were no complications due to anharmonic interactions at the MP2/VTZ + 1(Q) level, because the relevant interacting states are either sufficiently separated or the interaction is not strong enough ( $\nu_2/2\nu_3$ ), so that perturbationally and variationally determined anharmonic shifts of the respective fundamentals due to such cubic interactions differ by less than 1 cm<sup>−1</sup> in all cases. The theoretical fundamental wavenumbers  $\nu_i$  of <sup>28</sup>SiHF<sub>3</sub> and <sup>28</sup>SiDF<sub>3</sub> are reported in table 5 where they are compared with the experimental counterparts (see below).

In the following discussion (sections 4 and 5) the cubic force field of SiHF<sub>3</sub> is referred to. For the sake of completeness, table 6 lists all independent quadratic and cubic force constants of this molecule in terms of symmetry-adapted internal coordinates, as calculated at the MP2/VTZ + 1(Q) level of theory. In addition, table 7 contains the complete cubic force fields of <sup>28</sup>SiHF<sub>3</sub> and <sup>28</sup>SiDF<sub>3</sub> in reduced normal coordinates. There are 38 independent cubic constants (10  $a_1 a_1 a_1$ , 18  $a_1 e e$ , 10  $e e e$ ) which are listed in this order in tables 6 and 7 ( $a_1$  modes with indices  $s = 1, 2, 3$ ;  $e$  modes with indices  $t = 4, 5, 6$  and components  $t_a/t_b$  which are symmetric/antisymmetric with respect to one  $\sigma_v$  plane). The depen-

Table 4. Computed<sup>a</sup> and available experimental anharmonicity constants  $x_{ij}, g_{ij}$  (in  $\text{cm}^{-1}$ ) of  $^{28}\text{SiHF}_3$  and  $^{28}\text{SiDF}_3$ .

|                   | $ij$ | $^{28}\text{SiHF}_3$ |                      | $^{28}\text{SiDF}_3$ |                      |
|-------------------|------|----------------------|----------------------|----------------------|----------------------|
|                   |      | Calc.                | Exp. <sup>b</sup>    | Calc.                | Exp. <sup>b</sup>    |
| $x_{ij}$          | 1 1  | -34.02               | -31.3 (2)            | -17.60               | -15.5 (10)           |
|                   | 1 2  | -0.75                |                      | -0.59                |                      |
|                   | 1 3  | -0.62                |                      | -0.41                | $\sim 0$             |
|                   | 1 4  | +1.16                |                      | +2.44                | 2.29 (10)            |
|                   | 1 5  | -13.83               |                      | -5.67                |                      |
|                   | 1 6  | -0.23                | $\sim 0$             | -0.23                | 0.15 (15)            |
|                   | 2 2  | -1.44                |                      | -1.40                |                      |
|                   | 2 3  | +3.01                | 3.08 (8)             | +2.49                | 2.60 (15)            |
|                   | 2 4  | -4.39                |                      | -4.65                |                      |
|                   | 2 5  | -0.38                |                      | -0.12                |                      |
|                   | 2 6  | -0.81                | $\sim 0$             | -0.79                | $\sim 0$             |
|                   | 3 3  | -0.72                | -1.0912 <sup>c</sup> | -0.60                | -0.8906 <sup>c</sup> |
|                   | 3 4  | -1.83                |                      | -1.89                |                      |
|                   | 3 5  | +0.53                |                      | +0.48                |                      |
|                   | 3 6  | +0.62                | 0.5714 <sup>c</sup>  | +0.64                | 0.5795 <sup>c</sup>  |
|                   | 4 4  | -3.22                |                      | -3.16                |                      |
|                   | 4 5  | -2.35                |                      | -2.54                |                      |
|                   | 4 6  | -1.50                |                      | -1.54                |                      |
|                   | 5 5  | -1.03                |                      | -0.53                |                      |
|                   | 5 6  | +0.02                |                      | +0.57                |                      |
|                   | 6 6  | +0.11                |                      | -0.03                |                      |
| $g_{ij}$          | 4 4  | +2.02                |                      | +1.89                |                      |
|                   | 4 5  | +1.40                |                      | +1.37                |                      |
|                   | 4 6  | -0.17                |                      | -0.12                |                      |
|                   | 5 5  | +2.55                |                      | +1.43                |                      |
|                   | 5 6  | +0.44                |                      | -0.33                |                      |
|                   | 6 6  | +0.19                |                      | +0.11                |                      |
| $x_{56} + g_{56}$ |      |                      |                      | 0.24                 | 0.21 (3)             |

<sup>a</sup> MP2/VTZ-1(Q).

<sup>b</sup> Reference [11].

<sup>c</sup> Reference [47].

dent constants can be obtained from relations given elsewhere [29]. Finally, table 8 reports all independent quartic force constants  $\phi_{ijkl}$  ( $6 a_1 a_1 a_1 a_1, 9 a_1 a_1 e e, 9 e e e e$ ) from which the other dependent constants  $\phi_{ijkl}$  can be calculated [29]. These quartic constants are required in the perturbation formulas for the anharmonicity constants [25]. The specification  $t = 4, 5, 6$  for degenerate modes has been used instead of  $ta = 4a, 5a, 6a$  in tables 6–8 whenever this was possible without ambiguities. The calculated harmonic force field is found to be in good agreement with the previous experimental determination [9].

### 3. Hamiltonian model

The effective Hamiltonian  $H$  for a non-degenerate state  $v_s = 0, 1, \dots$  or for the first excited degenerate state  $v_t = 1$  of a  $\text{C}_{3v}$  molecule can be written as the

sum of vibration–rotation terms. The expressions for these terms in the quantum numbers  $v, J, k$  and  $l$  are given in appendix B. The symbols used are the degenerate ones, and their definition may be found in [1, 30]. The Hamiltonian of a non-degenerate state is obtained by taking the vibrational quantum number  $l$  equal to zero.

The coefficients of the Hamiltonian may be expressed as a function of the geometry and the force constants of the molecule. The order of the force constants involved plus the reference for the relation between the parameter and the force constants are listed in table 9.

It is important to note that the Hamiltonian given in appendix B is not unique because some of the terms in the Hamiltonian are not independent of each other and may be inherently bound together by some relations independent of the data. The problem was explained

Table 5. Computed<sup>a</sup> and experimental constants for trifluorosilane.<sup>b</sup>

|                         | SiHF <sub>3</sub> |         |                |      | SiDF <sub>3</sub> |             |                |      |
|-------------------------|-------------------|---------|----------------|------|-------------------|-------------|----------------|------|
|                         | Calc.             | Exp.    | Exp - Calc (%) | Ref. | Calc.             | Exp.        | Exp - Calc (%) | Ref. |
| $\zeta_4$               | 0.613             | 0.593   | -3.4           | [38] | 0.550             | 0.536       | -2.6           | [14] |
| $\zeta_5$               | 0.829             |         |                |      | 0.818             | 0.833       | 1.8            | [46] |
| $\zeta_6$               | -0.569            | -0.570  | 0.1            | [38] | -0.532            | -0.530      | -0.4           | [15] |
| $\nu_1/\text{cm}^{-1}$  | 2362              | 2316.9  | -1.9           | [47] | 1721              | 1689.6      | -1.9           | [47] |
| $\nu_2/\text{cm}^{-1}$  | 860               | 856     | -0.5           | [9]  | 856               | 854         | -0.2           | [11] |
| $\nu_3/\text{cm}^{-1}$  | 425               | 425     | 0.0            | [11] | 421               | 422         | 0.2            | [11] |
| $\nu_4/\text{cm}^{-1}$  | 1008              | 998     | -1.0           | [38] | 1002              | 994.3       | -0.8           | [14] |
| $\nu_5/\text{cm}^{-1}$  | 858               | 844     | -1.7           | [11] | 637               | 627.2       | -1.6           | [46] |
| $\nu_6/\text{cm}^{-1}$  | 306               | 305.5   | -0.2           | [38] | 303               | 302.3       | -0.2           | [15] |
| $\alpha_1^B/\text{MHz}$ | 5.114             |         |                |      | 7.618             | 8.283       | 8.0            | [47] |
| $\alpha_2^B/\text{MHz}$ | 29.324            | 20.79   | 2.2            | [9]  | 17.819            | 21.90       | <u>18.6</u>    | [9]  |
| $\alpha_3^B/\text{MHz}$ | -4.865            | -4.478  | -8.7           | [47] | -4.882            | -4.533      | -7.7           | [47] |
| $\alpha_4^B/\text{MHz}$ | 15.251            | 15.129  | -0.8           | [38] | 15.476            | 15.278      | -1.3           | [14] |
| $\alpha_5^B/\text{MHz}$ | 1.528             | 1.80    | <u>15.1</u>    | [9]  | -0.272            | -0.325      | <u>15.9</u>    | [46] |
| $\alpha_6^B/\text{MHz}$ | -6.934            | -6.816  | -1.7           | [38] | -5.099            | -4.937      | -3.3           | [15] |
| $\alpha_1^C/\text{MHz}$ | 0.963             |         |                |      | 0.852             | 1.239       | <u>31.3</u>    | [47] |
| $\alpha_2^C/\text{MHz}$ | 12.026            |         |                |      | 11.813            |             |                |      |
| $\alpha_3^C/\text{MHz}$ | -4.235            | -4.105  | -3.1           | [47] | -4.165            | -4.057      | -2.7           | [47] |
| $\alpha_4^C/\text{MHz}$ | 8.965             | 8.729   | -2.7           | [38] | 9.929             | 10.038      | 1.1            | [14] |
| $\alpha_5^C/\text{MHz}$ | -2.196            |         |                |      | -2.814            | -2.850      | 1.2            | [46] |
| $\alpha_6^C/\text{MHz}$ | 3.744             | 3.8175  | 1.9            | [38] | 4.015             | 4.054       | 1.0            | [15] |
| $q_4/\text{MHz}$        | -3.6869           | -3.6275 | -1.6           | [38] | -3.3490           | -3.2873 (4) | -1.9           | [14] |
| $q_5/\text{MHz}$        | -5.3267           | -4.90   | <u>-8.6</u>    | [11] | -2.0289           | -1.7189     | <u>-18.0</u>   | [46] |
| $q_6/\text{MHz}$        | -3.4345           | -3.2931 | -4.3           | [38] | -3.0415           | -2.8906 (1) | -5.2           | [15] |

<sup>a</sup> MP2/VTZ + 1(Q).<sup>b</sup> Large differences are underlined.

in 1965 by Watson [31, 32] who has shown that the indeterminacies observed are caused by the existence of a block-diagonal unitary transformation which transforms the values of the spectroscopic constants in the effective Hamiltonian:

$$\tilde{H} = e^{iS_v} H_v^{\text{eff}} e^{-iS_v} \quad (1)$$

for the vibrational state  $v$  in question without changing its eigenvalues. The reduction method has later been extended also to the Hamiltonians for the rotation-vibration states of symmetric top molecules [30, 33–35].

#### 4. Comparison of *ab initio* parameters with experiment

##### 4.1. Resonances

It is crucial to identify first those excited vibrational states which are well isolated because, otherwise, their constants may be quite sensitive even to weak resonances. For that goal, it is sufficient to consider the fundamental frequencies, at least for a preliminary rough estimate. It is rather obvious that only the two lowest excited states,  $\nu_6$  and  $\nu_3$ , are well isolated. On the other hand, all the other states may be affected by resonances.

The analysis of the infrared spectrum [11] revealed a strong Fermi resonance between  $2\nu_3$  and  $\nu_2$  for both SiHF<sub>3</sub> and SiDF<sub>3</sub>. It was later analysed by Hoy *et al.* [9]. Furthermore, for SiHF<sub>3</sub>, there is a Coriolis resonance between  $\nu_5$  and  $2\nu_3$  as well as a Fermi resonance between  $\nu_1$  and  $2\nu_4 + \nu_6$ . A Coriolis resonance between  $\nu_2$  and  $\nu_5$  is possible but it should be quite weak because the corresponding coupling constant is quite small:  $|\zeta_{25}^v| = 0.0022$  [MP2/VTZ + 1(Q)]. For SiDF<sub>3</sub>, a resonance is probable between  $\nu_5$  and  $2\nu_6$ . A more detailed study of the resonances will be presented once the accuracy of the force field has been assessed.

##### 4.2. 'Classical' rotational parameters

The best way to check the quality of the quadratic (harmonic) force field is to use parameters which depend only on the quadratic force constants. These are the Coriolis  $\zeta$  constants and the equilibrium quartic centrifugal distortion constants. The Coriolis  $\zeta^2$  constants are usually determined from the  $(C\zeta)_r$  constant, neglecting the vibrational dependence of both  $C$  and  $(C\zeta)_r$ . This limits the precision to a few per cent, pro-

# Ab initio force field and structure of trifluorosilane

Table 6. Computed<sup>a</sup> quadratic and cubic symmetry force constants  $F_{ij}, F_{ijk}$  of  $\text{SiHF}_3$ .<sup>a</sup>

| $i\ j\ k$ | $F_{ij}, F_{ijk}$ | $i\ j\ k$ | $F_{ijk}$ |
|-----------|-------------------|-----------|-----------|
| 1 1       | 3.429             | 1 4 6     | 0.006     |
| 1 2       | 0.111             | 1 5 5     | -0.225    |
| 1 3       | -0.053            | 1 5 6     | 0.029     |
| 2 2       | 6.696             | 1 6 6     | -0.014    |
| 2 3       | 0.182             | 2 4 4     | -21.035   |
| 3 3       | 1.019             | 2 4 5     | -0.082    |
| 4 4       | 6.108             | 2 4 6     | 0.500     |
| 4 5       | 0.197             | 2 5 5     | -0.340    |
| 4 6       | -0.225            | 2 5 6     | 0.097     |
| 5 5       | 0.587             | 2 6 6     | -0.994    |
| 5 6       | -0.163            | 3 4 4     | 0.016     |
| 6 6       | 0.832             | 3 4 5     | 0.198     |
|           |                   | 3 4 6     | 0.367     |
| 1 1 1     | -15.782           | 3 5 5     | 0.157     |
| 1 1 2     | -0.042            | 3 5 6     | 0.264     |
| 1 1 3     | -0.042            | 3 6 6     | -1.042    |
| 1 2 2     | -0.295            | 4 4 4     | -14.588   |
| 1 2 3     | 0.176             | 4 4 5     | -0.063    |
| 1 3 3     | -0.141            | 4 4 6     | -0.324    |
| 2 2 2     | -22.032           | 4 5 5     | -0.187    |
| 2 2 3     | -0.695            | 4 5 6     | 0.019     |
| 2 3 3     | -0.789            | 4 6 6     | 0.327     |
| 3 3 3     | 0.722             | 5 5 5     | -0.481    |
| 1 4 4     | -0.136            | 5 5 6     | 0.204     |
| 1 4 5     | -0.169            | 5 6 6     | -0.231    |
|           |                   | 6 6 6     | -0.550    |

<sup>a</sup> MP2/VTZ + 1(Q).

<sup>b</sup> Units are consistent with energies in aJ, bond lengths in Å, and bond angles in rad.

Table 7. Computed<sup>a</sup> cubic normal coordinate force constants  $\phi_{ijk}$  (in  $\text{cm}^{-1}$ ) of  $^{28}\text{SiHF}_3$  and  $^{28}\text{SiDF}_3$ .<sup>b</sup>

| $i\ j\ k$ | $^{28}\text{SiHF}_3$ | $^{28}\text{SiDF}_3$ | $i\ j\ k$ | $^{28}\text{SiHF}_3$ | $^{28}\text{SiDF}_3$ |
|-----------|----------------------|----------------------|-----------|----------------------|----------------------|
| 1 1 1     | -1342.1              | -818.0               | 2 5 5     | -38.0                | -15.1                |
| 1 1 2     | -2.7                 | -24.7                | 2 5 6     | 2.8                  | -2.6                 |
| 1 1 3     | -5.5                 | 3.2                  | 2 6 6     | 23.6                 | 22.6                 |
| 1 2 2     | -3.4                 | 2.0                  | 3 4 4     | -6.1                 | -6.1                 |
| 1 2 3     | 9.2                  | 11.3                 | 3 4 5     | -6.8                 | -3.2                 |
| 1 3 3     | -3.7                 | -4.7                 | 3 4 6     | -0.6                 | -1.5                 |
| 2 2 2     | -123.0               | -123.5               | 3 5 5     | 32.2                 | 21.3                 |
| 2 2 3     | -41.7                | -39.6                | 3 5 6     | 2.2                  | 3.9                  |
| 2 3 3     | 23.8                 | 23.6                 | 3 6 6     | -15.2                | -14.7                |
| 3 3 3     | -2.0                 | -2.2                 | 4 4 4     | -139.0               | -150.4               |
| 1 4 4     | 56.5                 | 28.7                 | 4 4 5     | -33.8                | -11.8                |
| 1 4 5     | -122.7               | -47.6                | 4 4 6     | -15.1                | -16.0                |
| 1 4 6     | -21.3                | -12.9                | 4 5 5     | -7.7                 | -6.9                 |
| 1 5 5     | 314.0                | 191.8                | 4 5 6     | 0.3                  | 0.9                  |
| 1 5 6     | 51.4                 | 42.1                 | 4 6 6     | -19.8                | -21.7                |
| 1 6 6     | 7.6                  | 6.5                  | 5 5 5     | -54.7                | -27.8                |
| 2 4 4     | -161.5               | -169.6               | 5 5 6     | -27.5                | -18.0                |
| 2 4 5     | -39.4                | -20.6                | 5 6 6     | -18.8                | -12.3                |
| 2 4 6     | 21.9                 | 21.3                 | 6 6 6     | -26.4                | -27.4                |

<sup>a</sup> MP2/VTZ + 1(Q).

<sup>b</sup> According to the potential energy distribution matrix, each normal mode of  $\text{SiHF}_3$  is dominated by a particular symmetry coordinate. The positive phases of the normal coordinates were selected to correspond to a positive contribution of the respective dominant symmetry coordinate.

accuracy of the cubic force field. Experimental equilibrium sextic constants have been determined only in a few rare cases because it is difficult to obtain precise (it requires high  $J$  and high  $K$  transitions which are not easily measurable) and unperturbed (as a rule, the sextic constants are extremely sensitive to interactions between states) sextic constants from the analysis of the spectrum. It is worth noting that for both the isotopic species  $\text{SiHF}_3$  and  $\text{SiDF}_3$  the sextic splitting constants  $h_3$  could be determined accurately. This constant  $h_3$  is quite sensitive to the reduction, the relation between the reduced constant  $\tilde{h}_3$  and the unreduced one  $h_3$  being

$$\tilde{h}_3 = h_3 - \xi. \quad (2)$$

In the usual case where the molecule is not a quasi-spherical top, reduction  $A$  is chosen. This reduction eliminates the term with  $\varepsilon$  in the Hamiltonian (equation (B 4)) and therefore

$$\xi = \frac{\varepsilon^2}{C - B} = \frac{\tau_{xxxz}^2}{16(C - B)}. \quad (3)$$

The other sextic centrifugal distortion constants also depend on the reduction, but the dependence is much smaller although significantly larger than the accuracy

vided  $C_0$  is known. A better method is to use  $(C\zeta)_i$  determined from the fundamental  $\nu_i = 1$  and the overtone  $\nu_i = 2$ , which allows us to take into account the vibrational dependence. This second method could be used for  $\nu_6 = 1, 2$  in  $\text{SiHF}_3$ , it gives  $\zeta_6 = -0.568$  instead of  $\zeta_6 = -0.570$  with the first approximate method mentioned. In 1960 Maes [36] derived the theoretical expression of the vibrational dependence of  $(C\zeta)_i$  which is a function both of the cubic and quartic force fields. Thus, in principle, it should be possible to obtain  $(C\zeta)_e = C_e \cdot \zeta^2$  but the expression given by Maes is too complicated to be useful in numerical work.

The ground state centrifugal distortion constants are not expected to be identical to the *ab initio* equilibrium constants because the ground state constants are affected by a small vibrational dependence. However, there is a large volume of documented evidence which shows that the difference between the ground state and equilibrium constants is small (a few per cent). The same conclusion is likely to be true for the sextic centrifugal distortion constants, which may be used to check the

Table 8. Computed<sup>a</sup> quartic normal coordinate force constants  $\phi_{ijkl}$  (in  $\text{cm}^{-1}$ ) of  $^{28}\text{SiHF}_3$  and  $^{28}\text{SiDF}_3$ .

| $i\ i\ j\ j$ | $^{28}\text{SiHF}_3$ | $^{28}\text{SiDF}_3$ |
|--------------|----------------------|----------------------|
| 1 1 1 1      | 684.2                | 353.4                |
| 1 1 2 2      | -0.2                 | 0.0                  |
| 1 1 3 3      | -0.5                 | -0.3                 |
| 1 1 4 4      | -41.3                | -7.8                 |
| 1 1 5 5      | -300.9               | -157.8               |
| 1 1 6 6      | -6.2                 | -6.0                 |
| 2 2 2 2      | 14.0                 | 14.4                 |
| 2 2 3 3      | -6.7                 | -6.8                 |
| 2 2 4 4      | 24.5                 | 25.9                 |
| 2 2 5 5      | 2.1                  | 0.4                  |
| 2 2 6 6      | -6.9                 | -6.6                 |
| 3 3 3 3      | 6.8                  | 6.8                  |
| 3 3 4 4      | -13.1                | -13.6                |
| 3 3 5 5      | 0.9                  | 1.2                  |
| 3 3 6 6      | 3.6                  | 3.5                  |
| 4 4 4 4      | 44.4                 | 47.7                 |
| 4 4 5 5      | 24.9                 | 4.0                  |
| 4 4 6 6      | -3.8                 | -4.5                 |
| 5 5 5 5      | 163.7                | 84.3                 |
| 5 5 6 6      | 1.8                  | 2.7                  |
| 6 6 6 6      | 11.8                 | 11.0                 |
| 4a 4a 5b 5b  | 8.4                  | 0.8                  |
| 4a 4a 6b 6b  | -16.0                | -16.5                |
| 5a 5a 6b 6b  | -2.3                 | -0.6                 |

<sup>a</sup> MP2/VTZ + 1(Q).

of the constants. The relation between the reduced (with tilde) and unreduced (without tilde) constants is

$$\tilde{H}_J = H_J - 2\xi, \quad (4)$$

$$\tilde{H}_{JK} = H_{JK} + 18\xi, \quad (5)$$

$$\tilde{H}_{KJ} = H_{KJ} - 30\xi. \quad (6)$$

The vibration-rotation interaction constants  $\alpha$  and the  $l$ -type doubling constants (for a degenerate excited state) may be used to check the accuracy of the cubic force field, but only for unperturbed states.

The experimental and computed constants are given in tables 5 and 10. For Coriolis constants and the ground state centrifugal distortion constants there is extremely good agreement between theory and experiment, the only exception being the calculated constant  $\tilde{h}_3$  of  $\text{SiDF}_3$ , which is significantly smaller than the experimental value (21.6%). Although the experimental value was obtained from only 6 splittings, it seems to be quite reliable, particularly because the value for the  $v_6 = 1$  state is very similar,  $\tilde{h}_3 = -0.763$  (2) mHz [15]. The vibrational dependence,  $\tilde{h}_3^e - \tilde{h}_3^0$  of the unreduced

Table 9. Relation between the spectroscopic constants and the force constants.

| Parameter          | Description                       | Order of force constant | Ref.     |
|--------------------|-----------------------------------|-------------------------|----------|
| $\omega_l$         | harmonic wavenumber               | 2                       | [42]     |
| $D$                | quartic centrifugal distortion    | 2                       | [42]     |
| $\zeta$            | Coriolis coupling constant        | 2                       | [42]     |
| $\nu_l$            | vibrational frequency             | 2, 3, 4                 | [42]     |
| $x_{rs}, g_{t,t'}$ | vibrational anharmonicity         | 2, 3, 4                 | [25, 42] |
| $\alpha_r$         | vibration-rotation constants      | 2, 3                    | [25, 42] |
| $q_t, r_t$         | $l$ -type doubling constants      | 2, 3                    | [25, 42] |
| $H$                | sextic centrifugal distortion     | 2, 3                    | [42]     |
| $\eta_J, \eta_K$   | diagonal Coriolis coupling        | 2, 3                    | [39]     |
| $d$                | $\Delta K = \pm 3$ matrix element | 2, 3                    | [41]     |

parameter is expected to be small, as for the other parameters, but this is no longer true for the reduced value because it is the difference between two terms which have the same order of magnitude. Actually, a large vibrational dependence was already observed for  $\text{AsF}_3$  [37]. This could explain the large difference between the *ab initio*  $\tilde{h}_3^e$  and the experimental  $\tilde{h}_3^0$ .

For the  $v_5 = 1$  state of both isotopic species, the vibration-rotation interaction constants  $\alpha^B$  and the  $l$ -type doubling constant  $q$  are not reproduced well (differences up to 18%). This indicates that the  $v_5 = 1$  state is likely to be in interaction with other states (which will be confirmed below). The same conclusion is valid for the  $v_2 = 1$  state of  $\text{SiDF}_3$ . On the other hand, the agreement is extremely good for the isolated states  $v_3 = 1$ ,  $v_4 = 1$  and  $v_6 = 1$ .

Usually, only the absolute value of the  $l$ -type doubling constant  $q$  is determined from pure rotational spectra. Actually, it was possible to determine the signs of  $q$  for the vibrational states  $v_6 = 1$  and  $v_4 = 1$  of both  $\text{SiHF}_3$  and  $\text{SiDF}_3$  using high resolution infrared spectra. They agree with the calculated ones.

It may be noted that there is no experimental value for the ground state centrifugal distortion constant  $D_K^0$  although its excited state value could be determined without a problem for the degenerate excited states  $v_4 = 1$  and  $v_6 = 1$ . Quite recently, Gnida *et al.* [38] determined an approximate value of  $D_K^0$  in fitting the rotational and  $l$ -type resonance transitions of the  $v_6 = 2$  state of  $\text{SiHF}_3$ . Its value, 5.96(10) kHz, although not accurate (it is highly correlated with the corresponding excited state parameter,  $\rho = 0.99997$ ), is in extremely good agreement with the *ab initio* prediction, see table 10. We also tried to determine  $D_K^0$  using the Aliev and Watson sum rule [39, 40]. This sum rule relates  $\eta_J$  and  $\eta_K$  to the quartic centrifugal distortion constants:

# Ab initio force field and structure of trifluorosilane

Table 10. Compare<sup>a</sup> and experimental centrifugal distortion constants for trifluorosilane.

| Species                                 |                    | $D_J/\text{kHz}$ | $D_{JK}/\text{kHz}$ | $D_K/\text{kHz}$ | $H_J/\text{Hz}$ | $H_{JK}/\text{Hz}$ | $H_{KJ}/\text{Hz}$ | $H_K/\text{Hz}$ | $h_3/\text{Hz}$ | $\xi/\text{Hz}$ |
|-----------------------------------------|--------------------|------------------|---------------------|------------------|-----------------|--------------------|--------------------|-----------------|-----------------|-----------------|
| <sup>28</sup> SiHF <sub>3</sub><br>[38] | calc.              | 7.4612           | -12.3508            | 5.784            | 0.022 594       | -0.089 0           | 0.1121             | -0.045 11       | -0.001 030      | -0.000 206 4    |
|                                         | exp.               | 7.5744           | -12.551             | 5.96             | 0.022 581       | -0.083 8           | 0.1010             |                 | -0.001 103      |                 |
|                                         | diff. <sup>b</sup> | 1.5              | 1.6                 | 3.0              | 0.0             | -6.7               | -7.1               |                 | 6.6             |                 |
| <sup>29</sup> SiHF <sub>3</sub><br>[38] | calc.              | 7.4093           | -12.253             | 5.739            | 0.022 4         | -0.088 33          | 0.1112             | -0.044 77       | -0.000 993      | -0.000 211      |
|                                         | exp.               | 7.5223           | -12.450             |                  | 0.023 0         | -0.085 3           | 0.1069             |                 |                 |                 |
|                                         | diff. <sup>b</sup> | 1.5              | 1.6                 |                  | 2.7             | -3.6               | -4.0               |                 |                 |                 |
| <sup>30</sup> SiHF <sub>3</sub><br>[38] | calc.              | 7.3595           | -12.160             | 5.695            | 0.022 22        | -0.087 65          | 0.1104             | -0.044 43       | -0.000 958      | -0.000 216      |
|                                         | exp.               | 7.4730           | -12.354             |                  | 0.023 73        | -0.085 56          | 0.1067             |                 |                 |                 |
|                                         | diff. <sup>b</sup> | 1.5              | 1.6                 |                  | 6.4             | -2.4               | -3.5               |                 |                 |                 |
| <sup>28</sup> SiDF <sub>3</sub><br>[14] | calc.              | 6.2726           | -9.861              | 4.483            | 0.017 13        | -0.066 52          | 0.0835             | -0.033 60       | -0.000 60       | -0.000 235      |
|                                         | diff. <sup>b</sup> | 6.3492           | -9.969              | 4.31             | 0.016 42        | -0.061 19          | 0.0774             |                 | -0.000 76       |                 |
|                                         | diff. <sup>b</sup> | 1.2              | 1.1                 | -3.9             | -4.3            | -8.7               | -7.9               |                 | 21.6            |                 |
| <sup>29</sup> SiDF <sub>3</sub><br>[14] | calc.              | 6.2374           | -9.798              | 4.455            | 0.017 0         | -0.066 2           | 0.0831             | -0.033 44       | -0.000 57       | -0.000 239      |
|                                         | exp.               | 6.3145           | -9.907              | -9.907           | 0.016 9         | -0.062 3           | 0.0781             |                 |                 |                 |
|                                         | diff. <sup>b</sup> | 1.2              | 1.1                 |                  | -0.5            | -6.2               | -6.5               |                 |                 |                 |
| <sup>30</sup> SiDF <sub>3</sub><br>[14] | calc.              | 6.2036           | -9.736              | 4.427            | 0.016 9         | -0.065 9           | 0.0828             | -0.032 29       | -0.000 55       | -0.000 243      |
|                                         | exp.               | 6.2791           | -9.843              |                  | 0.016 5         | -0.061 8           | 0.0766             |                 |                 |                 |
|                                         | diff. <sup>b</sup> | 1.2              | 1.1                 |                  | -2.4            | -6.6               | -8.0               |                 |                 |                 |
| median                                  | diff. <sup>b</sup> | 1.4              | 1.3                 |                  | -0.3            | -6.4               | -6.8               |                 | 13.9            |                 |
| std <sup>c</sup>                        | diff. <sup>b</sup> | 0.2              | 0.3                 |                  | 3.8             | 2.3                | 2.3                |                 | 10.9            |                 |

<sup>a</sup> MP2/VTZ + 1(Q).

<sup>b</sup> Exp - calc in %.

<sup>c</sup> Standard deviation.

$$\sum_{i=4}^6 (u_i - \frac{1}{4}\eta_{iJ}) = 3D_K^0 - \frac{1}{4}D_{JK}^0 - \frac{1}{2}D_J^0, \quad (7)$$

where

$$u_i = D_K^0 - \frac{1}{4}\eta_{iK} \quad (8)$$

is the true determinable quantity because  $D_K^0$  and  $\eta_{iK}$  are fully correlated and  $\eta_{iK}$  was obtained by fixing  $D_K^0$  to its force field value. The sum rule should allow the determination of  $D_K^0$  for SiDF<sub>3</sub> because all three degenerate states have been analysed. The result is  $D_K^0 = 4.31$  kHz whereas the force field value is 4.48 kHz. The agreement is not bad, and, as will be explained below, the small discrepancy is probably due to the fact that the  $v_5 = 1$  state of SiDF<sub>3</sub> is perturbed, and, consequently, its constants  $\eta_J$  and  $\eta_K$  are only effective constants.

## 4.3. Vibrational parameters

The accuracy of the force field may be assessed also by comparing the theoretical and the experimental wavenumbers of the fundamentals. Table 5 shows that the agreement is almost perfect, the greatest discrepancy being only 1.9% for the SiH stretching mode  $\nu_1$  which is the highest vibration, and most sensitive to anharmonicity.

The vibrational band origins of the overtone, combination, and hot bands which were previously assigned

by Bürger *et al.* [11] also may be used to check the accuracy of the force field. The experimental and calculated values are gathered in table 11 for SiHF<sub>3</sub> and table 12 for SiDF<sub>3</sub>. The overall agreement is rather good. The calculated values are slightly larger than the experimental ones, the difference increasing almost linearly with the frequency. The maximum deviation is only 2.11% for the hot band  $\nu_1 + \nu_3 - \nu_3$  of SiHF<sub>3</sub>. As anticipated from the previous discussion, there is also good agreement between the experimental and *ab initio* anharmonicity constants which are both listed in table 4.

## 4.4. Rotational parameters affected by the reduction

There is still a need to discuss the parameters of degenerate excited states which are sensitive to the reduction of the Hamiltonian. These are the two diagonal elements  $\eta_J$  and  $\eta_K$ , the (2, -1) *l*-resonance constant  $q_{12}$  ( $=r$ ) and the parameter  $d$  of the *l*-dependent  $\Delta K = \pm 3$  matrix elements. The explicit expressions for the constants  $\eta_J$  and  $\eta_K$  have been derived by Aliev and Watson [39] and that for  $d$  by Sarka and Demaison [41], whereas the expression for  $q_{12}$  has been known for a long time [25, 42, 43], see table 9. They all depend on the force field up to cubic terms. These four constants cannot be determined simultaneously by fitting the experimental data. One of these constants has to be constrained because of

Table 11. Band centres of the infrared spectrum of SiHF<sub>3</sub> (in cm<sup>-1</sup>).

| Assignment                    | Calc. <sup>a</sup> | Exp. <sup>b</sup>    | e - c (%) |
|-------------------------------|--------------------|----------------------|-----------|
| $\nu_6$                       | 305.86             | 305.46               | -0.13     |
| $3\nu_3 - 2\nu_3$             | 421.63             | 419.4                | -0.53     |
| $2\nu_3 - \nu_3$              | 423.08             | 421.85 <sup>c</sup>  | -0.29     |
| $\nu_3$                       | 424.53             | 424.03 <sup>c</sup>  | -0.12     |
| $\nu_3 + \nu_6 - \nu_6$       | 425.15             | 424.60 <sup>c</sup>  | -0.13     |
| $\nu_2 - \nu_3$               | 435.72             | 434.4                | -0.30     |
| $\nu_5$                       | 857.58             | 843.6                | -1.66     |
| $2\nu_3$                      | 847.61             | 845.87 <sup>c</sup>  | -0.21     |
| $2\nu_3 + \nu_6 - \nu_6$      | 848.86             | 846.60 <sup>c</sup>  | -0.27     |
| $2\nu_3 + 2\nu_6 - 2\nu_6$    | 850.10             | 846.4                | -0.44     |
| $\nu_2$                       | 860.24             | 859.35 <sup>c</sup>  | -0.10     |
| $\nu_2 + \nu_3 - \nu_3$       | 863.26             | 862.20 <sup>c</sup>  | -0.12     |
| $\nu_4$                       | 1008.44            | 999.58               | -0.88     |
| $\nu_4 + \nu_6$               | 1310.59            | 1303.2               | -0.57     |
| $2\nu_4$                      | 2006.40            | 1995.0               | -0.57     |
| $2\nu_1 - \nu_1$              | 2294.47            | 2253.0               | -1.84     |
| $2\nu_4 + \nu_6$              | 2309.07            | 2301.6               | -0.32     |
| $\nu_1 + \nu_3 - \nu_3$       | 2361.88            | 2313.1               | -2.11     |
| $\nu_1$                       | 2362.50            | 2316.91 <sup>c</sup> | -1.97     |
| $\nu_1 + \nu_3$               | 2786.41            | 2740.0               | -1.69     |
| $\nu_1 + \nu_4$               | 3372.10            | 3319.9               | -1.57     |
| $2\nu_1$                      | 4656.97            | 4568.0               | -1.95     |
| Largest deviation             |                    |                      | -2.11     |
| Median of absolute deviations |                    |                      | 0.48      |

<sup>a</sup> MP2/VTZ+1(Q). For the overtone and combination bands only the  $\sum l_i = 0$  component is given.

<sup>b</sup> Reference [11] if not otherwise quoted.

<sup>c</sup> Reference [47].

the correlation among them. In the Q reduction, the constraint is  $q_{12} = 0$  and the values determined for the parameters (denoted by the superscript Q) are actually the combination of the 'true' parameters (without superscript):

$$\eta_J^Q = \eta_J - 8 \frac{(q_{12})^2}{F}, \quad (9)$$

$$\eta_K^Q = \eta_K + 8 \frac{(q_{12})^2}{F}, \quad (10)$$

$$d_Q = d - 4 \frac{q_{12}q_{22}}{F}, \quad (11)$$

where

$$F = 2(C\zeta)_t^2 + C_t - B_t, \quad (12)$$

while in the alternative D reduction the constraint is  $d = 0$  and the determined parameters (with superscript D) are again the combination of the 'true' parameters (without superscript):

Table 12. Band centres of the infrared spectrum of SiDF<sub>3</sub> (in cm<sup>-1</sup>).

| Assignment                         | Calc. <sup>a</sup> | Exp. <sup>b</sup>    | e - c (%) |
|------------------------------------|--------------------|----------------------|-----------|
| $\nu_6$                            | 302.68             | 302.29 <sup>c</sup>  | -0.39     |
| $3\nu_3 - 2\nu_3$                  | 418.98             | 416.4                | -0.62     |
| $2\nu_3 - \nu_3$                   | 420.18             | 419.15 <sup>d</sup>  | -0.25     |
| $\nu_3$                            | 421.39             | 420.93 <sup>d</sup>  | -0.11     |
| $\nu_3 + \nu_6 - \nu_6$            | 422.03             | 421.51 <sup>d</sup>  | -0.12     |
| $\nu_3 + 2\nu_6 - 2\nu_6$          | 422.67             | 422.09 <sup>d</sup>  | -0.14     |
| $\nu_2 - \nu_3$                    | 434.60             | 433.3                | -0.30     |
| $\nu_5$                            | 636.87             | 628.4                | -1.35     |
| $\nu_3 + \nu_6$                    | 724.71             | 724.5                | -0.03     |
| $4\nu_3 - 2\nu_3$                  | 836.74             | 835                  | -0.21     |
| $3\nu_2 - \nu_3$                   | 839.16             | 836.8                | -0.28     |
| $3\nu_3 + \nu_6 - \nu_3 - \nu_6$   | 840.43             | 837.4                | -0.36     |
| $3\nu_3 + 2\nu_6 - \nu_3 - 2\nu_6$ | 841.71             | 838                  | -0.44     |
| $2\nu_3$                           | 841.57             | 840.10 <sup>d</sup>  | -0.18     |
| $2\nu_3 + \nu_6 - \nu_6$           | 842.85             | 840.93 <sup>d</sup>  | -0.23     |
| $2\nu_3 + 2\nu_6 - 2\nu_6$         | 844.12             | 841.1                | -0.36     |
| $2\nu_3 + 3\nu_6 - 3\nu_6$         | 845.40             | 841.9                | -0.42     |
| $\nu_2$                            | 855.99             | 854.85 <sup>d</sup>  | -0.13     |
| $\nu_2 + \nu_3 - \nu_3$            | 858.48             | 857.40 <sup>d</sup>  | -0.13     |
| $\nu_2 + 2\nu_3 - 2\nu_3$          | 860.97             | 858.2                | -0.32     |
| $\nu_4$                            | 1002.26            | 994.30 <sup>c</sup>  | -0.61     |
| $\nu_3 + \nu_5$                    | 1058.73            | 1061.9               | 0.30      |
| $2\nu_5$                           | 1269.82            | 1250.6               | -1.54     |
| $\nu_4 + \nu_6$                    | 1301.40            | 1278.7               | -1.78     |
| $\nu_4 + \nu_5$                    | 1633.27            | 1613.2               | -1.24     |
| $\nu_1$                            | 1721.15            | 1689.57 <sup>d</sup> | -1.87     |
| $\nu_1 + \nu_4 - \nu_4$            | 1723.59            | 1692.6               | -1.83     |
| $2\nu_4$                           | 1994.43            | 1990                 | -0.22     |
| $\nu_1 + \nu_6$                    | 2023.48            | 1990                 | -1.68     |
| $\nu_1 + \nu_3$                    | 2142.13            | 2114.9               | -1.29     |
| $2\nu_1$                           | 3407.10            | 3349.14 <sup>d</sup> | -1.73     |
| Largest deviation                  |                    |                      | -1.87     |
| Median of absolute deviations      |                    |                      | 0.32      |

<sup>a</sup> MP2/VTZ+1(Q). For the overtone and combination bands only the  $\sum l_i = 0$  components is given.

<sup>b</sup> Reference [11] if not otherwise quoted.

<sup>c</sup> Reference [15].

<sup>d</sup> Reference [47].

<sup>e</sup> Reference [14].

$$q_{12}^D = q_{12} - \frac{Fd}{4q_{22}}, \quad (13)$$

$$\eta_J^D = \eta_J - 4 \frac{q_{12}d}{q_{22}} + \frac{Fd^2}{2(q_{22})^2}, \quad (14)$$

$$\eta_K^D = \eta_K + 4 \frac{q_{12}d}{q_{22}} - \frac{Fd^2}{2(q_{22})^2}. \quad (15)$$

The computed and experimental parameters in both reductions are compared in table 13 for the isolated states  $\nu_4 = 1$  and  $\nu_6 = 1$  of both isotopic species. The parameters of the  $\nu_5 = 1$  state are given only for

Table 13. Computed<sup>a</sup> and experimental constants (in kHz) in reductions Q and D of trifluorosilane.

| Species<br>Ref.           |                  | <i>Ab initio</i><br>unreduced | $Q_{\text{exp.}}$ | $Q_{\text{calc.}}$ | $Q(e-c)$ | $Q(e-c)$<br>% | $D_{\text{exp.}}$ | $D_{\text{calc.}}$ | $D(e-c)$ | $D(e-c)$<br>% |
|---------------------------|------------------|-------------------------------|-------------------|--------------------|----------|---------------|-------------------|--------------------|----------|---------------|
| SiHF <sub>3</sub><br>[38] | $\nu_4 = 1$      | $q_{12}$                      | 2071.832          | 0                  | 0        |               | 3139.1 (22)       | 3046.5             | 92.7     | 2.95          |
|                           |                  | $\eta_J$                      | 11.029            | -7.250 (13)        | -6.316   | -0.934 12.88  | 36.002 (65)       | 31.1868            | 4.815    | 13.37         |
|                           |                  | $\eta_K$                      | -11.772           | 6.612 (37)         | 5.573    | 1.039 15.71   | -36.642 (72)      | -31.929            | -4.713   | 12.86         |
|                           |                  | $d$                           | 7.260             | 25.128 (27)        | 22.693   | 2.434 9.69    | 0                 | 0                  |          |               |
|                           | [38] $\nu_6 = 1$ | $q_{12}$                      | -275.658          | 0                  | 0        |               | 2687.53 (2)       | 2714.236           | -26.702  | -0.99         |
|                           |                  | $\eta_J$                      | -33.531           | -33.888 (1)        | -33.453  | -0.436 1.29   | -41.320 (1)       | -41.035            | -0.285   | 0.69          |
|                           |                  | $\eta_K$                      | 31.331            | 31.455 (9)         | 32.253   | 0.202 0.64    | 38.887 (9)        | 38.836             | 0.051    | 0.13          |
|                           |                  | $d$                           | -5.285            | -4.552 3 (1)       | -4.798   | 0.245 -5.39   | 0                 | 0                  |          |               |
|                           | [14] $\nu_4 = 1$ | $q_{12}$                      | 2168.5154         | 0                  | 0        |               | 3042.2 (11)       | 2968.422           | 73.812   | 2.43          |
|                           |                  | $\eta_J$                      | 11.594            | -11.025 (7)        | -9.631   | -1.393 12.64  | 33.490 (33)       | 30.141             | 3.349    | 10.00         |
|                           |                  | $\eta_K$                      | -10.433           | 12.178 (15)        | 10.793   | 1.385 11.38   | -32.354 (33)      | -28.980            | -3.374   | 10.43         |
|                           |                  | $d$                           | 6.046             | 23.997 (15)        | 22.436   | 1.561 6.50    | 0                 | 0                  |          |               |
|                           | [46] $\nu_5 = 1$ | $q_{12}$                      | 1293.495          |                    | 0.000    |               | -1143.9 (59)      | -1189.3            | 45.4     | -3.97         |
|                           |                  | $\eta_J$                      | 14.030            | 12.158 (14)        | 10.670   | 1.488 12.24   | 14.706 (26)       | 13.510             | 1.196    | 8.14          |
|                           |                  | $\eta_K$                      | -10.543           | -5.778 (75)        | -7.183   | 1.405 -24.31  | -8.36 (27)        | -10.023            | 1.664    | -19.91        |
|                           |                  | $d$                           | -5.058            | fixed              | 2.423    |               |                   |                    |          |               |
|                           | [15] $\nu_6 = 1$ | $q_{12}$                      | -297.996          | 0                  | 0        |               | 2601.931 (47)     | 2619.972           | -18.041  | -0.69         |
|                           |                  | $\eta_J$                      | -31.074           | -31.403 (3)        | -30.975  | -0.428 1.36   | -38.9818 (28)     | -38.646            | -0.336   | 0.86          |
|                           |                  | $\eta_K$                      | 29.109            | 29.743 (32)        | 29.010   | 0.733 2.46    | 37.283 (33)       | 36.681             | 0.602    | 1.61          |
|                           |                  | $d$                           | -4.959            | -4.210 64 (8)      | -4.453   | 0.242 -5.75   | 0                 | 0                  |          |               |

<sup>a</sup> MP2/VTZ + 1(Q).

SiDF<sub>3</sub> because, for SiHF<sub>3</sub>, they are affected by a strong Coriolis resonance. For the  $\nu_6 = 1$  state the agreement is extremely good, but it is slightly worse for the  $\nu_4 = 1$  state, indicating that probably this state is less well isolated, as will be confirmed below. It may be noted also that the harmonic contribution is larger than the anharmonic one for  $\eta_J$  and  $\eta_K$  whereas the contrary is true for  $q_{12}$  and  $d$ . Finally, it is worth remarking that for the rotational parameters (which do not depend on the quartic force field), the difference between the calculated and the experimental values is of the same order of magnitude as the expected vibrational dependence. In conclusion, it does not seem useful to try to refine the *ab initio* cubic force field from the experimental data.

#### 4.5. Analysis of the resonances

The accuracy of the force field seems to be good enough to calculate the relative position of the vibrational energy levels from the *ab initio* harmonic frequencies  $\omega_r$  and anharmonic constants  $x_{rs}$  (see equation (B 1)). The levels likely to interact are gathered in table 14 together with the type of interaction and the value of the interaction constant calculated from the *ab initio* normal coordinate force constants. This table confirms that the levels  $\nu_3 = 1$  and  $\nu_6 = 1$  are well isolated,

although the Coriolis constant linking these two states is not zero. All the other fundamental states may be affected by an interaction. In SiHF<sub>3</sub>, the three levels  $\nu_2/\nu_5/2\nu_3$  form a triad through Fermi and Coriolis interactions whereas, in SiDF<sub>3</sub>, the triad is formed from  $\nu_2/2\nu_3/3\nu_6$  through Fermi and quartic anharmonic resonances. Hoy *et al.* [9] analysed the Fermi resonance in both isotropic species, neglecting the other interactions. This oversight explains why their interaction constants are so different for the two isotropic species and also so different from the *ab initio* values. In SiHF<sub>3</sub>, there is a quartic anharmonic resonance between  $\nu_4 = 1$  and  $\nu_6 = 3$ . In SiDF<sub>3</sub>, a similar quartic anharmonic resonance occurs between  $\nu_4 = 1$  and  $\nu_3 = 1$ ,  $\nu_6 = 2$ . Furthermore, there is a Fermi resonance between  $\nu_5 = 1$  and  $\nu_6 = 2$ . Finally, the  $\nu_1 = 1$  state is perturbed in both isotopic species. In conclusion, the  $\nu_5 = 1$  state is likely to be perturbed in both isotopic species. This perturbation, although weaker for the  $\nu_4 = 1$  state, is probably not negligible either. These findings agree with our previous conclusions and explain the discrepancies observed in table 5.

All this confirms that the *ab initio* values are very close to experiment if the experimental data are unperturbed, and much more reliable than experimental data in the case of perturbations which are not accounted for.

Table 14. Possible interactions in trifluorosilane.

| Species           | First level | Other interaction level           | $\Delta E/\text{cm}^{-1}$ | Parameter <sup>a</sup>  |
|-------------------|-------------|-----------------------------------|---------------------------|-------------------------|
| SiHF <sub>3</sub> | $\nu_6 = 1$ | $\nu_3 = 1$                       | 118.9                     | $\zeta_{36}^y = 0.423$  |
|                   | $\nu_2 = 1$ | $\nu_5 = 1$                       | 5.2                       | $\zeta_{25}^y = 0.0022$ |
|                   | $\nu_2 = 1$ | $\nu_3 = 2$                       | 12.6                      | $\phi_{233} = 23.8$     |
|                   | $\nu_5 = 1$ | $\nu_3 = 2$                       | 7.4                       | Coriolis ?              |
|                   | $\nu_4 = 1$ | $\nu_6 = 1$                       | 30.9                      | $\phi_{4666} = 1.8$     |
|                   | $\nu_1 = 1$ | $\nu_4 = 2, \nu_6 = 1$            | 53.4                      | $\phi_{1446} = 0.2$     |
|                   | $\nu_1 = 1$ | $\nu_3 = 1, \nu_4 = 2$            | 64.8                      | $\phi_{1344} = 0.74$    |
|                   | $\nu_6 = 1$ | $\nu_3 = 1$                       | 118.9                     | $\zeta_{36}^y = 0.441$  |
| SiDF <sub>3</sub> | $\nu_2 = 1$ | $\nu_3 = 2$                       | 14.4                      | $\phi_{233} = 23.6$     |
|                   | $\nu_2 = 1$ | $\nu_6 = 3$                       | 31.1                      | $\phi_{2666} = 2.4$     |
|                   | $\nu_4 = 1$ | $\nu_3 = 1, \nu_6 = 2$            | 27.4                      | $\phi_{3455} = 0.4$     |
|                   | $\nu_5 = 1$ | $\nu_6 = 2$                       | 30.4                      | $\phi_{566} = 12.3$     |
|                   | $\nu_1 = 1$ | $\nu_2 = 2$                       | 12.0                      | $\phi_{122} = 2.0$      |
|                   | $\nu_1 = 1$ | $\nu_3 = 1, \nu_4 = 1, \nu_6 = 1$ | 0.4                       | Coriolis ?              |
|                   |             |                                   |                           |                         |
|                   |             |                                   |                           |                         |

<sup>a</sup> Absolute value given. The interaction matrix elements are proportional to the corresponding normal coordinate force constants (in  $\text{cm}^{-1}$ ).

Table 15. Rotational constants and vibrational corrections for trifluorosilane (in MHz).

|                      | <sup>28</sup> SiHF <sub>3</sub> | <sup>29</sup> SiHF <sub>3</sub> | <sup>30</sup> SiHF <sub>3</sub> | <sup>28</sup> SiDF <sub>3</sub> | <sup>29</sup> SiDF <sub>3</sub> | <sup>30</sup> SiDF <sub>3</sub> |
|----------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| $B_0^a$              | 7208.054                        | 7195.753                        | 7183.794                        | 6890.105                        | 6880.209                        | 6870.578                        |
| $B_e - B_0^b$        | 20.132                          | 20.0247                         | 19.9247                         | 20.382                          | 20.246                          | 20.118                          |
| $B_e(\text{exp})^c$  | 7228.186                        | 7215.778                        | 7203.719                        | 6910.487                        | 6900.455                        | 6890.696                        |
| $B_e(\text{calc})^d$ | 7228.197                        | 7215.778                        | 7203.710                        | 6910.497                        | 6900.453                        | 6890.687                        |
| $C_0^a$              | 4134.162                        |                                 |                                 | 4133.696                        |                                 |                                 |
| $C_e - C_0^b$        | 14.890                          | 14.793                          | 14.702                          | 15.380                          | 15.283                          | 15.193                          |
| $C_e(\text{exp})^c$  | 4149.052                        |                                 |                                 | 4149.076                        |                                 |                                 |
| $C_e(\text{calc})^d$ | 4149.061                        |                                 |                                 | 4149.061                        |                                 |                                 |

<sup>a</sup> Reference [14] for SiHF<sub>3</sub> and reference [38] for SiDF<sub>3</sub>.

<sup>b</sup> *Ab initio* MP2/VTZ + 1(Q) values.

<sup>c</sup> Calculated from experimental  $B_0/C_0$  and *ab initio*  $B_e - B_0/C_e - C_0$ .

<sup>d</sup> Calculated using the parameters of last line of table 1.

These perturbations are not always easy to detect experimentally, but a discrepancy between *ab initio* and experimental parameters is a good indicator of a possible perturbation. In this case, it is better to use *ab initio*  $\alpha$  constants for the structure determination rather than experimental values (or 'hybrid' sets).

### 5. Structure

The theoretical rotation-vibration interaction constants deduced from the *ab initio* cubic force field were combined with the experimental ground state rotational constants  $B_0$  and  $C_0$  of the different isotopic species to

yield the semiexperimental equilibrium rotational constants  $B_e$  and  $C_e$  reported in table 15. It is interesting to note that the values of  $C_e$  are equal (within their uncertainty) for both isotopic species, as they should be. This is a good test of the quality both of the  $C_0$  constants and the force field. If we assume that the accuracy of the vibrational correction is about 5%, the accuracy of the equilibrium rotational constants is about 1 MHz.

The equilibrium structure was calculated from a least-squares fit of the equilibrium moments of inertia, and is given in the last line of table 1. A first fit, without

# Ab initio force field and structure of trifluorosilane

Table 16. Structures of  $\text{XH}_n\text{F}_{4-n}$ ,  $\text{X} = \text{Si}, \text{C}$ ;  $n = 0-4$ .<sup>a</sup>

|                          | $r(\text{X}-\text{H})$ | $r(\text{X}-\text{F})$ | $\angle\text{HXH}$ | $\angle\text{FXF}$ | $\angle\text{HXF}$ | Ref.      |
|--------------------------|------------------------|------------------------|--------------------|--------------------|--------------------|-----------|
| $\text{SiH}_4$           | 1.4734 (4)             |                        | 109.47             |                    |                    | [28]      |
| $\text{SiH}_3\text{F}$   | 1.470 (2)              | 1.591 (2)              | 110.55 (20)        |                    | 108.37 (20)        | [44]      |
| $\text{SiH}_2\text{F}_2$ | 1.464 (2)              | 1.576 (2)              | 114.25 (20)        | 107.75 (20)        | 108.66 (20)        | [45]      |
| $\text{SiHF}_3$          | 1.449 (1)              | 1.563 (1)              |                    | 103.23 (20)        | 110.69 (20)        | this work |
| $\text{SiF}_4$           |                        | 1.552 (2)              |                    | 109.47             |                    | [48]      |
| $\text{CH}_4$            | 1.0860 (3)             |                        | 109.47             |                    |                    | [49]      |
| $\text{CH}_3\text{F}$    | 1.0872 (3)             | 1.3826 (3)             | 110.24 (4)         |                    | 108.69 (4)         | [50]      |
| $\text{CH}_2\text{F}_2$  | 1.087 (1)              | 1.353 (1)              | 113.28 (20)        | 108.36 (20)        | 108.77 (20)        | [51]      |
| $\text{CHF}_3$           | 1.085 (2)              | 1.328 (3)              |                    | 108.58 (34)        | 110.35 (35)        | [52, 53]  |
| $\text{CF}_4$            |                        | 1.315 (2)              |                    | 109.47             |                    | [54]      |

<sup>a</sup> Distances in Å, angles in deg.

weighting, established that the residuals are several orders of magnitude smaller than the estimated accuracy ( $0.01 \mu\text{Å}^2$ ) and confirmed that the  $C_e$  values are less accurate than the  $B_e$  values. A final weighted fit was made using an accuracy of  $0.0005 \mu\text{Å}^2$  for  $I_B$  and  $0.003 \mu\text{Å}^2$  for  $I_C$ . It was checked that the results are not sensitive to the weighting scheme. Although the fit seems to be well behaved and the standard deviation of the derived parameters is low, it does not prove that the derived structure is reliable because, actually, the three structural parameters were calculated from only seven independent moments of inertia (the  $I_C$  value being the same for both isotopic species).

A comparison with the previous structure of Hoy *et al.* [9], which is also given in table 1, may give a first indication of the accuracy of our results, since both our rotational constants and our force field are more accurate, so that the derived structure should also be more accurate. A good agreement between the two structures is an indication of accuracy. However, certainly it is much better to compare the semiexperimental structure with the *ab initio* structure which is given in table 1. An MP2 calculation with a very large basis set is expected to provide bond angles with an accuracy generally better than  $0.3^\circ$ . For bond lengths, the situation is more difficult because the theoretical values are still affected by small and (mainly) systematic errors due to the approximate treatment of the electron correlation (at the MP2 level), to basis set incompleteness and, possibly, to core-correlation effects which may be rather large for second-row atoms. As described in section 2, the theoretical bond lengths in  $\text{SiHF}_3$  have been improved by applying corrections obtained from  $\text{SiH}_4$  and  $\text{SiF}_2$  at the same level of theory (same method, same basis set, with and without frozen core approximation). Clearly it would be better to derive the correction for the SiF bond length from another structurally similar fluorosilane, but the

experimental equilibrium structures of monofluorosilane,  $\text{SiH}_3\text{F}$  [44] and difluorosilane,  $\text{SiH}_2\text{F}_2$  [45] are not known accurately enough for this purpose, and there are no other suitable experimental data. The *ab initio*  $r(\text{SiH})$  value in  $\text{SiHF}_3$ ,  $1.450 \text{ Å}$ , is only marginally larger than the semiexperimental value,  $1.449 \text{ Å}$ , and the difference,  $0.001 \text{ Å}$ , does not exceed the expected accuracy. The *ab initio*  $r(\text{SiF})$  value,  $1.563 \text{ Å}$ , is in perfect agreement with the experimental value. Likewise, the difference between the *ab initio* and experimental  $\angle\text{FSiF}$ ,  $0.14^\circ$ , is small and consistent with the expected accuracy of the two methods. In conclusion, the present semiexperimental structure probably is accurate to better than  $0.001 \text{ Å}$  for the distances and  $0.2^\circ$  for the angles.

Table 16 gathers the structures of the two series  $\text{SiH}_n\text{F}_{4-n}$  and  $\text{CH}_n\text{F}_{4-n}$ ,  $n = 0-4$ . Both the SiF and SiH bond lengths decrease as the number of fluorine atoms increases. The behaviour of the SiF bond length is similar to that of the CF bond the length of which also decreases with increasing F substitution. Actually, there is an almost perfect linear correlation between these two bond lengths. On the other hand, the variation in the CH bond length seems to be extremely small with increasing substitution. The bond angles also behave similarly for the two series, i.e., an increase with increasing substitution. A linear correlation is also found between the angles of the two series. It is interesting to note that the variation is small when going from the monofluoro to the difluoro compounds, whereas it is large when going from difluoro to the trifluoro species.

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**Appendix A**  
Symmetry internal coordinates of SiHF<sub>3</sub>

$$\begin{aligned}
 S_1(a_1) &= r, \\
 S_2(a_1) &= \frac{1}{\sqrt{3}}(R_1 + R_2 + R_3), \\
 S_3(a_1) &= \frac{1}{\sqrt{3(1+K^2)}} \\
 &\quad \times (K\alpha^{12} + K\alpha_{13} + K\alpha_{23} - \beta_1 - \beta_2 - \beta_3), \\
 S_{4a}(e) &= \frac{1}{\sqrt{6}}(2R_1 - R_2 - R_3), \\
 S_{5a}(e) &= \frac{1}{\sqrt{6}}(2\beta_1 - \beta_2 - \beta_3), \\
 S_{6a}(e) &= \frac{1}{\sqrt{6}}(2\alpha_{23} - \alpha_{12} - \alpha_{13}), \\
 S_{4b}(e) &= \frac{1}{\sqrt{2}}(R_2 - R_3), \\
 S_{5b}(e) &= \frac{1}{\sqrt{2}}(\beta_2 - \beta_3), \\
 S_{6b}(e) &= \frac{1}{\sqrt{2}}(\alpha_{13} - \alpha_{12}),
 \end{aligned}$$

where  $r$  is the SiH bond length,  $R_i$  are the SiF<sub>*i*</sub> bond lengths,  $\alpha_{ij}$  are the F<sub>*i*</sub>SiF<sub>*j*</sub> bond angles, and  $\beta_i$  are the F<sub>*i*</sub>SiH bond angles. The angle redundancy has been removed in  $S_3$  by setting  $\Delta\alpha = -K\Delta\beta$  [55] with  $K = -3 \sin\beta \cos\beta / \sin\alpha = 1.038109$  for the MP2/VTZ+1(Q) equilibrium bond angles.  $S_{4a}$  and  $S_{4b}$  ( $t = 4-6$ ) are symmetric and antisymmetric, respectively, with regard to the plane containing the atoms H, Si and F<sub>1</sub>.

**Appendix B**  
Matrix elements of the Hamiltonian diagonal elements

$$\begin{aligned}
 E &= \sum_r \omega_r \left( v_r + \frac{d_r}{2} \right) + \sum_{r \geq s} x_{rs} \left( v_r + \frac{d_r}{2} \right) \left( v_s + \frac{d_s}{2} \right) \\
 &\quad + \sum_{t \geq t'} g_{tt'} l_t l_{t'} + \dots + B_v J(J+1) + C_v - B_v k^2 \\
 &\quad - D_J J^2(J+1)^2 - D_{JK} J(J+1)k^2 - D_K k^4 \\
 &\quad + H_J J^3(J+1)^3 + H_{JK} J^2(J+1)^2 k^2 \\
 &\quad + H_{KJ} J(J+1)k^4 + \dots - 2(C\zeta)kl \\
 &\quad + \eta_J J(J+1)kl + \eta_K k^3 l + \dots
 \end{aligned} \quad (B1)$$

The vibrational dependence is not included explicitly, and therefore the parameters are effective ones. For instance, the rotational constants may be expressed as

$$B_v = B_e - \sum_r \alpha_r^B \left( v_r + \frac{d_r}{2} \right) + \dots \quad (B2)$$

and

$$C_v = C_e - \sum_r \alpha_r^C \left( v_r + \frac{d_r}{2} \right) + \dots \quad (B3)$$

Non-diagonal elements (leading terms only)

$$\langle v, J, k \pm 3 | H | v, J, k \rangle = \epsilon(2k \pm 3) F_3^\pm(J, k), \quad (B4)$$

$$\langle v, J, k \pm 6 | H | v, J, k \rangle = h_3 F_6^\pm(J, k), \quad (B5)$$

$$\langle v_t = 1, J, k \pm 2, l = \pm 1 | h | v, J, k, l = \mp 1 \rangle = 2q_{22} F_2^\pm(J, k), \quad (B6)$$

$$\langle v_t = 1, J, k \mp 1, l = \pm 1 | H | v, J, k, l = \pm 1 \rangle = 2q_{12} F_1^\pm(J, k), \quad (B7)$$

$$\langle v_t = 1, J, k \pm 3, l = \pm 1 | H | v, J, j, l = \pm 1 \rangle = ld F_3^\pm(J, k), \quad (B8)$$

where

$$F_n^\pm(J, k) = \prod_{i=1}^n [J(J+1) - (k \pm i \mp 1)(k \pm 1)]^{1/2}. \quad (B9)$$

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# Equilibrium structure of $\text{SiF}_4$

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# Equilibrium structure of SiF<sub>4</sub>

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## Abstract

The equilibrium Si-F bond length in SiF<sub>4</sub> has been calculated ab initio at the MP2 and CCSD(T) levels using a polarized valence quadruple  $\zeta$  basis set. The  $r_e$  structure has also been estimated using the ground state rotational constant  $B_0$  reported by Jörissen *et al.* [Can. J. Phys. **67** (1989) 532] by harmonic corrections to derive  $B_z$  followed by empirical corrections for the effect of stretching anharmonicity and also by application of an empirically derived rovibrational interaction parameter. The  $r_e(\text{Si-F})$  values obtained from these different methods are in a narrow range 1.5516-1.5529 Å, their estimated standard deviation is 0.0005 Å and the mean value is 1.5524 (8) Å where the uncertainty shown in parentheses is given in the unit of the last digit and is 4 standard deviations which corresponds to a confidence level of 99%.

## 1. Introduction

It is now possible to determine a very accurate structure for a small molecule by high level ab initio calculations [1], at least when this molecule is only composed of first row atoms. When second row atoms are involved, the situation is more difficult because basis set convergence is harder to achieve, especially with regard to core correlation effects. Standard ab initio calculations are still very useful in such a case, but it is necessary to "calibrate" them with the help of experimental data to obtain a reliable structure. SiF<sub>4</sub> is a good example of such a molecule where ab initio calculations alone do not yet allow us to calculate an accurate Si-F

bond length. In this paper, we will show that it is possible to use structurally similar molecules whose geometry is accurately known to "calibrate" the ab initio calculations. We will also show that it is possible to evaluate an independent, but compatible, experimental equilibrium structure using the available ground state rotational constant [6]. The different methods used in this paper are well known but they are not often used in conjunction which might explain why an accurate equilibrium structure is still lacking for such a simple and, at the same time, important molecule.

There have been several attempts to determine the structure of the tetrahedral molecule silicon tetrafluoride, SiF<sub>4</sub>, but the results are not very satisfactory. The  $r_a$  bond length was determined by two simultaneous electron diffraction studies [2, 3], but the derived  $r_g$  bond lengths, although compatible, are not in very good agreement:  $r_g = 1.556(2)$  Å [2] or  $r_g = 1.553(1)$  Å [3]. The given uncertainty corresponds to one standard deviation and includes estimates of systematic error. The effective structure was also determined using an estimate of the ground state rotational constant giving  $r_o = 1.55982(17)$  Å [4]. However, it was later found that the used rotational constant is in error by more than 30 MHz [5, 6] which corresponds to a bond length decrease of almost 0.006 Å. The equilibrium structure of SiF<sub>4</sub> was also recently calculated at the CCSD(T)/cc-pVQZ+1 level, the result being,  $r_e$  (Si-F) = 1.56043 Å [7]. This value presumably calculated within the frozen core approximation is in accidental good agreement with the  $r_o$  structure from Ref. [4] which is known to be inaccurate.

The goal of the present note is twofold: i) to evaluate a reliable experimental equilibrium structure using the experimental data taken from the literature, and particularly the ground state rotational constant  $B_o$  reported by Jörissen *et al.* [6] ii) to obtain an independent equilibrium structure from high level ab initio calculations. The combined use of these different methods will allow us to improve the precision and estimate the accuracy of the derived structure.

## 2. Experimental structure

From the electron diffraction distance  $r_a$  determined at  $T = 298$  K, it is possible to estimate the average  $r_z$  bond length using Eq. (1) [8, 9],

$$r_a - r_z = \frac{3}{2} a [u_T^2 - u_{T=0}^2] + K_0 - \frac{u_T^2}{r_e} + \delta r_T \quad (1)$$

where:

- $\delta r_T = 0.00027 \text{ \AA}$  is a small centrifugal correction at temperature  $T$
- $K_0 = 0.00173 \text{ \AA}$  is the mean square perpendicular amplitude correction (at 0 K)
- $u_T$  is the mean amplitude of vibration at temperature  $T = 298 \text{ K}$
- $a$  is the Morse anharmonicity parameter

$\delta r_T$ ,  $K_0$ , and  $u_T$  are calculated from the harmonic force field [4]. The Morse anharmonicity parameter  $a$  is usually determined from the corresponding diatomic radical (here SiF) [9] assuming that it is identical for all Si-F bonds. The result of Eq. (1) is not sensitive to this assumption but this is no more true for the correction  $r_z - r_e$  which will be calculated below. Although it is well established that the range of variation of the Morse parameter is generally quite small [9], this does not imply that the diatomic value is always appropriate. In fact, it is sometimes a rather rough approximation [10]. Halonen [11] tried to determine  $a(\text{SiF})$  in  $\text{SiF}_4$ . He found two possible solutions:  $a = 1.903 \text{ \AA}^{-1}$  or  $a = 1.992 \text{ \AA}^{-1}$ . Although these different values of  $a$  give compatible structures (i.e. deviations not larger than  $0.001 \text{ \AA}$ ), it is possible to estimate the right value of  $a$  because it is known that  $a$  varies with the bond length [12, 13]. The parameter  $a(\text{SiF})$  can be determined for  $\text{SiF}_2$  and  $\text{SiHF}_3$  from the known harmonic and cubic force fields using Eq. (2):

$$f_{rrr} = -3af_{rr} \quad (2)$$

The results are gathered in Table 1 and plotted in Figure 1. The observed bond-length dependence indicates that the right value of  $a$  for  $\text{SiF}_4$  is  $1.903 \text{ \AA}^{-1}$ .

The  $r_z$  structure is then converted into  $r_e$  value using the approximate Kuchitsu's formula [8, 9, 14, 15]

$$r_z = r_e + \frac{3}{2} au^2 - K \quad (3)$$

where all parameters are calculated from the harmonic force field at  $T = 0 \text{ K}$ . Table 2 also reports the experimental values of the mean amplitude for the Si-F bond determined by electron diffraction. The mean value is  $r_e(\text{Si-F}) = 1.550(2) \text{ \AA}$ . It indicates that the equilibrium bond length is likely to be much smaller than the published ab initio value,  $1.56043 \text{ \AA}$  [7].

The accurate ground state rotational constant determined by Jörissen *et al.* [6] allows us to calculate a very precise effective structure:  $r_o(\text{Si-F}) = 1.5540 \text{ \AA}$ . The  $r_e$  value is expected to be slightly smaller. Actually, it is possible to obtain it by estimating the vibrational correction from the structurally similar molecule  $\text{SiHF}_3$  [16] with the help of the empirical equation of Demaison and Nemes [17, 18] which states that the vibrational correction  $\varepsilon = I_o - I_e$  varies approximately as  $\sqrt{I}$ . For a heavy, rigid molecule like  $\text{SiF}_4$  whose structure can be determined from the rotational constant of only one isotopic species, this method should be accurate enough. It gives:  $r_e(\text{Si-F}) = 1.5524(10) \text{ \AA}$ . The given uncertainty corresponds to an uncertainty of 50% on the vibrational correction.

The average structure,  $r_z$  can also be calculated by correcting the ground state rotational constant for the harmonic contribution to the vibration-rotation interaction constants  $\alpha_i$  which are obtained from the harmonic force field [4]. The derived value,  $B_z = 4126.05 \text{ MHz}$  gives  $r_z = 1.5549 \text{ \AA}$ . This value can be converted into  $r_e$  value using Eq. (3). The results are also given in Table 2. The main source of error is due to the approximate nature of Eq. (3) and it is roughly estimated to be 30% of the correction  $r_z - r_e$  [10], i.e. about  $0.001 \text{ \AA}$ . The main approximation is that Eq. (3) neglects all the anharmonic constants except the bond stretching anharmonicity. This assumption was carefully checked in many different molecules and was found to be a reasonable one [9]. It is also possible to verify the validity of this assumption by using Eq. (3) to determine the structure of similar molecules whose equilibrium structure is already accurately known. The molecules  $\text{SiF}_2$  [19] and  $\text{SiHF}_3$  [16] are appropriate for this comparison. As the  $r_z$  structure of  $\text{SiHF}_3$  cannot be determined from only one isotopic species, primary as well secondary isotopic differences in bond lengths were taken into account. They were estimated by Eq. (4) which may be easily derived from Eq. (3):

$$\delta r_z = \frac{3}{2} a \delta(u^2) - \delta K \quad (4)$$

The results given in Table 3 indicate that the method seems to be particularly accurate in the particular case of the Si-F bond length.

### 3. Ab initio calculations

The equilibrium bond length in SiF<sub>4</sub> (point group T<sub>d</sub>) has been calculated at the correlated levels of second-order Møller-Plesset perturbation theory (MP2) [20] and coupled cluster theory with single and double excitations [21] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [22]. These calculations were performed with GAUSSIAN94 [23] and MOLPRO94 [24, 25]. The correlation consistent polarized valence quadruple-zeta basis VQZ+1 which has been defined elsewhere [16, 26] was used throughout. At the stationary points of SiF<sub>4</sub> the associated internal gradients did not exceed 10<sup>-5</sup> au. When applying the frozen core approximation, the silicon 1s2s2p-like and the fluorine 1s-like core molecular orbitals were required to remain doubly occupied.

The computed bond lengths in SiF<sub>4</sub> are shown in Table 4 together with analogous theoretical results [16, 26] for the equilibrium structure of SiF<sub>2</sub>. The equilibrium geometry of this triatomic molecule has been determined experimentally [19] with sufficient accuracy (see Table 3) so that the errors in the calculated bond distances of SiF<sub>2</sub> can easily be established at all presently chosen theoretical levels. These errors are then used to correct the corresponding theoretical  $r_e$  values of the target molecule SiF<sub>4</sub>. This approach leads to four consistent estimates for the equilibrium bond length in SiF<sub>4</sub> which are in the narrow range 1.5516-1.5529 Å (see Table 4; the empirically corrected  $r_e$  values are given in parentheses). The mean value of these estimates is 1.5524 Å which is fortuitously identical with the spectroscopic  $r_e$  values from this work reported in Table 2. As might have been expected, the CCSD(T) calculation which takes core correlation into account predicts the most reliable  $r_e$  value for SiF<sub>4</sub> (1.5516 Å), the deviation from the spectroscopic value is essentially the same as in the case of SiF<sub>2</sub> (0.0007 Å, see Tables 3-4).

### 4. Conclusion

We have at our disposal 6 different structures (4 from ab initio calculations and 2 from spectroscopy, see Tables 2 and 4) which are in a narrow range 1.5516-1.5529 Å. Their mean value is identical to their median value, 1.55235 Å, which is a further indication that there is no outlier. The number of data ( $n = 6$ ) is small, thus, it might seem that it is not enough to calculate a reliable standard deviation using the standard procedure. However, in the present case (no

outlier,  $n = 6$  data), the range  $R$  of the data (interval from the lowest to the highest value) gives us a quick and reliable estimate of the standard deviation  $s$  of the data [27],

$$s = \frac{R}{1.40n^{1/3}} \quad (5)$$

Eq. (5) gives  $s = 0.0005 \text{ \AA}$ . In conclusion, the equilibrium value for the bond length in  $\text{SiF}_4$  is  $r_e(\text{Si-F}) = 1.5524(8) \text{ \AA}$  where the uncertainty shown in parentheses is given in the unit of the last digit and is 4 standard deviations which corresponds to a confidence level of 99%.

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Table 1  
Morse anharmonicity parameter  $a$  for the Si-F bond length

| Molecule          | $r_e$ (Å) | Ref.      | $a$ (Å <sup>-1</sup> ) | Ref. |
|-------------------|-----------|-----------|------------------------|------|
| SiF               | 1.601     | [28]      | 1.980                  | [9]  |
| SiF <sub>2</sub>  | 1.590     | [19]      | 1.975                  | [19] |
| SiHF <sub>3</sub> | 1.563     | [16]      | 1.928                  | [16] |
| SiF <sub>4</sub>  | 1.552     | this work | 1.903                  | [11] |
| SiF <sub>4</sub>  | 1.552     | this work | 1.992                  | [11] |

Table 2  
Si-F bond length (Å) in SiF<sub>4</sub> <sup>a</sup>

|                  | Electron diffraction |           | Spectroscopy |                         |
|------------------|----------------------|-----------|--------------|-------------------------|
|                  | [2]                  | [3]       | from $B_0$   | from $B_z$ <sup>b</sup> |
| $r_a$            | 1.555 (2)            | 1.552 (1) |              |                         |
| $r_z$            | 1.554 (2)            | 1.551 (1) |              | 1.5549 (2)              |
| $r_e$            | 1.551 (2)            | 1.548 (2) | 1.5524 (10)  | 1.5523(10)              |
| $u$ <sup>c</sup> | 0.029 (7)            | 0.043 (2) |              | 0.039 <sup>d</sup>      |

<sup>a</sup> See text for details.

<sup>b</sup> With the help of Eq. (4).

<sup>c</sup> Mean amplitude of vibration measured at  $T = 298$  K.

<sup>d</sup> Calculated from the force field:  $u(298\text{ K}) = 0.03907\text{ Å}$  and  $u(0\text{ K}) = 0.0387\text{ Å}$ .

Table 3  
Structures <sup>a</sup> of SiF<sub>2</sub> and SiHF<sub>3</sub>

| Molecule          | Type of structure  | $r(\text{Si-H})$ | $r(\text{Si-F})$ | $\angle(\text{FSiF})$ |
|-------------------|--------------------|------------------|------------------|-----------------------|
| SiF <sub>2</sub>  | $r_z$              |                  | 1.5947           | 100.89                |
|                   | $r_e$ <sup>b</sup> |                  | 1.5903 (13)      | 100.89                |
|                   | exp. <sup>c</sup>  |                  | 1.5901(1)        | 100.77(2)             |
| SiHF <sub>3</sub> | $r_z$              | 1.4526           | 1.5666           | 108.18                |
|                   | $r_e$ <sup>b</sup> | 1.4497 (9)       | 1.5636 (9)       | 108.18                |
|                   | exp. <sup>d</sup>  | 1.44872 (3)      | 1.56266 (1)      | 108.2271 (4)          |

<sup>a</sup> Bond lengths in Å, bond angles in degree.

<sup>b</sup> Calculated from  $r_z$  value with the help of Eq. (3). The uncertainty is assumed to be 30% of the correction  $r_z - r_e$ .

<sup>c</sup> Ref. [19].

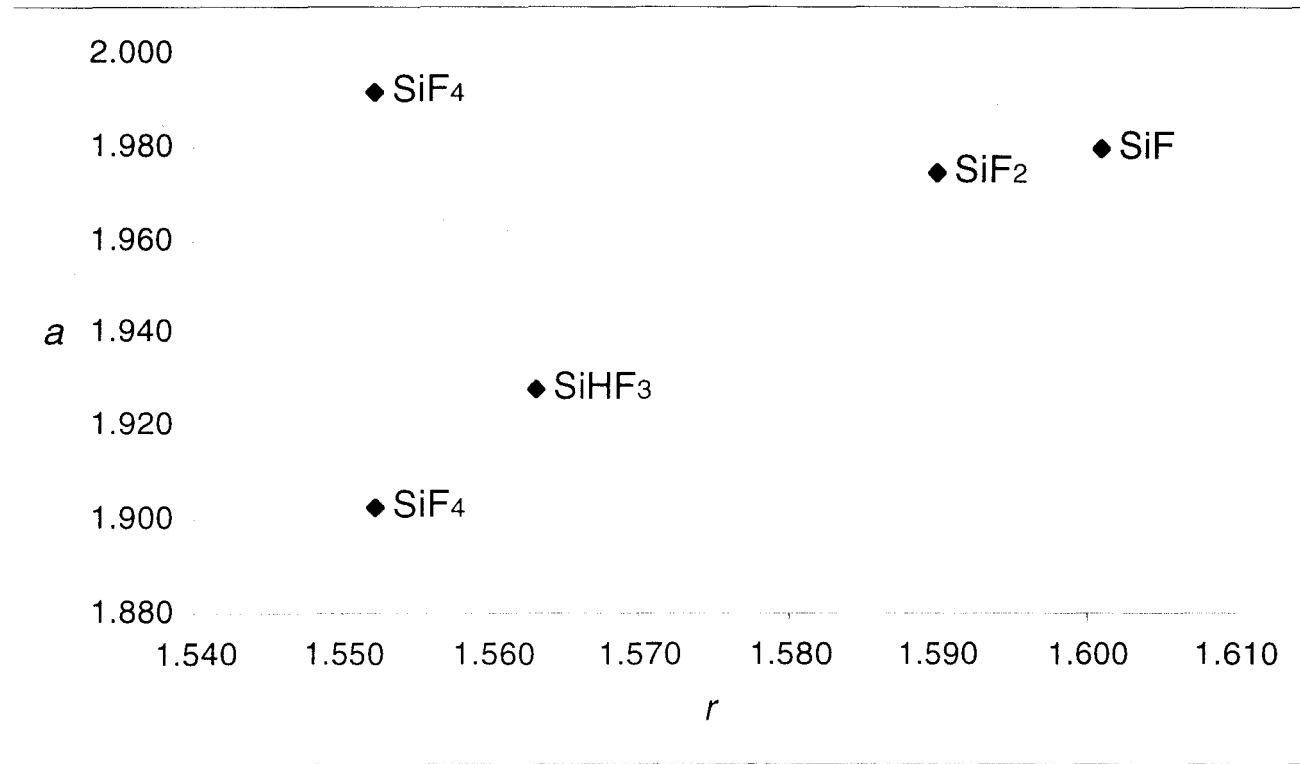
<sup>d</sup> Ref. [16].

Table 4  
 Computed equilibrium geometries <sup>a</sup> of SiF<sub>4</sub> and SiF<sub>2</sub>

| Molecule         | Method <sup>b</sup> | <i>r</i> (Si-F) <sup>c</sup> | ∠(FSiF) | Ref. |
|------------------|---------------------|------------------------------|---------|------|
| SiF <sub>4</sub> | MP2 ae              | 1.5546 (1.5516)              |         |      |
|                  | MP2 fc              | 1.5633 (1.5526)              |         |      |
|                  | CCSD(T) ae          | 1.5516 (1.5523)              |         |      |
|                  | CCSD(T) fc          | 1.5598 (1.5529)              |         |      |
| SiF <sub>2</sub> | MP2 ae              | 1.5931                       | 101.06  | [16] |
|                  | MP2 fc              | 1.6008                       | 100.95  | [16] |
|                  | CCSD(T) ae          | 1.5894                       | 100.98  | [26] |
|                  | CCSD(T) fc          | 1.5970                       | 100.86  | [26] |

<sup>a</sup> Bond lengths in Å, bond angles in degree.  
<sup>b</sup> Basis set VQZ+1; ae = all electrons correlated, fc = frozen core approximation.  
<sup>c</sup> Empirically corrected values in parentheses (see text).

Fig .1  
Plot of  $a(\text{SiF})$  [ $\text{\AA}^{-1}$ ] as a function of  $r(\text{SiF})$  [ $\text{\AA}$ ]





## Conclusion

L'objectif de ce travail était de vérifier la théorie des réductions pour les états dégénérés d'une toupie symétrique  $C_{3v}$ . Il consistait aussi à estimer la précision des calculs de chimie quantique pour la détermination de paramètres moléculaires.

Cela nous a amené à utiliser six spectromètres différents pour déterminer des paramètres très précis, et à faire des calculs de chimie quantique de haut niveau avec trois programmes différents. La combinaison de résultats théoriques et expérimentaux permet d'obtenir les paramètres moléculaires les plus fiables.

Nous avons analysé les bandes de vibration fondamentales du trifluorosilane pour avoir un maximum de paramètres et les comparer à ceux calculés à partir du champ de force *ab initio*. Nous voulions d'abord évaluer la précision du champ de force en confrontant certains paramètres comme les fréquences de vibration, et les constantes de distorsion centrifuges de l'état fondamental. La précision de champ de force calculé étant bonne, nous avons pu l'utiliser sans le recalibrer.

Nous avons ensuite entrepris de calculer les paramètres réduits à partir des relations données par la théorie des réductions entre ces paramètres et les constantes de force, puis nous les avons comparés aux valeurs expérimentales. L'accord entre ces paramètres calculés et ceux obtenus expérimentalement était très bon, ce qui confirme bien la théorie des réductions. Les paramètres déterminables expérimentalement ont donc un sens clairement défini, et peuvent être reliés aux constantes de force qui ont un réel sens physique.

Pour les réductions des Hamiltoniens des toupies  $C_{3v}$ , les relations sont donc vérifiées expérimentalement et théoriquement. Il reste un cas pour lequel il n'existe pas encore de confirmation expérimentale. Pour les toupies asymétriques, il est théoriquement possible, avec une molécule toupie quasi-sphérique ( $A \approx B \approx C$ ) d'utiliser un Hamiltonien non réduit. En effet les constantes de distorsion quartique ne sont pas affectées par la transformation de Van Vleck, il est donc possible de déterminer ces six constantes. Nous pensons pouvoir le vérifier avec l'étude de la molécule  $SO_2F_2$ .

Une partie des travaux a été consacrée aux calculs de structures à l'équilibre par des méthodes *ab initio*. Mais nous avons constaté que la méthode de convergence reste aujourd'hui difficilement applicable à la plupart des molécules : elle est limitée à des molécules ayant peu d'atomes, et ces atomes doivent être légers. Les principales limitations sont dues aux temps de calcul et aux ressources informatiques (mémoire vive, espace disque).

La technique de calibration est très utilisée, des écarts (offset) existent pour les liaisons les plus courantes C-H et C=O, mais ils ne sont pas toujours fiables et disponibles pour d'autres types de liaison. Des structures expérimentales précises n'existent pas toujours, et les écarts n'ont pas été calculés avec un niveau de calcul suffisamment élevé pour qu'ils soient constants.

Pour l'instant la méthode qui fournit les structures les plus précises, et qui est applicable à un grand nombre de molécules est celle qui utilise les moments d'inertie à l'équilibre obtenus par correction des moments d'inertie expérimentaux dans l'état fondamental de vibration avec le champ de force *ab initio*. Les résultats obtenus par association des données expérimentales et théoriques sont plus fiables que ceux fournis par les deux types de données séparément. Les moments d'inertie fournis par la spectroscopie de ro-vibration sont en effet très fiables, de même que les champs de force *ab initio* sont eux aussi très précis avec des niveaux de calcul relativement peu élevés par rapport à ceux nécessaires pour calculer une bonne structure. Celui du trifluorosilane a permis de très bien reproduire les données expérimentales avec le niveau de calcul MP2/cc-pvTZ+1.

La précision des nouvelles structures de SiHF<sub>3</sub> et SiF<sub>4</sub> que nous avons déterminées confirme bien la fiabilité de cette méthode.

Les calculs *ab initio* permettent d'obtenir des données très intéressantes, et combinés à des paramètres expérimentaux fournissent des résultats très utiles. Ils sont très précieux pour faire une première prévision des spectres préalable à l'analyse expérimentale, ou pour calculer des paramètres que l'on ne peut atteindre expérimentalement...

Dans le domaine des calculs *ab initio*, l'évolution très rapide des matériels informatiques permettra d'ici quelques années d'utiliser des bases très étendues qui pourront calculer exactement les corrélations de cœur- valence et les fonctions diffuses. La méthode de convergence sera sûrement applicable pour un plus grand nombre de molécules, il est vraisemblable que les bases quadruple zéta ne seront qu'un calcul intermédiaire d'ici deux à trois ans.

A plus court terme nous voulons vérifier sur d'autres molécules si les très bonnes précisions que nous avons obtenues avec notre champ de force n'étaient pas accidentelles. En effet, les calculs de champ de force anharmonique au niveau MP2 sont récents, et n'étaient menés auparavant qu'avec la méthode Hartree-Fock. Un bon candidat serait la molécule  $\text{CHF}_3$  pour laquelle il existe des données expérimentales fiables. Cette molécule ne possède que des atomes de la 1<sup>ère</sup> ligne, mais les liaisons sont beaucoup plus polaires : il faudra sûrement tenir compte de l'influence des fonctions diffuses.



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