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Thesis defended by **Tamara SHAABAN**

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Speciality **Theoretical physical analytical chemistry**

Theoretical and Experimental Exploration of the Physico-Chemical and Spectroscopic Properties of Protactinium(V)

Thesis supervised by Valérie VALLET Supervisor
Florent RÉAL Co-Supervisor

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Keywords: actinide, protactinium, x-ray absorption spectroscopy, quantum chemistry

Mots clés : actinides, protactinium, spectroscopie d'absorption de rayons x, chimie quantique

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THEORETICAL AND EXPERIMENTAL EXPLORATION OF THE PHYSICO-CHEMICAL AND SPECTROSCOPIC PROPERTIES OF PROTACTINIUM(V)**Abstract**

Protactinium (Pa, $Z = 91$) occupies a unique position between transition metals and the heavier actinides, as both its 5f and 6d orbitals contribute to the ground-state electronic configuration. In aqueous solution, protactinium exists mainly in the +V oxidation state; however, unlike uranium or neptunium, it does not form a stable di-oxo cation (PaO_2^+). Instead, it can form a mono-oxo bond (Pa–O) in solution, for which only limited experimental information exists. Because of its scarcity, strong radioactivity, and marked tendency toward hydrolysis, polymerization, and sorption onto solids, experimental investigations of protactinium chemistry remain highly challenging. This thesis therefore combines advanced quantum-chemical modeling and high-resolution X-ray spectroscopy to elucidate the stability, structure, and spectroscopic signatures of Pa(V) mono-oxo complexes.

A theoretical framework was developed to evaluate the thermodynamics of oxo-bond formation and ligand-dependent stabilization in aqueous media using relativistic density functional theory (DFT) and correlated wave-function methods. The Gibbs free energy of the reaction $\text{Pa}(\text{OH})_4(\text{X}) \longrightarrow \text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ was computed for a series of monodentate ligands, hydroxide (OH^-), halides (F^- , Cl^- , Br^- , I^-), and thiocyanate (SCN^-) as well as for bidentate ligands such as nitrate (NO_3^-), sulfate (SO_4^{2-}), and oxalate ($\text{C}_2\text{O}_4^{2-}$). These calculations showed that Cl^- , Br^- , I^- , SO_4^{2-} , SCN^- , and NO_3^- effectively stabilize the mono-oxo bond and that the Pa–O interaction exhibits triple-bond character. The derived thermodynamic trends provided quantitative guidance for subsequent experimental work.

These predictions were validated by X-ray Absorption Spectroscopy (XANES and EXAFS) measurements performed at the SOLEIL synchrotron within the ANR-CHESS project. For the first time, a persistent Pa–O bond was observed in concentrated hydrochloric acid, revealing the formation of $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ even in 12 M HCl. The experimental Pa–O bond length of 1.83 Å agrees remarkably well with theoretical predictions, resolving a discrepancy between theory and experiment. At lower acidities (3 M HCl), mixed hydroxo-oxo species such as $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ were identified, confirming the coexistence of multiple Pa(V) species depending on acidity.

To interpret the HERFD-XANES spectra at the M_4 -edge of PaF_7^{2-} and $\text{PaO}(\text{C}_2\text{O}_4)_3^{3-}$, core-excited states were modeled using two-component relativistic TD-DFT (2c-TDA-CAM-B3LYP) and multireference RASPT2 methods. Both approaches gave consistent results, indicating that the main transitions are localized on the Pa and Pa–O fragments of the respective complexes, with minimal ligand-to-metal charge transfer.

Overall, this work provides the first coherent theoretical–experimental description of Pa(V) speciation in aqueous media. It establishes a predictive computational framework for anticipating complex stability and guiding synchrotron experiments. The results demonstrate that the mono-oxo Pa–O bond can persist in highly acidic environments and that theoretical models can now reproduce experimental bond distances and spectral features with good accuracy.

Keywords: actinide, protactinium, x-ray absorption spectroscopy, quantum chemistry

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EXPLORATION THÉORIQUE ET EXPÉRIMENTALE DES PROPRIÉTÉS PHYSICO-CHIMIQUES ET SPECTROSCOPIQUES DU PROTACTINIUM(V)**Résumé**

Le protactinium (Pa, $Z = 91$) occupe une position unique entre les métaux de transition et les actinides lourds, car ses orbitales 5f et 6d contribuent toutes deux à sa configuration électronique à l'état fondamental. En solution aqueuse, il se trouve principalement à l'état d'oxydation +V; toutefois, contrairement à l'uranium ou au neptunium, il ne forme pas de cation dioxo stable (PaO_2^+), mais peut établir une liaison mono-oxo (Pa–O), encore peu caractérisée expérimentalement. La rareté, la radioactivité et la forte réactivité du protactinium compliquent considérablement son étude.

Cette thèse combine modélisation quantique avancée et spectroscopie X à haute résolution pour étudier la stabilité, la structure et les signatures spectroscopiques des complexes mono-oxo de Pa(V). À l'aide de DFT relativiste et de méthodes à fonction d'onde corrélée, un protocole théorique a été développé pour évaluer la thermodynamique de formation des liaisons oxo $\text{Pa}(\text{OH})_4(\text{X}) \longrightarrow \text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$, notamment pour des ligands monodentés (hydroxyde, halogénures, thiocyanate) et bidentés (nitrate, sulfate, oxalate). Les résultats montrent que plusieurs de ces ligands stabilisent efficacement la liaison Pa–O, qui présente un caractère de triple liaison. Ces tendances ont guidé les investigations expérimentales.

Les prédictions théoriques ont été validées par des mesures XANES et EXAFS réalisées au synchrotron SOLEIL (projet ANR-CHESS). Une liaison Pa–O persistante a été observée pour la première fois en milieu fortement acide, confirmant la formation de $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ dans une solution concentrée, 12 M HCl, avec une longueur de liaison expérimentale (1.83 Å) en excellent accord avec les valeurs théoriques. À plus faible acidité, des espèces mixtes hydroxo–oxo, telles que $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ ou $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ ont également été identifiées, confirmant la coexistence de plusieurs espèces de Pa(V) en fonction de l'acidité.

Enfin, les spectres HERFD-XANES au seuil M_4 de complexes modèles ont été interprétés par modélisation des états excités à l'aide de la méthode TD-DFT relativiste à deux composantes (2c-TDA-CAM-B3LYP) ainsi que par la méthode multiréférence RASPT2. Les deux approches ont donné des résultats cohérents, indiquant que les principales transitions sont localisées sur les fragments Pa et Pa–O des complexes respectifs, avec un transfert de charge ligand-métal négligeable.

Ce travail fournit la première description intégrée, à la fois théorique et expérimentale, de la spéciation du Pa(V) en solution aqueuse. Il démontre la stabilité de la liaison mono-oxo en milieu acide et confirme la capacité des modèles quantiques modernes à prédire avec fiabilité les propriétés structurales et spectrales du protactinium.

Mots clés : actinides, protactinium, spectroscopie d'absorption de rayons x, chimie quantique

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Table of contents

Abstract	xiii
Acknowledgments	xv
Table of contents	xvii
List of Tables	xix
List of Figures	xxi
General Introduction	1
References	4
1 Protactinium(V) in Aqueous Media	7
1.1 Discovery of Protactinium	7
1.2 Applications of Protactinium	9
1.3 Electronic structure and oxidation states	10
1.4 Formation of PaO_2^+ in gas phase	11
1.5 Experimental Challenges in Manipulating Pa(V) in Solution . .	13
1.6 Complexation of Pa(V) with ligands	14
1.7 Objectives of the Thesis	19
1.8 References	22
2 Theoretical Methods	29
2.1 Introduction to Quantum Chemistry	29
2.2 The Schrödinger equation	30
2.2.1 Born-Oppenheimer Approximation	31
2.3 Constraints on the wave-function	32
2.4 Hartree-Fock self-consistent field method	33
2.5 Configuration Interaction Methods (CI)	36
2.6 Møller-Plesset many-body perturbation theory	37
2.7 Coupled-Cluster method	38

2.8	Density Functional Theory	40
2.8.1	The Kohn-Sham equation	41
2.8.2	Approximate exchange-correlation functionals	44
2.9	Relativistic Quantum Chemistry	52
2.9.1	The Dirac Equation	53
2.9.2	The Many-Electron Dirac Hamiltonian	56
2.9.3	Two-Components Relativistic Hamiltonians	57
2.10	Basis sets	62
2.11	Solvent Effects	66
2.11.1	Continuum Models	68
2.12	Time-Dependent Density Functional Theory	73
2.12.1	Time-Dependent Kohn-Sham Equations	74
2.12.2	Adiabatic Approximation	74
2.12.3	Real-Time TD-DFT	75
2.12.4	Linear-Response TD-DFT	75
2.13	Multi-Configurational Self-Consistent Field (MCSCF)	78
2.13.1	Post-MCSCF Perturbation Theory	79
2.13.2	Spin-Orbit Coupling: The Two-Step RASSI-SO Approach	80
2.14	References	82
3	The Protactinium(V) Mono-oxo Bond	97
3.1	Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations	98
3.2	Is the protactinium(V) mono-oxo bond weaker than what we thought?	133
3.3	References	154
4	Speciation of Pa(V) in solution with XAS	157
4.1	Synchrotron Physics	160
4.2	X-ray Absorption Spectroscopy	161
4.2.1	Principles	161
4.2.2	X-ray Absorption Near Edge Structure (XANES)	166
4.2.3	Resonant Inelastic X-ray Scattering (RIXS)	169
4.2.4	High-Energy Resolution Fluorescence Detection XANES (HERFD-XANES)	170
4.2.5	Extended X-ray Absorption Fine Structure (EXAFS)	175
4.2.6	Derivation of the EXAFS Equation	176
4.2.7	EXAFS Data Reduction	179
4.2.8	EXAFS limitations	186
4.3	EXAFS analysis of Pa(V) in hydrochloric acid	188
4.4	RIXS maps and HERFD-XANES of Pa(V) solutions in HF and H ₂ C ₂ O ₄	206

4.5	Conclusion	210
4.6	References	211
5	The core-excited states of protactinium(V) complexes	217
5.0.1	Introduction	217
5.0.2	Computational Modeling	218
5.0.3	TD-DFT Calculations	219
5.0.4	RASSCF Calculations	222
5.1	Results	224
5.1.1	M ₄ - edge of [Pa] ⁵⁺	224
5.1.2	M ₄ -edge of [PaO] ³⁺	225
5.1.3	M ₄ -edge of [PaF ₇] ²⁻	227
5.1.4	M ₄ -edge of [PaO(C ₂ O ₄) ₃] ³⁻	233
5.1.5	Comparison of the M ₄ -edge of [PaF ₇] ²⁻ and [PaO(C ₂ O ₄) ₃] ³⁻	235
5.2	Conclusion	238
5.3	References	239
6	Conclusions and Perspectives	241
6.1	Theoretical insights into the stabilization of the mono-oxo bond	242
6.2	Experimental validation in hydrochloric acid media	242
6.3	Perspectives for ligand chemistry	243
6.4	Advances in X-ray spectroscopy and theoretical interpretation	244
6.5	Broader outlook and long-term perspectives	245
6.6	References	245
Scientific contributions		247
	Publications	247
	Oral presentations (first author was the presenter)	247
	Poster presentations	248

List of Tables

1.1	Suggested chloro complexes of Pa(V) as a function of HCl concentration and at Pa trace-level concentrations.	17
3.1	Electronic energies ΔE (in kJ mol^{-1}) for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$, calculated using CCSD(T) and various DFT functionals, grouped by functional type.	102
4.1	Summary of Pa(V) and Pa(IV) samples shown in Figure 4.1, prepared at IJCLab, Orsay, with their respective Pa and ligand concentrations. Spectroscopic analyses (HERFD-XANES, RIXS, EXAFS) performed at the MARS beamline of the SOLEIL synchrotron at the Pa L_3 -edge during the experimental campaign conducted from February 14 th to 19 th , 2024. Shaded rows indicate samples that could not be measured.	160
4.2	Recommended parameter ranges in EXAFS fitting.	184
5.1	Summary of the active spaces defined and the number of roots (singlets and triplets) calculated for each system.	224
5.2	Absolute energies in eV of the main peak A in the Pa M_4 -edge of $[\text{Pa}]^{5+}$ and $[\text{PaF}_7]^{2-}$. Comparison for DZ, TZP, TZ2P and QZ4P basis sets in TDA-CAMB3LYP calculations and for VTZP basis sets at the SO-RASSCF and SO-RASPT2 levels	225
5.3	Summary of electronic transitions contributing to the M_4 -edge of PaO^{3+} , computed at the SO-RASPT2 level. Dominant orbital characters (5f, 6d, and O 2p) and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the $3d_{3/2}$ electron is excited into. The peak labels correspond to Figure 5.7b.	228

5.4	Summary of electronic transitions contributing to the M_4 -edge of $[\text{PaO}]^{3+}$, computed at the SO-CAM-B3LYP level with TZ2P basis set. Dominant orbital characters (5f, 6d, and O 2p) and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the $3d_{3/2}$ electron is excited into. The peak labels correspond to Figure 5.5.	229
5.5	Absolute energies in eV of the main peaks A and B in the Pa M_4 -edge of $[\text{PaO}]^{3+}$ and of the main peak A in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. The B peak is barely visible in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. Comparison for DZP, TZP, TZ2P and QZ4P basis sets in 2c-TDA-CAMB3LYP calculations and for VTZP basis sets at the SO-RASSCF and SO-RASPT2 levels.	230
5.6	Summary of electronic transitions contributing to the M_4 -edge of $[\text{PaF}_7]^{2-}$, computed at the SO-RASPT2 level. Pa and fluoride contributions and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the $3d_{3/2}$ electron is excited into.	233

List of Figures

1	Periodic table of elements.	2
1.1	Partial decay scheme of ^{238}U , showing the production of ^{234}Pa .	8
1.2	Partial decay scheme of ^{235}U showing the production of ^{231}Pa .	9
1.3	Speciation diagram of Pa(V) hydrolyzed species at ultra-trace concentration in aqueous solution ($I = 1 \text{ M NaClO}_4$, $T = 198 \text{ K}$) [trubertHydrolysisProtactiniumV	
2.1	Functional classification based on Perdew’s “Jacob’s ladder [bursch_best-practice_2022].	4
2.2	Illustration of areas treated in the basis set concept.	63
2.3	PCM solute cavity of Pa(OH) ₅ complex.	71
3.1	The model systems of Pa(V) complexes.	101
4.1	EXAFS cells containing protactinium samples prepared at IJCLab (Orsay) for measurements at the MARS beamline of the SOLEIL synchrotron. The sample numbering corresponds to Table 4.1. The analyses were performed at the Pa L ₃ -edge during an experimental campaign conducted from February 14 th to 19 th , 2024.	159
4.2	Schematic representation of a synchrotron light source. Electrons (blue) are generated by an electron gun and accelerated in a linear accelerator (LINAC) before being injected into a storage ring. Bending magnets (red) alter the electron trajectory, causing the emission of synchrotron radiation (yellow), which is directed toward experimental stations [5].	162
4.3	Representation of the atomic energy levels with the K-, L-, and M-shells and their corresponding absorption edges.	163
4.4	Decay of the excited state: X-ray fluorescence (left) and Auger effect (right; dashed lines represent non-radiative process.). . .	165
4.5	XAS spectrum of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L ₃ -edge at the MARS beamline of the SOLEIL synchrotron.	166

4.6	Plutonium L ₃ -edge XANES spectra for aqueous solution of Pu(III)-Pu(VI) with Pu(IV) colloids [vitovaExploringElectronicStructure2018].	168
4.7	(a) Schematic representation of resonant inelastic X-ray scattering (RIXS) processes. An incident photon of energy Ω excites a core electron into an unoccupied state, creating an intermediate state. The system then relaxes either via a core-level transition (core-to-core RIXS) or through a valence electron decay (core-to-valence RIXS), emitting a photon of energy ω . The energy transfer $\Omega - \omega$ corresponds to the energy of the final state excitation. (b) Example of a 2D RIXS map showing emission intensity as a function of incident energy and energy transfer at the U L ₃ -edge of UO ₂ [kvashninaRoleResonantInelastic2014].	170
4.8	U L ₃ -edge of UO ₂ and UO ₂ (NO ₃) ₂ ·6H ₂ O measured in total fluorescence yield (TFY) and HERFD modes [10].	171
4.9	U M ₄ -edge of UO ₂ measured in total fluorescence yield (TFY) and HERFD modes [14].	172
4.10	HERFD-XANES spectra at the uranium M ₄ -edge for various uranium oxide compounds (U ₄ O ₉ , U ₃ O ₇ , U ₃ O ₈). Solid lines represent the experimental spectra, while dotted lines and open circles correspond to component spectra obtained through Iterative Target Transformation (ITT), scaled according to the calculated weight fractions. The labeled spectral features (1, 2, 3/3*) correlate with uranium in formal oxidation states U(IV), U(V), and U(VI), respectively [leindersEvolutionUraniumChemical2017].	173
4.11	Uranium M ₄ -edge HERFD-XANES spectra of four U(VI) compounds: Sr ₃ UO ₆ (O _h), CaUO ₄ (D _{3d}), β -SrUO ₄ (D _{4h}), and Cs ₂ UO ₂ Cl ₄ (D _{4h}). Experimental spectra (thick lines), simulated spectra (thin lines), and uranium <i>f</i> -projected DOS (dotted lines) are shown [amidaniProbingLocal2017].	174
4.12	Normalized XAS spectrum with subtracted background of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L ₃ -edge at the MARS beamline of the SOLEIL synchrotron.	180
4.13	The $\chi(k)$ of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L ₃ -edge at the MARS beamline of the SOLEIL synchrotron: (a) unweighted, (b) weighted by <i>k</i> , and (c) weighted by <i>k</i> ³	181
4.14	Fourier transform (FT) magnitude of EXAFS data from Pa(V) sample in concentrated hydrofluoric acid, acquired at the L ₃ -edge at the MARS beamline of the SOLEIL synchrotron.	182
4.15	Workflow for EXAFS data reduction and fitting.	185

4.16	Optimized geometries of the complexes: (a) $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ identified in 12 M HCl, and (b) $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and (c) $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ identified in 3 M HCl. All geometries were optimized in the COSMO solvent model at the scalar relativistic (SR-ZORA) level using the PBE0 functional, and were used for EXAFS fitting.	191
4.17	(a) $2p3d$ RIXS schematic at the Pa L_3 -edge; (b-c) experimental RIXS maps of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, performed at the MARS beamline of the SOLEIL synchrotron at the Pa L_3 -edge during the experimental campaign conducted from February 14 th to 19 th , 2024.	206
4.18	Optimized geometries of (a) $[\text{PaF}_7]^{2-}$ and (b) $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. The geometries were optimized in the COSMO solvent model at the scalar relativistic (SR-ZORA) level using the PBE0 functional.	207
4.19	Pa L_3 -edge HERFD-XANES of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$	208
4.20	(a) Schematic illustration of the $3d4f$ RIXS process at the Pa M_4 -edge. (b) and (c) Experimental RIXS maps of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, respectively, measured at the MARS beamline of the SOLEIL synchrotron in 2022 [4].	209
4.21	Pa M_4 -edge HERFD-XANES of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ [4].	210
5.1	Optimized geometries of selected Pa and PaO complexes, computed at the SR-ZORA/PBE0/TZ2P level in the COSMO solvent model. Color code: navy blue (Pa), dark green (F), red (O), black (C), white (H).	219
5.2	Schematic orbital diagram of $[\text{PaO}]^{3+}$, computed at the scalar relativistic level with the SAOP functional. The atomic contributions (weight in %) are highlighted in red for Pa(5f), blue for Pa(6d) and black for other orbitals (Pa(7s), Pa(7p), O(2p)).	220
5.3	2c-TDA-CAM-B3LYP Pa M_4 -edge XAS of $[\text{Pa}]^{5+}$ with DZP, TZP, TZ2P, and QZ4P (full virtual orbital space; no oscillator strength cutoff). A Lorentzian broadening with FWHM 1.5 eV is applied. (a) Basis set convergence. (b) DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions.	226
5.4	M_4 -edge spectrum of $[\text{Pa}]^{5+}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.	227
5.5	M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the 2c-TDA-CAMB3LYP level of theory with TZ2P basis set, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 0.3 eV.	230

5.6	Comparison of 2c-TDA-CAMB3LYP XAS at the Pa M_4 -edge of $[\text{PaO}]^{3+}$ for DZP, TZP, TZ2P, and QZ4P basis sets, using virtual space restrictions and an oscillator strength cutoff. A Lorentzian broadening with FWHM 1.5 eV is applied. (a) Basis set convergence. (b) DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions. (c) Effect of the selection $\tau_{\text{osc}} > 10^{-5}$ (OS-5) and the virtual space restriction (OS-5-VS), compared to neither oscillator strength cutoff nor virtual space restriction (Full-VS), for the TZ2P basis set.	231
5.7	M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the SO-RASPT2 level of theory. Lorentzian broadening parameter is set to a FWHM of either 1.5 eV or 0.3 eV.	232
5.8	Comparison of 2c-TDA-CAMB3LYP XAS at the Pa M_4 -edge of $[\text{PaF}_7]^{2-}$ for DZP, TZP, TZ2P, and QZ4P basis sets, using virtual space restrictions and an oscillator strength cutoff. A Lorentzian broadening with FWHM 1.5 eV is applied. (a) Basis set convergence. (b) DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions. (c) Effect of the selection $\tau_{\text{osc}} > 10^{-5}$ (OS-5) and the virtual space restriction (OS-5-VS), compared to neither oscillator strength cutoff nor virtual space restriction (Full-VS), for the TZ2P basis set.	234
5.9	M_4 -edge spectrum of $[\text{PaF}_7]^{2-}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.	235
5.10	M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory with different choices of active spaces, (a) 5f, 6d in RAS3; (b) 5f, 6d, 7s in RAS3; and (c) 5f, 6d in RAS3 with bonding orbitals included in RAS2. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.	236
5.11	2c-TDA-CAMB3LYP spectra with TZ2P basis set at the Pa M_4 -edge of $[\text{PaO}]^{3+}$ for different Pa–O _{oxo} distances, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.	237
5.12	2c-TDA-CAMB3LYP spectra with TZ2P basis sets at the Pa M_4 -edge of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.	237

General Introduction

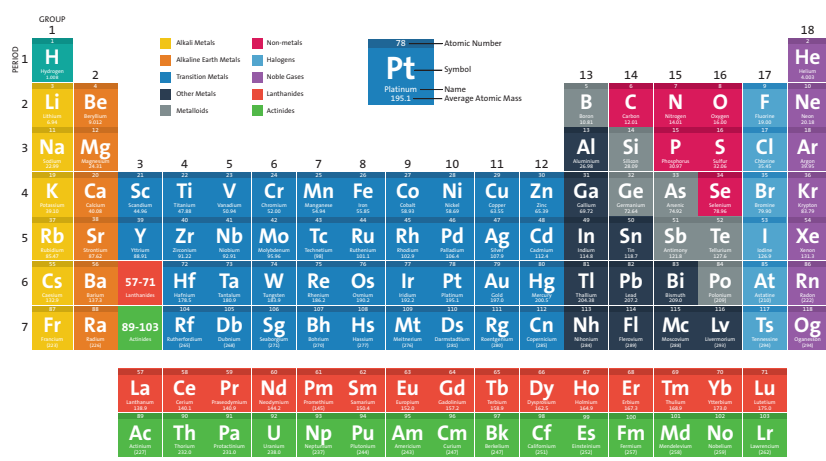
Actinides are 5f-block elements located in the last row of the periodic table (see Figure 1). A defining feature of this family is that all isotopes are radioactive with half-lives spanning many orders of magnitude. Only a few actinides, such as ^{232}Th , ^{235}U , and ^{238}U , occur naturally in significant amounts because their half-lives are comparable to the age of the Earth. Others, such as ^{231}Pa are present in nature as members of long-lived uranium decay chains that occur due to natural nuclear reactions. Beyond these primordial and radiogenic nuclides, additional actinides arise from anthropogenic activities, being produced by neutron irradiation in reactors or during nuclear weapon tests. Their dual origin has made actinides central not only to the history of nuclear science but also to contemporary issues in energy production, weapons, and environmental contamination.

Actinides are characterized by their large number of electrons and by the presence of partially filled 5f and 6d orbitals. With atomic numbers ranging from 89 (actinium) to 103 (lawrencium), their ground-state electronic configurations extend from $\text{Ac}:[\text{Rn}]6d^1 7s^2$ to $\text{Lr}:[\text{Rn}]5f^{14} 7s^2 7p^1$. This electronic structure allows them to adopt different oxidation states, and in some cases coexisting in the same system. For example, plutonium is well known for exhibiting four oxidation states simultaneously in aqueous solution [1]. Such flexibility gives rise to a remarkably complex chemistry in which redox transformations, ligand coordination, and subtle electronic effects jointly govern determine reactivity.

The importance of actinide chemistry is clearly illustrated by its central role in the nuclear fuel cycle. Uranium and plutonium are the primary sources of nuclear fuels, making nuclear energy one of the principal low-carbon energy technologies available today. While nuclear energy plays a key role in mitigating


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PERIODIC TABLE OF ELEMENTS



The periodic table is color-coded by groups: Alkali Metals (yellow), Alkaline Earth Metals (orange), Transition Metals (blue), Other Metals (grey), Non-metals (red), Halogens (green), Noble Gases (purple), Lanthanides (pink), and Actinides (dark pink). A callout for Platinum (Pt) shows its atomic number (78), symbol, name, and average atomic mass (195.1).

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Figure 1: Periodic table of elements.

climate change by substantially reducing greenhouse gas emissions, offsetting approximately 8 million tons of CO₂ per GWe of capacity each year when replacing coal-based generation [2], it simultaneously produces considerable quantities of spent nuclear fuel. By 2020, around 400 000 tonnes of heavy metal had been discharged from nuclear power plants as spent nuclear fuel, of which about 30% had been reprocessed into high-level radioactive waste according to the annual report of the International Atomic Energy Agency in 2020 [3]. Managing these materials remains a major challenge, involving decisions about reprocessing, storage, and eventual geological disposal. The scientific question underlying all these strategies is the same: how do actinides behave over the timescales of hundreds of thousands of years?

Because of their potential mobility in the environment, whether resulting from nuclear accidents, reprocessing activities, nuclear weapon testing, or long-term storage, understanding actinide behavior is of fundamental importance. Once released, radionuclides can migrate through multiple environmental compartments including the atmosphere, hydrosphere, biosphere, and lithosphere.

Their transport and fate depend strongly on oxidation state, solubility, complexation, precipitation, and sorption processes. For instance, Pu(IV) is relatively insoluble and tends to be immobile, whereas Pu(V) is more soluble and can migrate more readily. Among these compartments, the hydrosphere is of particular importance, since water is capable of transporting radionuclides over long distances [4]. In aqueous environments, natural organic matter further influences actinide speciation by stabilizing or destabilizing particular oxidation states. Depending on its concentration and the prevailing chemical conditions, organic matter can either enhance or limit mobility, underscoring the complexity of predicting their behavior in real environments [5].

For both technological applications and environmental safety, advancing our understanding of actinide chemistry requires detailed knowledge of their electronic structure. The distribution of electrons among 5f, 6d, and 7s orbitals controls redox chemistry, bonding, and coordination, ultimately determining how these elements interact with ligands and matrices. Uranium and plutonium have been extensively investigated because of their central role in nuclear energy and weapons [6, 7], but other actinides remain far less explored.

Among them, protactinium (Pa, $Z = 91$) stands out as a particularly intriguing element. Its electronic structure is unique in that both the 5f and 6d orbitals contribute to the ground state configuration, placing it at the intersection between transition metals and the heavier actinides [8].

In aqueous solution, protactinium primarily exists in two oxidation states, +IV and +V, with the latter being the predominant form. Unlike its heavier congeners, however, Pa(V) does not form a di-oxo bond in solution, even though the PaO_2^+ cation is known to be stable in the gas phase [9]. Only a limited number of experimental studies have investigated Pa(V) species in aqueous media, as experimental work is strongly constrained by the element's scarcity, high radioactivity, and pronounced tendency toward hydrolysis and sorption onto solid surfaces [10, 11].

Nevertheless, protactinium remains a valuable element for probing physico-chemical and spectroscopic properties using a combined theoretical and experimental approach. This thesis aims to advance this understanding through the combination of quantum-chemical modeling and X-ray absorption and emission

spectroscopies, as outlined in the following plan:

- In chapter 1, an overview of protactinium is presented, covering its discovery, isotopes, and main applications. This chapter also discusses the formation of PaO_2^+ , the experimental challenges associated with handling protactinium, and the chemistry of Pa(V) in aqueous media with different ligands, concluding with the objectives of this thesis.
- In chapter 2, the quantum-chemical methods employed in this work are described. This includes both wave function-based and density functional approaches, together with the treatment of relativistic effects and solvation models, as well as the methodologies used to compute core-excited states.
- chapter 3, chapter 4, and chapter 5 present the main results obtained throughout this thesis. In particular, chapter 4 provides an overview of X-ray absorption and emission spectroscopic techniques applied to actinide systems.
- Finally, chapter 6 summarizes the main conclusions of this work and outlines perspectives for future research.

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Protactinium(V) in Aqueous Media: Discovery, Properties, and Speciation

1.1 Discovery of Protactinium

In 1871, Mendeleev predicted the existence of an element between thorium and uranium in his periodic system. A vacant position was left in group V, below tantalum, which he referred to as eka-tantalum, with an estimated atomic mass of 235. From this prediction, researchers attempted to identify this missing element by looking for tantalum-like chemistry, which delayed its discovery.

In 1900, William Crookes separated a highly radioactive substance from uranium residues during studies on the radioactivity of uranium. Although he did not recognize it as a distinct element, he designated it as *Uranium-X* (UX) [1].

The gap was first filled in 1913, when Fajans, Russell, and Soddy discovered ^{234}Pa , a member of the ^{238}U decay series (Figure 1.1), using radioactive displacement laws [2–4]. In the same year, Fajans and Göhring identified a short-lived isomer of ^{234}Pa , called ^{234m}Pa , for which they proposed the name brevium (Latin for “short”) [5]. These isotopes exhibit half-lives of 6.7 hours for ^{234}Pa and 1.17 minutes for ^{234m}Pa , respectively, and are produced in the ^{238}U decay chain through the β -decay of ^{234}Th , followed by further decay to ^{234}U (Figure 1.1).

A few years later, in 1917-1918, Meitner and Hahn in Germany, and inde-

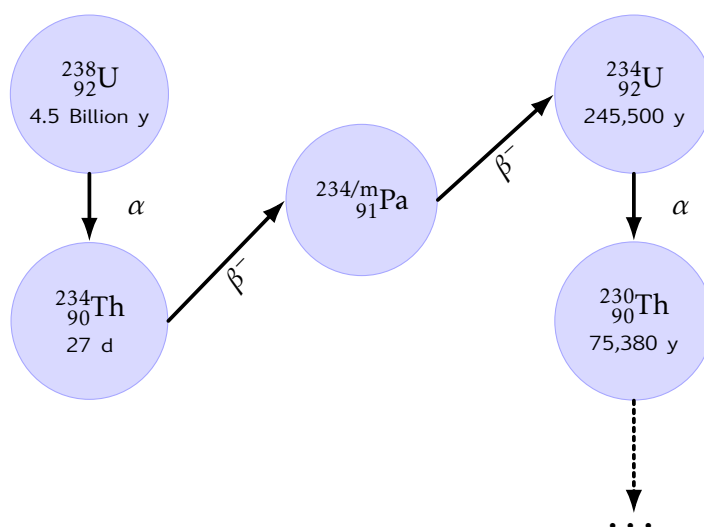


Figure 1.1: Partial decay scheme of ^{238}U , showing the production of ^{234}Pa .

pendently Soddy and Cranston in the United Kingdom, succeeded in isolating the much longer-lived isotope ^{231}Pa ($t_{1/2} = 32760$ years) [6, 7]. This firmly established element 91 as a new chemical element. Since ^{231}Pa belongs to the ^{235}U decay series and decays to ^{227}Ac through α emission (Figure 1.2), Meitner proposed the name protoactinium (“parent of actinium”).

In 1949, the International Union of Pure and Applied Chemistry (IUPAC) shortened the name to protactinium (Pa) [8, 9].

A total of twenty-nine isotopes of protactinium have been reported so far. Among these, ^{230}Pa , ^{231}Pa , ^{233}Pa , ^{234}Pa , and its isomeric form ^{234m}Pa are of particular significance for chemical investigations [10]. The naturally occurring isotopes are ^{231}Pa and $^{234m}/^{234}\text{Pa}$, which originate from the decay chains of ^{235}U ($4n+3$ series) and ^{238}U ($4n+2$ series), respectively, as mentioned above. Estimates of their crustal inventories amount to 3.2×10^7 t for ^{231}Pa and only about 42 kg for ^{234}Pa [11].

Several isotopes are also produced artificially. Neutron irradiation of ^{232}Th generates both ^{233}Pa , which serves as the precursor of the fissile isotope ^{233}U [12], and ^{231}Pa through the $(n, 2n)$ reaction. Proton bombardment of ^{232}Th provides another pathway, yielding ^{230}Pa [13]. In addition, ^{233}Pa is obtained as a daughter product of ^{237}Np [14]. In this work, the experimentally studied protactinium is

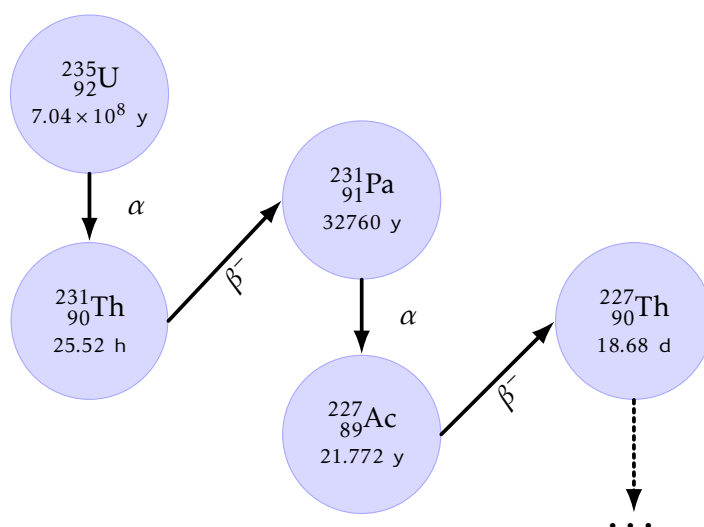


Figure 1.2: Partial decay scheme of ^{235}U showing the production of ^{231}Pa .

^{231}Pa .

1.2 Applications of Protactinium

The practical applications of protactinium are scarce, mainly because the element is extremely rare, highly radioactive, and chemically insufficiently characterized. However, some of its isotopes play a role in a variety of disciplines.

In geoscience, protactinium is central to age U-containing materials. The $^{231}\text{Pa}/^{235}\text{U}$ system provides a sensitive chronometer for U-bearing samples on timescales up to 200 000 years [15–17], and in combination with the $^{230}\text{Th}/^{238}\text{U}$ ratio, it allows precise age determinations as well as reconstructions of sedimentation rates [18].

In addition, the $^{231}\text{Pa}/^{235}\text{U}$ ratio has forensic importance, as it can be used to determine the age of enriched uranium. Even though the ingrowth of ^{231}Pa is very small for young samples (<100 years), the high content of ^{235}U makes the ratio measurable with good precision. This information is valuable for security and safeguards, since it can help determine when the uranium was enriched and trace the origin of confiscated nuclear material [19, 20].

In marine studies, the $^{231}\text{Pa}/^{230}\text{Th}$ ratio serves as a tracer of particle transport

and ocean circulation, with direct implications on the environment because it is related to climate change [21–23].

In the nuclear domain, protactinium appears in the thorium-based fuel cycle, where ^{233}Pa is produced as an intermediate in the breeding of ^{233}U , while ^{231}Pa is generated as a byproduct that contributes significantly to the long-term radiotoxicity of spent fuel [24–26]. The behavior of protactinium is therefore an important factor in reprocessing strategies and waste storage, and must also be considered in the context of uranium tailings and mining activities, where ^{231}Pa can accumulate in the environment [27].

More recently, medical applications have been proposed, in particular the use of ^{230}U for targeted α -therapy or as a generator of ^{226}Th . This isotope can be produced either through proton or deuteron irradiation of natural thorium via the intermediate formation of ^{230}Pa , or by direct irradiation of ^{231}Pa . These production routes highlight the role of protactinium isotopes in emerging medical applications [13, 28–30].

1.3 Electronic structure and oxidation states

Protactinium is the first actinide to exhibit simultaneously occupied 5f and 6d orbitals in its free-atom ground-state configuration, $[\text{Rn}]5f^2 6d^1 7s^2$, where the 5f and 6d orbitals are nearly degenerate in energy. This near-degeneracy enables strong interactions between the 5f and 6d valence orbitals, positioning Pa at the intersection between transition metals, which display predominantly 6d character, and the heavier actinides, which exhibit increasingly 5f character [31].

In aqueous media, protactinium exists mainly in two oxidation states, +IV and +V, with the latter being the most stable and predominant form, similar to its group-5 analogues niobium (Nb) and tantalum (Ta). Pa(IV) is relatively unstable and is readily oxidized to Pa(V) unless a strong reducing agent is present [32, 33]. Oxidation states lower than +IV have never been observed in aqueous solution. However, in chloride-based molten salts, reduction to the +III and +II oxidation states has been reported through co-crystallization with divalent lanthanides [34]. Given that Pa(V) is by far the most stable oxidation state under typical conditions, the present work focuses on its chemistry.

1.4 Formation of PaO_2^+ in gas phase

As with uranium and neptunium, the PaO_2^+ cation is stable in the gas phase. Gibson and Haire attributed this stability to its electronic structure: the protactinium center is considered "valence saturated". This saturation renders PaO_2^+ an "essentially inert species," a characteristic it shares with its uranium analogue, UO_2^+ . Experimental confirmation of this inertness was achieved through ion-molecule reactions with iso-butene: both PaO_2^+ and UO_2^+ formed only adducts (association complexes, $\text{AnO}_2\text{C}_4\text{H}_8^+$) and exhibited no further reactivity. This contrasts sharply with the Pa^+ and PaO^+ ions, which were found to be extremely reactive.

Furthermore, comparative studies suggest that the pentavalent PaO_2^+ species is apparently more robust than UO_2^+ and NpO_2^+ . This conclusion is supported by estimates of the metal-oxygen bond dissociation energies (BDEs). The first bond dissociation energy, $\text{BDE}[\text{Pa}^+ - \text{O}]$, is approximately 800 kJ mol^{-1} , and the second, $\text{BDE}[\text{OPa}^+ - \text{O}]$ is about 800 kJ mol^{-1} . This indicates that the second Pa–O bond in protactinium is as strong as the first one, which explains the strong stability of the PaO_2^+ unit [35].

Despite the high stability of the PaO_2^+ unit, it undergoes oxo-exchange with water much faster than the UO_2^+ unit in the gas phase. Dau et al. demonstrated experimentally that the hydrated form, $\text{PaO}_2^+(\text{H}_2\text{O})$, rapidly hydrolyzes to $\text{PaO}(\text{OH})_2^+$. The corresponding reaction are substantially endothermic, by at least 50 kJ mol^{-1} ($\text{PaO}_2^+(\text{H}_2\text{O}) \rightarrow \text{PaO}(\text{OH})_2^+$). These results place Pa(V) at a turning point in the actinide series regarding the relative stabilities of the hydrated oxo versus hydroxo species [36].

High-level electronic structure calculations (CCSD(T)) by Vasiliu et al. further showed that $\text{PaO}_2^+(\text{H}_2\text{O})$ and $\text{PaO}(\text{OH})_2^+$ are essentially isoenergetic in the gas phase ($\Delta H_{\text{hydrolysis}} = 0.6 \text{ kJ mol}^{-1}$), suggesting that the two structures can coexist. This stands in sharp contrast to later actinyls (U, Np, Pu), where the hydrate to hydroxide conversion is strongly endothermic [37].

Subsequent work by Dau et al. confirmed that PaO_2^+ can further hydrolyze to $\text{Pa}(\text{OH})_4^+$, a result supported by both experimental and theoretical evidence [38]. The formation of a highly symmetric tetrahedral (T_d) $\text{Pa}(\text{OH})_4^+$ complex is

particularly striking, as it underscores the pronounced *d*-block character of Pa(V) [38].

In agreement, Jian et al. showed theoretically that PaO_2^+ undergoes hydrolysis and oxo-exchange more readily than any other AnO_2^+ , despite having the highest bond dissociation energy [39].

By contrast, PaO_2^+ cation is unstable in solution [10, 33, 40]. Its instability arises from the strong propensity of Pa(V) to undergo hydrolysis, irreversible polymerization, and sorption on solid surfaces, which complicate the chemical studies (section 1.5). This is supported by quantum-chemical calculations from Toraishi et al., who showed that PaO_2^+ is not a stable form in aqueous media. From an energetic point of view, the formation of the dioxo cation is not favored. Density functional theory calculations indicated that forming the second Pa–O bond is highly endothermic ($111.36 \text{ kJ mol}^{-1}$), unlike the spontaneous and exothermic formation of UO_2^+ [41].

In addition, molecular orbital analysis by Toraishi et al. indicated that in PaO_2^+ , the involvement of Pa(V) 6d orbitals creates a destabilizing effect. Specifically, the 6d – 2p antibonding interaction interferes with the 5f – 2p bonding network, which weakens the overall π bonding framework. In contrast, for the uranyl cation (UO_2^{2+}), the 6d orbitals of U(VI) engage in bonding with the oxygen 2p orbitals, and this bonding interaction can coexist at an angle with the 5f – 2p bonds due to electron correlation. This orbital arrangement avoids the destructive overlap observed in protactinium, thereby accounting for the stability of the uranyl unit [41].

Instead of forming a stable PaO_2^+ in aqueous media, Pa(V) exists in solution as mono-oxo ion PaO^{3+} making it a truly unique actinide or as a bare cation Pa^{5+} . Since this thesis focuses on the chemistry of Pa(V) in aqueous media, the following section provides an overview of the literature on the chemistry of Pa(V) in aqueous media in the presence of ligands.

1.5 Experimental Challenges in Manipulating Pa(V) in Solution

Before discussing the complexation of Pa(V) with ligands in solution, it is important to note the considerable experimental challenges associated with manipulating protactinium, which include hydrolysis, sorption onto solids, and irreversible polymerization.

Pa(V) has a strong tendency to hydrolyze in non- or weakly complexing media, which rapidly leads to the formation of radiocolloids and irreversible polymerization. This instability becomes more pronounced with increasing pH or protactinium concentration.

At constant ionic strength (3 M), and within the range $10^{-5} \text{ M} < [\text{H}^+] < 3 \text{ M}$, the hydrolyzed cation detected at trace levels is $\text{PaO}(\text{OH})^{2+}$. As the proton concentration decreases below 1 M, this species forms more readily and becomes predominant around $\text{pH} \approx 3$. At higher pH values, further hydrolysis produces the neutral pentahydroxo complex $\text{Pa}(\text{OH})_5$ (Figure 1.3), whereas under extremely acidic conditions ($[\text{H}^+] > 8 \text{ M}$), the existence of the mono-oxo cation PaO^{3+} has been suggested [42].

To overcome these difficulties and maintain Pa(V) in true solution, experimental procedures typically employ tracer-level concentrations ($C_{\text{Pa}} \leq 10^{-10} \text{ M}$) to avoid polymerization and hydrolysis.

In addition, Pa(V) strongly sorbs on solid surfaces, particularly silica materials such as glass, silica gel, or quartz, with sorption ratios reported as high as 97-99% in perchlorate media. To mitigate this problem, the container walls are often chemically pretreated, for example, by saturating the surface with protactinium hydroxo species or applying protective polymer coatings such as parylene C, in order to reduce adsorption [33].

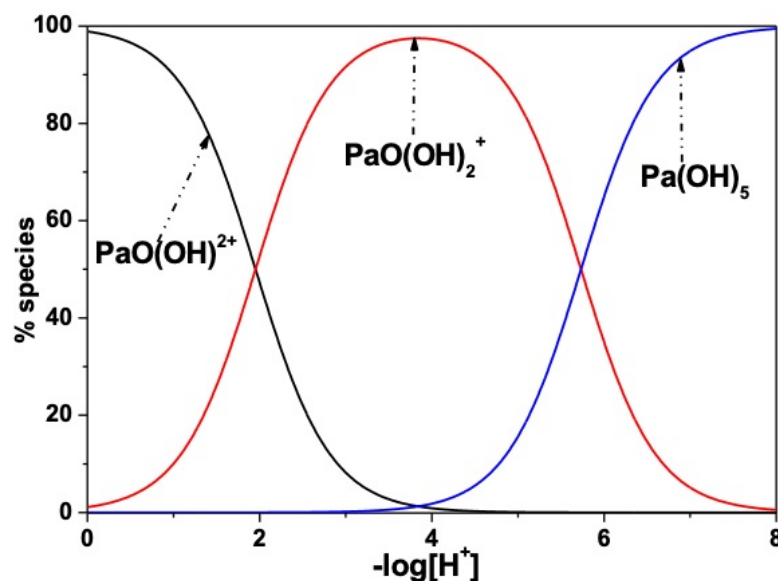
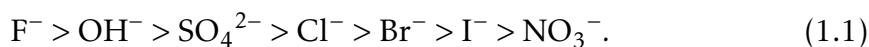


Figure 1.3: Speciation diagram of Pa(V) hydrolyzed species at ultra-trace concentration in aqueous solution ($I = 1 \text{ M NaClO}_4$, $T = 198 \text{ K}$) [42].

1.6 Complexation of Pa(V) with ligands

Inorganic Ligands

Pa(V) has a strong tendency to form complexes with different inorganic ligands. Depending on the solution conditions, it may exist as simple Pa^{5+} coordination complexes, or as oxo- and hydroxo-containing species. The relative affinity of Pa(V) for common inorganic ligands follows the scale:



In the following, a brief overview of the complexes formed between Pa(V) and different inorganic ligands is presented. For a more detailed discussion, the reader is referred to [10, 40].

Pa(V) in Hydrofluoric Acid (HF) The behavior of Pa(V) in hydrofluoric acid solutions was extensively investigated during the 1960s and 1970s using both

tracer-scale methods (such as solvent extraction and ion exchange) and macroscopic techniques including potentiometry, conductimetry, and spectrophotometry. These studies demonstrated that the speciation of Pa(V) is strongly influenced by both the proton concentration and the free fluoride content. Complexes with stoichiometries ranging from 1:1 to 1:8 were identified, with homoleptic fluoro complexes prevailing at high fluoride concentrations (1:5-1:8), and mixed oxo- or hydroxo-fluoro species dominate at lower fluoride to protactinium ratios.

The heptafluoro complex $[\text{PaF}_7]^{2-}$ is the main species in solutions containing HF concentrations between 10^{-3} M and 4-8 M, while the $[\text{PaF}_8]^{3-}$ forms in highly concentrated fluoride media under low proton conditions ($C_{\text{H}^+}=10^{-7}$ - 10^{-2} M). At lower HF concentrations ($<10^{-3}$ M), $[\text{PaF}_7]^{2-}$ is replaced by complexes with fewer fluoride ligands, such as $[\text{PaF}_6]^{-}$ and $[\text{PaF}_5]^{2-}$. In this region, oxo and hydroxo-fluoro species, including PaOF_3 , $[\text{PaOF}_2]^{+}$, and $[\text{PaOF}]^{2+}$ are also formed, while $[\text{PaOF}_4]^{-}$ and $[\text{PaF}_4]^{+}$ have not been experimentally detected [10, 40].

With the advent of synchrotron-based X-ray absorption spectroscopy (XAS), the coordination chemistry of protactinium in HF could be revisited at the molecular scale. The first XANES and EXAFS experiments at the L_3 -edge of Pa(V) (16 733 eV) were performed in 2005 at ESRF (Grenoble) [43]. The absence of the characteristic actinyl shoulder in the XANES spectrum confirmed that no linear trans-dioxo unit is present in the fluoro complexes. The corresponding EXAFS data, collected in 0.5 M HF, indicated a first coordination shell of seven ligands at (2.16 ± 0.02) Å, consistent with PaF_7^{2-} , although partial substitution of one fluoride by H_2O could not be excluded because of the similar scattering properties of O and F atoms.

Subsequent studies extended this investigation over a broader HF concentration range. De Sio and Wilson reported that in concentrated HF (27 M) the spectrum is best fitted with PaF_8^{3-} (Pa-F 2.174 Å), while in the intermediate region (2.5-10 M HF) a mixture of PaF_7^{2-} and PaF_8^{3-} is consistent with the data. At lower concentrations (0.01-1 M HF), one water molecule is likely to replace a fluoride in the first coordination sphere, at a distance of 2.54-2.57 Å [44]. Giandomenico et al. investigated more dilute conditions (0.5 M, 0.05 M, and 5 mM HF). They confirmed that a single coordination shell of 7 ligands is consistent with

0.5 M and 0.05 M HF, though they did not exclude PaF_6^- or $[\text{PaF}_6(\text{H}_2\text{O})]^-$. In the most dilute case (5 mM of HF), their fits required two distinct contributions: one short Pa-O distance at 1.71 Å and six O/F atoms at 2.27 Å [45].

Pa(V) in Sulfuric Acid (H_2SO_4) Early studies on the complexation of Pa(V) with sulfate (SO_4^{2-}) suggested the formation of complexes of 1:1 and 1:2 stoichiometry, typically formulated as $[\text{PaO}(\text{SO}_4)]^+$ and $[\text{PaO}(\text{SO}_4)_2]^-$, which are present in 0.1 M H_2SO_4 and in 0.5–3 M H_2SO_4 , respectively. At higher acid concentrations, the mono-oxo bond was reported to disappear, giving rise to the formation of Pa^{5+} sulfate complexes such as $[\text{Pa}(\text{SO}_4)_3]^-$ and $[\text{Pa}(\text{SO}_4)_4]^{3-}$ [8, 11, 40, 46].

Modern structural studies using XAS (XANES and EXAFS) have since confirmed the persistent presence of the mono-oxo bond in 4 M and 13 M H_2SO_4 . The L_3 -edge XANES spectra of these samples lack the characteristic feature associated with a linear trans-dioxo bond, while EXAFS analysis unambiguously reveals a short Pa mono-oxo bond at 1.72 Å. This finding confirms the presence of the mono-oxo bond for Pa(V) species in concentrated sulfuric acid, contrary to earlier interpretations. The coordination of Pa to sulfate ligands remains ambiguous – both monodentate and bidentate binding modes appear possible [43, 47].

Furthermore, solvent extraction experiments designed to determine the thermodynamic parameters of Pa(V)-sulfate complexation indicate that $[\text{PaO}(\text{SO}_4)_3]^{3-}$ is the most stable species in solution [47–49].

Pa(V) in Hydrochloric Acid (HCl) The complexation behavior of Pa(V) in hydrochloric acid has been investigated mainly through partition and diffusion experiments performed at tracer concentrations ($C_{\text{Pa}} \leq 1 \times 10^{-10}$ M), which examined the effects of proton and chloride concentrations on speciation [50–53]. The reported stoichiometry of Pa(V)-chloride complexes ranges from 1:1 to 1:7, depending on the acidity of the medium.

In dilute solutions (<2 M HCl), hydrolyzed species such as $[\text{PaO}(\text{OH})]^{2+}$ predominate, whereas in highly acidic media (>8 M HCl), fully halogenated complexes such as $[\text{PaCl}_6]^-$ and $[\text{PaCl}_7]^{2-}$ are formed, a intriguing conclusion espe-

[HCl]	Suggested Species	Reference
< 3	$[\text{PaO}(\text{OH})]^{2+}$, $[\text{PaO}(\text{OH})]^+$	[11, 53]
2–4	$[\text{PaO}(\text{OH})\text{Cl}]^+$	[50]
3	$[\text{PaOCl}_4]^-$	[54]
	$[\text{Pa}(\text{OH})_3\text{Cl}]^+$	[51]
3–6	$[\text{PaO}(\text{OH})\text{Cl}]^+$, $\text{PaO}(\text{OH})\text{Cl}_2$, $[\text{PaOCl}_3]^-$, $[\text{PaOCl}_4]^-$, $[\text{PaOCl}_5]^{2-}$	[53]
	$[\text{Pa}(\text{OH})\text{Cl}_3]^+$, $\text{Pa}(\text{OH})_2\text{Cl}_3$, $[\text{Pa}(\text{OH})_2\text{Cl}_4]^-$, $[\text{Pa}(\text{OH})\text{Cl}_5]^-$, $[\text{PaCl}_6]^-$	[52]
6	$[\text{PaOCl}_5]^{2-}$	[54]
6–10	$[\text{PaOCl}_5]^{2-}$, $[\text{PaOCl}_6]^{3-}$	[53]
> 6	$[\text{PaOCl}_5]^{2-}$, $[\text{PaCl}_7]^{2-}$, $[\text{Pa}(\text{OH})\text{Cl}_7]^{3-}$	[55]
6–8	$[\text{Pa}(\text{OH})\text{Cl}_6]^{2-}$, $[\text{PaCl}_6]^-$	[50]
8	$[\text{PaOCl}_6]^{3-}$	[56]
8–10	$[\text{Pa}(\text{OH})\text{Cl}_5]^{2-}$, $[\text{PaCl}_7]^{2-}$, $[\text{Pa}(\text{OH})\text{Cl}_7]^{3-}$	[57]
10	$[\text{PaOCl}_6]^{3-}$	[58]
10–12	$[\text{PaCl}_7]^{2-}$	[52]

Table 1.1: Suggested chloro complexes of Pa(V) as a function of HCl concentration and at Pa trace-level concentrations.

cially with respect to the confirmed presence of the mono-oxo bond in highly concentrated sulfuric acid solution. Between these two regimes, oxo-chloro, hydroxo-chloro, or oxo-hydroxo-chloro complexes are expected to form depending on the chloride concentration, although this interpretation remains contradictory among different studies, as shown in Table 1.1.

However, there remains some disagreement regarding the persistence of the mono-oxo bond under strongly acidic conditions. UV-Vis spectra of freshly prepared Pa(V) solutions (1–11 M HCl) show a strong absorption band near 210 nm, which has been attributed to the presence of a Pa–O bond even under highly acidic conditions [53]. Other studies, however, have suggested that in concentrated hydrochloric acid, Pa(V) forms only fully chlorinated species [50, 52].

To date, no structural study (XAS or crystallographic) of Pa(V) in hydrochloric acid has been reported, leaving its coordination environment in this medium unresolved. This issue will be addressed in chapter 4 through the combined analysis of EXAFS data and theoretical calculations.

Pa(V) in Hydrobromic acid (HBr) and Hydroiodic acid (HI) No experimental data are currently available on the behavior or speciation of Pa(V) in hydrobromic or hydroiodic acid solutions [10].

Pa(V) in nitric acid HNO_3 In nitric acid solution, several Pa(V) species of the general formula $\text{Pa}(\text{OH})_x(\text{NO}_3)_y^{(5-x-y)+}$ (with $y \leq 4$) have been proposed, depending on HNO_3 concentration [59]. In 3 M HNO_3 , the dominant complex exhibits a 1:4 stoichiometry. When the acid concentration increases to approximately 4-5 M, a gradual transition from cationic to anionic species occurs. The anionic species formed under these conditions are believed to contain six or seven coordinated nitrate ligands, consistent with the absence of oxo or hydroxo groups in the coordination environment of Pa(V) [10, 60].

To date, no structural (XAS or crystallographic) studies of Pa(V) in nitric acid have been reported.

Organic Ligands

Pa(V) can form complexes with different organic ligands, such as polyaminocarboxylate acids and oxalic acid, which will be discussed below. For detailed studies on complexation with polyaminocarboxylic acids, readers are referred to [40, 61, 62].

Pa(V) in Oxalic Acid ($\text{H}_2\text{C}_2\text{O}_4$) Prior to 1971, only a few investigations had examined the speciation of Pa(V) in oxalic acid solutions, and their conclusions were often inconsistent. These early works proposed several possible oxalate complexes with stoichiometries ranging from 1:1 to 1:4, differing in the presence or absence of oxo and hydroxo groups, while the reported stability constants were sometimes contradictory or not clearly related to well-defined equilibria [40].

Later, Mendes et al. refined the speciation picture through solvent extraction experiments, determining the thermodynamic parameters of Pa(V)-oxalate complexation at various temperatures and at an ionic strength of 3 M [63]. Their results demonstrated that Pa(V) forms three main successive oxalate complexes, all retaining the mono-oxo bond ($\text{Pa}-\text{O}$). These species are characterized by their stoichiometry: the mono-complex $[\text{PaO}(\text{C}_2\text{O}_4)]^+$, the di-complex $[\text{PaO}(\text{C}_2\text{O}_4)_2]^-$,

and the tri-complex $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, with stability increasing progressively across the series.

In addition, Mendes et al. performed X-ray absorption spectroscopy (XAS) measurements (XANES and EXAFS) at the L_3 -edge on two Pa(V) samples in 0.8 M and 1 M $\text{H}_2\text{C}_2\text{O}_4$ solutions. These analyses confirmed that Pa(V) in oxalic acid does not exhibit the linear trans-dioxo bond typical of actinyl cations (AnO_2^+), but instead features a single short Pa–O bond of 1.75 Å. Complementary capillary electrophoresis coupled with inductively coupled plasma mass spectrometry (CE-ICP-MS) verified that the tris(oxalato) complex carries an overall charge of -3 . Each oxalate ligand coordinates to Pa(V) in a bidentate, side-on fashion [63].

1.7 Objectives of the Thesis

Protactinium occupies a unique position in the actinide series, both historically and chemically. Its discovery filled the gap predicted by Mendeleev between thorium and uranium, yet its chemistry remains among the least explored of the early actinides. This limited understanding arises mainly from its scarcity, intense radioactivity, and the experimental challenges associated with its strong tendency toward hydrolysis, polymerization, and sorption onto solid surfaces.

In this context, the ANR project CHEmistry, Spectroscopy and Speciation of Protactinium (ANR-CHESS) was established to combine theoretical and experimental efforts in order to bridge existing gaps in our knowledge of protactinium chemistry.

The objective of this thesis, which is part of the ANR-CHESS project, is to investigate the speciation of Pa(V) in aqueous media, with particular emphasis on the formation and stabilization of the mono-oxo species PaO^{3+} . While the dioxo cation PaO_2^+ is stable in the gas phase, the existence of the mono-oxo form PaO^{3+} in solution makes protactinium a truly unique actinide.

Experimental studies suggest that the formation of the Pa–O bond strongly depends on both the nature and concentration of the coordinating ligands. Available structural data exist only Pa(V) complexes in hydrofluoric, sulfuric, and oxalic acid media, where X-ray absorption spectroscopy revealed fitted

Pa–O bond distances in the range of 1.71-1.75 Å [43, 45, 63]. These values differ from the longer distances predicted by theoretical calculations for $\text{PaO}(\text{C}_2\text{O}_4)_3^{3-}$ and $\text{PaO}(\text{SO}_4)_3^{3-}$ ($\text{Pa}-\text{O} \approx 1.86$ Å) [64].

To gain a broader understanding prior to new experimental investigations, a systematic theoretical study was performed, exploring a variety of inorganic and organic ligands to determine their ability to stabilize the mono-oxo bond, elucidate the electronic nature of the Pa–O interaction, and investigate the discrepancy between theoretical and experimental bond distances.

This work, presented in chapter 3, aims to answer three central questions:

- Which types of ligands are capable of stabilizing the mono-oxo bond of Pa(V)?
- What is the electronic nature of the Pa–O bond in these complexes?
- Why do experimental Pa–O bond distances (1.72-1.75 Å) differ from theoretical predictions (1.86 Å)? Are these discrepancies due to theoretical limitations or experimental uncertainties?

Note that the theoretical methods employed in this work are presented in chapter 2.

Building on these theoretical insights, several Pa(V) samples were prepared and measured at the SOLEIL synchrotron, under a variety of ligand environments, including sulfuric, oxalic, and hydrochloric acid, as well as other inorganic (HNO_3 , HCl and HBr) and organic media (diethylenetriaminepentaacetic (DTPA) and mellitic acids). Among these systems, the hydrochloric acid solution is of particular interest, as no structural data had previously been reported for Pa(V) in this medium. It was therefore especially important to analyze this system to determine whether the mono-oxo bond can be stabilized in concentrated HCl . Several key questions were addressed:

- Does the Pa–O bond persist in concentrated HCl medium, despite previous diffusion and partition studies suggesting otherwise?
- Is there agreement between theoretical and the new experimental results regarding the stability of the Pa–O bond in HCl ?

- Are the experimentally determined Pa–O bond distances consistent with theoretical predictions?

Previous studies by Le Naour et al. on Pa(V) in HF and H₂SO₄ [43], and by Mendes et al. on Pa(V) in H₂C₂O₄ [63], demonstrated through XANES measurements the absence of a di-oxo bond, based on the lack of a characteristic shoulder approximately 15 eV above the absorption edge. However, confirming the presence of a mono-oxo Pa–O bond required complementary EXAFS analysis.

With the advancement of X-ray emission spectroscopies, particularly Resonant Inelastic X-ray Scattering (RIXS) and High Energy Resolution Fluorescence Detection (HERFD), it is now possible to provide L₃- and M₄-edges spectra with much higher precision. Therefore, it is timely to perform L₃-edge measurements on Pa(V) in HF and H₂C₂O₄, even though previous M₄-edge investigations were inconclusive due to similar M₄-edge RIXS maps and HERFD-XANES spectra PaF₇²⁻ and PaO(C₂O₄)₃³⁻ [65]. This aspect will be further discussed in chapter 4.

Since such experimental measurements cannot be fully interpreted without theoretical support to characterize the underlying electronic transitions, core-excitation simulations were also performed. These simulations focused on modeling XANES spectra at the M₄-edge to evaluate whether variations in excitation energy could yield distinct spectral features. The results of this theoretical work are presented in chapter 5.

The spectroscopic investigation thus raised the following additional questions:

- Can the L₃-edge High Energy Resolution Fluorescence Detection (HERFD) and Resonant Inelastic X-ray Scattering (RIXS) techniques provide clearer spectroscopic signatures of the Pa–O bond compared to previous M₄-edge studies?
- How accurately do the theoretical core-excitation simulations reproduce the experimental spectra, what insights do they provide into the nature of the electronic transitions?

After presenting the objectives of the thesis, these questions will be addressed in chapter 3, chapter 4, and chapter 5.

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Theoretical Methods

2.1 Introduction to Quantum Chemistry

Computational chemistry is an invaluable tool for probing atomic and molecular properties. It employs methods grounded in the principles of quantum mechanics enabling the investigation of molecular structures, reactivities, and spectroscopic parameters. Several key criteria are considered to evaluate these methods and determine their quality and applicability:

Variational Principle: A variational method provides a calculated energy that is always an upper bound to the true ground state energy.

Size Extensivity: This ensures that the computed energy scales linearly with the size of the system (i.e., the number of electrons). It implies that the total energy of a system composed of non-interacting fragments should equal the sum of the energies of the individual fragments, which is related to the following criterion.

Size Consistency: This principle concerns the behavior of a method when two or more fragments are separated. It states that the energy calculated for the fragments should remain the same, regardless of their spatial separation. Size consistency is essential for accurately describing dissociation processes and the energetics of chemical reactions.

Agreement with Experimental Data: The method should be able to reproduce experimental data such as bond lengths, vibrational frequencies, and reaction

energies with high accuracy (within approximately 4 kJ mol^{-1} [1]). Achieving consistency with experimental data is not straightforward but is crucial for validating the reliability of the method in predicting and understanding chemical phenomena. This is because experimental validation ensures that the theoretical models and computational methods accurately reflect real-world behavior. Without such validation, the predictive power of these methods remains uncertain, potentially leading to incorrect conclusions and hindering scientific progress.

This chapter provides an overview of the quantum mechanical methods pertinent to the study of actinide complexes, particularly protactinium.

2.2 The Schrödinger equation

One of the main goals in molecular quantum mechanics is to solve the time-independent Schrödinger equation (Equation 2.1), which describes the evolution of the wave-function Ψ of the system in its stationary state,

$$\hat{H}|\Psi\rangle = E|\Psi\rangle \quad (2.1)$$

where $|\Psi\rangle$ is the total wave-function, E is the total energy and $\hat{H}$ is the Hamiltonian operator of the system. Depending on the system the Hamiltonian can be relativistic or not, where the relativistic effects should be considered when dealing with systems containing atoms with large atomic numbers. Relativistic effects will be discussed in a separate section 2.9. The non-relativistic Hamilto-

nian of a molecular system is written as a sum of five main contributions:

$$\begin{aligned}
 \widehat{H} = & - \sum_i \frac{1}{2} \nabla_i^2 && \text{(electron kinetic energies)} \\
 & - \sum_A \frac{1}{2M_A} \nabla_A^2 && \text{(nucleus kinetic energies)} \\
 & - \sum_{i,A} \frac{Z_A}{r_{iA}} && \text{(electron-nucleus Coulomb attractions)} \\
 & + \frac{1}{2} \sum_{i<j} \frac{1}{r_{ij}} && \text{(electron-electron repulsions)} \\
 & + \frac{1}{2} \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} && \text{(nuclear repulsions),}
 \end{aligned} \tag{2.2}$$

where i, j represent electrons and A, B represent nuclei. r_{ij} is the distance between the electrons i and j , R_{AB} is the distance between the two nuclei A and B , and r_{iA} is the distance between the electron i and its corresponding nucleus A . M_A corresponds to the ratio of the mass of the nucleus A to the mass of an electron corresponds Z_A is the atomic number of the nucleus A .

This equation can be solved analytically for systems containing one electron, while for many-body systems mathematical approximations have to be adopted. The Born-Oppenheimer approximation [2] is the first among several approximations used to simplify the Schrödinger equation.

2.2.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation is based on the fact that the nuclei are much heavier than the electrons. Because of this difference, the electrons move quickly and adapt almost instantaneously to the positions of the nuclei. Thus the nuclei are considered to be in fixed position compared to the fast movement of the electrons. According to this approximation, the kinetic energies of the nuclei are neglected and the nuclei repulsions are considered constant in Equation 2.2. Then the total Hamiltonian of the system can be separated into an electronic part and a nuclear part:

$$\widehat{H} = \widehat{H}_{el} + \widehat{H}_{nuc}, \tag{2.3}$$

where the nuclear part is constant for our systems of interest, and the electronic part is:

$$\widehat{H}_{el} = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{i < j} \frac{1}{r_{ij}}. \quad (2.4)$$

With this approximation, the problem is reduced to solving the electronic Schrödinger equation in the field of fixed nuclei:

$$\widehat{H}_{el} |\Psi_{el}(r, R)\rangle = E_{el}(R) |\Psi_{el}(r, R)\rangle. \quad (2.5)$$

Even with this approximation, the solution of electronic Schrödinger equation is still not straightforward due to the Coulombic interaction term of the electrons that depends on their coordinates. Therefore several methods, presented further down, have been developed with different levels of approximation to solve this equation numerically.

Once the electronic problem is solved and the electronic wave-function is known, it is possible to solve for the nuclei under the same assumptions used to formulate the electronic problem. Since the electrons move much faster than the nuclei, then it is possible to replace the electronic coordinates in Equation 2.4 by their average values, which are averaged over the electronic wave-function. By varying the positions of the nuclei in space, we can construct the potential energy surface (PES), which describes the energy of the system as a function of the nuclear coordinates. The optimal geometry for a molecule, representing its most stable configuration, corresponds to the minimum energy point on the PES. Finding this minimum energy configuration allows us to determine the equilibrium geometry of the molecule.

2.3 Constraints on the wave-function

To simplify the electronic Schrödinger equation of a many-body system, the electrons can be treated as independent particles. This allow us to express the

N -body wave-function Ψ as a product of N one-particle orbitals ϕ .

$$\Psi(r_1, \dots, r_N) = \phi(r_1) \dots \phi(r_N). \quad (2.6)$$

However, electrons are fermions with spin $\frac{1}{2}$, then the electronic wave-function should obey the Pauli exclusion principle which states that two particles cannot occupy the same quantum state simultaneously. Therefore the wave function must be anti-symmetric with respect to the interchange of the coordinates r (both space and spin) of any two electrons [3]:

$$\Psi(r_1, \dots, r_N) = -\phi(r_N) \dots \phi(r_1). \quad (2.7)$$

To fulfill this requirement, the wave-function Ψ is expressed as a Slater determinant composed of N orthonormal spin-orbitals:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_2(\mathbf{r}_1) & \dots & \phi_N(\mathbf{r}_1) \\ \phi_1(\mathbf{r}_2) & \phi_2(\mathbf{r}_2) & \dots & \phi_N(\mathbf{r}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(\mathbf{r}_N) & \phi_2(\mathbf{r}_N) & \dots & \phi_N(\mathbf{r}_N) \end{vmatrix}, \quad (2.8)$$

with the spin-orbitals in a row and the electron coordinates in a column. $\frac{1}{\sqrt{N!}}$ is a normalization factor.

2.4 Hartree-Fock self-consistent field method

One of the fundamental concepts in quantum chemistry is the variational principle. The basic idea of this principle is to approximate the true wave-function to an approximate wave-function that minimizes the energy of the system to a value greater than or equal to the exact ground-state energy. By applying the variational principle to the Schrödinger equation where the trial wave-function is expressed as one single Slater determinant (Equation 2.8), one can derive the pseudo-eigenvalues Hartree-Fock (HF) equations:

$$\widehat{F}_i \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}). \quad (2.9)$$

Here, $\widehat{F}_i$ is the one-electron Fock operator, ϕ_i is the molecular spin-orbital of the electron i and ϵ_i is the corresponding orbital energy. The Fock operator is composed of the one-electron Hamiltonian and the contributions from the Coulomb and exchange interactions:

$$\widehat{F}_i = \widehat{h}_i + \sum_r (2\widehat{J}_r - \widehat{K}_r). \quad (2.10)$$

$\widehat{h}_i$ is the one-electron Hamiltonian, which corresponds to the sum of the kinetic energy of the electron i and the electron(i)-nucleus(A) potential energy:

$$\widehat{h}_i(\mathbf{r}) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^N \frac{Z_A}{r_{iA}}, \quad (2.11)$$

J_r and K_r , in Equation 2.10, are the Coulomb and exchange operators respectively. J_r represents the interaction of electron i with electron j , and K_r takes into account the effect of spin correlation. By applying these operators on ϕ_i we obtain:

$$\widehat{J}_r \phi_i(\mathbf{r}_i) = \left[\int \frac{\phi_j^*(\mathbf{r}_j) \phi_j(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j \right] \phi_i(\mathbf{r}_i) \quad (2.12)$$

$$\widehat{K}_r \phi_i(\mathbf{r}_i) = \left[\int \frac{\phi_j^*(\mathbf{r}_j) \phi_i(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j \right] \phi_j(\mathbf{r}_i), \quad (2.13)$$

The Coulomb operator (Equation 2.12) of a spin orbital represents the repulsion an electron at a point in space would experience with the average charge distribution of the other electrons. This makes Hartree-Fock a "mean-field" theory. The exchange operator (Equation 2.13) does not have a similarly straightforward classical interpretation, and arises only due to quantum effects.

By bracketing the Fock operator, the energy of the orbital i in Equation 2.9 is obtained.

$$\epsilon_i = \langle \phi_i | \widehat{F}_i | \phi_i \rangle = h_{ii} + \sum_{j=1}^N (2J_{ij} - K_{ij}), \quad (2.14)$$

with the following notation definition $h_{ii} = \langle \phi_i | \widehat{h}_i | \phi_i \rangle$, $J_{ij} = \langle \phi_i | \widehat{J}_j | \phi_i \rangle$ and $K_{ij} = \langle \phi_i | \widehat{K}_j | \phi_i \rangle$. For an atom or a molecule with closed-shell electronic configuration,

the total Hartree-Fock energy E_{HF} of the N -electron system reads

$$E_{HF} = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) = \sum_{i=1}^N \left(\epsilon_i + \frac{1}{2} \sum_{j=1}^N (2J_{ij} - K_{ij}) \right), \quad (2.15)$$

Equation 2.15 shows that E_{HF} is not just the sum of the orbital energies. This is explained by the fact that the Coulomb and exchange operators include the interaction between electron i and the electrons occupying other spin orbitals (including j). They as well include the interaction of electron j with electrons occupying other spin orbitals (including i). Thus the sum of orbital energies counts the electron-electron interactions twice, giving rise to the $\frac{1}{2}$ factor in the correct expression of the total energy E_{HF} relative to the sum of the orbital energies (Equation 2.14).

The calculation of E_{HF} involves a self-consistent procedure. The molecular orbitals are expressed as linear combination of atomic orbitals (LCAO-MO approach) and are solutions of the HF equations. Each spatial wave-function ϕ_i is written as a linear combination of basis functions χ (see section 2.10) which, for molecular systems, are usually atomic orbitals:

$$\phi_i = \sum_j^{N_b} c_{ij} \chi_j, \quad (2.16)$$

where c_{ij} are unknown coefficients and N_b is the number of basis functions used. The search of the optimal ϵ_i and ϕ_i implies finding the optimal coefficients c_{ij} . Thus Equation 2.9 should be solved, but the Fock operator is as function of J_r and K_r which also depend on ϕ_i . Therefore trial coefficients c_{ij} are first suggested and consequently a first ϕ_i is calculated, then one computes J_r and K_r . Once they are computed, Equation 2.9 is solved and ϵ_i is obtained. Then this cycle is repeated again with new ϕ_i until E_{HF} is converged. This is the self-consistent procedure.

In the Hartree-Fock approximation the electrons are uncorrelated because the instantaneous Coulombic interactions between the electrons are not introduced. But in real systems, the electrons are interacting and these interactions are

described by the electron-correlation energy. Thus Hartree-Fock solution of the Schrödinger equation does not recover the total energy, where the electron-correlation energy, crucial to get an accurate description of the properties of the system, is missed. Then the correlation energy E_{corr} is defined as the difference between E_{HF} and the exact energy E_{exact} :

$$E_{corr} = E_{exact} - E_{HF}, \quad (2.17)$$

This makes the Hartree-Fock method a less accurate but computationally inexpensive method, which generally scales as N^4 , where N is the number of basis functions.

The correlation energy can be divided into dynamic and non-dynamic (static) components. The dynamic component relates to the electron motion, where electrons avoid each other. On the other hand, the non-dynamic component comes from nearly degenerate energy levels of the Hartree-Fock occupied and virtual orbitals, and these have multi-reference character. In this work, we have investigated the contribution of the dynamical correlation. Different approaches (post-HF methods) have been developed to account for the dynamical correlation energy, and they will be discussed in the following sections.

2.5 Configuration Interaction Methods (CI)

The Configuration-Interaction (CI) method is one of the most direct post-Hartree-Fock (HF) approaches. It involves expanding the n -electron wave-function into an infinite series of Slater determinants:

$$|\Psi_n\rangle = C_0^{(n)} |\Psi_0\rangle + \sum_{a,r} C_a^{r(n)} |\Psi_a^r\rangle + \sum_{r<s, a<b} C_{ab}^{rs(n)} |\Psi_{ab}^{rs}\rangle + \sum_{r<s<t, a<b<c} C_{abc}^{rst(n)} |\Psi_{abc}^{rst}\rangle + \dots, \quad (2.18)$$

where a, b, c stand for the occupied orbitals and r, s, t for the unoccupied ones. All the possible arrangements of electrons in the Hartree-Fock orbitals that are empty in the HF determinant $|\Phi_0\rangle$ are included. These arrangements are represented by singly excited determinants $|\Phi_a^r\rangle$, doubly excited determinants $|\Phi_{ab}^{rs}\rangle$,

triply excited determinants $|\Phi_{abc}^{rst}\rangle$, and so on. These determinants are commonly referred to as Singles (S), Doubles (D), Triples (T), Quadruples (Q), etc. If the expansion is complete, yielding all possible determinants, the solution is exact and referred to as full CI (FCI). A full CI gives high accuracy if a large basis set is used but one has to expect that it is computationally expensive even for small systems with minimal basis sets being used. Therefore, the truncated CI methods are a common approach that can be applied to larger systems. Depending on the determinant at which the Equation 2.18 is cut, one can obtain Singles (CIS), Singles and Doubles (CISD), and Singles, Doubles, and Triples (CISDT) CI methods. This offers a compromise by including a subset of determinants. It is important to note that the FCI method is size consistent but the truncated CI methods lack size-consistency, which can limit their applicability. Possible corrections such as the Davidson correction [4], could be applied to recover partly the size-consistency.

Now will be discussed two post-HF approaches that have the advantage of being size consistent: Møller-Plesset many-body perturbation theory and the coupled-cluster theory.

2.6 Møller-Plesset many-body perturbation theory

An improvement over the Hartree-Fock approximation can be obtained by adding a perturbative Hamiltonian $\widehat{H}'$, which accounts to the interaction energy between the electrons, to the zeroth-order Hamiltonian $\widehat{H}_0$ which is the Hartree-Fock Hamiltonian,

$$\widehat{H} = \widehat{H}_0 + \widehat{H}'. \quad (2.19)$$

The zeroth-order wave-function is the Hartree-Fock wave-function, $|\Psi_0\rangle$. By expanding both the wave-function, $|\Psi_0\rangle$, and the energy as a Taylor expansion in powers of a perturbation parameter λ that defines the strength of the perturbation, the MBPT expressions can be written as:

$$E_{PT} = \lambda_0 E_0 + \lambda_1 E_1 + \lambda_2 E_2 + \dots, \quad (2.20)$$

$$|\Psi_{PT}\rangle = \lambda_0 |\Psi_0\rangle + \lambda_1 |\Psi_1\rangle + \lambda_2 |\Psi_2\rangle + \dots \quad (2.21)$$

The perturbation added to the reference wave-function is included by excited Slater determinants, in which one or more electrons are excited from the occupied to the unoccupied orbitals. Thus the first order of correction is the excitation of one electron to an unoccupied orbital and by that we obtain Møller-Plesset correction to the 1st order (MP1), for which the energy correction is strictly zero because of the Brillouin theorem (states that singly excited configurations do not contribute to the first-order correction to the wave-function) [5]. By exciting two electrons we obtain the Møller-Plesset correction to the 2nd order (MP2) and so on for MP3, MP4 and MP5. For instance, the MP2 total energy reads:

$$E_{MP2} = E_{HF} + E_{\text{corr}}^{MP2}. \quad (2.22)$$

The MP2 method is considered the computationally cheapest post-HF method which scales N^5 , where N is the number of basis functions, and it is widely used. Although this approach is not variational and may lead to energies lower than the true ground state energy with respect to the perturbation order n , it is size-extensive. This property is crucial if one wants to compute reaction/dissociation energies. On the other hand MP2 may fail due to divergence or large errors for systems with small HOMO-LUMO gaps. In this case multi-reference methods [3] like multi-reference configuration interaction (MRCI) method provides a robust alternative.

2.7 Coupled-Cluster method

To go beyond perturbative methods, such as MP2, one can use another non-variational and size-consistent method to recover the dynamic correlation energy which is called the coupled-cluster method (CC). In this method, the electronic wave-function, $|\Psi_{CC}\rangle$, is written as:

$$|\Psi_{CC}\rangle = e^{\hat{T}} |\Psi_0\rangle, \quad (2.23)$$

where $|\Psi_0\rangle$ is the HF wave-function and $e^{\widehat{T}}$ is an exponential operator of the cluster operator $\widehat{T}$. In order to understand its effect on $|\Psi_0\rangle$, $e^{\widehat{T}}$ can be defined by the following series expansion,

$$e^{\widehat{T}} = 1 + \widehat{T} + \frac{1}{2!}\widehat{T}^2 + \dots + \frac{1}{N!}\widehat{T}^N, \quad (2.24)$$

where the cluster operator $\widehat{T}$ is the sum of cluster operators of different excitation levels:

$$\widehat{T} = \widehat{T}_1 + \widehat{T}_2 + \dots + \widehat{T}_N, \quad (2.25)$$

with $\widehat{T}_1$ being the one-electron excitation operator, $\widehat{T}_2$ the two-electron excitation operator,..., $\widehat{T}_N$ the N-electron excitation operator. An excitation operator $\widehat{T}_i$ acting on the Hartree-Fock (HF) wave-function generates all possible i^{th} excited Slater determinants. For instance the excitation operator reads:

$$\widehat{T}_1 |\Psi_0\rangle = \sum_{a,p} t_a^p |\Psi_a^p\rangle, \quad (2.26)$$

$$\widehat{T}_2 |\Psi_0\rangle = \sum_{a,b,p,q} t_{ab}^{pq} |\Psi_{ab}^{pq}\rangle, \quad (2.27)$$

where Ψ_a^p and Ψ_{ab}^{pq} represents a singly and doubly excited Slater determinants respectively. t_a^p and t_{ab}^{pq} are the single- and double-excitation amplitudes, respectively.

For a N -electron system, $|\Psi_{CC}\rangle$ is exact if the coupled-cluster expansion reaches the N -electron excitation operator, this is equivalent to full CI. In reality, due to the computational cost we restrict the QM calculations to triple excitations at most. In case of "coupled cluster doubles" (CCD), $\widehat{T}$ is approximated by $\widehat{T}_2$ only which scales N^6 , where N is the number of basis sets. CCD is a more computationally efficient variant of the coupled cluster methods, but it is less commonly used because it does not account for the effects of single excitations, which can be important for accurately describing electron correlation in many systems [6]. Then considering $\widehat{T}_1 + \widehat{T}_2$ is known as the "coupled cluster singles and doubles" (CCSD) which scales as well N^6 . One can add also triple excitations to reach CC with single, double and triple (CCSDT) by limiting the cluster operator

to $\widehat{T}_1 + \widehat{T}_2 + \widehat{T}_3$, but the cost reaches N^8 . CCSDT price is reduced by replacing the triple excitations with perturbative triple excitations which is known as CCSD(T). CCSD(T) is considered the "gold standard" in quantum chemistry, and it scales as N^7 .

Although the CC method is very accurate and size consistent, it is single determinant approach. Therefore, it is essential to check the multi reference character of the resulting wavefunction. For that the $\widehat{T}_1$ diagnostic (Equation 2.28) value is an important descriptor to determine whether the electronic wave-function is adequately described by single-reference methods, CC methods [7]:

$$\widehat{T}_1 = \frac{\|t_1\|}{\sqrt{N_{elec}}}. \quad (2.28)$$

If $\widehat{T}_1$ exceeds a threshold ($\widehat{T}_1 > 0.02$), it indicates that the CC method may not be able to capture all the necessary electron correlation effects. In this case, it is advisable to consider multi-reference methods, such as multi-reference configuration interaction (MRCI discussed in section 2.5) or multi-configurational self-consistent field (MCSCF discussed in section 2.13) [3], which can better handle the correlation effects in such systems.

While wave-function theory provides a detailed quantum mechanical description of electronic systems by solving the Schrödinger equation for the many-body wave-function, it becomes computationally intractable for large systems due to its exponential scaling with system size.

2.8 Density Functional Theory

Density Functional Theory (DFT) has been developed as an alternative to wave-function theory based methods, and it is based on the electron density, ρ , rather than from the many-body wavefunction. This approach simplifies the problem of solving the Schrödinger equation, as it reduces the complexity associated with many-body interactions. It is based on the Hohenberg-Kohn [8] theorems which postulate that total electron density determines the ground-state energy and all other ground-state electronic properties. The Hohenberg-Kohn theorems

express the ground-state energy in an external potential (v_{ext}) as a function of the ground-state electron density $\rho(r)$:

$$E[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] + \int \rho(\mathbf{r})v_{ext}(\mathbf{r})d\mathbf{r}, \quad (2.29)$$

where v_{ext} is an external potential, felt by the electrons, such as, for instance, the potential created by the nuclei.

ρ , the electron density of N electrons, is defined as:

$$\rho(\mathbf{r}) = N \int d\mathbf{r}_2 \dots d\mathbf{r}_N d\sigma_1 \dots d\sigma_N |\psi(\mathbf{r}_1\sigma_1 \mathbf{r}_2\sigma_2, \dots, \mathbf{r}_N\sigma_N)|^2, \quad (2.30)$$

where the integration is carried out over all spin and spatial coordinates apart from one set of spatial coordinates which is electron 1 in this case.

The first term of the Equation 2.29 is the universal functional, $F[\rho(\mathbf{r})]$, which depends only on the total density, and contains the kinetic energy functional $T[\rho(\mathbf{r})]$ and the electron energy functional (total Coulomb interaction energy + exchange term), $V_{ee}[\rho(\mathbf{r})]$:

$$F[\rho(\mathbf{r})] = T[\rho(\mathbf{r})] + V_{ee}[\rho(\mathbf{r})]. \quad (2.31)$$

In practice, the exact form of this density functional is not known and approximations are required to solve the equation and obtaining the energy of the system using variational principles.

2.8.1 The Kohn-Sham equation

The Hohenberg-Kohn theorems prove the existence of a density functional but does not provide an analytical form to express it. Within a year after the Hohenberg-Kohn theorems, Kohn and Sham (KS) proposed a solution [9]. The Kohn-Sham approach proposes to replace the interacting system by an effective non-interacting system of N electrons moving in the Kohn-Sham potential $V_{KS}(\mathbf{r})$.

The corresponding Kohn-Sham Hamiltonian is:

$$\widehat{H}_{\text{KS}} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i=1}^N V_{\text{KS}}(\mathbf{r}_i), \quad (2.32)$$

where the first term represents the kinetic energy operator and the second term is the effective potential Kohn-Sham potential experienced by each electron, defined as

$$V_{\text{KS}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}), \quad (2.33)$$

with $V_{\text{ext}}(\mathbf{r})$ is the external potential due to the atomic nuclei, $V_{\text{H}}(\mathbf{r})$ is the Hartree potential (classical electrostatic repulsion), and $V_{\text{xc}}(\mathbf{r})$ is the exchange-correlation potential.

Each of these terms is defined as follows:

1. The external potential $V_{\text{ext}}(\mathbf{r})$ is the Coulomb potential from atomic nuclei at positions $\mathbf{R}_A$ with charges Z_A :

$$V_{\text{ext}}(\mathbf{r}) = - \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|}. \quad (2.34)$$

2. The Hartree potential $V_{\text{H}}(\mathbf{r})$ represents the classical electrostatic repulsion between electrons:

$$V_{\text{H}}(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (2.35)$$

3. The exchange-correlation potential $V_{\text{xc}}(\mathbf{r})$ is derived from the exchange-correlation functional $E_{\text{xc}}[\rho]$, which is not known exactly must be approximated (e.g., LDA, GGA, hybrid functionals, see subsection 2.8.2).

The ground-state wave-function of this non-interacting system is expressed as a single Slater determinant, constructed from the Kohn-Sham orbitals ϕ_i , which satisfy the following eigenvalue equation:

$$\left(- \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i=1}^N V_{\text{KS}}(\mathbf{r}_i) \right) \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}), \quad (2.36)$$

where ϕ_i are the single-particle orbitals and ϵ_i are the corresponding eigenvalues. These orbitals represent the non-interacting reference system's particles, whose density exactly matches that of the interacting system.

These equations must be solved self-consistently, as $V_{KS}(\mathbf{r})$ depends on the electron density, which is computed from the KS orbitals:

$$\rho(\mathbf{r}) = \sum_i f_i |\phi_i(\mathbf{r})|^2. \quad (2.37)$$

This self-consistent procedure ensures that the KS orbitals yield the correct ground-state electron density for the system.

Now we can express the total energy $E[\rho(\mathbf{r})]$ of an interacting many-electron system in terms of the electron density $\rho(\mathbf{r})$. It is given as:

$$E[\rho] = T_s[\rho] + E_{\text{ext}}[\rho] + E_{\text{H}}[\rho] + E_{\text{xc}}[\rho], \quad (2.38)$$

where:

- $T_s[\rho]$ is the Kohn-Sham non-interacting kinetic energy
- $E_{\text{ext}}[\rho]$ is the external potential energy (electron-nucleus interaction)
- $E_{\text{H}}[\rho]$ is the Hartree energy (classical Coulomb interaction between electrons)
- $E_{\text{xc}}[\rho]$ is the exchange-correlation energy (quantum mechanical corrections)

Each of these terms is defined as follows:

1. The kinetic energy of the non-interacting KS electrons is:

$$T_s[\rho] = \sum_i^N \langle \phi_i | -\frac{1}{2} \nabla_i^2 | \phi_i \rangle. \quad (2.39)$$

This is an approximation to the true kinetic energy of interacting electrons. The kinetic energy correction $T[\rho] - T_s[\rho]$, also called correlation kinetic

energy, is unknown and is implicitly included in the exchange-correlation functional $E_{xc}[\rho]$.

2. The external potential energy represents the interaction with the external potential (e.g., due to atomic nuclei). It reads

$$E_{\text{ext}}[\rho] = \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (2.40)$$

3. The Hartree energy $E_{\text{H}}[\rho(\mathbf{r})]$ represents the classical electrostatic repulsion between electrons:

$$E_{\text{H}}[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (2.41)$$

It accounts for the mean-field Coulomb interaction.

4. The exchange-correlation energy $E_{xc}[\rho]$ contains all quantum mechanical exchange and correlation effects, as defined by the exchange correlation potential V_{xc} :

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) V_{xc}(\mathbf{r}) d\mathbf{r}. \quad (2.42)$$

The functional $E[\rho]$ (see 2.38) is minimized with respect to $\rho(\mathbf{r})$ to obtain the ground-state energy and electron density.

The quality of DFT calculations depends directly on the exchange-correlation functional, which lacks an exact mathematical expression and thus must be approximated. Several approximations, known as Jacob's ladder (See Figure 2.1) [10–12], have been proposed to systematically improve the accuracy of these functionals and will be described in the upcoming section.

2.8.2 Approximate exchange-correlation functionals

The exchange-correlation functional, $E_{xc}[\rho]$, can be decomposed into an exchange part $E_x[\rho]$ (representing exchange energy) and a correlation part $E_c[\rho]$

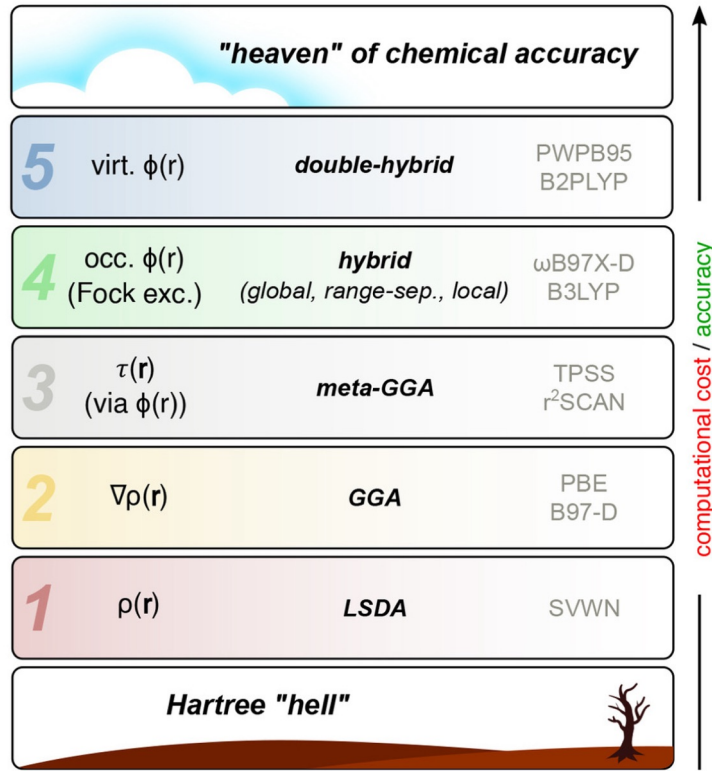


Figure 2.1: Functional classification based on Perdew's "Jacob's ladder" [13].

(representing the correlation energy):

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho]. \quad (2.43)$$

The exchange-correlation functional can also be defined in terms of the exchange and correlation energy per particle, ϵ_x and ϵ_c respectively:

$$E_x[\rho] = \int \rho(\mathbf{r}) \epsilon_x(\rho(\mathbf{r})) d\mathbf{r}, \quad (2.44)$$

$$E_c[\rho] = \int \rho(\mathbf{r}) \epsilon_c(\rho(\mathbf{r})) d\mathbf{r}. \quad (2.45)$$

One can also define the exchange energy as involving only electrons with identical spins (spin-up α and spin-down β). However, the correlation of electrons with the same spin is different and can, therefore, be separated from the correla-

tion of electrons with opposite spins:

$$E_x[\rho] = E_x^\alpha[\rho_\alpha] + E_x^\beta[\rho_\beta], \quad (2.46)$$

$$E_c[\rho] = E_c^{\alpha\alpha}[\rho_\alpha] + E_c^{\beta\beta}[\rho_\beta] + E_c^{\alpha\beta}[\rho_\alpha, \rho_\beta]. \quad (2.47)$$

with $\rho = \rho_\alpha + \rho_\beta$ and $\rho_\alpha = \rho_\beta$ for a closed-shell singlet state.

Local density approximation(LDA)

The Local Density Approximation (LDA) comes in the Jacob's ladder(Figure 2.1) as the first method for approximating the exchange-correlation energy. It assumes that the energy density at each point is the same as in a uniform electron gas (UEG) with the same local electron density. Mathematically, it is expressed as:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}^{UEG}[\rho(\mathbf{r})] d\mathbf{r} = E_x^{LDA} + E_c^{LDA}, \quad (2.48)$$

where $\epsilon_{xc}^{UEG}[\rho]$ is the exchange-correlation energy, per unit volume, of the UEG. The exchange energy is expressed by the Dirac formula:

$$E_x^{LDA}[\rho] = -C_x \int \rho(\mathbf{r})^{4/3} d\mathbf{r}, \quad C_x = \frac{3}{4} \left(\frac{3}{\pi} \right)^{1/3}. \quad (2.49)$$

The correlation energy ($E_c^{LDA}[\rho]$) does not have a simple analytical form and is typically obtained from quantum Monte Carlo calculations or other numerical methods [14].

The Local Density Approximation (LDA) functional approximates the exchange-correlation energy of an interacting electron system to that of a uniform electron gas with the same density, which means considering a slowly varying density. This approach often underestimates electron correlation effects, which results in overestimating binding energies and underestimating bond lengths. However, LDA can be suitable for solid-state systems where the electron density changes slowly. It has also proven to be a good approximation for actinides in highly symmetric systems, UF_6 , NpF_6 and PuF_6 , where there is good agreement between experimental and theoretical geometries and vibrational frequencies [15].

An extension of the Local Density Approximation (LDA) is the Local Spin

Density Approximation (LSDA) [16]. While LDA considers only the electron density, LSDA also takes into account the spin densities of electrons. This means that LSDA distinguishes between the densities of electrons with different spins (spin-up and spin-down), allowing for a more accurate description of systems with spin polarization. Within LSDA, the exchange-correlation functional is expressed as:

$$E_{xc}[\rho_\alpha, \rho_\beta] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho_\alpha(\mathbf{r}), \rho_\beta(\mathbf{r})) d\mathbf{r}. \quad (2.50)$$

In the context of LSDA, various parametrizations have been introduced. For example, Vosko, Wilk, and Nusair (VWN) introduced a series of parametrizations known as the VWN models [17], while Perdew and Wang developed their own parametrization known as PW92 [18], which remains widely used in spin-polarized calculations.

Generalized Gradient Approximation (GGA) and meta-GGA

The Generalized Gradient Approximation (GGA) is an extension of the Local Spin Density Approximation (LSDA). GGA accounts for the inhomogeneity of the electron density by involving the gradient of the density in the exchange-correlation energy. The exchange-correlation functional within the GGA is given by:

$$E_{xc}[\rho_\alpha, \rho_\beta] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho_\alpha, \rho_\beta, \nabla \rho_\alpha, \nabla \rho_\beta) d\mathbf{r}. \quad (2.51)$$

Many GGA functionals have been proposed for the exchange and correlation parts, such as Perdew-Burke-Ernzerhof (PBE) functional [19] and Lee-Yang-Parr (LYP) functional [20].

The addition of the first-order gradient correction to LDA functionals provides more accurate results when computing thermodynamic properties and molecular geometries [10].

GGAs can be further improved by considering details about the electron density and its gradient using the Laplacian and non-interacting kinetic energy, which are known as second-order corrections. This leads to the development of meta-GGA functionals. Among these functionals are the Tao-Perdew-Staroverov-Scuseria (TPSS) [21], the strongly constrained and appropriately

normed (SCAN) [22] and Minnesota 06-local (M06-L) [23] functionals which lead to more accurate predictions of thermodynamic properties compared to the LDA and the GGA ones [10].

Hybrid functionals

The exchange-correlation functional in DFT, LDA or even the more advanced approximations like GGA have limitations. They work well for homogeneous systems (like metals) but fail for systems where electron-electron interactions play a more complex role, such as in molecules and excited states. This is due to one of the most critical errors in actual DFT approximations, the so-called self-interaction error (SIE). The second error, related to the missing of long-range correlation effects that give rise to London dispersion, is discussed in subsubsection 2.8.2.

As explained in [13], self-interaction error (SIE) arises from an artificial residual interaction of an electron with itself due to the imperfect cancellation of the approximate exchange-correlation functional and self-Coulomb interaction. In contrast, Hartree-Fock theory is free from SIE because of a mathematical relationship between the integrals that describe the Coulomb and (exact) exchange interactions: these two effects perfectly cancel out when an electron interacts with itself. In practice, SIE in Density Functional Theory (DFT) often leads to an over-delocalization of electron density, causing an artificial stabilization of energy in delocalized electronic situations. SIE is present in all semi-local (meta-GGA and GGA) functionals.

Hybrid functionals aim to mitigate SIE by substituting a portion of the approximate DFT exchange with Fock exchange (e.g., B3LYP, which incorporates 20%, and PBE0, which includes 25%). Although this adjustment reduces SIE, it does not completely eliminate it, meaning that even hybrid functionals that include Fock exchange are still susceptible to SIE. Conversely, utilizing 100% Fock exchange results in poor performance as well. Generally, Fock exchange contributions of 5-25% are regarded as small, those of 25-40% as moderate, and contributions exceeding 40% as high.

The hybrid functional B3LYP (Becke's three-parameter exchange functional [24])

with the Lee-Yang-Parr correlation functional) is widely used in computational chemistry. This functional is a balance between the Hartree-Fock exchange and the $E_x[\rho]$ from the VWN LSDA functional [17], as well as the Becke 88 GGA functional [25]. For the correlation terms, it combines the VWN functional [17] with the LYP GGA functional [20], resulting in the following expression:

$$E_{xc}^{B3LYP} = aE_x^{HF} + (1-a)\Delta E_x^{VWN} + b\Delta E_x^{B88} + (1-c)\Delta E_x^{VWN} + c\Delta E_c^{LYP}, \quad (2.52)$$

where $a = 0.20$ (20% HF exchange), $b = 0.72$ and $c = 0.81$.

Another hybrid functional is PBE0 [26], which is the hybrid version of the GGA functional PBE [19]. It contains 25% HF exchange and is defined as follows:

$$E_{xc}^{PBE0} = \frac{1}{4}E_x^{HF} + \frac{3}{4}E_x^{PBE} + E_c^{PBE}. \quad (2.53)$$

The hybrid functionals improve the accuracy of chemical system descriptions, including atomization energies, bond lengths, and reaction barriers [10]. In the case of actinide systems, hybrid density functionals such as PBE0 or B3LYP are often effective in predicting molecular geometries. However, the same functionals may not reliably predict relative energies [27–29].

Meta-Hybrid GGA Approximation

Meta-hybrid GGA functionals are an extension of hybrid functionals that combine Hartree-Fock exchange along with meta-GGA exchange-correlation terms, which include the non-interacting kinetic energy. Among these functionals are M06 (27% HF exchange), M06-2X (54% HF exchange), and M06-HF (100% HF exchange), where the meta-GGA functional is M06-L [23, 30]. Another meta-hybrid functional is TPSSh (10% HF exchange) [21, 31], which is a hybrid version of the TPSS meta-GGA functional.

Range-separated hybrid approximations

Although hybrid functionals improve the description of bond interactions and reaction kinetics, they only partially address the self-interaction problem. For hybrid functionals, a way to improve SIE is to make the admixture of HF exchange

dependent on the interelectronic distance, leading to so-called range-separated hybrid (RSH) functionals. In RSH functionals, the exchange interaction is separated using an error function:

$$\frac{1}{r_{ij}} = \frac{1 - \text{erf}(\omega_{ij})}{r_{ij}} + \frac{\text{erf}(\omega_{ij})}{r_{ij}}. \quad (2.54)$$

The two terms of Equation 2.54 describe the short- and long-range part of the exchange interaction respectively. The parameter ω in the error function (erf) controls the balance between short- and long-range exchanges at intermediate r_{ij} value.

In 2001, Tsuneda and co-worker [32, 33] proposed a long-range correction (LRC) scheme where its general form is:

$$E_{XC}^{LC} = E_X^{HF,LR} + E_X^{DFT,SR} + E_c^{DFT}. \quad (2.55)$$

The term $E_X^{HF,LR}$ corresponds to the long-range HF exchange at long inter-electronic distances. The term $E_X^{DFT,SR}$ refers to the short-range DFT exchange (e.g. GGA or hybrid functionals) which is used at short inter-electronic distances. E_c^{DFT} is the standard DFT correlation functional. An example about LRC functionals is the LRC- ω PBE which includes a short-range version of the PBE exchange functional, the standard PBE correlation functional, and it has an ω value of 0.3.

In 2004, Yanai and co-workers [34] introduced two additional parameters, α and β , to Equation 2.54, and it becomes:

$$\frac{1}{r_{ij}} = \frac{1 - [\alpha + \beta \cdot \text{erf}(\omega_{ij})]}{r_{ij}} + \frac{\alpha + \beta \cdot \text{erf}(\omega_{ij})}{r_{ij}}. \quad (2.56)$$

This is called the Coulomb-Attenuating Method (CAM) approach in which fractions of HF-exchange are added at both short- and long-ranges. The general form CAM functional is:

$$E_{XC}^{CAM} = \alpha E_X^{HF,SR} + \beta E_X^{HF,LR} + (1 - \alpha) E_X^{DFT,SR} + (1 - \beta) E_X^{DFT,LR} + E_c^{DFT}. \quad (2.57)$$

Among these functionals, the CAM-B3LYP functional employs both short- and long-range versions of the Becke 88 (B88) exchange functional. Its correlation energy is the same as that used in B3LYP. The optimized parameters for CAM-B3LYP are $\alpha = 0.19$, $\beta = 0.65$, and $\omega = 0.33$. This approximation improves the charge-transfer excitation energies using Time-Dependent Density Functional Theory (TD-DFT) [35] which will be discussed later.

Dispersion corrections

Standard DFT functionals fail to capture long-range dynamic correlation well captured by usual post-HF methods such as MP2 or CCSD(T) [36]. To account for these interactions, it is proposed to add to the standard approximate functionals a semi-empirical dispersion correction of the form:

$$E_{dispersion} = -s \sum_{\alpha < \beta} f(R_{\alpha\beta}) \frac{C_6^{\alpha\beta}}{R_{\alpha\beta}^6}, \quad (2.58)$$

where $R_{\alpha\beta}$ is the distance between each pair of atoms, $C_6^{\alpha\beta}$ is the dispersion coefficient between these atoms, $f(R_{\alpha\beta})$ is a damping functional that is applied to smoothly transition between short and long distances, approaching 1 at large $R_{\alpha\beta}$ and 0 at short $R_{\alpha\beta}$, and s is a scaling parameter to adjust the dispersion contribution for different exchange-correlation functionals. This approach is called DFT-D which has been developed by Grimme and co-workers. Four different generations of DFT-D have been developed: D1 [37], D2 [38], D3 [39] which can be used either with the original damping function, D3(0), or the newer Becke-Johnson damping function, D3(BJ) [40], and D4 [41].

Another approach to describe dispersion interactions is to add to the standard approximate functionals a non-local Van Der Waals density functional. The two main categories of nonlocal correlation functionals are: the van der Waals density functionals (vdW-DF) of Langreth, Lundqvist [42, 43] and coworkers and the Vydrov-Van Voorhis (VV) functionals [44].

Double-hybrid functionals

To go beyond hybrid functionals, double-hybrid functionals have been developed by incorporating both exact exchange (as in hybrid functionals) and a part of second-order perturbation theory correlation energy, typically from MP2 (Møller-Plesset perturbation theory) [38, 45]. These functionals can improve the description of the systems where other DFT approximations fail [46].

To conclude, DFT is less computationally expensive than wavefunction-based methods, with a typical scaling of N^3 . However, it is important to maintain a balance between computational cost and accuracy. Therefore, it is necessary to evaluate the performance of functionals by benchmarking them against highly accurate wavefunction-based methods, especially when predicting relative energies [47].

2.9 Relativistic Quantum Chemistry

All the methods discussed so far fall under the non-relativistic approaches, and they are appropriate to describe elements with nuclear charge up to $Z = 36$ [48–50]. However, for heavier atoms, relativistic effects become significant. This is because the high atomic number implies that the electrons that are close to the nucleus have a velocity close to that of the speed of light, leading to a change in the atomic electronic structure description.

There are two categories of relativistic effects: the scalar ones (independent of the electron spin) which result from the relativistic mass increase of the electrons that are located close to the nucleus and move with a very high speed, and the spin-orbit effects (dependent on the electron spin) arising from the interaction of the electron spin with the magnetic field induced from the relative motion of the other charges. The two main consequences of scalar relativistic effects on the electronic structure are:

- The s and p orbitals contract and stabilize energetically, which is a direct relativistic effect.
- The d and f orbitals expand and destabilize, which is an indirect relativistic effect.

tic effect. This occurs because the contraction of inner s and p orbitals increases the screening of the nuclear charge for outer orbitals. As a result, the effective nuclear charge decreases, leading to the expansion and energetic destabilization of d and f orbitals.

In turn, the spin-orbit relativistic effect leads to the splitting of the orbitals with angular momenta greater than 1 (p, d, f, etc.), thus lifting degeneracy.

Relativistic quantum chemistry is based on the four-component Dirac equation, which combines quantum mechanics with laws of relativity in physics. In this section, we will discuss the four-component Dirac equation and its two-components approximations. Additionally, we will mention about the core approximations including frozen-core approximations and effective-core potentials.

2.9.1 The Dirac Equation

When we want to introduce relativistic effects into quantum systems, we cannot use the Schrödinger equation (Eq. 2.1) in its standard form, as it is not Lorentz invariant. This is because the equation is linear in time but quadratic in the spatial coordinates. To ensure Lorentz invariance, a different mathematical approach is required. One such approach is to consider a free particle, such as an electron, moving at relativistic velocities. The relativistic energy of a free particle with rest mass m_e and momentum p is given by:

$$E = \sqrt{p^2 c^2 + m_e^2 c^4}, \quad (2.59)$$

By applying this principle and introducing the interaction with electromagnetic fields, the energy expression becomes:

$$(E - q\phi)^2 = c^2 \pi^2 + m_e^2 c^4, \quad (2.60)$$

where,

$$\pi = \mathbf{p} - q\mathbf{A}, \quad (2.61)$$

$$E = E - q\phi, \quad (2.62)$$

with ϕ the scalar potential (associated with the electric field), and $\mathbf{A}$ the vector potential (associated with the magnetic field). This leads to the Klein-Gordon equation in the presence of electromagnetic fields:

$$\left(i\hbar\frac{\partial}{\partial t} - q\phi\right)^2 \psi = (c^2\boldsymbol{\pi}^2 + m_e^2c^4)\psi, \quad (2.63)$$

But the Klein-Gordon equation does not take into account the spin of the electron. To incorporate electron spin, Dirac proposed a linear, quantized form of the energy-momentum relation:

$$E - q\phi = c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta m_e c^2, \quad (2.64)$$

This led to the Dirac equation:

$$(c\boldsymbol{\alpha} \cdot \boldsymbol{\pi} + \beta m_e c^2 + q\phi)\psi = i\hbar\frac{\partial}{\partial t}\psi, \quad (2.65)$$

with α_i , $i = x, y, z$ are constructed from the Pauli matrices σ_i and β is a 4x4 matrix constructed from the 2x2 I_2 identity matrix:

$$\begin{aligned} \alpha_x &= \begin{bmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{bmatrix}, & \alpha_y &= \begin{bmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{bmatrix}, & \alpha_z &= \begin{bmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{bmatrix}, \\ \sigma_x &= \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, & \sigma_y &= \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, & \sigma_z &= \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \\ \beta &= \begin{bmatrix} I_2 & 0_2 \\ 0_2 & -I_2 \end{bmatrix}, \end{aligned} \quad (2.66)$$

The presence of the Pauli matrices implies that spin is embedded in the theory. The subscript 2 in I_2 indicates 2x2 matrices. As a result, both α_i and β are 4x4 matrices requiring the wave-function to be a four-component vector or 4-*spinor*,

yielding:

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \Psi_1(\mathbf{r}, t) \\ \Psi_2(\mathbf{r}, t) \\ \Psi_3(\mathbf{r}, t) \\ \Psi_4(\mathbf{r}, t) \end{pmatrix}, \quad (2.67)$$

with the components 1 and 3 corresponding to spin $\frac{1}{2}$ and the components 2 and 4 corresponding to spin $-\frac{1}{2}$.

Then the Dirac Hamiltonian can be written as 4×4 matrix:

$$H = \begin{bmatrix} m_e c^2 + q\phi & 0 & c\pi_z & c(\pi_x - i\pi_y) \\ 0 & m_e c^2 + q\phi & c(\pi_x + i\pi_y) & -c\pi_z \\ c\pi_z & c(\pi_x + i\pi_y) & -m_e c^2 + q\phi & 0 \\ c(\pi_x - i\pi_y) & -c\pi_z & 0 & -m_e c^2 + q\phi \end{bmatrix}, \quad (2.68)$$

The Dirac equation has both positive and negative energy solutions leading to two different physical states: electrons ($E > m_e c^2$) and positrons ($E < m_e c^2$). This result implies that an electron can occupy either a positive or a negative energy state separated by an energy gap of $2m_e c^2$. To prevent electrons from occupying negative energy states, Dirac proposed that all negative energy levels are fully occupied, known as the Dirac sea [51], consistent with the Pauli exclusion principle. If the energy spectrum is shifted by $-m_e c^2$, aligning it with the electron's rest mass energy (when $p = 0$), the Dirac equation can be reformulated so that the lower limit of the high-energy spectrum matches that of the non-relativistic Schrödinger equation.

$$\begin{pmatrix} VI_2 & c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} \\ c \boldsymbol{\sigma} \cdot \boldsymbol{\pi} & V - 2m_e c^2 \end{pmatrix} \begin{pmatrix} \Psi^L(\mathbf{r}) \\ \Psi^S(\mathbf{r}) \end{pmatrix} = E \begin{pmatrix} \Psi^L(\mathbf{r}) \\ \Psi^S(\mathbf{r}) \end{pmatrix}, \quad (2.69)$$

This lead us to introduce the large component Ψ^L (electrons) and the small component Ψ^S (positrons), each of them is a two component spinor that includes

the two-spin states α (spin-up) and β (spin-down):

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \Psi^L(\mathbf{r}) \\ \Psi^S(\mathbf{r}) \end{pmatrix} = \begin{pmatrix} \Psi_\alpha^L(\mathbf{r}) \\ \Psi_\beta^L(\mathbf{r}) \\ \Psi_\alpha^S(\mathbf{r}) \\ \Psi_\beta^S(\mathbf{r}) \end{pmatrix}, \quad (2.70)$$

Like the Schrödinger equation, the Dirac equation can be solved exactly only for single-electron systems. For many-electron systems, additional approximations are required.

2.9.2 The Many-Electron Dirac Hamiltonian

The one-electron Dirac Hamiltonian can be extended to an n -electron system, where it becomes essential to account for electron-electron interactions, primarily the Coulomb repulsion. In a relativistic context, however, moving electrons generate currents, which in turn produce magnetic fields. These lead to current-current (magnetic) interactions between electrons. Additionally, an electron can experience the magnetic field produced by the motion of another electron, resulting in velocity-dependent and retarded interactions. These effects are collectively included in the two-electron Breit term. Moreover, magnetic fields generated by moving electrons can couple to the spins of other electrons, giving rise to spin-other-orbit interaction (SOO).

All these relativistic effects are captured by the Dirac-Coulomb-Breit Hamiltonian [52], which forms the basis for accurate relativistic descriptions of multi-electron atoms and is written as:

$$\hat{H}^{DCB} = \sum_{i=1}^N \hat{h}_i + \sum_{i<j} \hat{g}_{ij}^{Breit}, \quad (2.71)$$

where $\hat{g}_{ij}^B$ is the two-electron Breit correction term:

$$\hat{g}_{ij}^{Breit} = \hat{g}_{ij}^{Gaunt} + \hat{g}_{ij}^{Gauge} = \frac{c\boldsymbol{\alpha}_i \cdot c\boldsymbol{\alpha}_j}{2c^2 r_{ij}^3} + \frac{(c\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{2c^2 r_{ij}^3}, \quad (2.72)$$

where, α_i and α_j are the Dirac matrices associated with electrons i and j , respectively, and $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is the relative position vector between the electrons.

The first term in parentheses is called Gaunt term, which computes the current-current interactions between electron spins and thus it is responsible for spin-other-orbit interaction (SOO) [53]. The second term is gauge-dependent and reflects the relativistic nature of the two-electron interactions [54, 55]. While these contributions are crucial for accurately describing core properties, their inclusion typically has almost no effect on computed values such as energies and molecular geometries, as demonstrated in studies [56, 57]. Although the Dirac-Coulomb-Breit Hamiltonian is effective in capturing relativistic effects, it requires solving the full four-component Dirac equation, which makes it computationally expensive in terms of both time and resources. Therefore, approximations are required, typically achieved by transforming the four-component equation into a simpler two-component form. These approximations will be discussed below.

2.9.3 Two-Components Relativistic Hamiltonians

Transforming the four-component equation into a two-component one involves the decoupling of the large and the small components, either by eliminating the small components (positronic states) or by applying a series of unitary transformations to achieve decoupling. Both approaches are based on the Foldy-Wouthuysen (FW) transformation [58]. Examples of the first approach are the Pauli Hamiltonian [59] and the Zeroth-Order Regular Approximation (ZORA) [60], while the second approach are Douglas-Kroll Hess (DKH) [61, 62] and exact-two component (X2C) Hamiltonians [63, 64], which will be discussed below. The advantage of these approaches is the separation of the Relativistic Hamiltonian in a way that they can be used with or without spin-orbit coupling (scalar relativistic calculation).

Pauli Approximation

The first-order of Foldy-Wouthuysen transformation [58] leads to the Pauli Hamiltonian by expanding in a power series in $\frac{1}{c^2}$,

$$\hat{H}^{Pauli} = V + \frac{p^2}{2m_e} - \underbrace{\frac{p^4}{8m_e^3c^2}}_{\text{mass-velocity}} + \underbrace{\frac{1}{8m_e^2c^2}(\nabla^2 V)}_{\text{Darwin}} + \underbrace{\frac{1}{4m_e^2c^2}\boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p})}_{\text{spin-orbit}}, \quad (2.73)$$

This Hamiltonian captures the scalar relativistic effects (mass-velocity and Darwin) and the spin-orbit interaction, making it more accurate than a purely non-relativistic approach and less sophisticated than full four-component methods.

One can focus on scalar relativistic effects and neglect spin-orbit coupling by dropping the spin-dependent term, this yields the scalar Pauli Hamiltonian:

$$\hat{H}_{SR}^{Pauli} = V + \frac{p^2}{2m_e} + \frac{p^4}{8m_e^3c^2} + \frac{1}{8m_e^2c^2}\nabla^2 V, \quad (2.74)$$

The Pauli Hamiltonian provides good first-order relativistic corrections, but it leads to variational collapse at higher orders. Therefore, it is typically used for light elements ($Z < 20$), where first-order corrections are sufficient.

Zeroth-Order Regular Approximation (ZORA)

The Zeroth-Order Regular Approximation (ZORA) is a variationally stable alternative to the Pauli Hamiltonian. It is obtained by coupling $\psi^L(\mathbf{r})$ and $\psi^S(\mathbf{r})$ (from Equation 2.69) by an energy-dependent factor χ :

$$\psi^S(\mathbf{r}) = \chi \psi^L(\mathbf{r}) \quad (2.75)$$

where

$$\chi = K(E, \mathbf{r}) \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2m_e c}, \quad (2.76)$$

with $K(E, \mathbf{r})$ being a multiplicative operator, defined as:

$$K(E, \mathbf{r}) = \left(1 - \frac{V - E}{2m_e c^2} \right)^{-1}, \quad (2.77)$$

which can be written,

$$K(E, \mathbf{r}) = \frac{2m_e c^2}{2m_e c^2 - V} \left(1 + \frac{E}{2m_e c^2 - V} \right)^{-1}, \quad (2.78)$$

and by expanding the term in parenthesis in a power series in $\frac{E}{2m_e c^2 - V}$, we obtain:

$$K(E, \mathbf{r}) = \frac{2m_e c^2}{2m_e c^2 - V} - \frac{(2m_e c^2 - V)^2}{2m_e c^2} E + \frac{(2m_e c^2 - V)^3}{2m_e c^2} E^2 + \dots \quad (2.79)$$

If we keep only the first term of the expansion in Equation 2.79, the Zeroth-Order Regular Approximation (ZORA) is obtained::

$$\hat{H}^{ZORA} = V + (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2m_e c^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}), \quad (2.80)$$

The ZORA Hamiltonian lacks mass velocity term and includes only parts of the Darwin term, which hampers the accurate prediction of core-energy levels. Spin-orbit interactions arising from nuclei are included implicitly due to the Pauli matrices (σ_i), which can be removed to obtain the scalar relativistic ZORA Hamiltonian. The scalar relativistic effects are fully included in the kinetic operator $\hat{T}_{SR}^{ZORA}$:

$$\hat{H}_{SR}^{ZORA} = V + \hat{T}_{SR}^{ZORA}, \quad (2.81)$$

with,

$$\hat{T}_{SR}^{ZORA} = \mathbf{p} \frac{c^2}{2m_e c^2 - V} \mathbf{p}, \quad (2.82)$$

This can be useful for systems and properties for which spin-orbit coupling is expected to be negligible, such as the case of closed-shell actinide molecules, as are pentavalent protactinium. In practice, the use of the scalar relativistic ZORA Hamiltonian instead of the two-component spin-orbit ZORA offers a computational cost reduction by a factor of 4-8. [65, 66].

Douglas-Kroll-Hess (DKH) Hamiltonian

The Douglas-Kroll-Hess (DKH) method is another two-component Hamiltonian, and it is widely used in quantum chemistry because it respects the variational principle. Unlike ZORA, DKH systematically eliminates the small-component contributions of the Dirac equation through a series of unitary transformations to the one-electron Dirac Hamiltonian, leading to the following matrix:

$$h_{DKH\infty} = \sum_{k=0}^{\infty} \epsilon_k = \sum_{k=0}^{\infty} \begin{pmatrix} \epsilon_{k+} & 0 \\ 0 & \epsilon_{k-} \end{pmatrix}, \quad (2.83)$$

where the ϵ_k terms are scalar operators, composed of a spin-free part, ϵ_k^{SF} , and a spin-dependent part, ϵ_k^{SD} .

$$h_{DKH\infty} = \sum_{k=0}^{\infty} \epsilon_k = \sum_{k=0}^{\infty} \begin{pmatrix} \epsilon_{k+}^{SF} + \epsilon_{k+}^{SD} & 0 \\ 0 & \epsilon_{k-}^{SF} + \epsilon_{k-}^{SD} \end{pmatrix}, \quad (2.84)$$

Since the matrix elements ϵ_k cannot be computed analytically due to the complicated operators, the infinite summation is truncated at a finite order, leading to the so-called DKH_n Hamiltonians, where n indicates the order of the expansion ($DKH2$, $DKH4$, $DKH6$, $DKH8$). The second-order DKH ($DKH2$) is commonly used for scalar relativistic corrections for valence properties, offering a good balance between accuracy and computational efficiency [62, 65]. However, for accurate core energy levels and core properties, one has to use third order $DKH3$ Hamiltonian [67].

eXact 2-Component (X2C) Hamiltonian

In the eXact Two-Component (X2C) Hamiltonian [63, 64] framework, the positive- and negative-energy solutions of the Dirac equation are decoupled by applying a single unitary transformation. This transformation fully eliminates the small components, resulting in a block-diagonal Hamiltonian:

$$\mathbf{U}^\dagger \begin{bmatrix} \mathbf{h}_{LL} & \mathbf{h}_{LS} \\ \mathbf{h}_{SL} & \mathbf{h}_{SS} \end{bmatrix} \mathbf{U} = \begin{bmatrix} \tilde{\mathbf{h}}_{++} & 0 \\ 0 & \tilde{\mathbf{h}}_{--} \end{bmatrix}, \quad (2.85)$$

A major advantage of the X2C method is that all operations are carried out in matrix form, eliminating the need to define or implement new operators. Additionally, X2C exactly reproduces the positive-energy spectrum of the Dirac Hamiltonian at the one-electron level, making it both accurate and computationally efficient.

Core Approximations

The electrons in an atom can be divided into two categories with respect to their location relative to the nucleus: the core electrons and the valence electrons. The core electrons are located close to the nucleus, whereas the valence electrons are located in the outermost part and they participate in chemical bonding. Since the core electrons are not participating in bonding, their treatment can be simplified through core approximations that reduce the computational cost. Two main forms of core approximation are the frozen-core approximation and the use of effective core potentials (ECPs) [68].

In the frozen-core approximation, core orbitals are considered chemically inert and have an atomic character, even within molecules or materials. To reduce computational cost, inner electrons of atoms can be frozen. This is not a pseudo potential because all electrons are still present, the cores are just frozen at their optimized atomic configuration during the self-consistent field (SCF) procedure. While this approach saves time, it may reduce accuracy and should therefore be applied with caution depending on the system under study.

Notice that in post-HF methods, frozen core approximation is particularly common because core electrons provide a stable potential that influences the valence electrons but not needed to be actively correlated. Therefore the core orbitals are explicitly calculated during the self-consistent field (SCF) procedure but are excluded from subsequent correlation treatments, such as MP2 or coupled cluster methods. This significantly reduces computational cost without compromising accuracy for properties dominated by valence electron behavior.

Another way to reduce the computational cost is to use an effective core potentials (ECPs), that remove the core electrons and replace them by an effective potential that reproduces their influence on the valence electrons. Then the

Hamiltonian can be reduced to the sum of interaction between the valence electrons and their interaction with the nucleus and core electrons, leading to the so-called valence Hamiltonian:

$$\hat{H}_v = \sum_i^{N_v} \hat{H}_i + \sum_{i<j}^{N_v} \frac{1}{r_{ij}} + V_{ECP}, \quad (2.86)$$

where N_v is the number of valence electrons and V_{ECP} is the effective core potential which has the following analytical form:

$$V_{ECP} = -\frac{Z_{eff}}{r} + \sum_{l_j} \left(\sum_k a_{l_j,k} r^{n_{l_j,k}-2} \exp(-\alpha_{l_j,k} r^2) \right) P_{l_j}, \quad (2.87)$$

$$P_{l_j} = \sum_{m_j=-j}^j |l_j m_j\rangle \langle l_j m_j|, \quad (2.88)$$

where $Z_{eff} = Z - N_{core}$, corresponds to the effective core charge and P_{l_j} to the angular projector operators, to make each valence orbitals feel the core effects. Thus, a , n , and α which are parameters related to the total angular momentum j , are determined by a fitting procedure of a n -term polynomial to reproduce the best all-electron relativistic reference calculations [69]. For actinides, two types of relativistic ECP (RECP) has been developed: small-core and large-core which include 60 and 78 (or more) electrons, respectively. The choice of the core size depends on the strength of interaction between the actinides' valence electrons and the ligands. To investigate protactinium complexes, I chose a small-core potential because it have been previously show that large-core potential would bias the results [70], whereas small-core potential are as accurate as all-electron results for geometries and valence transition energies [71, 72].

2.10 Basis sets

In section 2.3 it has been mentioned that the wave-function is described by a Slater determinant which is expressed in terms of orthonormal spin-orbitals.

The spin-orbital ϕ_i represents a specific orbital of a atom or molecule.

In practice, for a molecule, one can consider that each molecular orbital is expressed as a Linear Combination of Atomic Orbitals (LCAO) [73] ϕ_i , which, themselves are expanded over mathematical basis set functions χ_k , with the coefficients d_k ,

$$\phi_i = \sum_j^{N_{AO}} c_{ij} \phi_j = \sum_j^{N_{AO}} c_{ij} \sum_k^{N_b^j} d_k \chi_k \quad (2.89)$$

with N_{AO} is the number of atomic orbitals and N_b^j is the number of the basis functions used for a given atomic orbital ϕ_j . The atomic basis set functions χ_k used to represent the three main types of atomic orbitals, core, valence and diffuse ones (Figure 2.2). In quantum chemical calculations, the basis set functions can take the form of Slater-type orbitals (STO) [74] or Gaussian-type orbitals (GTO) [75]. Both are a product of a radial part $R_l(r)$ and a spherical harmonic function $Y_l^m(\theta, \phi)$. The STO is described as follows:

$$\chi_k(r, \theta, \phi) = N r^{n-1} \exp^{-\zeta r} Y_l^m(\theta, \phi) \quad (2.90)$$

where n is the principal quantum number, N is a normalization constant, r is the electron-nucleus distance and ζ is a constant related to the effective charge of the nucleus. The best values of ζ are determined by fitting STOs to atomic wave-functions computed numerically. However, they are less suited for molecular systems because two-electron integrals involving several centers cannot be computed analytically. Therefore, the Gaussian-type orbitals (GTOs) were introduced:

$$\chi_k(r, \theta, \phi) = N r^{n-1} \exp^{-\alpha r^2} Y_l^m(\theta, \phi) \quad (2.91)$$

where α is a positive exponent. A major advantage of GTOs is that the product of two Gaussians centered at different atoms results in another Gaussian centered at a weighted midpoint. This property allows complex multi-center integrals, such as two-electron integrals over three or four centers, to be reduced to simpler two-center integrals, greatly accelerating quantum chemical calculations. Even

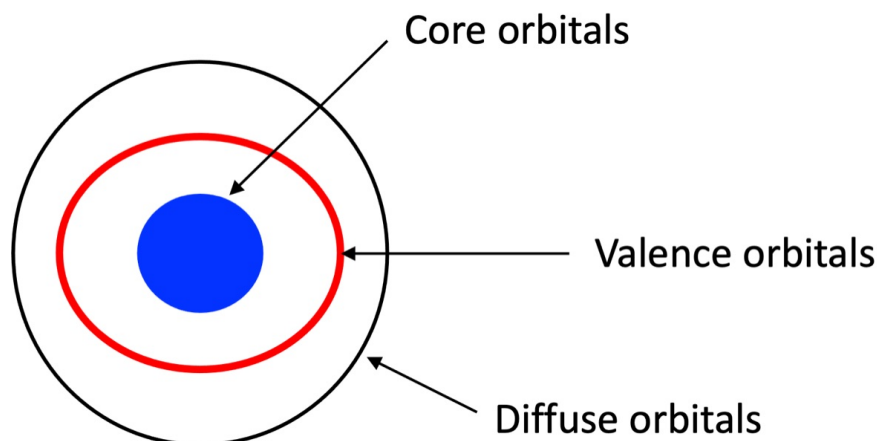


Figure 2.2: Illustration of areas treated in the basis set concept.

so GTOs provide computational efficiency but give a poorer description of the electrons behavior near the atomic nuclei due to the r^2 dependence. This leads to a rapid slope decline when moving away from the nucleus and a poor representation of the orbital "tail" compared to Slater-type orbitals (STOs). To overcome this limitation, each STO is approximated by a linear combination of primitive Gaussian functions, forming what are known as contracted Gaussian-type orbitals. There are two main types of contraction:

- Segmented contractions, where each primitive contributes to only one contracted function, offering simplicity and speed. Examples of segmented contracted basis sets are the Pople-type [76].
- General contractions, where all primitives on an atom contribute to all contracted functions, enhancing flexibility and accuracy at a higher computational cost. Examples of general contracted basis sets include the Atomic Natural Orbitals (ANOs) [77], the correlation-consistent basis sets (cc) developed by Dunning [78], and the Ahlrichs basis sets, including both the first generation (def) [79] and the second-generation (def2) [80] basis sets.

A minimal basis set has one basis function for each occupied orbital, defined as basis set of single ζ quality but it is usually not enough to obtain a chemical

description of the electronic density of the molecule. To improve the description, double- ζ basis (DZ) set is adopted where each basis function in the minimal basis set is replaced by two basis functions. Also the basis set can be extended to triple (TZ), quadrupole (QZ) and so on. For actinides, we need an accurate modeling of valence properties, TZ or QZ basis sets are required. To reduce computational cost, split-valence basis sets (SV) are used, where valence orbitals are described with multiple basis functions (two or more), while core orbitals are represented with fewer basis functions.

Further improvements to the basis sets can be made by adding:

- Polarization functions (P) with higher angular momentum functions (p-functions for hydrogen). These functions allow orbitals to distort in shape, which is important for describing chemical bonding, anisotropy in electron distribution and angular electronic correlation
- Double, triple, quadrupole (2P, 3P, 4P, etc. . .) functions, which add even more angular flexibility, improving correlation effects.
- Diffuse functions have small exponents, producing very "shallow" functions that extend far from the nucleus, which more accurately represent the "tail" portion of the atomic orbitals. These functions are added to better describe the long-range behavior of the electron density. They are especially important in systems where there are anions and weak intermolecular interactions (van der Waals forces).

An example of basis sets is the "aug-cc-pVnZ", where "aug" indicates the addition of diffuse functions, "cc" stands for correlation consistent, "pV" refers to polarized valence and nZ" indicates the zeta-quality level of the basis set, with $n = D, T, Q, 5, 6$ corresponding to double-, triple-, quadruple-, 5-, and 6-zeta(ζ), respectively.

For molecular systems of moderate size, such as those considered in this study, the use of basis sets of limited cardinality, typically triple- (T) or quadruple-zeta (Q), generally ensures a satisfactory description of geometrical structures and selected molecular properties. However, the accuracy of the total electronic energy remains significantly affected by basis set incompleteness, which constitutes a

major limitation, particularly in the context of thermodynamic property calculations. To mitigate this drawback and approach the complete basis set (CBS) limit, one can exploit the fact that modern basis sets are specifically designed to support systematic energy extrapolation, thereby enabling a smooth and controlled convergence toward the CBS limit. The total energy is divided into two components: the Hartree-Fock (HF) reference energy and the correlation energy. To extrapolate the total energy E^{CBS} to the complete basis set limit, we use two calculations and a formula that requires only two calculations to extrapolate separately the reference HF energy and the correlation energy.

The HF reference energies were extrapolated with the Karton and Martin formula [81]:

$$E_{\text{HF}}(n) = E_{\text{HF}}^{\text{CBS}} + A(n+1)e^{(-6.57\sqrt{n})}. \quad (2.92)$$

where $E_{\text{CBS}}^{\text{HF}}$ is the HF CBS energy, A is a parameter, and n corresponds to the cardinal number of the basis set (e.g., $n=3$ for cc-pVTZ, $n=4$ for cc-pVQZ).

The correlation energy is extrapolated using an inverse power law known as the L3 method [82]:

$$E_{\text{corr}}(n) = E_{\text{corr}}^{\text{CBS}} + An^{-3} \quad (2.93)$$

where $E_{\text{corr}}^{\text{CBS}}$ is the extrapolated correlation energy, and A is a fitting parameter.

2.11 Solvent Effects

So far, we have presented all the necessary tools to achieve the most accurate calculation on cluster systems limited to the molecule or ion of interest and basically their first coordination shell, limited to few ligands treated explicitly. Since our aim is to explore relative stability of systems in solution, long-range effects, i.e. beyond the first shell, have to be included. In computational chemistry, solvent effects can be treated using either explicit or implicit solvation models [83–86].

In explicit solvation models, a number of solvent molecules can be added around the solute and treated explicitly. In this case, the number of solvent molecules in the first and second coordination shells, their orientation and their placement with respect to the solute should be considered, leading to a large

number of possible conformers. Then, identifying the most stable conformer becomes essential but it is tedious. To overcome this, molecular dynamics (MD) simulations can be employed to determine the true model of the solute in the solvent. In molecular dynamics (MD) simulations, the solute is placed in a box filled with solvent molecules, and periodic boundary conditions are applied to replicate the box infinitely in all directions in order to mimic bulk solvent conditions. The system is then propagated over time by calculating forces and updating atomic positions at each time step, generating a trajectory. Several approaches fall under this category:

- **Classical molecular dynamics (MD) [87]:** In classical MD, solute-solvent interactions are modeled using a force field which refers to the functional form and parameter sets used to calculate the potential energy of a system on the atomistic level [88–90]. Force-field parameters are typically derived either by fitting to experimental data (e.g., neutron, X-ray and electron diffraction, NMR, infrared, Raman and neutron spectroscopy) or from quantum chemical calculations. However, for protactinium complexes, the lack of experimental data prevents such parameter fitting. While a quantum chemical parametrization has been proposed for tetravalent protactinium [91], no parameters currently exist for pentavalent species, neither for Pa^{5+} nor PaO^{3+} . Moreover, since we are not only interested by structural properties but also by relative stabilities of Pa(V) complexes, we explored chemical reactions, such as the one discussed in chapter 3 of this thesis, $\text{Pa(OH)}_4\text{X} \longrightarrow \text{PaO(OH}_2\text{)(X)(H}_2\text{O)}$. Accurately modeling such transformations requires a reactive force field capable of describing bond breaking and formation. Unfortunately, no such reactive parameters [92] exist for actinides at present.
- **Ab initio molecular dynamics (AIMD) [93–95]:** AIMD simulations compute interatomic forces directly from quantum mechanics, enabling a fully quantum mechanical treatment of both the solute and the solvent, and naturally accounting for all types of interactions. In this thesis AIMD simulations were performed for selected pentavalent protactinium complexes. The systems were embedded in large simulation boxes containing

around 100 water molecules and trajectories were propagated over a few picoseconds using 128 processors within a DFT framework. We employed the PBE GGA functional (See chapter 3). Two limitations affect these AIMD simulations. First, the short trajectory lengths (a few ps) are insufficient to ensure full thermalization or convergence of structural and thermodynamic properties, despite their computational cost of about two weeks per simulation. Second, the accuracy of the DFT functional itself is a concern, particularly for modeling the solvent and the metal-solvent interactions. Recent studies recommend hybrid or meta-hybrid functionals for improved water modeling [96], but these come with a significant increase in computational demand. More accurate post-Hartree-Fock methods such as CCSD(T), often referred as the "gold-standard" CCSD(T), remain computationally prohibitive for such systems. Similarly, simulating full reaction pathways using AIMD is currently unfeasible.

- **QM/MM (Quantum Mechanics / Molecular Mechanics) [97, 98]:** It is a hybrid approach where the solute and the first coordination shell of solvent molecules are treated quantum mechanically while the rest are described by molecular mechanics. In a word, the energy of the system is a combination of three energies:

$$E_{QM/MM} = E_{QM} + E_{QM/MM} + E_{MM}, \quad (2.94)$$

with E_{QM} the ab initio solute energy, E_{MM} the classical energy obtained thanks to a given force field, and last the $E_{QM/MM}$ energy which is the interaction between the QM and the MM part of the system, calculated classically by including the electrostatic effects and the Van der Waals interaction (Lennard-Jones potential) or more sophisticated terms like polarizable terms or bond breaking terms. This approach is a good compromise between computational time and accuracy but requires a well-parametrized and physically meaningful force field, that accounts for all the interactions, which is so far not available for either Pa^{5+} or PaO^{3+} species.

To overcome the high computational cost of molecular dynamics simulations and

the absence of parameterized force fields for pentavalent protactinium, implicit solvation models can be employed. In these models, the solvent is represented as a continuous dielectric medium rather than as discrete molecules, significantly reducing computational complexity while still capturing key solvation effects. In this work, continuum solvation models [99] have been used; they will be discussed in the following section.

2.11.1 Continuum Models

In continuum solvation models, the solvent is treated as a polarizable dielectric continuum with a dielectric constant, ϵ_r , while the solute is embedded within a molecular-shaped cavity inside this medium. The solute's charge distribution, ρ , induces polarization of the surrounding dielectric medium. In response, the polarized solvent generates a reaction field that acts back on the solute, modifying its structure, its energy, and properties[99, 100].

The interaction between the solute and the solvent is represented by a reaction potential $\hat{V}_{solv}[\sigma]$, that depends on the apparent surface charge distribution σ . This potential acts as a perturbation to the solute's gas-phase Hamiltonian $\hat{H}(S)$, describing the change in the system's electronic structure from the gas phase to the continuum-solvent environment. Then the effective Hamiltonian, $\hat{H}_{eff}$, in the continuum is expressed as:

$$\hat{H}_{eff} = \hat{H}(S) + \hat{V}_{solv}[\sigma], \quad (2.95)$$

The total electrostatic potential, $\Phi(\mathbf{r})$, including contributions from both the solute and the polarized solvent, satisfies the Poisson equation:

$$\nabla \cdot [\epsilon(\mathbf{r}) \nabla \Phi(\mathbf{r})] = -4\pi \rho(\mathbf{r}), \quad (2.96)$$

where $\rho(\mathbf{r})$ is the charge density of the solute, and $\epsilon(\mathbf{r})$ is the space-dependent dielectric permittivity (with $\epsilon = 1$ inside the cavity, and $\epsilon = \epsilon_r$ in the solvent region). The reaction potential, $\hat{V}_{solv}$, is then obtained by subtracting the vacuum electrostatic potential ($\epsilon = 1$) from the total potential.

The reaction potential $\hat{V}_{solv}$ is expressed in terms an induced charge density

on the cavity surface Γ . For practical calculations, the cavity surface is discretized into small regions called tesserae (Figure 2.3). Each tessera is characterized by the position of its center r_i , its area, a_i , and the normal vector, n_i , at its center. The surface charge distribution, $\sigma(s_i)$, is assumed constant within each tessera. The induced charge density, apparent surface charge distribution $\sigma(s)$, is determined from the solute's electrostatic potential at the cavity surface. Hence the surface charges and the solute-solvent interaction are solved self-consistently within a self-consistent reaction field (SCRF) framework, using an iterative procedure to obtain the solvated molecule's wave function and energy.

The free solvation energy ΔG_{sol} , is typically decomposed into three contributions:

$$\Delta G_{sol} = \Delta G_{cav} + \Delta G_{disp} + \Delta G_{elec}, \quad (2.97)$$

where ΔG_{cav} is the free energy required to create the solute cavity, ΔG_{disp} accounts for van der Waals interactions between the solute and the solvent, and ΔG_{elec} represents the electrostatic component arising from mutual polarization.

The two first contributions are generally determined empirically, while the electrostatic component, ΔG_{elec} , dominates the solvation free energy and must be computed accurately. This term can be formally calculated by using the following formula:

$$\Delta G_{elec} = \frac{1}{2} \int \rho(\mathbf{r}) \phi_{reaction}(\mathbf{r}) d\mathbf{r}, \quad (2.98)$$

where $\rho(\mathbf{r})$ is the solute's charge density and $\phi_{reaction}(\mathbf{r})$ denotes the electrostatic potential induced by the solvent, also known as the reaction field.

Several continuum solvation models have been developed, including the Polarizable Continuum Model (PCM), the Conductor-like PCM (C-PCM), and the Conductor-like Screening Model (COSMO), as well as its extension for thermodynamic properties, the Conductor-like Screening Model for Real Solvents (COSMO-RS). These models differ mainly in how they approximate the dielectric boundary conditions and calculate the surface charges.

Polarizable Continuum Model

The Polarizable Continuum Model (PCM) [101, 102] implements the general framework of continuum solvation theory discussed previously.

In PCM, the electrostatic interaction between the solute and the solvent is represented as an interaction between the solute's charge distribution, $\rho(\mathbf{r})$, and an induced surface charge distribution, $\sigma(\mathbf{s})$, known as the *the apparent surface charge*, which is spread over the cavity surface Γ . As discussed the cavity surface is discretized into small elements called tesserae.

The resulting system can be formulated as a set of linear equations:

$$\mathbf{S}\mathbf{q} = \mathbf{R}\mathbf{V}, \quad (2.99)$$

where:

- $\mathbf{q}$ is the vector of induced surface charges.
- $\mathbf{V}$ is the vector of the solute's electrostatic potential evaluated at the tesserae.
- $\mathbf{S}$ is the interaction matrix between cavity charges.
- $\mathbf{R}$ is the coupling matrix relating the solute's potential to the surface charges.

Once the system of equations (Equation 2.99) is solved and the apparent surface charge vector $\mathbf{q}$ is obtained, the electrostatic contribution to the solvation free energy can be computed as:

$$\Delta G_{elec} = \frac{1}{2} \mathbf{q} \mathbf{V} \quad (2.100)$$

where the factor of $\frac{1}{2}$ prevents double counting of the interaction energy, as both the solute and the dielectric medium respond to each other's fields.

In addition to the electrostatic term, non-electrostatic contributions, such as cavitation and dispersion-repulsion energies, are typically incorporated via empirical corrections to obtain the total solvation free energy.

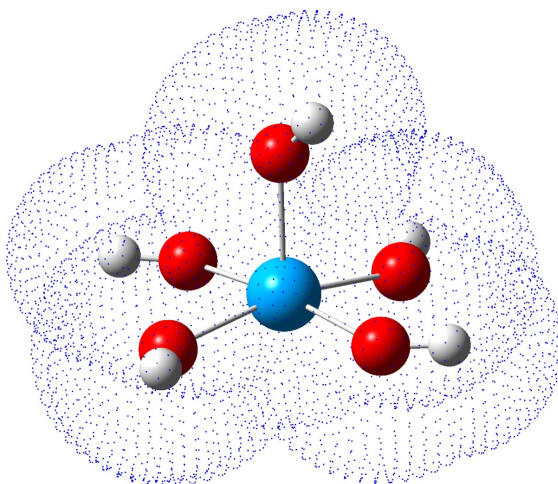


Figure 2.3: PCM solute cavity of $\text{Pa}(\text{OH})_5$ complex.

Conductor-like Polarizable Continuum Model (C-PCM)

The Conductor-like Polarizable Continuum Model (C-PCM) [103, 104] is a variant of PCM, and is considered one of the most successful solvation models.

In matrix form, C-PCM follows the same general structure as PCM but incorporates a scaled-conductor approximation. Within this approximation, the coupling matrix $\mathbf{R}$ simplifies to become a simple scalar times the identity matrix $\mathbf{1}$:

$$\mathbf{R} = -f(\epsilon_r)\mathbf{1}, \quad (2.101)$$

where the dielectric scaling factor is defined as:

$$f(\epsilon_r) = \frac{\epsilon_r - 1}{\epsilon_r}, \quad (2.102)$$

with ϵ_r being the relative permittivity of the solvent. In this C-PCM model, $\epsilon_r \rightarrow \infty$ is the true conductor limit. The scaling factor $f(\epsilon_r)$ (See Equation 2.102) interpolates between vacuum (0) and conductor (1). The resulting surface charges can then be used, as in standard PCM, to compute the electrostatic solvation energy.

Conductor-like Screening Model (COSMO)

The Conductor-like Screening Model (COSMO) [105, 106] further simplifies solute-solvent electrostatic interactions by treating the solvent as a perfect conductor with a scaled-conductor approximation. COSMO introduces a dielectric scaling factor:

$$f(\epsilon_r) = \frac{\epsilon_r - 1}{\epsilon_r + x}, \quad (2.103)$$

where the empirical parameter x adjusts to experimental data (typically $x = 0.5$ for neutral molecules and $x = 0$ for ions).

Once the apparent surface charges are obtained using this scaling, the electrostatic component of the solvation free energy, ΔG_{elec} , is computed exactly as in C-PCM by projecting the solute's electrostatic potential onto the scaled surface charges.

Conductor-like Screening Model for Real Solvents (COSMO-RS)

Traditional dielectric continuum models (PCM, C-PCM and COSMO) share a key limitation: they cannot distinguish between solvents with identical dielectric constants but different molecular interactions (e.g., cyclohexane vs. benzene). Moreover, by assuming a linear, homogeneous response, these models often fail to capture specific solvation phenomena, such as hydrogen bonding, directional interactions, and local solvent structure, especially in polar media where reorientation of permanent dipoles dominates.

COSMO-RS overcomes these shortcomings by combining quantum-chemical COSMO surface charges with a statistical thermodynamics treatment of explicit solute-solvent interactions [107, 108]. First, a standard COSMO calculation is performed on the isolated solute in the perfect-conductor limit, yielding its apparent surface charge distribution. These charges then serve as “interaction profiles” in a statistical ensemble of solvent and solute molecules, where pairwise segment interactions, both solvent-solvent and solute-solvent, are evaluated using empirical energy functions corresponding to COSMO-RS parameter datasets. By integrating over all possible configurations, COSMO-RS computes the chemical potential of each species in solution.

From these chemical potentials, COSMO-RS predicts a wide range of bulk thermodynamic properties – activity coefficients, solubility, vapor pressure, partition coefficients, and solvation free energies – across varying temperatures and solvent composition. This approach accurately accounts for specific interactions, including hydrogen bonding and dispersion, without requiring explicit solvent geometries.

Because COSMO-RS uses precomputed COSMO charges rather than self-consistent polarization in a particular solvent, it excels at predicting thermodynamic properties but cannot capture solvent-induced changes to a solute’s geometry or vibrational frequencies. As a result, COSMO-RS is limited to single-point energy calculations and cannot be used for geometry optimizations or frequency analysis. Nonetheless, its ability to account for specific solute-solvent interactions makes it ideal for computing the solvation free energies of protactinium complexes, as detailed in chapter 3.

2.12 Time-Dependent Density Functional Theory

Ground-state density functional theory discussed in section 2.8 provides only a static description of the electronic ground state. To access excited-states and real-time electron dynamics, one uses its time-dependent extension, time-dependent density functional theory (TD-DFT) [109–112].

In TD-DFT, the system in its ground state is subjected to a time-dependent external potential $V_{ext}(\mathbf{r}, t)$, such as an electric field or a laser pulse. This perturbation drives the evolution of the electron density $\rho(\mathbf{r}, t)$. Accordingly, the static Kohn-Sham potential in Equation 2.33 is replaced by a time-dependent potential, and the time-dependent Kohn-Sham (TD-KS) Hamiltonian becomes:

$$\widehat{H}_{KS}(t) = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 + \sum_{i=1}^N V_{KS}(\mathbf{r}_i, t), \quad (2.104)$$

where $V_{KS}(\mathbf{r}, t) = V_{ext}(\mathbf{r}, t) + V_H(\mathbf{r}, t) + V_{xc}(\mathbf{r}, t)$ combines the external, Hartree, and exchange-correlation potentials.

Runge and Gross [113] provided a TD-DFT analogue to the Hohenberg-Kohn

theorem: there is one-to-one mapping between the time-dependent external potential, $V_{ext}(\mathbf{r}, t)$ (up to a purely time-dependent gauge) and $\rho(\mathbf{r}, t)$, so that all observables are functionals of the time-dependent density alone.

2.12.1 Time-Dependent Kohn-Sham Equations

To make the problem tractable, one introduces non-interacting Kohn-Sham orbitals $\phi_i(\mathbf{r}, t)$ evolving under an effective Hamiltonian that reproduces the exact density, $\rho(\mathbf{r}, t)$. The time-dependent Kohn-Sham (TD-KS) equations are:

$$\hat{H}_{KS}(t) \phi_i(\mathbf{r}, t) = i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t), \quad (2.105)$$

with $\hat{H}_{KS}(t)$ defined by Equation 2.104.

2.12.2 Adiabatic Approximation

Since the exact functional V_{xc} is unknown, TD-DFT implementation often invokes the *adiabatic approximation*, which neglect memory of past densities

$$V_{xc}(\mathbf{r}, t) \approx \left. \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \right|_{\rho=\rho(\mathbf{r}, t)}, \quad (2.106)$$

using any standard ground-state functional $E_{xc}[\rho]$. This “no-memory” ansatz simplifies computations but cannot capture inherently time-nonlocal phenomena (e.g. double excitations).

2.12.3 Real-Time TD-DFT

In *real-time TD-DFT*, one directly propagates the TD-KS equations under a time-dependent perturbation (e.g. a short delta-pulse) [114]. Observables such as the dipole moment are recorded as functions of time and then Fourier-transformed to yield excitation spectra, including nonlinear and ultrafast responses.

2.12.4 Linear-Response TD-DFT

For weak perturbations, *linear-response TD-DFT (LR-TD-DFT)* suffices.

One begins with the time-dependent density response to a small external perturbation,

$$\delta\rho(\mathbf{r}, t) = \int_{-\infty}^t dt' \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; t - t') \delta V_{\text{ext}}(\mathbf{r}', t') \quad (2.107)$$

where $\chi(\mathbf{r}, \mathbf{r}'; t - t')$ is the density-density response function. To turn this convolution in time into a simple product, we Fourier-transform both sides with respect to t :

$$\delta\rho(\mathbf{r}, \omega) = \int d\mathbf{r}' \chi(\mathbf{r}, \mathbf{r}'; \omega) \delta V_{\text{ext}}(\mathbf{r}', \omega). \quad (2.108)$$

The poles of $\chi(\omega)$ in the complex ω -plane correspond to the system's excitation energies.

Casida [115, 116] reformulated the search for those poles as a matrix eigenvalue problem in the space of single Kohn-Sham orbital transitions ($i \rightarrow a$). Defining the coupling matrices,

$$A_{ia,jb} = (\varepsilon_a - \varepsilon_i) \delta_{ij} \delta_{ab} (ia|jb) + f_{ia,jb}^{\text{xc}}, \quad B_{ia,jb} = (ia|bj) + f_{ia,bj}^{\text{xc}} \quad (2.109)$$

one shows that the excitation energies ω satisfy

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix} = \omega \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{X} \\ \mathbf{Y} \end{pmatrix}. \quad (2.110)$$

Here

- $\varepsilon_i, \varepsilon_a$ are occupied and virtual KS orbital energies,
- $(ia|jb)$ are two-electron Coulomb integrals,
- $f_{pq,rs}^{\text{xc}} = \iint \phi_p^*(1) \phi_q(1) \frac{\delta^2 E_{\text{xc}}}{\delta \rho(1) \delta \rho(2)} \phi_r^*(2) \phi_s(2) d_1 d_2$ is the exchange-correlation kernel matrix.

Solving this non-Hermitian eigenvalue problem yields pairs $(\omega_n, \mathbf{X}_n, \mathbf{Y}_n)$ whose ω_n are the excitation energies, and $\mathbf{X}_n$, and $\mathbf{Y}_n$ are the transitions vectors.

In addition to these, oscillator strengths associated with the excitations can be computed from the $\mathbf{X}_n$, $\mathbf{Y}_n$ eigenvectors. The oscillator strengths are the probability of the transition from the ground state to the excited states.

In practice one often applies the *Tamm-Dancoff approximation (TDA)* [117] by setting $\mathbf{B} = 0$, reducing the problem to the Hermitian eigenvalue equation

$$\mathbf{A}\mathbf{X} = \omega\mathbf{X}, \quad (2.111)$$

which retains most of the accuracy for single excitations while improving numerical stability. TDA/TD-DFT is a widely used and a good approximation to full TD-DFT [118, 119], and it is employed in this work (See chapter 4).

While LR-TD-DFT has been successful for describing valence [119] and core excitations [120] of molecular systems, it has several limitations. TD-DFT is restricted to the treatment of single excitations. The neglect of orbital relaxation in (A)LDA-based LR-TD-DFT can be questioned in situations where the excited electron and the hole it leaves behind occupy very different spatial regions or electronic environments. We can quote in particular [121–123]:

- long-range charge-transfer states. When an excitation moves electron density from one fragment (or chromophore) to another distant fragment, the ground-state orbitals are a poor starting point and fail to relax to the correct donor-acceptor distribution.
- Rydberg Excitations: Rydberg states involve promotion of an electron into very diffuse, high-lying orbitals. The remaining core orbitals should contract (orbital relaxation) but cannot in a fixed-orbital framework.
- Core-Level Excitations: Removing a deep core electron induces significant reorganization of the valence manifold (orbital contraction and polarization) that TD-DFT cannot capture without explicit relaxation. The consequence of lacking orbital relaxation is a typically tendency to overestimate absolute core excitation energies by 10-20 eV (or more depending on the element and edge). However, the relative energies of core excited states is much less sensitive to missing relaxation. In practice, TD-DFT in the adiabatic approximation can often predict these relative peaks position to

within 0.5 eV or better, even though the absolute energies remain poorly placed. We will discuss this in the context of Pa core spectra in chapter 5 [124].

- Multiconfigurational or Diradical Systems: When the ground state already has mixed configuration character (e.g. diradicals or bond-breaking regions), both the occupied and virtual orbitals must adapt differently in the excited state, an effect absent in linear-response TD-DFT.

In addition, the exchange-correlation kernel f_{xc} is unknown. As discussed earlier, in the *adiabatic local density approximation*, the kernel is derived from the ground-state exchange-correlation functional. Consequently, the predicted transition energies and properties become highly dependent on the chosen functional [125]. This further limits the reliability of TD-DFT in systems with multi-configurational character or long-range correlation effects.

To overcome these limitations, wavefunction-based multi-reference methods [126, 127] can be used. In this work, both the Restricted Active Space Self-Consistent Field (RASSCF) method and its second-order perturbative extension RASPT2 were employed to investigate core excitations in pentavalent protactinium complexes. The theoretical foundations of RASSCF and RASPT2 methods will be discussed in the following section.

2.13 Multi-Configurational Self-Consistent Field (MCSCF)

As in full Configuration Interaction (FCI), discussed in section 2.5, the Multi-Configurational Self-Consistent Field (MCSCF) wave-function is expressed as a linear combination of Slater determinants. However, in MCSCF both the expansion coefficients C_i and the molecular orbitals are simultaneously optimized. In other words, MCSCF can be viewed as a self-consistent field version of CI, in which orbital relaxation is included at each step of the configuration interaction procedure.

While MCSCF provides an accurate and variational description of static

electron correlation, handling a large number of possible configurations is computationally expensive. To address this challenge, different approaches are available that can reduce the computational cost.

One such approach is the Complete Active Space Self-Consistent Field (CASSCF) method [128], which introduces a well-defined way to restrict the wavefunction expansion to the most important configurations. This is achieved by dividing the molecular orbitals into three subspaces: the inactive space, the active space and the virtual space. The orbitals are doubly occupied in the inactive space, empty in the virtual space, and are allowed to have partial electron occupations within the active space. Within the active space, a full CI expansion is performed, capturing the static correlation.

A critical point in CASSCF is the selection of the active space [129], as both its size and composition have a direct impact on the accuracy and computational cost of the calculation. Finding the right balance between precision and cost is essential, therefore the choice of active orbitals must be guided by chemical intuition.

When the active space required for CASSCF calculation becomes too large, the full CI expansion within that space becomes computationally expensive. In such cases, one can simplify the calculations by using Restricted Active Space Self-Consistent Field (RASSCF) method [130, 131]. In RASSCF, the active space from CAS is divided into three subspaces:

- **RAS 2** is the middle subspace, it corresponds to the regular conventional CASSCF active space where the full CI is performed.
- **RAS 1** is the lower subspace, it contains orbitals that are typically doubly occupied, and it allows only a certain number of electrons to be excited from it.
- **RAS 3** is the upper subspace, it consists of orbitals that are unoccupied, and allows only a certain number of electrons to be excited to it.

This partitioning allows the inclusion of more orbitals in the active space while maintaining a computationally feasible CI expansion. In addition to improving computational efficiency, it also enables the treatment of core excitations [132–

134], which often require the inclusion of deeply bound orbitals in the active space, and it is employed in this work. As in CASSCF, the molecular orbitals and the CI coefficients are optimized self-consistently, ensuring a balanced variationally consistent multi-configurational description of the electronic structure.

As discussed in section 2.4, the electron correlation can be separated into the dynamical and static components. CASSCF and RASSCF primarily account for static correlation. In order to incorporate the dynamic correlation, two main approaches are mostly used: either the configuration interaction methods (CI), such as Difference-Dedicated Configuration interaction (DDCI) [135] and Multi-reference CI with Single- and Double excitations (MR-CISD) [136] or the perturbation theory methods. While CI-based approaches are beyond the scope of this work, the second-order perturbative methods were used will be described in more detail below.

2.13.1 Post-MCSCF Perturbation Theory

To recover the dynamic correlation energy missing from CASSCF and RASSCF, second-order perturbation theory can be applied on top of the multiconfigurational wavefunction. Among the most commonly used approaches are the Complete Active Space Second-Order Perturbation Theory (CASPT2) [137, 138] and the Restricted Active Space Second-Order Perturbation Theory (RASPT2) methods.

These methods take the multiconfigurational reference wavefunction generated from CASSCF or RASSCF and apply perturbation theory to include dynamic correlation effects from the external (inactive and virtual) orbital spaces as in Møller-Plesset many-body perturbation theory. The total electronic energy is then given by:

$$E_{total} = E_{MCSCF} + E_{PT}^{(2)}, \quad (2.112)$$

where E_{MCSCF} is the self-consistent energy from CASSCF or RASSCF, and is $E_{PT}^{(2)}$ is the second-order energy correction obtained from perturbation theory.

RASPT2 is particularly useful when the size of the active space makes a full CAS treatment impractical, while still allowing for a proper description of ex-

cited states, transition metal complexes, or core-excited states. By building upon a flexible RASSCF reference, RASPT2 allows for an accurate and computationally efficient inclusion of dynamic correlation.

Special care must be taken in the choice of the zeroth-order Hamiltonian and in managing intruder states, which can affect the numerical stability of the perturbative correction. Techniques such as level shifting [128] or imaginary level shifting [139] are often employed to mitigate these issues.

2.13.2 Spin-Orbit Coupling: The Two-Step RASSI-SO Approach

After recovering the dynamic correlation through CASPT2 or RASPT2, spin-orbit coupling (SOC) can be incorporated using the two-step *CILS+SO* approach (Configuration Interaction in the Spin-free space followed by SOC), implemented in the *RASSI* module of *OpenMolcas* [140]. In this method, the treatment of electronic correlation and spin-orbit coupling is separated where SOC can be considered a perturbation, then treating the SOC after the first CI calculation should be accurate enough.

The first step consists of diagonalizing the spin-free Hamiltonian $\hat{H}^{el}$, typically using RASSCF or RASPT2, to obtain a set of spin-free eigenstates Ψ_k^{el} and their corresponding energies E_k^{el} . These eigenfunctions are expanded in terms of the underlying Slater determinants ϕ_i from the reference space:

$$|\Psi_k^{el}\rangle = \sum_i c_k^i |\phi_i\rangle \quad (2.113)$$

Once the spin-free states are obtained, spin-orbit effects are introduced by constructing the total Hamiltonian:

$$\hat{H}^{tot} = \hat{H}^{el} + \hat{H}^{SO}, \quad (2.114)$$

where $\hat{H}^{SO}$ is the spin-orbit coupling operator. The matrix representation of $\hat{H}^{tot}$ in the basis of spin-free eigenstates $|\Psi_k^{el}\rangle$ takes the form:

$$\begin{array}{c}
\langle \Psi_1^{\text{el}} | \\
\vdots \\
\langle \Psi_i^{\text{el}} | \\
\vdots \\
\langle \Psi_N^{\text{el}} |
\end{array}
\begin{array}{c}
| \Psi_1^{\text{el}} \rangle \quad \dots \quad | \Psi_i^{\text{el}} \rangle \quad | \Psi_N^{\text{el}} \rangle \\
\left[\begin{array}{ccccc}
E_1^{\text{el}} & \dots & \dots & \dots & H_{1N}^{\text{SO}} \\
\vdots & & \ddots & & \vdots \\
\dots & & E_i^{\text{el}} & \dots & H_{ij}^{\text{SO}} \\
\vdots & & \vdots & \dots & \ddots \\
H_{N1}^{\text{SO}} & \dots & H_{ij}^{\text{SO}} & \dots & E_N^{\text{el}}
\end{array} \right]
\end{array}
\quad (2.115)$$

The diagonal elements are the spin-free energies E_k^{el} , while the off-diagonal elements are spin-orbit coupling matrix elements between the spin-free states. Diagonalizing this matrix yields spin-orbit coupled states Ψ_k^{SO} , which are expressed as linear combinations of the original spin-free wavefunctions.

This approach, also referred to as *contracted SOC* (c-SOCI), is computationally efficient but has limitations. Since the SOC matrix is constructed in a truncated spin-free state space, some spin-orbit interactions—particularly those involving single excitations important for orbital relaxation and SOC polarization may be underestimated. Moreover, because SOC is added after orbital optimization, the resulting wavefunctions do not account for orbital relaxation induced by spin-orbit coupling.

These approximations can become inadequate in systems with strong spin-orbit interaction and tightly coupled correlation effects, as found in 6p elements [141–144]. In such cases, accurate results may require either a larger spin-free state basis in the SOC coupling step or the use of more advanced methods such as the Effective and Polarized CI+SO (EPCISO) approach [145].

2.14 References

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The Protactinium(V) Mono-oxo Bond

This chapter is based on two published articles:

- T. Shaaban et al., “Stability of the Protactinium(V) Mono-Oxo Cation Probed by First-Principle Calculations”, *Chemistry – A European Journal*, 2024, **30**, e202304068, DOI: 10.1002/chem.202304068

All quantum mechanics (QM) data, including the optimized coordinates for all species, are accessible on the open-access Zenodo repository with the following DOI: 10.5281/zenodo.10529027 (Version v1.1). Additional results and details are provided in the supporting information.

For this publication, I performed all quantum mechanical (QM) calculations, carried out the data analysis, prepared the first draft of the manuscript, and revised the text in collaboration with the co-authors.

- T. Shaaban et al., “Is the protactinium(V) mono-oxo bond weaker than what we thought?”, *Chemical Communications*, 2024, **60**, 14376–14379, DOI: 10.1039/D4CC04522J

The data supporting this article are included in the Supplementary Information, and the optimized structures can be accessed at the Zenodo repository via the following DOI: 10.5281/zenodo.13494221.

For this publication, I carried out all static DFT calculations, along with the associated bond analysis.

In the following sections, I provide an overview of the objectives of this work.

3.1 Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations

As explained in chapter 1, protactinium ($Z = 91$) is the first actinide to exhibit simultaneously occupied 5f and 6d orbitals in its free-atom ground-state configuration, $[\text{Rn}]5f^26d^17s^2$ [3]. This electronic structure enables unique interactions between 5f and 6d valence orbitals, placing Pa at the intersection of transition metal and actinide chemistry. Despite its fundamental interest, our understanding of protactinium chemistry remains limited due to its rarity, radio-toxicity, and the practical challenges associated with conducting experiments on radioactive species. Working experimentally with protactinium is complex for many reasons [4]:

- such experiments are never routine and require strict safety protocols;
- it is often difficult to reach concentrations high enough to enable standard spectroscopic techniques;
- protactinium may precipitate into unidentified solid forms, further reducing its concentration in solution.

In solution, protactinium can adopt both tetravalent (Pa(IV)) and pentavalent (Pa(V)) oxidation states. However, Pa(V) dominates in solution because Pa(IV) is unstable and readily oxidizes to Pa(V) in the absence of strong reducing agent [5]. Accordingly, the thesis work focuses exclusively on the chemistry of pentavalent protactinium. The speciation of Pa(V) depends on the chemical environment. Like its heavier actinide counterparts, uranium, neptunium, and plutonium, the PaO_2^+ cation is stable in the gas phase [6]. In solution, however, the dioxo species PaO_2^+ has not been observed and this is supported by state-of-the-art quantum calculations [7].

In aqueous media, Pa(V) exists either as Pa^{5+} or in a mono-oxo form PaO^{3+} , making it a truly unique actinide. To date, only one crystal structure, $[\text{NEt}_4]_2[\text{PaOCl}_5]$ [8] provides evidence of a short $\text{Pa}\equiv\text{O}$ bond of 1.74 Å.

In solution the strength and persistence of the $\text{Pa}\equiv\text{O}$ bond appear to be highly sensitive to the concentration and coordination environment. Pa(V) exhibits

good solubility in hydrofluoric, sulfuric, as well as in oxalic acid media. In dilute HF, mono-oxo fluoride complexes such as $[\text{PaOF}]^{2+}$, $[\text{PaOF}_2]^+$, and PaOF_3 have been proposed [9, 10]. A short $\text{Pa}\equiv\text{O}$ bond is also observed in strongly acidic, non-fluoride environments – concentrated sulfuric acid (12 M) and oxalic acid [11, 12]. By contrast, in HF the $\text{Pa}\equiv\text{O}$ bond is destabilized as fluoride loading increases: for F/Pa ratios exceeding 5, the oxo bond disappears and stable non-oxo fluoro-complexes dominate, ranging from PaF_6^- to PaF_8^{3-} [10, 13].

In chloride media, the situation is less clear. Because chloride is a weaker ligand than fluoride or oxalate, the $\text{Pa}\equiv\text{O}$ bond might be expected to persist under acidic conditions. In fact, tracer-level studies in 3 M HCl suggest oxo-hydroxo-chloro species such as $[\text{PaO}(\text{OH})\text{Cl}]^+$ [14], although other hydroxo-oxo-chloro and fully chlorinated species have also been proposed depending on the chloride and proton concentrations. Ultraviolet-visible absorption measurements at higher concentrations show an absorption band near 210 nm that has been linked to a $\text{Pa}\equiv\text{O}$ bond [15]. However, other investigations have instead argued for fully chlorinated complexes in concentrated HCl [16–19]. To date, no direct structural characterization of Pa(V) chloride species has been reported, leaving the stability of the $\text{Pa}\equiv\text{O}$ bond in HCl unresolved.

These observations raise a fundamental question: under which chemical conditions is the $\text{Pa}\equiv\text{O}$ bond stabilized or weakened, and how does this depend on the nature of the coordinating ligand (hydroxide, halides, thiocyanate, nitrate, sulfate, oxalate)?

Addressing this question experimentally is challenging; given the limitations of protactinium chemistry, a purely experimental, trial-and-error approach would be too time consuming and impractical. However, advances in computational chemistry now enable increasingly accurate and predictive studies of actinide systems [20–23]. Consequently, we decided to employ quantum chemical methods to provide theoretical insight and guide the design of future experiments.

In this context, previous theoretical studies offer a valuable foundation. Notably, Lontchi et al. investigated the hydrolysis reactions of the dioxo $\text{PaO}_2(\text{OH})$ system using relativistic quantum chemical methods [24]. Their results showed

that hydrolysis proceeds through two exothermic steps: first, the formation of a mono-oxo complex, $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$, and subsequently, the formation of $\text{Pa}(\text{OH})_5$. Importantly, in the absence of inorganic or organic ligands, they found that $\text{Pa}(\text{OH})_5$ is more stable than the mono-oxo species by 38.5 kJ mol^{-1} . However, their study was limited to the gas phase and did not account for solvent effect, which are known to be important for estimating thermodynamic stabilities in aqueous phase.

Building on this approach, we aimed to extend the study to the aqueous phase in order to better approximate experimental conditions and assess solvation effects on the stability of protactinium complexes. In particular, we investigated how substituting one hydroxide ligand with other chemical groups affects the mono-oxo species by comparing two stoichiometrically equivalent neutral complexes: $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ (Figure 3.1). This comparison corresponds to a proton-transfer reaction from the coordinated water molecule to the oxo group in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$. While these neutral complexes are unlikely to be soluble in aqueous conditions, they offer a framework for assessing how different X ligands affect the stability of the mono-oxo bond.

In these systems, the coordination number of pentavalent protactinium (Pa(V)) varies between five and six, depending on the nature of the ligand X, which may be monodentate or bidentate. To capture a broad range of chemical behavior, we selected a diverse set of ligands, primarily monodentate, including hydroxide (OH^-), the halide series (F^- , Cl^- , Br^- , and I^-) and thiocyanate SCN^- . In addition, bidentate ligands such as nitrate (NO_3^-), sulfate (SO_4^{2-}) and the organic oxalate ($\text{C}_2\text{O}_4^{2-}$) were considered. To evaluate the relative stabilities of the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes we calculated the Gibbs free energy ΔG_r of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ at room temperature ($T=298 \text{ K}$) and pressure ($P=1 \text{ bar}$). This was done by summing the scalar relativistic electronic energy obtained from CCSD(T) ($\Delta E_{\text{CCSD}(T)}$), the spin-orbit (SO) correction (ΔE_{SOC}), the thermal correction to the Gibbs free energy (ΔG_{corr}), and the COSMO-RS solvation free energy (ΔG_{sol}):

$$\Delta G_r = \Delta E_{\text{CCSD}(T)} + \Delta E_{\text{SOC}} + \Delta G_{\text{corr}} + \Delta G_{\text{sol}} \quad (3.1)$$

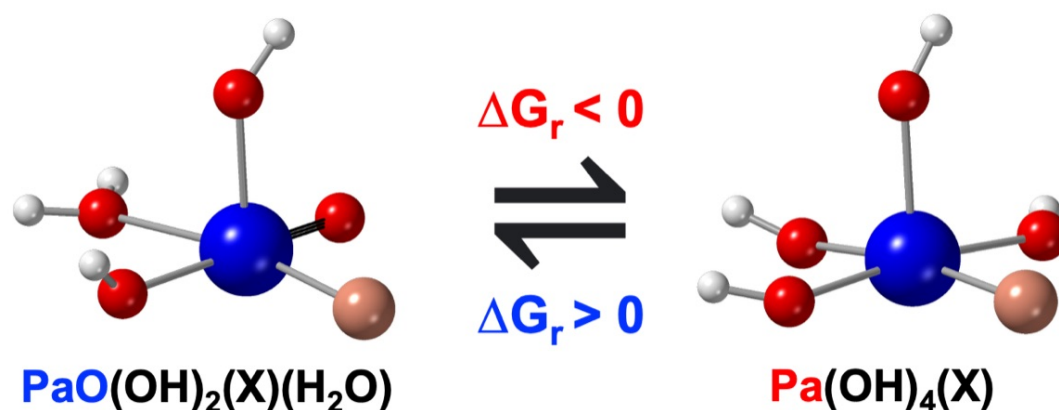


Figure 3.1: The model systems of Pa(V) complexes.

The choice of these components was guided by a thorough evaluation of the computational methodology, as in any theoretical study, to ensure accurate predictions of both geometries and thermodynamics. This benchmarking involved assessing the effects of basis set selection, spin-orbit coupling effect on geometries and energetics, and the choice of solvation model for reliable solvation energies. Additionally, various density functional theory (DFT) functionals were compared against high-level wavefunction-based results obtained from CCSD(T) calculations, in order to evaluate the performance of each functional in predicting reaction energetics to potentially using it for larger systems. This systematic benchmarking was performed with the ultimate goal of achieving chemical accuracy, i.e., errors within $1 \text{ kcal mol}^{-1} \approx 4.2 \text{ kJ mol}^{-1}$. Further details regarding the selection of basis sets, solvation models, and the SOC effect are provided in the Supplementary Information of this publication [1].

Beyond what is covered in the Supplementary Information regarding the benchmarking of various DFT functionals with respect to CCSD(T), we systematically compared the electronic reaction energies (ΔE) obtained with different DFT functionals against the CCSD(T) reference values for the reaction $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa(OH)}_4(\text{X})$ for the ligands $\text{X}=\text{OH}^-$ and Cl^- (see Table 3.1). Among the tested functionals, M06 shows the best agreement with CCSD(T) for both OH^- and Cl^- ligands, with deviations under 3 kJ mol^{-1} . In addition ω -B97X and M06-L also perform well (within $2\text{--}3 \text{ kJ mol}^{-1}$). By con-

trast, most GGA and hybrid functionals and the meta-GGA hybrid M06-2X significantly overestimate reaction exothermicity, with M06-2X showing the largest deviations among the functionals tested. It is worth mentioning that dispersion corrections as tested with the PBE0 functional, PBE0-D3(BJ) and PBE0-D4, are negligible and do not significantly reduce these discrepancies.

In light of these results, DFT was employed for geometry optimizations. However, because of the variability observed across DFT functionals and the challenges of accurately describing the energetics of protactinium(V) complexes, the CCSD(T) method was chosen to determine the reaction energies in this study.

Table 3.1: Electronic energies ΔE (in kJ mol^{-1}) for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$, calculated using CCSD(T) and various DFT functionals, grouped by functional type.

Type	Method	OH^-	Cl^-
Wavefunction	CCSD(T)	−48.3	−27.5
GGA	PBE	−56.9	−39.7
	BP86	−59.2	−42.2
Meta-GGA	M06-L	−51.5	−31.5
	TPSS	−60.6	−43.5
Meta-hybrid	M06	−46.8	−25.1
	M06-2X	−70.1	−46.6
	TPSSH	−59.0	−40.2
Hybrid	B3LYP	−60.9	−40.7
	PBE0	−55.2	−33.9
Hybrid-Dispersion	PBE0-D3(BJ)	−55.0	−33.8
	PBE0-D4	−55.5	−34.3
Long-range	ω -B97X	−50.5	−25.4
	CAM-B3LYP	−61.5	−38.6

A detailed discussion of the results can be found in the corresponding article. This study demonstrated that several ligands including Cl^- , Br^- , I^- , SCN^- , (NO_3^-) and (SO_4^{2-}) can stabilize the mono-oxo bond. These findings motivated the design of a new experimental campaign in which different samples were pre-

pared at the IJCLab in Orsay and analyzed using X-ray absorption spectroscopy at the SOLEIL synchrotron. The results of this experimental work are presented and discussed in detail chapter 4.



Stability of the Protactinium(V) Mono-Oxo Cation Probed by First-Principle Calculations

Tamara Shaaban,^[a] Florent Réal,^[a] Rémi Maurice,^[b] and Valérie Vallet*^[a]

This study explores the distinctive behavior of protactinium ($Z = 91$) within the actinide series. In contrast to neighboring elements like uranium or plutonium, protactinium in the pentavalent state diverges by not forming the typical dioxo protactinyl moiety PaO_2^+ in aqueous phase. Instead, it manifests as a monooxo PaO^{3+} cation or a Pa^{5+} . Employing first-principle calculations with implicit and explicit solvation, we investigate two stoichiometrically equivalent neutral complexes: $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$, where X represents various monodentate and bidentate ligands. Calculating the Gibbs free energy for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa}(\text{OH})_4(\text{X})$, we find

that the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized with Cl^- , Br^- , I^- , NCS^- , NO_3^- , and SO_4^{2-} ligands, while it is not favored with OH^- , F^- , and $\text{C}_2\text{O}_4^{2-}$ ligands. Quantum Theory of Atoms in Molecules (QTAIM) and Natural Bond Orbital (NBO) methods reveal the Pa mono-oxo bond as a triple bond, with significant contributions from the 5f and 6d shells. Covalency of the Pa mono-oxo bond increases with certain ligands, such as Cl^- , Br^- , I^- , NCS^- , and NO_3^- . These findings elucidate protactinium's unique chemical attributes and provide insights into the conditions supporting the stability of relevant complexes.

Introduction

Understanding and predicting the physico-chemical properties of radionuclides, in particular actinides, is at the heart of the challenges posed by multiple applications related to environment, energy or health. Questions related to the management of the nuclear fuels used are at the heart of the concerns of our Western societies, and the integrated radioactivity of these nuclei makes them interesting for nuclear medicine. Better understanding of the physical and chemical properties of actinide (An) complexes in the solvated phase, that is to say, their speciation, the nature of the chemical bonds between actinides and their environment partners, their thermodynamic properties, can have direct contributions in societal and industrial applications.

Protactinium ($Z = 91$) stands out as the first actinide element to possess actual 5f electrons in its free-atom ground state ($[\text{Rn}]5f^2 6d^1 7s^2$). This unique electronic configuration allows for an interplay between the valence 6d and 5f orbitals, making it an intriguing element.^[1] However, it also presents challenges in our understanding of its chemistry, as it is one of the most

complex and less studied radioactive elements.^[2] Protactinium can exist in both the pentavalent and tetravalent oxidation states, similarly to the transition metals niobium and tantalum within the same chemical group. In solution, Pa^{V} is predominant because Pa^{IV} is unstable and readily oxidizes to Pa^{V} unless strong reducing conditions are at play.^[3]

In this paper, our focus centers on Pa^{V} . Like its heavier counterparts, uranium, neptunium and plutonium, PaO_2^+ is stable in the gas phase.^[4,5] Both high-level electronic structure calculations and experimental data suggest the monohydrate $\text{PaO}_2^+(\text{H}_2\text{O})$ and the $\text{PaO}(\text{OH})_2^+$ dihydroxyl complex are isoenergetic.^[6–9] However, in solution, the dioxo moiety PaO_2^+ has not yet been identified.^[10–12] Indeed the protactinyl(V) ion is a much stronger acid than its successors in the actinide series and, in fact, the least hydrolyzed species of Pa(V) appears to be $\text{PaO}(\text{OH})^{2+}$.^[10] Pa^{V} may exist as a mono-oxo ion PaO^{3+} , in highly acidic media, rendering it a truly unique actinide^[12,13] or a solecation Pa^{5+} .^[14] However, studying Pa^{V} presents formidable challenges due to its strong tendency towards hydrolysis, polymerization, precipitation and sorption on any solid.^[12] To mitigate these competitive reactions, careful control of Pa concentrations and complexing media is essential. Pa^{V} displays high solubility in hydrofluoric and sulfuric acids, as well as in oxalic acids. Depending on the concentrations and the medium, it can either form oxo complexes or hydroxocomplexes. For instance, Pa^{V} mono-oxo ion complexes, such as $[\text{PaOF}]^{2+}$, $[\text{PaOF}_2]^+$, PaOF_3 , have been postulated in fluoride media under specific hydrofluoric acid concentrations.^[15] In concentrated sulfuric acid^[16] and oxalic acid,^[17] $[\text{PaOL}_n]^{3-2n}$ (where $\text{L} = \text{SO}_4^{2-}$ and $\text{C}_2\text{O}_4^{2-}$) with stoichiometries ranging from 1:1 to 1:3 have been observed.^[11] In cases of higher stoichiometry, X-ray absorption spectroscopy at the Pa_{LIII} edge has proven useful for confirming the presence or absence of the mono-oxo bond.^[13,16–18]

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To date, only one crystal structure $[\text{NET}_4]_2[\text{PaOCl}_5]^{[19]}$ provides evidence of a short Pa–O bond of 1.74 Å. The apparent strength of the Pa–O bond, however, is highly dependent on the concentration and medium, prompting questions about how coordinated ligands and solvent media influence its stability. This issue can be addressed through state-of-the-art quantum calculations. In a study conducted by Toraishi *et al.*, it was concluded that, in the presence of water molecules, Pa^{V} mono-oxo ionic complexes are the preferable species and that PaO_2^+ does not exist.^[20] In our research, we also employ quantum chemical methods to compare the relative stability of the two possible basic units of Pa^{V} , namely the bare Pa^{5+} and the Pa mono-oxo cation PaO^{3+} . Given that the mono-oxo PaO^{3+} moiety can be regarded as half of an actinyl dioxo cation, it is chemically relevant to discuss the nature of the Pa–O bond in the context of known uranyl complexes for the isoelectronic hexavalent uranium.

Since, Pa^{V} exhibits a closed-shell electronic ground state in most chemical complexes, we will apply single-reference approaches of the density functional theory (DFT) and wave-function Theory (WFT) based approaches, namely the coupled-cluster with single, double and perturbative triple excitations (CCSD(T)), within a relativistic framework. Although relativistic effects, i.e. scalar and spin-orbit ones, are typically considered relevant for open-shell systems, we will also quantify the impact of the spin-orbit coupling on properties of these closed-shell systems, as Vasiliu *et al.*^[21] pointed out can amount to about 10 kJ in Pa^{V} hydrates and hydroxide species.

Choice of Systems

Lontchi *et al.*^[22] explored the hydrolysis reactions of the dioxo $\text{PaO}_2(\text{OH})$ system using relativistic quantum chemical methods. They found that the hydrolysis leads to the exothermic formation of a mono-oxo complex $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$ in the first step and $\text{Pa}(\text{OH})_5$ in the second step. Their study demonstrated that $\text{Pa}(\text{OH})_5$ is more stable by 38.5 kJ than the mono-oxo complex $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$. This led us to investigate how the substitution of hydroxide OH^- by other ligands influences the stability or instability of the mono-oxo basic form by computing the relative energies of *ad hoc* isomeric complexes. In practice, we chose to expand the study by Lontchi *et al.*^[22] by examining two stoichiometrically equivalent neutral complexes $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$, which imply a proton-transfer reaction from the coordinated water molecule to the mono-oxo group in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$. Although these neutral complexes may not be soluble in aqueous solution, our modeling objective is to probe how the X ligands influence their relative stability. In these complexes, the coordination number of Pa^{V} can vary between 5 and 6 depending on the ligand X. X may be a monodentate or a bidentate ligand. To encompass a wide range of chemical possibilities, we have intentionally selected various ligands, including monodentate ligands, taking as X (X = hydroxide ion OH^- , the halide series F^- (illustrated in Figure 1), Cl^- , Br^- , I^- , with decreasing binding energies with actinide centers,^[23] and a monodentate coordinated thiocyanate

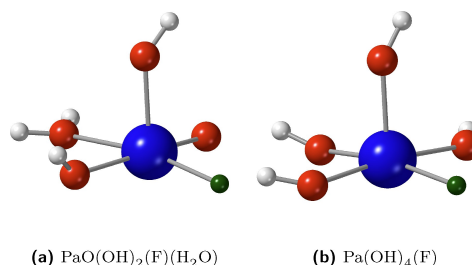
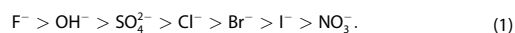
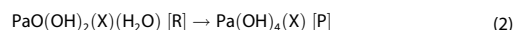


Figure 1. Perspectives of $\text{PaO}(\text{OH})_2(\text{F})(\text{H}_2\text{O})$ (a) and $\text{Pa}(\text{OH})_4(\text{F})$ (b) complexes in water. Color code: navy blue (Pa), dark green (F), red (O), white (H).

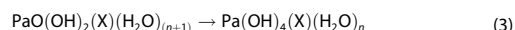
ligand (NCS^-), as well as bidentate ligands: X = nitrate (NO_3^-), sulfate (SO_4^{2-}), that are dominant in natural aquatic systems^[10] and the organic oxalate ($\text{C}_2\text{O}_4^{2-}$) ligand. Sulfate and oxalate are known to form complexes with Pa^{V} .^[13,17] The relative complexing tendencies of inorganic anions with respect to Pa^{V} are:^[10]



Our primary goal is to provide valuable insights for the experimental community regarding the possible Pa^{V} complexes that can be formed. To address this question, we will calculate the relative Gibbs free energy corresponding to the reaction:



Beyond the gas-phase molecular model, we will extend our modeling of $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes to the bulk phase by considering solvent effects, specifically water. Solvent effects can be accounted for either implicitly or explicitly. In implicit solvation models, the molecule is enclosed within a cavity surrounded water, which is modeled as a polarizable dielectric continuum. In explicit solvation models, a certain number n of water molecules are included in the first coordination sphere of the complex, and outer hydration shells are modeled by a polarizable continuum model, allowing us to discuss the following reactions for monodentate X ligands:



where the variable n can take on the value 1, 2 or 3, representing different water coordinations, and making the first-sphere coordination number rise formally from 5 to 8. As discussed later, complexes with three water molecules in the first coordination sphere turned out to be not stable, as one of the water molecules is pushed out to the second coordination sphere, resulting in a maximum coordination number of 7, as found by Oher *et al.*^[24]

Results and discussion

Solvent effect on geometries with implicit solvation models

The optimization of complex geometries in a solvent like water is essential because it accounts for the influence of the solvent on the molecular structures. In this work, the complexes $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_5$ (Figure 2) have demonstrated significant structural changes when transitioning from the gas phase to a solvent environment like water. The relaxation effect,

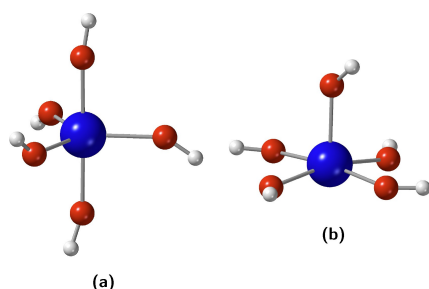


Figure 2. $\text{Pa}(\text{OH})_5$ structures in gas phase (a) and in water (COSMO model) (b). Color code: navy blue (Pa), red (O), white (H).

Table 1. Bond distances r (in Å), with their standard deviations within the $\text{Pa}(\text{OH})_4(\text{X})$ complexes optimized in the COSMO water solvent at the scalar relativistic level with the B3LYP functional.

X	$r(\text{Pa}-\text{OH})$	$r(\text{Pa}-\text{X})$
OH^-	2.134 ± 0.002	
F^-	2.115 ± 0.010	2.142
Cl^-	2.094 ± 0.006	2.706
Br^-	2.091 ± 0.006	2.876
I^-	2.088 ± 0.019	3.130
NCS^-	2.094 ± 0.006	2.395
NO_3^-	2.094 ± 0.011	2.528 ± 0.007
SO_4^{2-}	2.125 ± 0.013	2.400 ± 0.016
$\text{C}_2\text{O}_4^{2-}$	2.132 ± 0.008	2.343 ± 0.001

Table 2. Bond distances r (in Å), with their standard deviations and the stretching frequencies ν (in cm^{-1}) of the $\text{Pa}-\text{O}$ bond within the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes optimized in the COSMO water solvent at the scalar relativistic level with the B3LYP functional.

X	$r(\text{Pa}-\text{O})$	$r(\text{Pa}-\text{OH})$	$r(\text{Pa}-\text{X})$	$r(\text{Pa}-\text{OH}_2)$	$\nu(\text{Pa}-\text{O})$
OH^-	1.879	2.164 ± 0.034		2.550	771
F^-	1.871	2.137 ± 0.025	2.181	2.521	779
Cl^-	1.857	2.117 ± 0.028	2.730	2.498	795
Br^-	1.855	2.114 ± 0.028	2.896	2.493	796
I^-	1.852	2.111 ± 0.028	3.140	2.487	799
NCS^-	1.858	2.119 ± 0.026	2.422	2.505	793
NO_3^-	1.860	2.119 ± 0.044	2.547 ± 0.015	2.485	798
SO_4^{2-}	1.873	2.149 ± 0.036	2.440 ± 0.008	2.508	779
$\text{C}_2\text{O}_4^{2-}$	1.881	2.165 ± 0.040	2.372 ± 0.021	2.525	763

quantified by the energy difference between the gas phase and solvent phase structures, is substantial. In the case of $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$, the complex is stabilized by -76.3 kJ when subjected to geometry optimization in the solvent. Similarly, for $\text{Pa}(\text{OH})_5$, it experiences a stabilization of -28.0 kJ in a solvent environment. This emphasizes the importance of considering solvent effects in studying these complexes, as the solvent can significantly impact their stability and geometry.

The comparison of bond lengths between the gas phase and solvent phase structures of $\text{Pa}(\text{OH})_4(\text{X})$ and $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes provides valuable insights into the influence of the solvent on these complexes. In the case of $\text{Pa}(\text{OH})_4(\text{X})$ complexes, we observe that the $\text{Pa}-\text{X}$ distance increases by approximately 0.1 Å with various ligands when transitioning from gas phase structures (see Table S6 of the SI) to solvent phase structures (Table 1). Similarly, the $\text{Pa}-\text{OH}$ distances generally increase by up to 0.1 Å with all ligands, except when using the SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ ligands. This suggests that the solvent environment has a slight elongating effect on these bond distances. However, there does not seem to be a clear trend regarding the $\text{Pa}-\text{OH}$ distance. On the other hand, for the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, the $\text{Pa}-\text{O}$ distance increases by a maximum of 0.02 Å, and the $\text{Pa}-\text{X}$ distance increases by up to 0.1 Å with different ligands when transitioning from gas phase (see Table S7 of the SI) to solvent phase structures (Table 2). Interestingly, the $\text{Pa}-\text{OH}_2$ distance decreases by 0.2 Å in water, favoring closer interaction with the central atom Pa.

Overall, these observations emphasize the importance of considering solvent effects when studying these complexes, as they can significantly impact the structural parameters and bonding characteristics of the molecules in a realistic solution environment.

Solvent effect on geometries with explicit solvation models

In the bare $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes, the coordination number of Pa^{V} can be either 5 or 6 depending on whether the ligand is monodentate or bidentate. However, it is worth noting that Pa^{V} can have a coordination number of up to

8.^[11,24] This raises the possibility of accommodating additional water molecules in the first coordination sphere of Pa^{V} in the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes. To investigate this hypothesis, we filled the first coordination sphere of $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1}$ and $\text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ complexes with up to $n=3$ water molecules, as depicted in Figure 3. Our results show that both complexes can accommodate 1 ($n=1$) and 2 ($n=2$) additional water molecules. However, when we introduce three water molecules ($n=3$), the third water molecule migrates to

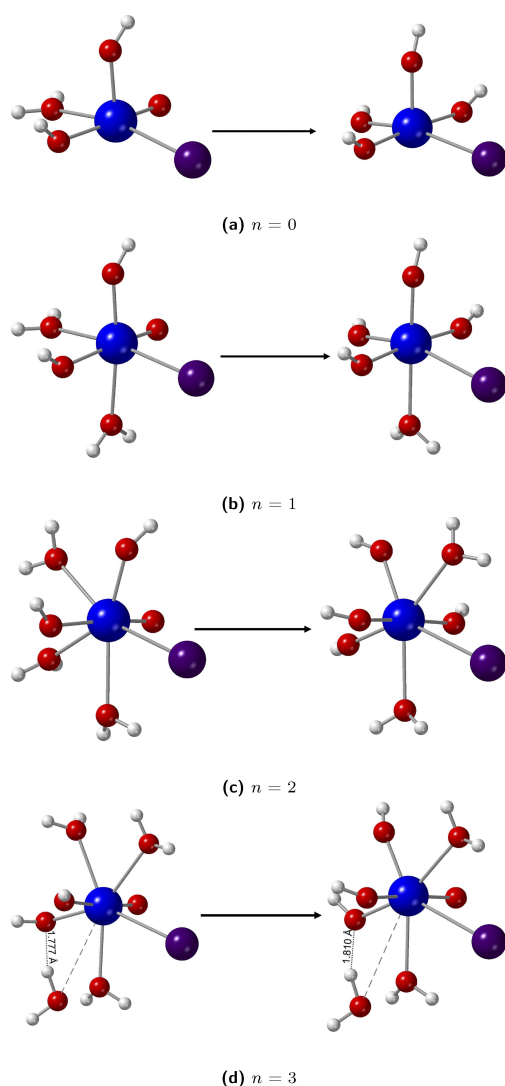


Figure 3. Perspective views of $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1}$ and $\text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ complexes with $n=0$ (a), $n=1$ (b); $n=2$ (c); $n=3$ (d). Color code: navy blue (Pa), purple (O), red (O), white (H).

the second coordination sphere, where it forms a hydrogen bond with a first-coordination sphere hydroxide in both complexes, enhancing the overall stability. This suggests that the coordination number of Pa^{V} is 7 and with monodentate ligands, and could rise up to 8 with bidentate ligands.

To assess the impact of these two additional water molecules on the relative stability of the $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1}$ and $\text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ complexes, we calculated the Gibbs free energies for the reaction $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1} [\text{R}] \rightarrow \text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n [\text{P}]$ for $n=0, 1$, and 2. Note here that we are looking at difference with respect to the $n=0$ reaction, computing $\Delta\Delta G_r(n) = \Delta G_r(n) - \Delta G_r(n=0)$. For $n > 0$ (Table 3), we observed that first $\Delta\Delta G_r$ are small, and second that the $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1}$ complexes remain more stable than the $\text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ ones, indicating that the addition of up to two water molecules has little impact on the relative stability of the $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1}$ and $\text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ complexes. Given the little impact and that explicit hydration is always tricky, there is no evidence that the corrected $\Delta G_r(n)$ values are there significantly more accurate than the uncorrected one. Therefore, in the remainder of our study, we will focus on discussing the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes, without considering explicit hydration.

Effect of Spin-Orbit (SO) Coupling on reaction Gibbs free energies

The spin-orbit coupling (SOC) is typically considered to have a negligible effect on the ground-state properties of closed-shell molecular systems such as molecular geometries, which applies to our case. However, since both the compared complexes [P] and [R] display different bonding patterns, it is still possible that the SOC play a secondary but not negligible role on ΔG_r . To test this hypothesis, we calculated the SOC contributions at the scalar relativistic geometries, which in fact amount almost the same order of magnitude to the electronic energies for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa}(\text{OH})_4(\text{X})$ with different ligands, as presented in Table 4. Notably, ΔE_{SO} is negative, in fact remarkably constant $-5.7 \pm 0.4 \text{ kJ}^{-1}$, indicating that SOC has a more significant stabilizing impact on the Pa complexes compared to the PaO ones. Due to the magnitude of the SOC contribution to ΔG_r , and since we have not found an easy and obvious explanation for this from the 5f and 6d population analysis (see Table S8 of the SI), we just conclude that we cannot disregard the influence of the SOC for the precise determination of the thermodynamics of these reactions.

Table 3. Difference of reaction free energy $\Delta\Delta G_r$ (kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{O})(\text{H}_2\text{O})_{n+1} \rightarrow \text{Pa}(\text{OH})_4(\text{O})(\text{H}_2\text{O})_n$ computed at CCSD(T) level, with respect to the reference $n=0$.

n	1	2	3
$\Delta\Delta G_r\text{-SO}$	0.2	2.4	3.3

Table 4. Comparison of the electronic reaction energies ΔE_r (kJ mol⁻¹) for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa}(\text{OH})_4(\text{X})$ computed at the CCSD(T) level in the gas phase with scalar relativistic effects (SR) and with spin-orbit coupling (SO), with the SO contribution ($\Delta\Delta E_r(\text{SO})$) computed at the B3LYP level in the gas phase.

X	$\Delta E_r(\text{SR})$	$\Delta\Delta E_r(\text{SO})$	$\Delta E_r(\text{SR} + \text{SO})$
OH ⁻	-48.3	-5.3	-53.6
F ⁻	-37.5	-5.6	-43.1
Cl ⁻	-27.5	-5.7	-33.2
Br ⁻	-25.4	-6.1	-31.5
I ⁻	-25.6	-6.7	-32.3
NCS ⁻	-24.7	-5.7	-30.4
NO ₃ ⁻	-53.4	-5.9	-59.3
SO ₄ ²⁻	-87.2	-5.2	-92.4
C ₂ O ₄ ²⁻	-68.6	-5.3	-73.9

Effect of ligands (X) on the geometries

The geometries optimized at the DFT/B3LYP level of $\text{Pa}(\text{OH})_4(\text{X})$ and $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes are reported in Table 1 and Table 2, respectively. It is noteworthy that in the case of the bidentate ligands NO₃⁻, SO₄²⁻, and C₂O₄²⁻, they form bonds with the Pa^V center through oxygen atoms. When considering NCS⁻, there are two possible binding configurations to the Pa^V center, either through the nitrogen atom or through the sulfur atom. Upon optimizing the $\text{Pa}(\text{OH})_4(\text{NCS})$ and $\text{Pa}(\text{OH})_4(\text{SCN})$ complexes at DFT/B3LYP level, it is observed that $\text{Pa}(\text{OH})_4(\text{NCS})$ is energetically more favorable by 33.5 kJ mol⁻¹ compared to $\text{Pa}(\text{OH})_4(\text{SCN})$. This implies that the Pa^V center prefers to bind to NCS⁻ through the nitrogen atom rather than the sulfur atom. A similar preference has been reported for An(IV) actinides (An = Th, U and Pu) in a study by Carter *et al.*^[25]

For the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes (see Table 2) and the $\text{Pa}(\text{OH})_4(\text{X})$ complexes (see Table 1), a noticeable trend is observed in the variation of the $r(\text{Pa}-\text{X})$ distance. The shortest Pa–X distance is found for the OH⁻ ligand because it is the least bulky ligand. As the halides become heavier (F⁻ < Cl⁻ < Br⁻ < I⁻), $r(\text{Pa}-\text{X})$ lengthens by up to 0.9 Å compared to the (Pa–F) bond length. Similarly, in the case of bulky ligands such as NO₃⁻, SO₄²⁻, and C₂O₄²⁻, which form bidentate bonds with Pa, the $r(\text{Pa}-\text{X})$ is longer by up to 0.4 Å compared to $r(\text{Pa}-\text{OH})$. When substituting one hydroxide ligand in the $\text{PaO}(\text{OH})_3(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_5$ complexes with X ligands, $r(\text{Pa}-\text{OH})$ becomes shorter by at most 0.05 Å in the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes again because OH⁻ is the least bulky group. The distance to the water molecule, $r(\text{Pa}-\text{OH}_2)$, remains almost the same among the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes. In terms of the $r(\text{Pa}-\text{O})$ distance in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, it is relevant at this stage to compare the mono-oxo Pa–O bond distances to the dioxo U–O₂ bond distances found in uranyl(VI) complexes with tetra- or pentavalent coordination (refer to values from the literature listed in Table S9 of the SI). In both the Pa and uranyl complexes, the shorter the An–X distance, the longer the An–O one. We will further discuss the relationship between the coordinated ligand and the Pa–O in the

context of its energetic stability. In the literature, experimental values for $r(\text{Pa}-\text{O})$ are reported as shorter, such as 1.75 Å in the $\text{PaO}(\text{C}_2\text{O}_4)_3^{3-}$ complex.^[16] On the other hand, using the DFT/PBE0 approach,^[24] it is 1.86 Å, falling within the same range as $r(\text{Pa}-\text{O})$ distances we have reported for the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes. The origin of this experimental/computational discrepancy is still unclear and requires further investigations both experimentally and computationally, as already mentioned elsewhere.^[24]

Pa-ligand bonding analyses

NBO analysis

In uranyl (UO₂²⁺), both U–O formal bond orders are three.^[26] In the PaO^{3+} cation, the NBO analysis also reveals a triple bond character (see Figure 4), consisting of one σ bond and two π bonds between Pa and O atoms, all three having occupation numbers nearing 2. In these σ and π bonding orbitals both the 5f and 6d shells are involved in bonding, with the 5f shell formally receiving more electron from the ligands than the 6d one in both types of orbitals (see Table S10 in the Supporting Information). Note that we consider the Pa⁵⁺ ion as a reference, and that thus the population of the 5f and 6d shells is conceived as arising from donation from the ligands.

In the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, the Pa mono-oxo bond retains its triple bond character as confirmed by the NBO analysis presented in Table 5 and Figure 5. This analysis reveals that both the σ and two π Pa–O bonds are strongly asymmetrical (polarized) toward the oxygen atom ($\approx 83\%$ oxygen weight), as found in uranyl complexes^[27] and that both the 5f and 6d electron contributions from Pa compete in shaping the

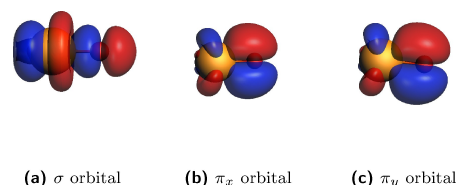
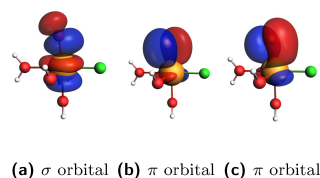
**Figure 4.** Plots of the σ (a) and two π_{xy} ((b) and (c)) PaO bonding orbitals within the bare PaO^{3+} cation. Color code: yellow (Pa), red (O). The isosurface cutoff is 0.03.**Figure 5.** Plots of the σ (a) and two π ((b) and (c)) Pa–O bonding orbitals within the $\text{PaO}(\text{OH})_2(\text{F})(\text{H}_2\text{O})$ complex. Color code: yellow (Pa), green (F), red (O), white (H). The isosurface cutoff is 0.03.

Table 5. Pa (5f and 6d orbitals) and O atomic orbital contributions to the σ and π Pa–O natural localized molecular orbitals (NLMOs) within the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes.

X	σ			π		
	Pa(5f)	Pa(6d)	O(s/p)	Pa(5f)	Pa(6d)	O(s/p)
OH^-	16.1	5.9	77.3	8.4	7.9	83.5
F^-	16.6	5.7	77.0	8.6	7.9	83.3
Cl^-	17.4	5.6	76.2	8.9	8.2	82.6
Br^-	17.6	5.6	76.1	8.9	8.2	82.6
I^-	17.7	5.6	76.0	8.9	8.2	82.6
NCS^-	16.9	5.9	76.4	9.0	7.9	82.7
NO_3^-	17.3	5.6	76.2	9.1	8.0	82.5
SO_4^{2-}	16.1	5.6	77.5	8.8	8.1	82.8
$\text{C}_2\text{O}_4^{2-}$	15.7	5.8	77.7	8.5	8.0	83.2

nature of these bonds. For the σ -bond, the 5f and 6d contributions decrease by approximately by 4% and 3%, respectively, when compared to the PaO^{3+} bare cation, implying that the σ bond is more borne by the oxygen atom in the complexes than in the bare PaO^{3+} . In terms of the π bonds, the 5f contribution decreases slightly by 1.9%, while the 6d contributions marginally increases by 0.6% in the various $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes compared to PaO^{3+} . Consequently, this makes the 5f and 6d contributions to the π orbitals nearly equivalent in all the studied $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, and the Pa–O π bonds quite close to the limit of oxygen lone pairs.

QTAIM analysis

To complement the NBO analyses, QTAIM analyses have been performed for the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes. These analyses provide a range of bonding descriptors defined at the bond critical points (BCPs) which aid in the classification of the nature of the Pa mono-oxo bond, as proposed by Nakainishi *et al.*^[28] and Pilmé *et al.*^[29] for instance. QTAIM analysis was extensively used to assess the nature of actinide ligand bonds after the pioneering work by Ingram *et al.*^[30] In the Supporting Information (see Table S11, Table S12, Table S13, Table S14), we have compiled various bonding BCP descriptors including the electron density (ρ), the Laplacian of the density ($\nabla^2\rho$), kinetic energy density (G), the potential energy density (V), the ratio between the absolute value potential energy density to the kinetic energy one ($|V|/G$), and the charges of the different atoms. The delocalisation index (DI) between two bonded atoms is indicative of the bond order between them. A DI value equal to or lower than 1 suggests a single bond. This criterion applies to the Pa–X, Pa–OH and Pa–OH₂ bonds within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes. In contrast, the DI for the Pa–O bond is approximately 1.8, a value closely resembling that found in uranyl complexes (1.87 to 1.92),^[31] where the uranyl bond is recognized as a strongly dissymmetric triple bond. This similarity, in conjunction with the NBO analysis discussed previously, confirms that the Pa–O bond is a formal triple bond.

In terms of the electron density (ρ), a value of $\rho > 0.2$ a.u. indicates a closed-shell covalent interaction. This criterion applies to the Pa–O bond, while the Pa–X, Pa–OH and Pa–OH₂ bonds within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes are best described as ionic bonds. This classification is further supported by the values of the Laplacian of the density $\nabla^2\rho$ at the BCPs, which are significantly smaller for the Pa–O bond in comparison to the Pa–X, Pa–OH and Pa–OH₂ bonds. Moreover, the ratio between the absolute value potential energy density to the kinetic energy one ($|V|/G$) is a good indicator to describe the chemical bonds. A ratio exceeding 1 suggests a covalent interaction. Significantly, $|V|/G$ is higher by 0.5 for the Pa–O bond when compared to that of the Pa–X, Pa–OH and Pa–OH₂ bonds. Thus all QTAIM descriptors collectively support the conclusion that the Pa–O bond exhibits a strong covalent character, while the Pa–X, Pa–OH, and Pa–OH₂ bonds display an ionic character.

Effect of ligands (X) on the relative stabilities of the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes

The primary objective of this study was to investigate the influence of inorganic and organic ligands on the relative stability of Pa^{5+} and PaO^{3+} complexes, aiming to identify which ligands can stabilize the Pa^{V} mono-oxo bond stable making it a truly actinide-like.

To determine the relative stability, Gibbs free energies for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa}(\text{OH})_4(\text{X})$ with different X ligands are compared (see Figure 6). A positive ΔG , translates into a preference for the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ over the $\text{Pa}(\text{OH})_4(\text{X})$ complex. This is the case for Cl^- , Br^- , I^- , NCS^- , NO_3^- and SO_4^{2-} ligands. Conversely, a negative ΔG , indicates that the $\text{Pa}(\text{OH})_4(\text{X})$ complex is energetically favored over the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complex. This is observed with OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$. Note that for thiocyanate ligand, the ΔG , is close to zero and thus, may be not the most suitable candidate to explore the relative stability in real conditions. It is noteworthy that the trends in the relative stabilities found in the solvent mirror those in the gas phase (see Figure S1, and Table S17 of the Supporting Information).

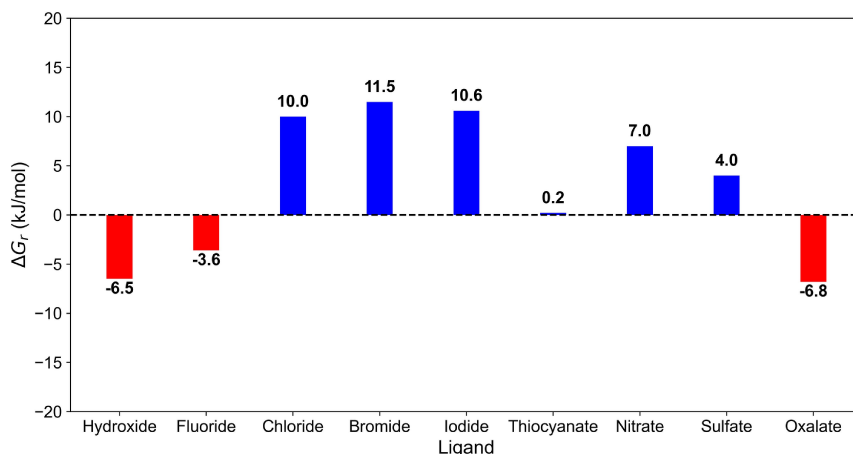


Figure 6. Gibbs free energies (ΔG_r) of the reaction $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa(OH)}_4(\text{X})$ for the different X ligands in the aqueous phase. The red bars refer to systems in which the X ligand stabilizes $\text{Pa(OH)}_4(\text{X})$, and blue bars correspond to $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ being energetically favored.

The relative stability of these two Pa^{V} forms can be explained by several factors. One key factor is the length of the Pa–O bond. When the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized (as is the case with the Cl^- , Br^- , I^- , NCS^- and NO_3^- ligands), the Pa–O bond is shorter (see Table 2), with a difference of up to 0.03 Å, with respect to the OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$ ligands. Additionally, the stretching frequency of the Pa–O bond in these complexes is greater by up to 36 cm^{-1} compared to complexes with OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$ ligands. A shorter Pa–O bond and a higher stretching frequency indicate a stronger Pa–O bond. This phenomenon is observed with Cl^- , Br^- , I^- , NCS^- , and NO_3^- ligands where the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized over the $\text{Pa(OH)}_4(\text{X})$ complex.

Another crucial factor is the length of the Pa–X bond. The Pa–X bond length is longer by up to 0.9 Å with the Cl^- , Br^- , I^- , NCS^- and NO_3^- ligands compared to the one with the OH^- , F^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ ligands. Thus, when the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized, the Pa^{V} center exhibits more affinity for the oxygen atom than for the X ligand ($\text{X} = \text{Cl}^-$, Br^- , I^- , NCS^- and NO_3^-), leading to the formation of a mono-oxo bond. This is not the case of the OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$ where the $\text{Pa(OH)}_4(\text{X})$ complex is stabilized and the Pa–X bond length is shorter indicating stronger bonding between the Pa^{V} center and these ligands.

In addition, from QTAIM analyses we obtain another important, not fully independent indicator: the DI. It increases as the bond becomes more covalent. This increase in DI is observed when the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized over the $\text{Pa(OH)}_4(\text{X})$ with Cl^- , Br^- , I^- , NCS^- and NO_3^- ligands (see Table S11 of the Supporting Information). In these cases, the DI is greater by 0.1, compared to the complexes with OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$ ligands.

Concerning the SO_4^{2-} ligand, even if the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is slightly more stable than the $\text{Pa(OH)}_4(\text{X})$ complex,

we note that the Pa–O bond distance and the DI deviate from the values obtained for the other ligands Cl^- , Br^- , I^- , NCS^- and NO_3^- , suggesting a weaker Pa–O bond. Thus the SO_4^{2-} ligand may not be a good candidate to observe the Pa mono-oxo bond in experimental conditions.

In summary, a shorter Pa–O bond, a higher stretching frequency, and a larger Pa–O DI all indicate a stronger Pa mono-oxo bond (see Figure 7). This helps explain why the $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ complex is stabilized with Cl^- , Br^- , I^- , NCS^- , and NO_3^- ligands, while the $\text{Pa(OH)}_4(\text{X})$ complex is favored with OH^- , F^- and $\text{C}_2\text{O}_4^{2-}$ ligands.

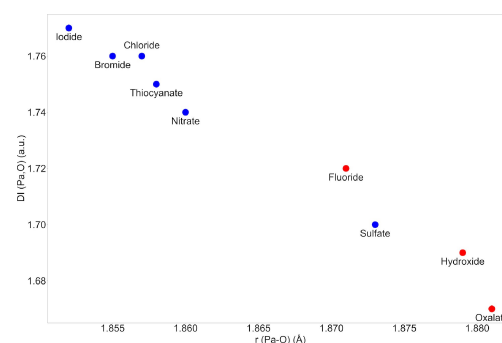


Figure 7. Correlation between the Pa–O bond length ($r(\text{Pa-O})$) and the delocalisation index of the Pa–O bond ($\text{DI}(\text{Pa-O})$). The red circles refer to systems in which the X ligand stabilizes $\text{Pa(OH)}_4(\text{X})$, and blue circles correspond to $\text{PaO(OH)}_2(\text{X})(\text{H}_2\text{O})$ being energetically favored.

Conclusions

In our study, our primary objective was to delve into the stability of the Pa–O bond in the presence of various inorganic ligands. Employing advanced quantum chemical methods, we calculated the Gibbs free energy (ΔG) for the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \rightarrow \text{Pa}(\text{OH})_4(\text{X})$ under standard conditions. Remarkably, even in closed-shell systems, the inclusion of spin-orbit (SO) coupling significantly impacted the relative electronic energies, and consequently the ΔG values. To determine these electronic energies, we utilized the CCSD(T) method, known for its accuracy despite its computational expense. The solvent, water, played a substantial role in structural properties, necessitating geometry optimizations within a water continuum model. Our study introduced additional water molecules to saturate the first coordination sphere, uncovering variations in coordination numbers without affecting the relative stability. The COSMO-RS solvation model was employed for calculating solvation energy (ΔG_{sol}). Additionally, we delved into the nature of the Pa–O bond in both the PaO^{3+} cation and $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, confirming a triple bond reference (though it is strongly dissymmetrical, as the uranyl di-oxo ones).

Predictions regarding the stability of the Pa–O bond indicated preferences for certain ligands, such as the heavier halides (chlorides, bromides, and iodides), as well as nitrates and sulfates. Conversely, hydroxide and oxalate ligands were found to trigger the preferential formation of $\text{Pa}(\text{OH})_4(\text{X})$ complexes. We anticipate that these theoretical predictions will serve as a catalyst for future experiments, validating and expanding our understanding of protactinium chemistry.

Computational Details

The geometry optimizations of $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})_{n+1}$ and $\text{Pa}(\text{OH})_4(\text{X})(\text{H}_2\text{O})_n$ complexes in their ground state were carried out with ADF.^[32,33] These optimizations were performed at the density functional theory (DFT) level employing the B3LYP exchange-correlation functional.^[34,35] The solvent effect is taken into account by Conductor-like Screening Model (COSMO).^[36–38] All atoms were described using triple-zeta plus polarization (TZ2P) basis sets^[39] without freezing core orbitals. To incorporate relativistic effects, two approaches were employed: the scalar relativistic (SR) and spin-orbit (SO) ZORA all-electron Hamiltonians.^[40–42] To evaluate the impact of the SOC on the geometries, optimizations were carried out with and without SO for complexes featuring ligands with light atoms (for instance $\text{X}=\text{OH}^-$) and a heavier halides (for instance $\text{X}=\text{I}^-$). The results, detailed in Table S15 of the Supporting Information, reveal that SO leads to a slight shortening of the Pa–ligand bond distances, with a maximum reduction of 0.015 Å. This effect is considered negligible, and therefore, structures optimized at the SR level were used. Nevertheless, it is worth noting that the SOC impact on the single-point electronic energies cannot be neglected and was introduced in the calculation of the ΔG values by means of a simple correction to the electronic energy ΔE , namely ΔE_{SOC} . To ensure that the optimized structures represent minima (no imaginary frequency), harmonic vibration frequency calculations were performed. These calculations also allowed for the determination of the thermodynamics contributions to the Gibbs free energy (ΔG_{corr}).

To calculate the solvation Gibbs free energies (ΔG_{sol}), we have chosen the COSMO-RS^[43,44] real-solvent continuum model, using the COSMO-RS atomic radii^[45] (Table S1) to construct the continuum model cavities, an approach that is superior to united atom models.^[46] COSMO-RS was also found to be superior to other continuum models for the prediction of oxidation potentials.^[47] We have validated the COSMO-RS model, by a comparison to other continuum models (PCM and COSMO) for the reaction of interest with $\text{X}=\text{OH}^-$ and $\text{X}=\text{C}_2\text{O}_4^{2-}$, as is discussed and justified in the Supporting Information.

The COSMO-RS solvation model^[43,44] as implemented in the COSMOtherm program, utilized files generated by single-point calculations performed with the Gaussian 16 program.^[48] In this context the BP86 functional is used, together with def-TZVP basis sets and small core relativistic pseudopotential^[49] (60 core electrons) for Pa; and all other atoms were described with def2-TZVP basis sets.^[50]

Recognizing that DFT may not provide the ultimate accuracy for determining electronic energies in chemical reactions involving heavy cations,^[51–54] additional single-point energy calculations were performed at the CCSD(T)^[55] level of theory ($\Delta E_{\text{CCSD(T)}}$). CCSD(T) is widely recognized as the reference method in quantum chemistry^[56] and is known for its exceptional accuracy, which has motivated the choice of Lontchi *et al.* to explore the Pa^{V} complexes stability.^[22] A discussion of the benchmarking of CCSD(T) versus DFT functionals given in the Supporting Information, supports this assessment.

The CCSD(T) calculations were carried out using the Molpro 2020 software.^[57] In the CCSD(T) calculations, relativistic effects were taken into account using all-electron Hamiltonians. Specifically, the choice between the exact two-component relativistic Hamiltonian (X2C)^[58] and the Douglas-Kroll-Hess (DKH) Hamiltonian^[59] depended in practice on the availability of adequate relativistic atomic basis sets. The aug-cc-pVTZ-X2C basis sets^[60–62] were applied for H, O, C, N, S, F, and Cl, while the aug-cc-pVTZ-DK basis sets^[63] were utilized for complexes containing $\text{Br}^{[64,65]}$ and $\text{I}^{[66]}$. Pa was described appropriately by cc-pVTZ-X2C or cc-pVTZ-DK basis sets.^[67] It is worth noting that in CCSD(T) calculations, all valence electrons were correlated, while the core electrons were frozen, except in the case of iodine, for which we had to correlate the outer-core 4d electrons. As it is recognized that CCSD(T) results are sensitive to the quality of the basis sets employed, a basis set quality effects exploration has been operated. Therefore, to attain convergence and determine the most appropriate basis sets, the energy of the reaction 2 with $\text{X}=\text{OH}^-$ was computed using two different basis sets: VTZ and VQZ. Subsequently, these results were extrapolated to the complete basis set (CBS) limit, which effectively represents an infinitely large basis set (further details are available in the Supplementary Information). The energies obtained for the reaction Equation 2 with $\text{X}=\text{OH}^-$ using either the VTZ or VQZ basis sets were found to be -48.3 kJ^{-1} and -48.7 kJ^{-1} , respectively. When extrapolated to the CBS limit, the reaction energy was determined to be -48.5 kJ^{-1} (see Table S5 of the SI). This convergence study demonstrates that both the VTZ and VQZ basis sets yield reaction electronic energy values very close to the CBS limit. Consequently, it can be concluded that VTZ basis sets are sufficiently accurate for determining the reaction's energy at the CCSD(T) level.

To discuss the relative stabilities of $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes we calculated the Gibbs free energy ΔG , of the reaction Equation 2 at room temperature ($T=298 \text{ K}$) and at $T=319 \text{ K}$ and pressure ($P=1 \text{ bar}$) summing up the CCSD(T) scalar relativistic energy ($\Delta E_{\text{CCSD(T)}}$), the SO correction (ΔE_{SOC}), the thermodynamics correction to the Gibbs free energy (ΔG_{corr}) and the COSMO-RS

solvation free energy (ΔG_{sol}) (see contributions in Table S17 and Table S18 of the SI):

$$\Delta G_r = \Delta E_{\text{CCSD(T)}} + \Delta E_{\text{SOC}} + \Delta G_{\text{corr}} + \Delta G_{\text{sol}} \quad (4)$$

The Gibbs free energies reported in Table S16 change by at most 2.4 kJ when increasing the temperature from 298 K to $T = 319$ K. Therefore in the rest of the article, only room temperature values will be discussed.

In order to investigate the nature of the chemical bond between Pa and O in the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes and to assess the extent of involvement of the 5f electrons in chemical bonding, two complementary approaches are employed: natural bond orbital (NBO) analysis and the quantum theory of atoms in molecules (QTAIM), by performing single-point calculations with the B3LYP functional and the COSMO solvent using the ADF software where the NBO6 version^[68] is employed. This analysis provides insights into the bonding interactions within molecules, including bond types and electron density distributions. It can reveal the extent to which the 5f and 6d Pa orbitals participate in chemical bonding in the studied complexes. QTAIM provides information about the topology of electron density, such as bond critical points and bond paths. This analysis can help confirm and complement the findings from NBO analysis regarding the nature of chemical bonding in the complexes.

Supporting information

All quantum mechanics (QM) data, including the optimized coordinates for all species, are accessible on the open-access Zenodo repository with the following DOI: 10.5281/zenodo.10529027. Version v1.1. Additional results and details are provided in the supporting information PDF file.

Note

A preprint version of this work was deposited at ChemRxiv.^[69]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in Zenodo at 10.5281/zenodo.10529027.

Keywords: bond analyses · coordination chemistry · protactinium · quantum chemistry · solvation · stability

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Supporting Information:

Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations

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List of Tables

S1	COSMO-RS atomic radii ^{S1} used to construct the continuum model cavities. .	S-5
S2	Solvation Gibbs free energies of the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes for hydroxide and oxalate ligands ($\text{X} = \text{OH}^-$ and $\text{X} = \text{C}_2\text{O}_4^{2-}$) and their relative solvation Gibbs free energies ΔG_{sol} (in kJ mol^{-1}) computed with the COSMO-RS, COSMO and PCM solvation models.	S-6
S3	Electronic energies ΔE (in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for different X ligands (OH^- , I^- and $\text{C}_2\text{O}_4^{2-}$) computed at the CCSD(T) and DFT levels, with various DFT functionals (B3LYP, B3LYP-D3(BJ), PBE0 and M06).	S-7

S4	CPU time (h) required to perform a single point calculation of $\text{Pa}(\text{OH})_5$ complex at the DFT/B3LYP with TZ2P and at the CCSD(T) level with aug-cc-pVTZ. Both calculations were performed on the same node of model Intel(R) Xeon(R) CPU E5-2690 v4 @ 2.60GHz and with same number of processors. .	S-7
S5	Electronic reaction energy, $\Delta E_{\text{CCSD(T)}}$ in kJ mol^{-1} of $\text{PaO}(\text{OH})_3(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_5$ computed at the scalar relativistic CCSD(T) level with increasing atomic basis set quality, VTZ, VQZ, and CBS.	S-8
S6	Bond distances r (in Å), with their standard deviations within the $\text{Pa}(\text{OH})_4(\text{X})$ complexes optimized in the gas phase at the scalar relativistic (SR-ZORA) level with B3LYP functional, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)).	S-9
S7	Bond distances r (in Å), with their standard deviations within the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes optimized in the gas phase at the scalar relativistic (SR-ZORA) level with B3LYP functional, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)).	S-9
S8	Natural electronic contribution of 7s, 5f and 6d electrons of the Pa atom in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes obtained from the NBO analyses.	S-10
S9	Bond distances r (in Å) in various uranyl(VI) complexes, taken from DFT (B3LYP) quantum chemical calculations in gas phase (GP) or continuum water solvent model or from X-ray diffraction experiments.	S-10
S10	Pa and O atomic orbital contributions to the σ and π (π_x and π_y) natural localized molecular orbitals (NLMOs) within PaO^{3+}	S-10
S11	QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–O _{yl} bond within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)).	S-11

- S12 QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–X bond within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)). S-11
- S13 QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–OH bonds within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center). S-11
- S14 QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–O_w bond within the different $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)). S-12
- S15 Bond distances r (in Å) within the $\text{Pa}(\text{OH})_4(\text{X})$ and $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes optimized in the water solvent (COSMO) with the B3LYP functional, either at the scalar relativistic (SR-ZORA) or spin-orbit (SO-ZORA) levels. S-12
- S16 Composite Gibbs free energies of reaction, ΔG_r (in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands at room temperature (T=298 K) and at T=319 K. S-12
- S17 Composite Gibbs free energies of reaction in the gas phase, ΔG_r , with the different contributions to it ($\Delta E_{\text{CCSD(T)}}$, ΔG_{corr} and ΔE_{SOC}) (all values are in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands. The geometries of all complexes were optimized in the gas phase, at the scalar relativistic (SR-ZORA) level of theory with the B3LYP functional. S-13

S18	Composite Gibbs free energies of reaction in the aqueous solvent (COSMO-RS), ΔG_r , with the different contributions to it ($\Delta E_{\text{CCSD(T)}}$, ΔG_{corr} , ΔE_{SOC} and ΔG_{sol}) (all values are in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands. The geometries of all complexes were optimized in the COSMO solvent, at the scalar relativistic (SR-ZORA) level of theory with the B3LYP functional.	S-14
S19	QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–OH bond within the $\text{Pa}(\text{OH})_5$ and $\text{Pa}(\text{OH})_4(\text{F})$ complexes.	S-14
S20	QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–F bond within the $\text{Pa}(\text{OH})_4(\text{F})$ complex.	S-14
S21	Gibbs free energies (ΔG_r in kJ mol^{-1}) of reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ computed at the B3LYP level with TZ2P basis sets in the gas phase, GP (with the scalar relativistic (SR-ZORA) Hamiltonian) and in the water solvent (either with the scalar relativistic (SR-ZORA) or the spin-orbit (SO-ZORA) Hamiltonians).	S-15

Benchmarking of solvation models and choice of COSMO-RS

In this section, we compare three different solvation continuum models for the reaction:



for $\text{X} = \text{OH}^-$ and $\text{X} = \text{C}_2\text{O}_4^{2-}$. These models include the PCM,^{S2} the COSMO model,^{S3} and the extension of the COSMO model known as COSMO-RS.^{S4,S5} For all these models, we utilized the COSMO-RS atomic radii^{S1} (listed in Table S1) to construct the continuum model cavities. This atomic based cavity construction is considered superior to united atom models.^{S6}

Table S1: COSMO-RS atomic radii^{S1} used to construct the continuum model cavities.

Atom	Pa	H	O	N	S	C	F	Cl	I	Br
Klamt radii Å	2.00	1.30	1.72	1.83	2.16	2.00	1.72	2.05	2.32	2.16

For the COSMO solvation model, single-point calculations were performed at the B3LYP level using T2ZP basis sets to describe all the atoms in the ADF software.^{S7,S8} In the case of the PCM solvation model, implemented in the Gaussian software,^{S9} single-point calculations were conducted with a small core relativistic pseudopotential^{S10} (60 core electrons) for Pa and the corresponding segmented basis sets.^{S11,S12} All other atoms were described with def2-TZVP basis sets.^{S13}

The COSMO-RS solvation model,^{S4,S5} as implemented in the COSMOtherm program, utilized files generated by single-point calculations performed with Gaussian 16.^{S9} In this context the BP86 functional is used, together with def-TZVP basis sets and small core relativistic pseudopotential^{S10} (60 core electrons) for Pa; and all other atoms were described with def2-TZVP basis sets.^{S13}

The solvation energies are presented in Table S2. Notably both the COSMO and PCM

solvation models yield the similar relative solvation Gibbs free energies (ΔG_{sol}), within 7.4 kJ mol^{-1} but different absolute solvation energies G_{sol} for the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes. Furthermore, both PCM and COSMO solvation models underestimate COSMO-RS relative free solvation energies. Consequently, we have chosen to utilize the COSMO-RS solvation model,^{S4,S5} an approach parameterized to quantitative prediction of solvation free energies,^{S6} in this study to determine the solvation energies.

Table S2: Solvation Gibbs free energies of the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes for hydroxide and oxalate ligands ($\text{X} = \text{OH}^-$ and $\text{X} = \text{C}_2\text{O}_4^{2-}$) and their relative solvation Gibbs free energies ΔG_{sol} (in kJ mol^{-1}) computed with the COSMO-RS, COSMO and PCM solvation models.

Continuum Model	X	$G_{sol}(\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}))$	$G_{sol}(\text{Pa}(\text{OH})_4(\text{X}))$	ΔG_{sol}
COSMO-RS	OH^-	-116.15	-56.10	60.06
	$\text{C}_2\text{O}_4^{2-}$	-369.44	-289.51	79.93
COSMO	OH^-	-153.2	-104.97	48.23
	$\text{C}_2\text{O}_4^{2-}$	-331.24	-269.48	61.76
PCM	OH^-	-133.39	-84.68	48.70
	$\text{C}_2\text{O}_4^{2-}$	-345.64	-284.46	61.18

CCSD(T) and DFT benchmarking

When comparing the electronic energy of the reaction 1 for different X ligands (OH^- , I^- , and $\text{C}_2\text{O}_4^{2-}$) at both the CCSD(T) and DFT levels with various DFT functionals (B3LYP, B3LYP-D3(BJ), PBE0,^{S14,S15} and M06^{S16}), several interesting observations can be made, as summarized in Table S3.

First, it becomes apparent that the B3LYP functional tends to overestimate the electronic energy for all three ligands. This overestimation, ranging from 12 to 9 kJ mol^{-1} can likely be attributed to the fact that the B3LYP functional does not account for dispersion effects. To test this hypothesis, calculations were performed using the B3LYP-D3(BJ) functional, which includes the D3 dispersion correction with Becke damping.^{S17,S18} As a result, the electronic

Table S3: Electronic energies ΔE (in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for different X ligands (OH^- , I^- and $\text{C}_2\text{O}_4^{2-}$) computed at the CCSD(T) and DFT levels, with various DFT functionals (B3LYP, B3LYP-D3(BJ), PBE0 and M06).

Ligand	$\Delta E_{\text{CCSD(T)}}$	ΔE_{B3LYP}	$\Delta E_{\text{B3LYP-D3(BJ)}}$	ΔE_{PBE0}	ΔE_{M06}
OH^-	-48.3	-60.9	-60.8	-55.2	-46.8
I^-	-25.6	-39.1	-39.4	-39.1	-23.2
$\text{C}_2\text{O}_4^{2-}$	-68.6	-76.7	-76.8	-71.3	-64.0

energies obtained with B3LYP and B3LYP-D3(BJ) are very close, suggesting that the D3 correction does not play a role for this reaction. Second, the PBE0 functional exhibits good agreement with CCSD(T) for the iodide ligand (I^-), but discrepancies of at least 6 kJ mol^{-1} arise for the hydroxide (OH^-) and oxalate ($\text{C}_2\text{O}_4^{2-}$) ligands. Similarly, the M06 functional is in good agreement with CCSD(T) for the hydroxide ligand, but discrepancies become evident for the iodide and oxalate complexes, with differences of 5 kJ mol^{-1} .

Considering these findings, it is apparent that while DFT functionals can provide reasonably accurate geometries, the choice of functional can significantly impact the accuracy of the electronic energy calculations, especially for different ligand types. Therefore, for the utmost accuracy in describing the electronic energies of the studied complexes, CCSD(T) will be employed, despite its computational demand where a single point calculation at the CCSD(T) level needs 56 times more time than to perform a single point calculation at the DFT/B3LYP level with same number of processors for the $\text{Pa}(\text{OH})_5$ complex Table S4.

Table S4: CPU time (h) required to perform a single point calculation of $\text{Pa}(\text{OH})_5$ complex at the DFT/B3LYP with TZ2P and at the CCSD(T) level with aug-cc-pVTZ. Both calculations were performed on the same node of model Intel(R) Xeon(R) CPU E5-2690 v4 @ 2.60GHz and with same number of processors.

Mehod	DFT/B3LYP	CCSD(T)
Time (h)	0.04	2.24
Number of processors	8	8

Complete basis set extrapolation

The extrapolation of the CCSD(T) energies to the complete basis set limit (CBS) uses two calculations with quality sequentially increased from triple- ζ ($n = 3$) to quadruple- ζ ($n = 4$). The HF reference energies were extrapolated with the Karton and Martin formula^{S19}

$$E_n^{\text{HF}} = E_{\text{CBS}}^{\text{HF}} + A(n+1)e^{(-6.57\sqrt{n})}. \quad (2)$$

For the correlation energies, we have used the L3 method^{S20} with the formula:

$$E_n^{\text{corr}} = E_{\text{CBS}}^{\text{corr}} + An^{-3}. \quad (3)$$

The sum of these two CBS limits yields the total E_{CBS} . As the HF and correlation energies are extrapolated with different formula the values CBS reaction Gibbs free energies are not trivially following a smooth trend with respect to the triple- ζ and quadruple- ζ ones (See Table S5).

Table S5: Electronic reaction energy, $\Delta E_{\text{CCSD(T)}}$ in kJ mol^{-1}) of $\text{PaO}(\text{OH})_3(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_5$ computed at the scalar relativistic CCSD(T) level with increasing atomic basis set quality, VTZ, VQZ, and CBS.

Basis set	VTZ	VQZ	CBS
$\Delta E_{\text{CCSD(T)}}$	-48.3	-48.7	-48.6

Supplementary tables

Table S6: Bond distances r (in Å), with their standard deviations within the $\text{Pa}(\text{OH})_4(\text{X})$ complexes optimized in the gas phase at the scalar relativistic (SR-ZORA) level with B3LYP functional, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)).

X	$r(\text{Pa}-\text{OH})$	$r(\text{Pa}-\text{X})$
HO^-	2.113 ± 0.011	
F^-	2.101 ± 0.007	2.086
Cl^-	2.092 ± 0.014	2.604
Br^-	2.089 ± 0.014	2.768
I^-	2.085 ± 0.015	3.013
NCS^-	2.092 ± 0.013	2.298
NO_3^-	2.082 ± 0.003	2.476 ± 0.005
SO_4^{2-}	2.149 ± 0.012	2.322 ± 0.001
$\text{C}_2\text{O}_4^{2-}$	2.156 ± 0.010	2.283 ± 0.001

Table S7: Bond distances r (in Å), with their standard deviations within the $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes optimized in the gas phase at the scalar relativistic (SR-ZORA) level with B3LYP functional, with NCS^- (N bound), NO_3^- , SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ (bound through O to the Pa(V) center)).

X	$r(\text{Pa}-\text{O})$	$r(\text{Pa}-\text{OH})$	$r(\text{Pa}-\text{X})$	$r(\text{Pa}-\text{OH}_2)$
OH^-	1.858	2.150 ± 0.040		2.646
F^-	1.853	2.148 ± 0.046	2.120	2.628
Cl^-	1.841	2.123 ± 0.020	2.626	2.602
Br^-	1.845	2.100 ± 0.004	2.837	2.631
I^-	1.835	2.114 ± 0.028	3.063	2.634
NCS^-	1.851	2.111 ± 0.006	2.337	2.627
NO_3^-	1.850	2.117 ± 0.004	2.516 ± 0.013	2.613
SO_4^{2-}	1.862	2.224 ± 0.077	2.307 ± 0.027	2.741
$\text{C}_2\text{O}_4^{2-}$	1.861	2.321 ± 0.072	2.291 ± 0.004	2.723

3.1. Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations 123

Table S8: Natural electronic contribution of 7s, 5f and 6d electrons of the Pa atom in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ and $\text{Pa}(\text{OH})_4(\text{X})$ complexes obtained from the NBO analyses.

Ligand	$\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$			$\text{Pa}(\text{OH})_4(\text{X})$		
	n(7s)	n(5f)	n(6d)	n(7s)	n(5f)	n(6d)
OH^-	0.11	1.34	1.21	0.10	1.36	1.22
F^-	0.09	1.35	1.17	0.10	1.30	1.18
Cl^-	0.12	1.40	1.26	0.13	1.35	1.28
Br^-	0.13	1.40	1.27	0.13	1.35	1.29
I^-	0.14	1.39	1.26	0.14	1.34	1.30
NCS^-	0.11	1.37	1.20	0.12	1.32	1.23
NO_3^-	0.12	1.42	1.24	0.13	1.36	1.29
SO_4^{2-}	0.12	1.42	1.27	0.13	1.38	1.30
$\text{C}_2\text{O}_4^{2-}$	0.12	1.42	1.29	0.14	1.40	1.30

Table S9: Bond distances r (in Å) in various uranyl(VI) complexes, taken from DFT (B3LYP) quantum chemical calculations in gas phase (GP) or continuum water solvent model or from X-ray diffraction experiments.

Complex	Method	$r(\text{U}-\text{O})$	$r(\text{U}-\text{L})$	Reference
$[\text{UO}_2(\text{OH})_4]^{2-}$	B3LYP-COSMO	1.846	2.264	Ref. S21
$[\text{UO}_2\text{F}_5]^{3-}$	B3LYP-COSMO	1.838	2.274	Ref. S21
$[\text{UO}_2\text{F}_4]^{2-}$	B3LYP-GP	1.824	2.229	Ref. S22
$[\text{UO}_2\text{Cl}_4]^{2-}$	B3LYP-GP	1.776	2.749	Ref. S22
$[\text{UO}_2\text{Br}_4]^{2-}$	B3LYP-GP	1.769	2.922	Ref. S22
$[\text{UO}_2\text{I}_4]^{2-}$	X-Ray	1.763	3.053	Ref. S23
$[\text{UO}_2(\text{NCS})_5]^{3-}$	B3LYP-GP	1.788	2.439	Ref. S21
$[\text{UO}_2(\text{NO}_3)_3]^-$	B3LYP-GP	1.79	2.51	Ref. S24
$[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})]^{2-} \cdot (\text{H}_2\text{O})_2$	B3PW91-CPCM	1.768	2.40	Ref. S25
$[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$	HF-CPCM	1.730	2.427	Ref. S26

Table S10: Pa and O atomic orbital contributions to the σ and π (π_x and π_y) natural localized molecular orbitals (NLMOs) within PaO^{3+} .

Bond	Pa(5f)	Pa(6d)	O(s/p)
σ	21.2	8.8	69.4
$\pi_{x,y}$	10.7	7.5	80.2

Table S11: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–O_{yl} bond within the different PaO(OH)₂(X)(H₂O) complexes, with NCS[−] (N bound), NO₃[−], SO₄^{2−} and C₂O₄^{2−} (bound through O to the Pa(V) center)).

Ligand	DI (Pa,O)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	q(Pa), a.u.	q(O), a.u.
OH [−]	1.69	0.23	0.36	0.25	−0.43	1.72	3.06	−1.13
F [−]	1.72	0.24	0.35	0.32	−0.56	1.75	3.10	−1.12
Cl [−]	1.76	0.25	0.35	0.34	−0.59	1.74	3.02	−1.09
Br [−]	1.76	0.25	0.35	0.34	−0.59	1.74	2.99	−1.08
I [−]	1.77	0.25	0.35	0.34	−0.60	1.76	2.96	−1.09
NCS [−]	1.75	0.25	0.35	0.34	−0.59	1.74	3.07	−1.10
NO ₃ [−]	1.74	0.25	0.34	0.34	−0.58	1.71	3.06	−1.09
SO ₄ ^{2−}	1.70	0.24	0.36	0.32	−0.55	1.72	3.05	−1.12
C ₂ O ₄ ^{2−}	1.67	0.23	0.36	0.31	−0.53	1.71	3.05	−1.14

Table S12: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–X bond within the different PaO(OH)₂(X)(H₂O) complexes, with NCS[−] (N bound), NO₃[−], SO₄^{2−} and C₂O₄^{2−} (bound through O to the Pa(V) center)).

Ligand	DI (Pa,X)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	q(Pa), a.u.	q(X), a.u.
F [−]	0.62	0.10	0.38	0.13	−0.16	1.23	3.10	−0.79
Cl [−]	0.55	0.05	0.13	0.04	−0.06	1.50	3.02	−0.78
Br [−]	0.55	0.05	0.09	0.03	−0.04	1.33	2.99	−0.76
I [−]	0.54	0.04	0.06	0.02	−0.03	1.50	2.96	−0.75
NCS [−]	0.44	0.06	0.21	0.07	−0.08	1.14	3.07	−1.10
NO ₃ [−]	0.28	0.05	0.18	0.05	−0.06	1.10	3.06	−0.61
SO ₄ ^{2−}	0.38	0.06	0.20	0.06	−0.07	1.17	3.05	−1.37
C ₂ O ₄ ^{2−}	0.43	0.07	0.23	0.08	−0.09	1.13	3.05	−1.23

Table S13: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–OH bonds within the different PaO(OH)₂(X)(H₂O) complexes, with NCS[−] (N bound), NO₃[−], SO₄^{2−} and C₂O₄^{2−} (bound through O to the Pa(V) center)).

Ligand	DI (Pa,OH)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	q(Pa), a.u.	q(X), a.u.
OH [−]	0.80	0.11	0.33	0.13	−0.18	1.41	3.06	−1.26
F [−]	0.85	0.12	0.34	0.14	−0.20	1.43	3.10	−1.24
Cl [−]	0.90	0.13	0.35	0.15	−0.19	1.23	3.02	−1.22
Br [−]	0.91	0.13	0.35	0.16	−0.22	1.39	2.99	−1.22
I [−]	0.92	0.13	0.35	0.15	−0.22	1.47	2.96	−1.21
NCS [−]	0.89	0.13	0.35	0.15	−0.21	1.45	3.07	−1.10
NO ₃ [−]	0.88	0.12	0.35	0.15	−0.21	1.37	3.06	−1.23
SO ₄ ^{2−}	0.84	0.12	0.33	0.14	−0.19	1.41	3.05	−1.24
C ₂ O ₄ ^{2−}	0.81	0.12	0.32	0.13	−0.18	1.39	3.05	−1.25

3.1. Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations 125

Table S14: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–O_w bond within the different PaO(OH)₂(X)(H₂O) complexes, with NCS[−] (N bound), NO₃[−], SO₄^{2−} and C₂O₄^{2−} (bound through O to the Pa(V) center)).

Ligand	DI (Pa,O _w)	ρ, a.u.	∇ ² ρ	G, a.u.	V, a.u.	V /G	q(Pa), a.u.	q(X), a.u.
OH [−]	0.27	0.04	0.17	0.04	−0.04	1.00	3.06	−1.19
F [−]	0.29	0.05	0.18	0.05	−0.05	1.00	3.10	−1.20
Cl [−]	0.30	0.05	0.19	0.05	−0.05	1.00	3.02	−1.20
Br [−]	0.30	0.05	0.19	0.05	−0.06	1.20	2.99	−1.19
I [−]	0.31	0.05	0.19	0.05	−0.06	1.20	2.96	−1.19
NCS [−]	0.29	0.05	0.19	0.05	−0.05	1.00	3.07	−1.19
NO ₃ [−]	0.31	0.05	0.20	0.05	−0.06	1.20	3.06	−1.19
SO ₄ ^{2−}	0.29	0.05	0.19	0.05	−0.05	1.00	3.05	−1.19
C ₂ O ₄ ^{2−}	0.28	0.05	0.18	0.05	−0.05	1.00	3.05	−1.19

Table S15: Bond distances *r* (in Å) within the Pa(OH)₄(X) and PaO(OH)₂(X)(H₂O) complexes optimized in the water solvent (COSMO) with the B3LYP functional, either at the scalar relativistic (SR-ZORA) or spin-orbit (SO-ZORA) levels.

Method	X	Pa(OH) ₄ (X)		PaO(OH) ₂ (X)(H ₂ O)			
		<i>r</i> (Pa–OH)	<i>r</i> (Pa–I)	<i>r</i> (Pa–OH)	<i>r</i> (Pa–O _{yl})	<i>r</i> (Pa–O _w)	<i>r</i> (Pa–I)
SR-ZORA	OH [−]	2.134		2.167	1.879	2.550	
	I [−]	2.088	3.130	2.111	1.852	2.487	3.140
SO-ZORA	OH [−]	2.131		2.164	1.882	2.540	
	I [−]	2.086	3.120	2.107	1.856	2.478	3.129

Table S16: Composite Gibbs free energies of reaction, Δ*G_r* (in kJ mol^{−1}) of the reaction PaO(OH)₂(X)(H₂O) → Pa(OH)₄(X) for the different X ligands at room temperature (T=298 K) and at T=319 K.

Ligand	Δ <i>G_r</i> _{298 K}	Δ <i>G_r</i> _{319 K}
OH [−]	−6.5	−8.6
F [−]	−3.6	−5.3
Cl [−]	10.0	8.9
Br [−]	11.5	10.5
I [−]	10.6	9.0
NCS [−]	0.2	−1.6
NO ₃ [−]	7.0	5.6
SO ₄ ^{2−}	4.0	1.8
C ₂ O ₄ ^{2−}	−6.8	−9.2

Table S17: Composite Gibbs free energies of reaction in the gas phase, ΔG_r , with the different contributions to it ($\Delta E_{CCSD(T)}$, ΔG_{corr} and ΔE_{SOC}) (all values are in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands. The geometries of all complexes were optimized in the gas phase, at the scalar relativistic (SR-ZORA) level of theory with the B3LYP functional.

Ligand	$\Delta E_{CCSD(T)}$	ΔG_{corr}	ΔE_{SOC}	ΔG_r
OH^-	-32.8	-11.5	-4.9	-49.1
F^-	-34.1	-7.5	-4.6	-46.2
Cl^-	-24.3	-13.0	-5.5	-42.8
Br^-	-16.2	-13.5	-5.5	-35.2
I^-	-12.9	-12.4	-6.0	-31.3
NCS^-	-26.6	-7.8	-4.9	-39.2
NO_3^-	-41.8	-9.6	-4.8	-56.3
SO_4^{2-}	-60.8	-6.2	-5.0	-72.0
$\text{C}_2\text{O}_4^{2-}$	-43.8	-12.9	-4.9	-61.6

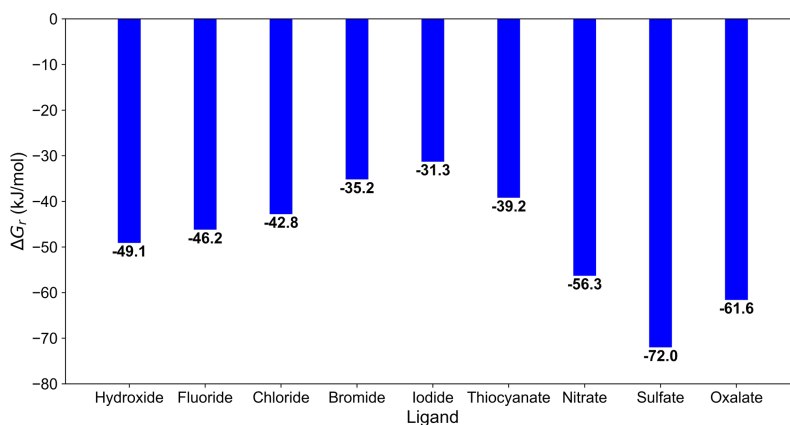


Figure S1: Gibbs free energies (ΔG_r) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands in the gas phase, with geometries optimized in the gas phase as well.

3.1. Stability of the protactinium(V) mono-oxo cation probed by first-principle calculations 127

Table S18: Composite Gibbs free energies of reaction in the aqueous solvent (COSMO-RS), ΔG_r , with the different contributions to it ($\Delta E_{CCSD(T)}$, ΔG_{corr} , ΔE_{SOC} and ΔG_{sol}) (all values are in kJ mol^{-1}) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ for the different X ligands. The geometries of all complexes were optimized in the COSMO solvent, at the scalar relativistic (SR-ZORA) level of theory with the B3LYP functional.

Ligand	$\Delta E_{CCSD(T)}$	ΔG_{corr}	ΔE_{SOC}	ΔG_{sol}	ΔG_r
OH^-	-48.3	-12.9	-5.3	60.1	-6.5
F^-	-37.5	-11.8	-5.6	51.4	-3.6
Cl^-	-27.5	-8.8	-5.7	52.1	10.0
Br^-	-25.4	-8.6	-6.1	51.6	11.5
I^-	-25.6	-9.9	-6.7	52.7	10.6
NCS^-	-24.7	-19.8	-5.7	50.4	0.2
NO_3^-	-53.4	-5.2	-5.9	71.5	7.0
SO_4^{2-}	-87.2	-3.3	-5.2	99.6	4.0
$\text{C}_2\text{O}_4^{2-}$	-68.6	-12.9	-5.3	79.9	-6.8

Table S19: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–OH bond within the $\text{Pa}(\text{OH})_5$ and $\text{Pa}(\text{OH})_4(\text{F})$ complexes.

Ligand	DI (Pa, O_w)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	q(Pa), a.u.	q(X), a.u.
OH^-	0.86	0.12	0.35	0.14	-0.20	1.40	3.16	-1.24
F^-	0.89	0.12	0.37	0.15	-0.21	1.38	3.21	-1.23

Table S20: QTAIM delocalization indices (DI) and Bond Critical Points (BCP) data for the Pa–F bond within the $\text{Pa}(\text{OH})_4(\text{F})$ complex.

Ligand	DI (Pa, F)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	q(Pa), a.u.	q(X), a.u.
F^-	0.70	0.11	0.38	0.14	-0.18	1.29	3.21	-0.75

Table S21: Gibbs free energies (ΔG_r in kJ mol^{-1}) of reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$ computed at the B3LYP level with TZ2P basis sets in the gas phase, GP (with the scalar relativistic (SR-ZORA) Hamiltonian) and in the water solvent (either with the scalar relativistic (SR-ZORA) or the spin-orbit (SO-ZORA) Hamiltonians).

X	GP	Water	
	SR-ZORA	SR-ZORA	SO-ZORA
OH^-	-58.0	-24.0	-28.6
F^-	-58.1	-17.8	-22.7
Cl^-	-41.9	-3.8	-9.1
Br^-	-39.8	-3.1	-8.5
I^-	-42.5	-1.4	-6.8
NCS^-	-44.1	-10.7	-16.1
NO_3^-	-60.8	-4.1	-9.1
SO_4^{2-}	-73.1	-15.6	-20.6
$\text{C}_2\text{O}_4^{2-}$	-67.2	-26.0	-30.5

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3.2 Is the protactinium(V) mono-oxo bond weaker than what we thought?

In a previous study [25] on protactinium mono-oxo complexes, the optimized geometries of the complexes $[\text{PaO}(\text{SO}_4)_3]^{3-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ were found to overestimate the $\text{Pa}\equiv\text{O}$ bond length relative to experimental values obtained from EXAFS. This discrepancy is noteworthy, since X-ray absorption spectroscopy has provided fitted $\text{Pa}\equiv\text{O}$ bond distances in the range of 1.72-1.75 Å [11, 12], depending on the experimental conditions and medium. It should also be noted that uranyl complexes were used as reference models in the EXAFS fitting procedures by Mendes et al. [12] which may introduce additional uncertainties.

Moreover, the only solid-state compound reported to contain a well-identified $\text{Pa}\equiv\text{O}$ bond, namely $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$, exhibits a bond length of (1.74 ± 0.09) Å, although the large standard deviation underscores the considerable uncertainty associated with this measurement.

In our own recent study [1], computed $\text{Pa}\equiv\text{O}$ bond distances in $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ complexes exceeded 1.8 Å. The same long distances exceeding 1.8 Å were found for $[\text{PaOX}_5]^{2-}$ (X being light halides) [26, 27]. This raises an important question: do current quantum chemical methods reliably reproduce the $\text{Pa}\equiv\text{O}$ bond length? The observed discrepancies may arise from several factors, including the choice of electronic structure method, the quality of the basis set, or the treatment of the solvation effects.

The objective of the present work is to revisit the issue using a more robust and diverse theoretical framework, going well beyond our previous studies on molecular Pa(V) complexes [1, 25]. To this end, the following computational approaches were adopted:

- Periodic density functional theory (DFT) calculations were performed on the only reported solid-state compound containing a well-defined $\text{Pa}\equiv\text{O}$ bond, namely $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ [8].
- Static quantum chemical calculations using a continuum dielectric model to simulate solvation effects, applied to the bare PaO^{3+} ion and the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$

complex.

- DFT-based molecular dynamics simulations on $\text{PaOF}_3(\text{H}_2\text{O})_3$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ to capture explicit solvent effects in solution and go beyond the capabilities of static QM simulations and implicit solvent models.

Across all methods employed, the $\text{Pa}\equiv\text{O}$ bond was consistently predicted to be slightly longer than 1.8 Å (a detailed discussion of these results can be found in the following article).

These findings contribute to the motivation for designing and conducting a new experimental campaign, including EXAFS measurements on protoactinium complexes. The results of this experimental work are presented and discussed in detail chapter 4.



Is the protactinium(v) mono-oxo bond weaker than what we thought?†

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The bond distance is the simplest and most obvious indicator of the nature of a given chemical bond. However, for rare chemistry, it may happen that it is not yet firmly established. In this communication, we will show that the formally-triple protactinium(v) mono-oxo bond is predicted to be longer than what was previously reported in the solid state and in solution, based on robust quantum mechanical calculations, supported by an extensive methodological study. Furthermore, additional calculations are used to demonstrate that the Pa–O_{oxo} bond of interest is more sensitive to complexation than the supposedly analogous U–O_{yl} ones, not only in terms of bond distance but also of finer bond descriptors associated with the effective bond multiplicity.

Protactinium (Pa, *Z* = 91) is an actinide with enigmatic physico-chemical properties^{1,2} that would differentiate the “transition-metal” like actinides (up to thorium, Th) from the heavier ones (starting with uranium, U).³ One of the key features of protactinium is its propensity to form a single oxo bond in solution in its pentavalent oxidation state,⁴ while this is not observed for the “transition-metal” like actinides and while dioxo bonds are observed for the heavier elements such as uranium, neptunium (Np), plutonium (Pu) and americium (Am).

This single oxo bond has been characterized by X-ray absorption spectroscopy in a couple of systems,^{5,6} in particular [PaO(C₂O₄)₃]^{3–} and [PaO(SO₄)₃]^{3–}, with a fitted Pa–O_{oxo} bond distance of

~1.72–1.75 Å, depending on the medium and conditions. The objective of the present article is to re-evaluate this bond distance from good theoretical grounds, by going well beyond our previous articles on molecular complexes that already pointed out a potential discrepancy between theory and experiment.^{7,8} To be free of any ambiguity related to speciation in solution, we include in our study the sole solid-state compound ever reported with an occurring Pa–O_{oxo} bond,⁹ namely [C₈H₂₀N]₂[PaOCl₅]. However, we must stress that post-Hartree-Fock methods are not generally available in periodic codes, which is why we have also performed a detailed methodological study on both model and actual molecular systems (*vide infra*).

Experimental lattice parameters and bond distances are reported in Table 1. In this structure, the [PaOCl₅]^{2–} molecular unit emerges, with one shorter axial Pa–Cl_{ax} bond distance and four longer equatorial Pa–Cl_{eq} bond distances (non equivalent in the reported *Cc* space group), together with a Pa–O_{oxo} bond distance of interest of 1.74(9) Å. Periodic density functional theory (DFT) calculations were performed with the VASP code.^{10,11} Both lattice parameters and atomic positions were optimized with various setups (see Table 1). For all reported calculations, the same plane-wave energy cutoff of 550 eV was applied. From the generic PBE¹² calculation, the *f* levels can be effectively pushed up by an *ad hoc* Hubbard *U* term¹³ or finer described by using a hybrid exchange–correlation functional such as PBE0,¹⁴ and on top of that a (post-SCF) dispersion correction may be applied.¹⁵

It is clear that for obtaining a fair agreement between the computed and experimental lattice parameters the introduction of a dispersion correction, namely D3(BJ),¹⁵ is required (see Table 1). Once it is applied, both the PBE and PBE0 functionals yield similar lattice parameters. While the Pa–O_{oxo} bond distance is typically increased by the +*U* correction, the introduction of Hartree-Fock exchange reduces it. Note that the dispersion correction keeps this bond distance untouched, with both the PBE and PBE0 functionals. With the more accurate PBE0 functional, we obtain a Pa–O_{oxo} bond distance of 1.83 Å, which lies within the confidence interval of the experimental distance, 1.74 ± 0.09 Å.

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Table 1 Optimized lattice parameters and relevant bond distances obtained for $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ by periodic density functional theory calculations. The results are compared with experiment (Cc space group)

$[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$	a (Å)	b (Å)	c (Å)	β (°)	$d[\text{Pa}-\text{O}]$ (Å)	$d[\text{Pa}-\text{Cl}_{\text{ax}}]$ (Å)	$d[\text{Pa}-\text{Cl}_{\text{eq}}]^a$ (Å)
PBE ¹²	14.281	14.951	13.596	91.34	1.859	2.648	2.689(6)
PBE+D3(BJ) ^{12,15}	13.301	14.840	12.745	91.65	1.859	2.624	2.673(17)
PBE+U+D3(BJ) ^{12,13,15} ($U_{\text{eff}} = 4$ eV)	13.295	14.797	12.825	91.36	1.890	2.631	2.690(14)
PBE0 ¹⁴	13.996	14.799	13.350	91.29	1.832	2.624	2.674(7)
PBE0+D3(BJ) ^{14,15}	13.153	14.665	12.518	91.59	1.832	2.608	2.659(19)
Expt. ⁹	14.131(8)	14.218(8)	13.235(9)	91.04(3)	1.74(9)	2.42(3)	2.64(6)

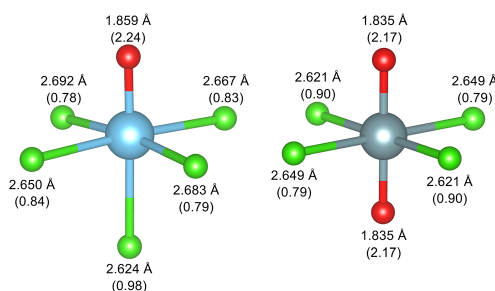
^a The four distances are crystallographically independent.**Table 2** Optimized lattice parameters and relevant bond distances obtained for $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ and $(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$, two representative uranyl compounds, by periodic density functional theory calculations. Results are compared with experiments ($P\bar{1}$ and $Pnma$ space groups)

$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	$d[\text{U}-\text{O}]$ (Å)	$d[\text{U}-\text{Cl}]^a$ (Å)
PBE+D3(BJ) ^{12,15} (dev.)	6.668 (+0.75%)	6.790 (+1.94%)	7.300 (−2.12%)	81.80 (−1.80%)	85.80 (−2.17%)	63.36 (+0.14%)	1.835	2.635(14)
Expt. ¹⁶	6.6183(6)	6.6609(6)	7.4578(6)	83.300(3)	87.703(3)	63.273(2)	1.786(3)	2.646(9)
$(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$	a (Å)	b (Å)	c (Å)	$d[\text{U}-\text{O}_{\text{w}}]$ (Å)		$d[\text{U}-\text{O}_{\text{yl}}]^b$ (Å)	$d[\text{U}-\text{Cl}]^a$ (Å)	
PBE+D3(BJ) ^{12,15} (dev.)	12.172 (−0.34%)	12.418 (−0.22%)	13.409 (−0.36%)	2.513		1.8035(5)	2.768(3)	
Expt. ¹⁷	12.2130(7)	12.4456(7)	13.4579(8)	2.499(3)		1.761(1)	2.765(3)	

^a The four distances are only crystallography equivalent two by two. ^b The two distances are crystallography independent.

Given the computational cost and for comparison purposes, we retained the PBE+D3(BJ) method^{12,15} for probing two well-resolved, recent, uranyl structures,^{16,17} namely $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ and $(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$. We note that a very good agreement with experiments is observed for the lattice parameters and for the U–Cl bond distances (see Table 2), which validates the chosen level of theory. Concerning the U–O_{yl} dioxo bond distances, we observe a standard overestimation of ~ 0.04 – 0.05 Å at this level of theory. If we correct the previous PBE+D3(BJ) Pa–O_{oxo} bond distance by the opposite amount, we obtain ~ 1.81 – 1.82 Å, which again lies within the experimental confidence interval. We thus conclude at this stage that the Pa–O_{oxo} bond distance is predicted to be slightly longer than 1.8 Å and thus also longer than the typical U–O_{yl} ones.⁸

Without entering yet in a detailed discussion concerning the Pa–O_{oxo} bond nature, we have performed additional periodic calculations with the PBE functional for the bare $[\text{PaO}]^{3+}$ and $[\text{UO}_2]^{2+}$ systems as well as determined integrated crystal orbital bond indices (ICOBIs)¹⁸ at the PBE+D3(BJ) level on the previous solid-state systems (see text below Table S1, ESI†). Note that the reference bonds in $[\text{PaO}]^{3+}$ and $[\text{UO}_2]^{2+}$ are both formally triple,⁸ with a subtle distinction: in $[\text{PaO}]^{3+}$ bonding orbitals may display mixed 6d/5f Pa characters, whereas in $[\text{UO}_2]^{2+}$, the 6d and 5f U characters are symmetry separated. In the bare systems, the Pa–O_{oxo} bond is slightly longer and displays a higher ICOBI. This is also true for the $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ and $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ solid-state systems (see Fig. 1). Naturally, the ICOBIs are there smaller than in the bare systems (longer distances). We note that the full crystal environment induces a lengthening of the Pa–O_{oxo} bond by 0.037 Å, larger than that found in uranyl, 0.024 Å. This, plus the shorter Pa–Cl_{ax} bond distance, indicates that the Pa–O_{oxo} bond is more sensitive to complexation since the *trans* position is not protected, unlike in $[\text{UO}_2]^{2+}$ and related compounds.

**Fig. 1** Schematic representation of the PBE+D3(BJ) atomic arrangements of the $[\text{PaOCl}_5]^{2-}$ (left) and $[\text{UO}_2\text{Cl}_4]^{2-}$ (right) units (visualization performed with VESTA¹⁹). The ICOBIs are given in brackets.

We now move on with complexes in solution. Static calculations, based on electronic structure theory and the application of a continuum dielectric model for solvation (implicit solvation model), lead to longer Pa–O_{oxo} bond distances^{5,7} than what was reported by EXAFS in solution, by ~ 0.10 – 0.15 Å, *i.e.* by more than the expected sum of the experimental and computational errors. Since this discrepancy can originate from the relative simplicity of the model used to mimic the complex in solution, we have chosen to initiate our analysis by comparing results from static quantum chemical (QC) calculations (with isolated systems) and QC molecular dynamics (MD) simulations (with systems embedded in large simulation boxes containing around 100 water molecules). Calculations and simulations were performed with the Abinit code.²⁰ For this part, we selected two prototypes: $\text{PaOF}_3(\text{H}_2\text{O})_3$, previously included in an *ab initio* molecular

3.2. Is the protactinium(V) mono-oxo bond weaker than what we thought? 137

ChemComm

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Communication

dynamics (AIMD) study,²¹ and the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ complex, previously studied by static approaches.^{5,7} In both cases, the protactinium(v) ion displays a coordination number of 7, which practically seems to be the largest possible one in solution for this ion,^{7,21} except in the peculiar $[\text{PaF}_8]^{3-}$ case.²²

First, we tested ten pure (*i.e.* nonhybrid) exchange–correlation functionals (see Table S2, ESI†). For the bare $[\text{PaO}]^{3+}$ system as well as for the isolated $\text{PaOF}_3(\text{H}_2\text{O})_3$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ complexes, we found very homogeneous results for the Pa–O_{oxo} bond distance of interest. Therefore, any of those ten functionals could have been used for the AIMD study. We selected the PBE functional¹² for the sake of homogeneity across our reported results. As can be seen in Table 3, the combined influence of the water bath and molecular dynamics has minimal impact on the Pa–O_{oxo} bond distance. More importantly, these effects together slightly increase the bond distance (by 0.003–0.004 Å). Therefore, the previously mentioned discrepancy between theory and EXAFS on $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ cannot be attributed to the static approach. Consequently, to facilitate a more in-depth methodological study, we will now exclusively use the static QC approach.

We have selected two protactinium(v) systems for this static study, namely $[\text{PaO}]^{3+}$, for obvious reasons, and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ as our primary case in solution. The sulfuric case⁶ is intentionally excluded due to the unclear coordination modes of the sulfate groups (monodentate *vs.* bidentate fashions), though a similar issue arises for the Pa–O_{oxo} bond distance.⁷ Calculations were performed with three computational chemistry codes, namely Gaussian,²³ Molpro²⁴ and ADF.²⁵

Since detailed results are reported in the ESI† (see in particular Tables S3 and S4), we only highlight our main conclusions here. First, both employed implicit solvation models lead to a slight Pa–O_{oxo} bond lengthening of less than 0.01 in the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ complex, which has a saturated protactinium(v) coordination sphere. Second, the spin–orbit coupling leads to an even more negligible Pa–O_{oxo} bond lengthening. Therefore, we report either scalar or spin–orbit relativistic values for comparison purposes, but to keep things simple, we have retained scalar relativistic values in Table 4. Third, we confirm that by going from PBE¹² to the hybrid PBE0¹⁴ functional, the Pa–O_{oxo} bond distance is reduced by ~ 0.03 Å, in accordance with the already discussed solid-state results (*vide supra*). Fourth, hybrid functionals such as B3LYP²⁶ and PBE0¹⁴ show good agreement with the higher level CCSD(T) method,²⁷ as does MP2.²⁸ Last, the application of a dispersion correction¹⁵ is bland on the Pa–O_{oxo} bond distance. All-in-all, we have reported the COSMO²⁹ scalar relativistic PBE0¹⁴ results in Table 4.

Before commenting on the obtained results with protactinium(v), we first assess the quality of the results obtained at the chosen level

Table 4 Scalar-relativistic An–O (An = Pa, U) bond distances obtained with the ADF code,²⁵ the COSMO implicit solvation²⁹ and the PBE0 exchange–correlation functional,¹⁴ together with the corresponding delocalisation indices (δ 's)³⁰ arising from the QTAIM³¹ analysis

Molecular system	<i>d</i> (Å)	δ
$[\text{PaO}]^{3+}$	1.710	2.33
$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$	1.858	1.69
$[\text{UO}_2]^{2+}$	1.702	2.15
$[\text{UO}_2\text{Cl}_4]^{2-}$	1.766	1.89
$[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$	1.7815(15)	1.84

of theory based on uranyl systems, namely $[\text{UO}_2]^{2+}$, the well-known $[\text{UO}_2\text{Cl}_4]^{2-}$ molecular unit (already present in the $(\text{C}_6\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ solid-state system), and the $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$ complex. The latter has been studied both experimentally and computationally³² and notably exhibits a uranium(vi) coordination number of 7, making it analogous to the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ case. As shown in Table S5 (ESI†), the influence of the spin–orbit coupling on the U–O_{yl} bond distance(s) is minimal, justifying our selection of a scalar relativistic level in Table 4. Note that the PBE0 gas-phase result for $[\text{UO}_2]^{2+}$ (1.68 Å) is in fair agreement with the reference 1.71 Å value of de Jong *et al.*³³ For $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$, our U–O_{yl} bond distance values in solution of 1.77 and 1.78 Å, respectively, are furthermore of quite exceptional match with the 1.77(1) and 1.79(4) Å experimental ones.^{32,34} Thus, we conclude that the values reported in Table 4 are of sufficient quality to allow for reliable comparisons between the protactinium(v) and uranium(vi) cases.

From Table 4, it is evident that while the An–O bond distance in the bare $[\text{PaO}]^{3+}$ system is slightly longer than that in $[\text{UO}_2]^{2+}$, it is much longer in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ than in $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$. In other words, even if $[\text{PaO}]^{3+}$ may be seen as a “half” $[\text{UO}_2]^{2+}$ unit, the coordination-induced bond lengthening is much more pronounced in the case of protactinium(v) (*ca.* +0.15) than in the uranium(vi) one (*ca.* +0.07), being in practice doubled. Thus, we definitely conclude that $[\text{PaO}]^{3+}$ exhibits a much stronger sensitivity to extra coordination compared to $[\text{UO}_2]^{2+}$.

To further check if this perspective on bond distance corroborates with the bonding perspective, we have also determined delocalisation indices (δ 's)³⁰ within the QTAIM framework³¹ (other indicators are given in Table S6, ESI†). We recall that δ values, by definition, correspond to the number of electron pairs shared between two atoms, reflecting the effective bond multiplicity. In the bare $[\text{UO}_2]^{2+}$ system, six bonding orbitals of $\sigma_{\text{u,g}}$ and $\pi_{\text{u,g}}$ are doubly occupied in the ground state,³⁵ the ungerade ones involving 5f orbitals of U and the gerade ones involving 6d orbitals of U. Thus, the U–O_{yl} bonds are formally triple bonds. As shown in Table 4, δ in there is much smaller than 3, which is due to the strong asymmetry of those bonds (“polar” character³⁶). Upon complexation, δ is reduced by ~ 0.3 in both $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$. Note that our 1.89 value for $[\text{UO}_2\text{Cl}_4]^{2-}$ is consistent with the 1.87 one of Wellington *et al.*³⁶

In the bare $[\text{PaO}]^{3+}$ system, three bonding orbitals are populated in the ground state. Note that due to the absence of a symmetry center, the 5f and 6d orbitals of Pa are not symmetry separated anymore. The obtained δ value, 2.33, is slightly higher

Table 3 Joint effect of explicit solvation and molecular dynamics on the Pa–O bond distance (Å) obtained with the Abinit code²⁰ and the PBE exchange–correlation functional¹²

Computational setup	$\text{PaOF}_3(\text{H}_2\text{O})_3$	$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$
Static, isolated molecule	1.833	1.869
Dynamic (298 K), water bath, 1.5 ps	1.836	1.873

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than in $[\text{UO}_2]^{2+}$, which is 2.15. This means that the slightly longer Pa–O_{oxo} bond distance goes together with a slightly more covalent Pa–O_{oxo} bond in $[\text{PaO}]^{3+}$ compared to the U–O_M ones in $[\text{UO}_2]^{2+}$. This is attributed to the smaller formal charge of protactinium(v) *versus* uranium(vi), and hence a larger ionic radius. After complexation, δ is reduced by ~ 0.6 in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. It is interesting to note that the observed factor of 2 in the complexation-induced bond lengthening perfectly correlates with the factor of 2 reduction in δ . Thus, these two bond descriptors point toward the exact same conclusion.

In this article, we have shown that the Pa–O_{oxo} bond is more sensitive to complexation than the U–O_M ones. We attribute this to the fact that the *trans* position is not protected in the $[\text{PaO}]^{3+}$ chemical moiety. This leaves room for coordination with specific bonding at this position in real chemical systems. For instance, it can occur in the solid-state $[\text{PaOCl}_5]^{2-}$ molecular unit (see Tables S7–S9 and the associated discussion on bonding, ESI†) or in the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ complex. Specifically, the distance to the *trans* ligands is expected to be shorter than that to the *cis* ones due to the inverse *trans* effect already observed and analyzed in actinide complexes.^{37–41} Since the Pa–O_{oxo} bond distance is predicted to be longer than the U–O_M one, the previous experimentally reported Pa–O_{oxo} bond distances must be revised. According to all of our calculations, this bond distance is in any case predicted to be slightly longer than 1.8 Å, indicating that it is weaker than previously thought. An obvious perspective of this work would consist in performing new experiments to confirm these findings. Furthermore, this work is already a key step in the exploration of the intriguing physico-chemical properties of the actinides since it confirms the peculiarity of protactinium, which definitely qualifies it as a trend separator within the actinide series.

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Data availability

The data supporting this article have been included as part of the ESI† and the optimized structures can be accessed at the Zenodo repository *via* the following <https://doi.org/10.5281/zenodo.1349422110.5281/zenodo.13494221>.

Conflicts of interest

There are no conflicts to declare.

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Supplementary Information (SI) for ChemComm.
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Supporting Information:

**Is the protactinium(V) mono-oxo bond weaker
than what we thought?**

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List of Tables

S1	Integrated crystal orbital bond indices (ICOBIs) ^{S1} obtained at the optimized structures (see Tables 1 and 2). Mean values are reported when related bonds are crystallography independent.	S-4
S2	Benchmark of ten exchange-correlation (XC) functionals based on the Abinit code ^{S2} for selected protactinium molecular systems. Only the Pa–O bond distance (Å) is reported.	S-5
S3	Role of implicit solvation (C-PCM ^{S3}) on the Pa–O bond distance (Å) obtained with Gaussian ^{S4} and the default radii (UFF ^{S5}).	S-6
S4	Role of implicit solvation (COSMO ^{S6}) on the Pa–O bond distance (Å) obtained with ADF ^{S7} and the default radii. ^{S8} The ZORA ^{S9} Hamiltonian was used. Values in red are reported from the main text for convenience.	S-7
S5	Role of implicit solvation (COSMO ^{S6}) on the U–O bond distance(s) (Å) obtained with ADF ^{S7} and the default radii. The ZORA ^{S9} Hamiltonian was used. Values in red are reported from the main text for convenience.	S-8
S6	QTAIM bonding indicators obtained at the An–O (An = Pa, U) bond critical points and Bader charges, based on ADF ^{S7} calculations with the COSMO implicit solvation ^{S6} and the PBE0 exchange-correlation functional. ^{S10} Distances and delocalisation indices are reported from the main text for convenience.	S-9
S7	Mayer ^{S11} and Wiberg ^{S12} bond indices of the Pa–O and Pa–Cl bonds within the [PaO(Cl) ₅] ²⁻ cluster, at the PBE+D3(BJ) solid-state geometry. Calculations were performed with ADF ^{S7} and the TZ2P basis sets. ^{S13}	S-10
S8	Pa (5f and 6d orbitals) and O atomic orbital contributions to the σ and π Pa–O natural localized molecular orbitals (NLMOs) ^{S14} within [PaO(Cl) ₅] ²⁻ cluster (same computational details as in Table S7).	S-10

3.2. Is the protactinium(V) mono-oxo bond weaker than what we thought? 141

S9	Pa (5f and 6d orbitals) and Cl atomic orbital contributions to the σ and π Pa–Cl natural localized molecular orbitals (NLMOs) ^{S14} within $[\text{PaO}(\text{Cl})_5]^{2-}$ cluster (same computational details as in Table S7).	S-10
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Table S1: Integrated crystal orbital bond indices (ICOBIs)^{S1} obtained at the optimized structures (see Tables 1 and 2). Mean values are reported when related bonds are crystallography independent.

$[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$	Pa–O	Pa–Cl _{ax}	Pa–Cl _{eq}
PBE+D3(BJ)	2.24	0.98	0.81
$(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$	U–O _{yl}		U–Cl
PBE+D3(BJ)	2.17		0.85
$(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$	U–O _{yl}	U–O _w	U–Cl
PBE+D3(BJ)	2.32	0.36	0.63

For assessing the impact of the “environment”, bare $[\text{PaO}]^{3+}$ and $[\text{UO}_2]^{2+}$ systems have been optimized at the PBE level within large cubic boxes, ensuring more than 10 Å of distance between two molecular units. The resulting bond distances were 1.822 and 1.811 Å, respectively, together with ICOBIs of 2.97 and 2.66. These values serve as references to assess the impact of coordination in the crystal structures on the bonding of the $[\text{PaO}]^{3+}$ and $[\text{UO}_2]^{2+}$ subunits. This impact on bonding, referred to as ΔICOB I, was found to be -0.73 for $[\text{PaO}]^{3+}$ in $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ and -0.49 and -0.34 in $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ and $(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$, respectively.

Note that the ICObI is larger in $(\text{C}_4\text{H}_{12}\text{N}_2)_2[\text{UO}_2\text{Cl}_4(\text{H}_2\text{O})]\text{Cl}_2$ than in $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{UO}_2\text{Cl}_4]$ by 0.15, corroborating the water-induced effective bond reinforcement observed by Rajapaksha et al.^{S15}. This bond reinforcement is concomitant with a reduction of the U–Cl ICObI, meaning that it is in fact indirect: by weakening the in-plane bonds with water addition, the uranyl bonds are effectively less destabilized, thus appearing reinforced.

Note that the valence 7p levels of Pa and U are omitted from the ICObI analysis by absence of such basis functions in the used program^{S16} (the procedure requires projection of the plane waves onto a localized basis). Since these atomic levels only have a limited impact on bonding, their omission does not significantly affect our analysis.

3.2. Is the protactinium(V) mono-oxo bond weaker than what we thought? 143

Table S2: Benchmark of ten exchange-correlation (XC) functionals based on the Abinit code^{S2} for selected protactinium molecular systems. Only the Pa-O bond distance (Å) is reported.

XC functional	[PaO] ³⁺	PaOF ₃ (H ₂ O) ₃	[PaO(C ₂ O ₄) ₃] ³⁻
PW91 ^{S17}	1.710	1.817	1.851
LDA (Wigner) ^{S18}	1.723	1.832	1.867
PBE ^{S19}	1.722	1.833	1.869
HTCH93 ^{S20}	1.710	1.813	1.842
HTCH120 ^{S21}	1.710	1.814	1.847
HTCH147 ^{S21}	1.710	1.813	1.845
HTCH407 ^{S22}	1.708	1.811	1.848
GGA (Wu) ^{S23}	1.715	1.824	1.860
HTBS ^{S24}	1.743	1.865	1.887
MOHLYP ^{S25}	1.730	1.842	1.874

Table S3: Role of implicit solvation (C-PCM^{S3}) on the Pa–O bond distance (Å) obtained with Gaussian^{S4} and the default radii (UFF^{S5}).

$[\text{PaO}]^{3+}$	Gas phase	C-PCM
B3PW91 ^{S26}	1.689	1.759
B3LYP ^{S27}	1.697	1.771
PBE ^{S19}	1.717	1.782
PBE0 ^{S10}	1.681	1.752
PBE0+D3(BJ) ^{S10,S28}	1.681	1.752
MP2 ^{S29}	1.714	1.766

$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$	Gas phase	C-PCM
B3PW91 ^{S26}	1.850	1.856
B3LYP ^{S27}	1.862	1.867
PBE ^{S19}	1.874	1.881
PBE0 ^{S10}	1.843	1.849
PBE0+D3(BJ) ^{S10,S28}	1.844	1.849
MP2 ^{S29}	1.857	1.857

The def2-TZVP basis sets^{S30} were used on all atoms except for Pa, which was treated with the ECP60MWB energy-consistent pseudopotential^{S31} along with its corresponding segmented basis set.^{S32} Overall, a bond lengthening of ~ 0.07 Å is observed for $[\text{PaO}]^{3+}$ and ~ 0.006 Å for $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, respectively. Notably, there was minimal variation when changing the underlying electronic structure theory method.

Additionally, calculations were conducted in the gas phase using Molpro,^{S33} yielding a scalar-relativistic CCSD(T)^{S34} value of 1.703 Å for $[\text{PaO}]^{3+}$. The MP2 and B3LYP calculations were also repeated for cross-checking, leading with this setup to 1.714 and 1.698 Å, respectively; values which are identical to those obtained using the Gaussian software.

3.2. Is the protactinium(V) mono-oxo bond weaker than what we thought? 145

Table S4: Role of implicit solvation (COSMO^{S6}) on the Pa–O bond distance (Å) obtained with ADF^{S7} and the default radii.^{S8} The ZORA^{S9} Hamiltonian was used. Values in red are reported from the main text for convenience.

$[\text{PaO}]^{3+}$	Relativity	Gas phase	COSMO
B3LYP ^{S27}	Scalar	1.705	1.729
	Spin-orbit	1.707	1.731
PBE0 ^{S10}	Scalar	1.688	1.710
	Spin-orbit	1.690	1.713

$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$	Relativity	Gas phase	COSMO
B3LYP ^{S27}	Scalar	1.871	1.878
	Spin-orbit	1.873	1.881
PBE0 ^{S10}	Scalar	1.852	1.858
	Spin-orbit	1.854	1.862

The TZ2P basis sets^{S13} were used on all atoms. By comparing Table S3 and Table S4, it is clear that the COSMO model leads to a lesser impact of solvation on the Pa–O bond distance than the C-PCM one. Test calculations have shown that this is essentially due to the use of the default UFF radii (rescaled by the 1.1 default α value). Despite this moderate discrepancy, the previous trend holds (solvation-induced bond lengthening).

Table S5: Role of implicit solvation (COSMO^{S6}) on the U–O bond distance(s) (Å) obtained with ADF^{S7} and the default radii. The ZORA^{S9} Hamiltonian was used. Values in red are reported from the main text for convenience.

$[\text{UO}_2]^{2+}$	Relativity	Gas phase	COSMO
PBE0 ^{S10}	Scalar	1.684	1.702
	Spin-orbit	1.687	1.705
$[\text{UO}_2\text{Cl}_4]^{2-}$	Relativity	Gas phase	COSMO
PBE0 ^{S10}	Scalar	1.763	1.766
	Spin-orbit	1.767	1.771
$[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$	Relativity	Gas phase	COSMO
PBE0 ^{S10}	Scalar	1.779(3)	1.7815(15)
	Spin-orbit	1.783(3)	1.786(2)

The TZ2P basis sets^{S13} were used on all atoms. As other deviation values reported in parenthesis in the main text for mean distances, the standard deviations have been computed using the following formula:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (d_i - \bar{d})^2} \quad (1)$$

where N is the number of distances entering the calculation of the mean $\bar{d}$ value. In other words, no Bessel's correction was applied.

3.2. Is the protactinium(V) mono-oxo bond weaker than what we thought? 147

Table S6: QTAIM bonding indicators obtained at the An-O (An = Pa, U) bond critical points and Bader charges, based on ADF^{S7} calculations with the COSMO implicit solvation^{S6} and the PBE0 exchange-correlation functional.^{S10} Distances and delocalisation indices are reported from the main text for convenience.

System	d (Å)	ρ , a.u.	$\nabla^2\rho$	G, a.u.	V, a.u.	$ V /G$	H, a.u.	$q(\text{An})$, a.u.	$q(\text{X})$, a.u.	δ
[PaO] ³⁺	1.710	0.36	0.33	0.58	-1.07	1.84	-0.50	3.69	-0.69	2.33
[PaO(C ₂ O ₄) ₃] ³⁻	1.858	0.25	0.36	0.34	-0.59	1.74	-0.25	3.09	-1.14	1.69
[UO ₂] ²⁺	1.702	0.36	0.39	0.59	-1.10	1.86	-0.49	3.53	-0.77	2.15
[UO ₂ Cl ₄] ²⁻	1.766	0.30	0.36	0.46	-0.83	1.80	-0.37	2.93	-0.97	1.89
[UO ₂ (C ₂ O ₄) ₃] ⁴⁻	1.7815(15)	0.29	0.36	0.44	-0.79	1.80	-0.35	2.41	-0.73	1.84

Table S7: Mayer^{S11} and Wiberg^{S12} bond indices of the Pa–O and Pa–Cl bonds within the $[\text{PaO}(\text{Cl})_5]^{2-}$ cluster, at the PBE+D3(BJ) solid-state geometry. Calculations were performed with ADF^{S7} and the TZ2P basis sets.^{S13}

	Pa–O	Pa–Cl _{ax}	Pa–Cl _{eq}
Mayer	2.02	0.91	0.79
Wiberg	2.07	1.03	0.91

Table S8: Pa (5f and 6d orbitals) and O atomic orbital contributions to the σ and π Pa–O natural localized molecular orbitals (NLMOs)^{S14} within $[\text{PaO}(\text{Cl})_5]^{2-}$ cluster (same computational details as in Table S7).

σ			π		
Pa(5f)	Pa(6d)	O(s/p)	Pa(5f)	Pa(6d)	O(s/p)
16.2	6.4	76.4	10.7	9.3	79.7

Table S9: Pa (5f and 6d orbitals) and Cl atomic orbital contributions to the σ and π Pa–Cl natural localized molecular orbitals (NLMOs)^{S14} within $[\text{PaO}(\text{Cl})_5]^{2-}$ cluster (same computational details as in Table S7).

	σ			π		
	Pa(5f)	Pa(6d)	Cl(s/p)	Pa(5f)	Pa(6d)	Cl(s/p)
Cl _{ax}	8.1	6.2	83.5	3.7	3.9	92.2
Cl _{eq}	4.7	7.2	85.3			

To cross-check our previous analysis of the solid-state $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ compound based on ICOBIs (see Table S1 and the related discussion), we have also performed bonding analyses within the molecular quantum chemistry framework, based on the $[\text{PaO}(\text{Cl})_5]^{2-}$ cluster, defined at the solid-state geometry. Clearly, the deviation to the ideal triple bond is confirmed with both the Mayer^{S11} and Wiberg^{S12} bond indices and the specificity of the Pa–Cl_{ax} bond is also reproduced. We have also computed atomic contributions per shell to the σ and π bonds between the atoms of interest, when applicable (see Tables S8 and S9). While both the Pa–O and Pa–Cl_{ax} bonds display actual π character, it is absent from the Pa–Cl_{eq} bonds. This, together with the shorter Pa–Cl_{eq} bond distance (compared to the Pa–Cl_{ax} ones), is in fact a signature for the inverse *trans* effect, expected for $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$.^{S35}

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Speciation of Protactinium(V) in Solution Using X-ray Absorption Spectroscopy

In chapter 3, we used theoretical simulations to investigate the types of ligands capable of stabilizing the mono-oxo bond in protactinium complexes. This study demonstrated that several ligands, including Cl^- , Br^- , I^- , SCN^- , NO_3^- and SO_4^{2-} , can stabilize the mono-oxo bond (see section 3.1 in chapter 3) [1]. However, these simulations also revealed a persistent discrepancy between theoretical and experimental mono-oxo bond lengths: the experimental distances are consistently shorter than those predicted by the quantum calculations. This led us to perform numerous theoretical investigations, including periodic density functional theory (DFT) calculations, static quantum chemical calculations and DFT-based molecular dynamics simulations aiming at understanding its origin (see section 3.2 in chapter 3), but no clear explanation could be identified, highlighting the need for new experiments [2].

To address this issue, our experimental collaborators within the ANR-CHESS project were successful in having beamtime at the MARS beamline (SOLEIL synchrotron) to characterize new protactinium samples (See Table 4.1). In addition to previously tested ligands such as fluoride, oxalate, and sulfate [3], new ligands including nitrate, bromide, and chloride were investigated. This

new study addressed several key questions:

- Under which chemical conditions does the mono-oxo bond persist?
- Can theoretical predictions be reconciled with experimental measurements?
- Does the Pa mono-oxo bond maintain a consistent length across different coordinating ligands?

These questions were investigated using X-ray absorption spectroscopy (XAS), a powerful technique for probing the local structure of actinide compounds. The samples were prepared at IJCLab, loaded into cells (Figure 4.1) and measured at the MARS beamline of SOLEIL synchrotron, at the Pa L_3 -edge (16 733 eV), during the experimental campaign conducted from February 14th to 19th, 2024, and which gathered the 24-hours monitoring of several ANR-CHESS actors, including myself.

Various measurements were performed, including RIXS, HERFD-XANES and XAS (See Table 4.1). It should be noted that two samples could not be measured: the Pa(V)–HNO₃ sample, which was unstable, and the Pa(V)–HBr sample, in which the K β 1 emission line (13 292 eV) of Br overlaps with the $L\alpha$ 1 emission line (13 291 eV) of Pa, thus preventing the acquisition of XAS spectra.

Additionally, a previous experimental campaign was conducted at the MARS beamline of the SOLEIL synchrotron in 2022, targeting the Pa M_4 -edge (3611 eV). During this campaign, M_4 -edge HERFD-XANES and RIXS measurements were performed on two samples: Pa(V) in concentrated HF and in H₂C₂O₄ [4].

Before presenting the results in section 4.3 and section 4.4, this chapter begins with an introduction to synchrotron physics, followed by the fundamentals of X-ray Absorption Spectroscopy (XAS). The discussion covers X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS), which are the two main components of XAS, as well as Resonant Inelastic X-ray Scattering (RIXS) and High-Energy-Resolution Fluorescence Detection XANES (HERFD-XANES), which are X-ray emission spectroscopic techniques (XES) frequently performed alongside XAS to provide complementary spectroscopic information. This part highlights the advantages of each method, describe



Figure 4.1: EXAFS cells containing protactinium samples prepared at IJCLab (Orsay) for measurements at the MARS beamline of the SOLEIL synchrotron. The sample numbering corresponds to Table 4.1. The analyses were performed at the Pa L_3 -edge during an experimental campaign conducted from February 14th to 19th, 2024.

#	Sample	C_{Pa} (M)	C_{ligand} (M)	HERFD-XANES	RIXS	EXAFS
1	Pa(V) in concentrated HF	9×10^{-3}	0.5	✓	✓	✓
2	Pa(V) in concentrated HCl	2×10^{-4}	12			✓
3	Pa(V)–HNO ₃	2×10^{-4}	1 M HCl/11.5 M HNO ₃			
4	Pa(V)–DTPA	1.7×10^{-4}	3 M HCl/0.5 M DTPA			✓
5	Pa(V) in diluted HCl	0.6×10^{-4}	3 M HCl/3 M HClO ₄			✓
6	Pa(V)–HBr	0.4×10^{-4}	3 M HBr / 3 M HClO ₄			
7	Pa(V)–H ₂ C ₂ O ₄	7×10^{-3}	1	✓	✓	✓
8	Pa(V)–H ₂ SO ₄	9.5×10^{-4}	4	✓		✓
9	Pa(V) in diluted HF	1.3×10^{-4}	3 M HCl / 2×10^{-3} M HF			✓
10	Pa(V)–mellitic	1×10^{-4}	1.3 M HCl / 1.3 M mellitic			✓
11	Pa(IV)–DTPA	4×10^{-4}	4.3 M HCl / 1.3×10^{-2} M DTPA			✓
12	Pa(IV)–HCl	4×10^{-4}	6.7			✓

Table 4.1: Summary of Pa(V) and Pa(IV) samples shown in Figure 4.1, prepared at IJ-CLab, Orsay, with their respective Pa and ligand concentrations. Spectroscopic analyses (HERFD-XANES, RIXS, EXAFS) performed at the MARS beamline of the SOLEIL synchrotron at the Pa L₃-edge during the experimental campaign conducted from February 14th to 19th, 2024. Shaded rows indicate samples that could not be measured.

the procedures for EXAFS data extraction and fitting, and discuss the main limitations of the technique.

4.1 Synchrotron Physics

The synchrotron is a cyclic accelerator in which a beam of particles, most commonly electrons, is accelerated by relativistic velocities generating electromagnetic radiations from 0.01 eV to beyond 100 keV.

The electron beam is initially produced by an electron gun through thermionic emission from a heated filament. These electrons are first accelerated to energies of approximately 100 MeV using a linear accelerator (LINAC) and subsequently transferred to a booster ring, where they are further accelerated to their final energy before being injected into the storage ring.

Inside the storage ring, electrons circulate at velocities approaching the speed of light. Their trajectory is maintained by bending magnets (BMs), which curve the path of the electrons and emit bending-magnet radiation as a result of the deflection. In addition to BMs, the storage ring includes insertion devices (IDs),

such as undulators and wigglers, which are placed in straight sections and are capable of producing significantly more intense and tunable synchrotron radiation (See Figure 4.2).

Over time, electron losses occur because of scattering with residual gas molecules and other beamline interactions, resulting in a gradual decline in beam current. To compensate for this, new electrons must be injected. This can be done either through discrete re-injections, which momentarily interrupt user experiments, or by operating in top-up mode. The top-up mode involves frequent, small injections of electrons to maintain a constant beam current, thereby enabling continuous and stable operation without disturbing ongoing measurements.

The synchrotron radiation produced in the storage ring is exceptionally intense, highly collimated, and tunable over a broad energy range. These properties make synchrotron light sources particularly suitable for techniques such as X-ray absorption spectroscopy (XAS) (See section 4.2), which is a powerful tool for studying the speciation of actinides. For radioactive elements like protactinium, synchrotrons allow for sensitive XAS measurements at low concentrations (around millimolar scale), where there are several synchrotrons beamlines dedicated for safe handling of actinides. Among those capable of studying protactinium are:

- **MARS beamline**, at SOLEIL synchrotron, operational since 2013 (France)
- **BM20 - ROBL beamline**, The Rossendorf beamline owned and operated by the Helmholtz-Zentrum Dresden Rossendorf (HZDR, Germany) operational since 1998, at the ESRF synchrotron (France)
- **12-BM**, APS - Argonne National Laboratory (USA)
- **INE / ACT - Beamlines**, KIT Light Source (Germany), established in 2004.



Figure 4.2: Schematic representation of a synchrotron light source. Electrons (blue) are generated by an electron gun and accelerated in a linear accelerator (LINAC) before being injected into a storage ring. Bending magnets (red) alter the electron trajectory, causing the emission of synchrotron radiation (yellow), which is directed toward experimental stations [5].

4.2 X-ray Absorption Spectroscopy

4.2.1 Principles

X-ray absorption spectroscopy is based on the photoelectric effect, where an incident X-ray beam is absorbed by a material, promoting a core electron, originating from an inner shell, into unfilled valence state or the continuum and leaving behind a core hole.

These core electrons have binding energies that lie within the X-ray range, typically ranging from 100 eV to 100 keV. Unlike valence electrons, they do not participate in chemical bonding and remain highly localized around their atomic nucleus. Furthermore, each inner shell of a given element has a well-defined binding energy, which is distinct from other shells within the same element and

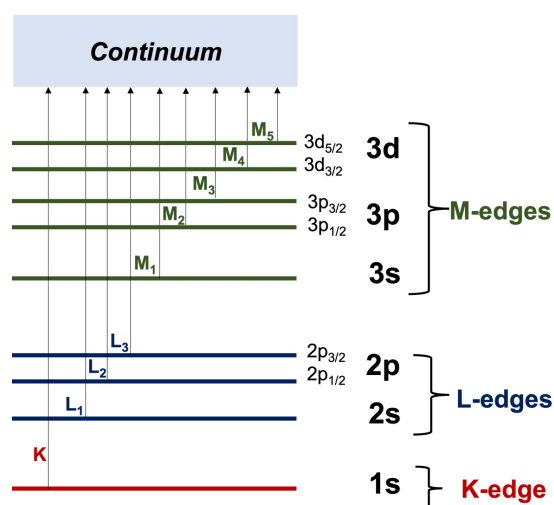


Figure 4.3: Representation of the atomic energy levels with the K-, L-, and M-shells and their corresponding absorption edges.

from core levels of different elements. This selectivity allows XAS to sensitively probe the local structural and electronic environments, making it a powerful technique for investigating actinide speciation.

Depending on the core level from which an electron is excited, a specific name is assigned to the corresponding X-ray absorption edge (See Figure 4.3). These are classified as follows:

- **K-edge:** excitation from the 1s orbital,
- **L-edges:** excitation from the 2s and 2p orbitals,
- **M-edges:** excitation from the 3s, 3p, and 3d orbitals,
- **N-edges:** excitation from the 4s, 4p, 4d, and 4f orbitals,
- **O-edges:** excitation from the 5s, 5p, 5d, and 5f orbitals.

For orbitals with angular momentum quantum number $l > 0$ (i.e., p, d, f), spin-orbit coupling lifts the degeneracy of the states, splitting them according to the total angular momentum quantum number $j = l \pm \frac{1}{2}$. This gives rise to multiple sub-edges, as illustrated in the following examples:

- For p orbitals ($l = 1$), the splitting yields $j = \frac{1}{2}$ and $j = \frac{3}{2}$. Excitation from the $2p_{1/2}$ level gives rise to the L_2 -edge, while excitation from the $2p_{3/2}$ level corresponds to the L_3 -edge.
- For d orbitals ($l = 2$), the resulting levels are $j = \frac{3}{2}$ and $j = \frac{5}{2}$, which give rise to the M_4 - and M_5 -edges, respectively.

The probability of these electronic transitions is governed by quantum mechanical selection rules. Under the electric dipole approximation, transitions are allowed only when the change in orbital angular momentum satisfies $\Delta l = \pm 1$ (e.g., $s \rightarrow p$, $p \rightarrow d$), and the spin state remains unchanged ($\Delta S = 0$). Quadrupole transitions with $\Delta l = \pm 2$ (e.g., $s \rightarrow d$, $p \rightarrow f$) are also possible but typically have intensities that are two or more orders of magnitude lower than dipole-allowed transitions. It must be noted that the final states usually are not purely atomic in character: hybridization and orbital mixing often occur, giving rise to additional features in the XAS spectrum.

X-ray absorption by a sample leads to a decrease in the intensity of the incident beam, governed by the Beer-Lambert law:

$$I = I_0 e^{-\mu d} \quad (4.1)$$

where I_0 is the incident X-ray intensity, I is the transmitted intensity, μ is the linear absorption coefficient, and d is the material thickness.

The absorption coefficient μ depends on several factors, including the photon energy E , the atomic number Z , the material density ρ , and the atomic mass A , following the relation:

$$\mu \propto \frac{\rho Z^4}{AE^3}. \quad (4.2)$$

After the photoelectric absorption, the core-hole is unstable and relaxes to the ground-state via either radiative or non-radiative processes. In the radiative case (X-ray fluorescence), an electron from a higher-energy shell fills the core hole and emits a secondary X-ray photon with energy equal to the difference between the two core levels. In the non-radiative case (Auger effect), the excess energy is transferred to another electron which is promoted to the continuum, as illustrated by Figure 4.4. Note that both processes occur at discrete energies

that are characteristic of the absorbing atom, and can be used to identify the absorbing atom.

To obtain an absorption spectrum, the variation of the absorption coefficient μ is measured as a function of the incident X-ray energy E . The scan is performed over a selected energy range, with small energy steps between points, enabling the detection of fine variations in absorption. The resulting spectrum reflects how the material interacts with X-rays across the energy range of interest.

In practice, two principal detection modes are commonly used:

- **Transmission mode:** The absorption is determined from the ratio of transmitted to incident intensity:

$$\mu(E) \propto -\ln\left(\frac{I}{I_0}\right). \quad (4.3)$$

- **Fluorescence mode:** The intensity of X-ray fluorescence emitted upon refilling the core hole is recorded. The absorption coefficient is proportional to the ratio:

$$\mu(E) \propto \frac{I_f}{I_0}, \quad (4.4)$$

where I_f is the fluorescence intensity.

The X-ray absorption spectrum is typically divided into two main regions: the X-ray Absorption Near Edge Structure (XANES) and the Extended X-ray Absorption Fine Structure (EXAFS) Figure 4.5. The distinction between the XANES and EXAFS regions can be understood in terms of the kinetic energy and wavelength of the ejected photoelectron. These regimes correspond to different photoelectron behaviors and reflect different underlying physical principles.

The kinetic energy of the photoelectron is related to its wavelength λ via the de Broglie relation:

$$E_{kin} = h\nu - E_{binding} = \frac{\hbar^2 k^2}{2m} = \frac{(2\pi)^2 \hbar^2}{2m\lambda^2} = \frac{h^2}{2m\lambda^2}, \quad (4.5)$$

where E_{kin} and $E_{binding}$ are the kinetic energy of the ejected electron, and the binding energy of the electron in the material, respectively. This relation shows

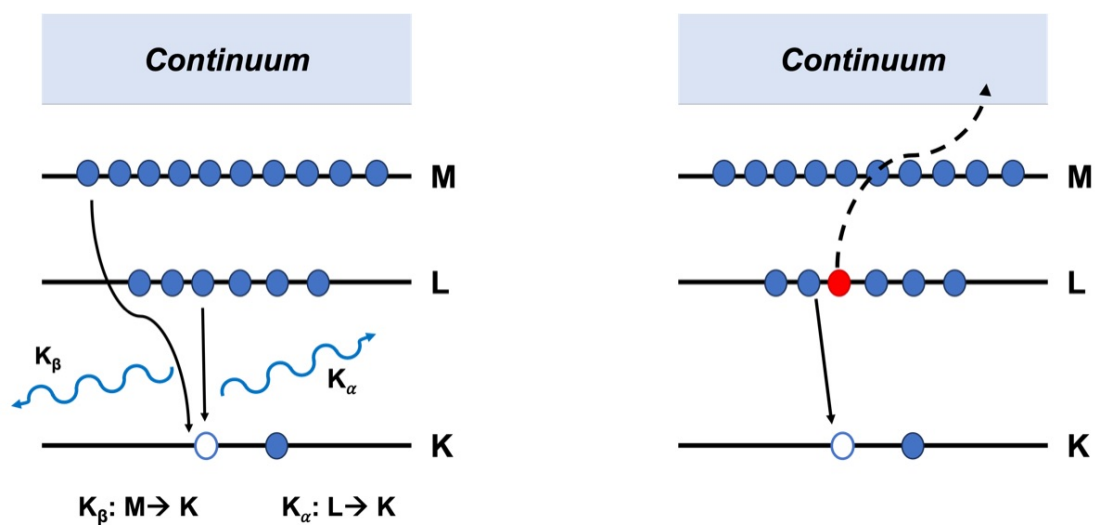


Figure 4.4: Decay of the excited state: X-ray fluorescence (left) and Auger effect (right; dashed lines represent non-radiative process.).

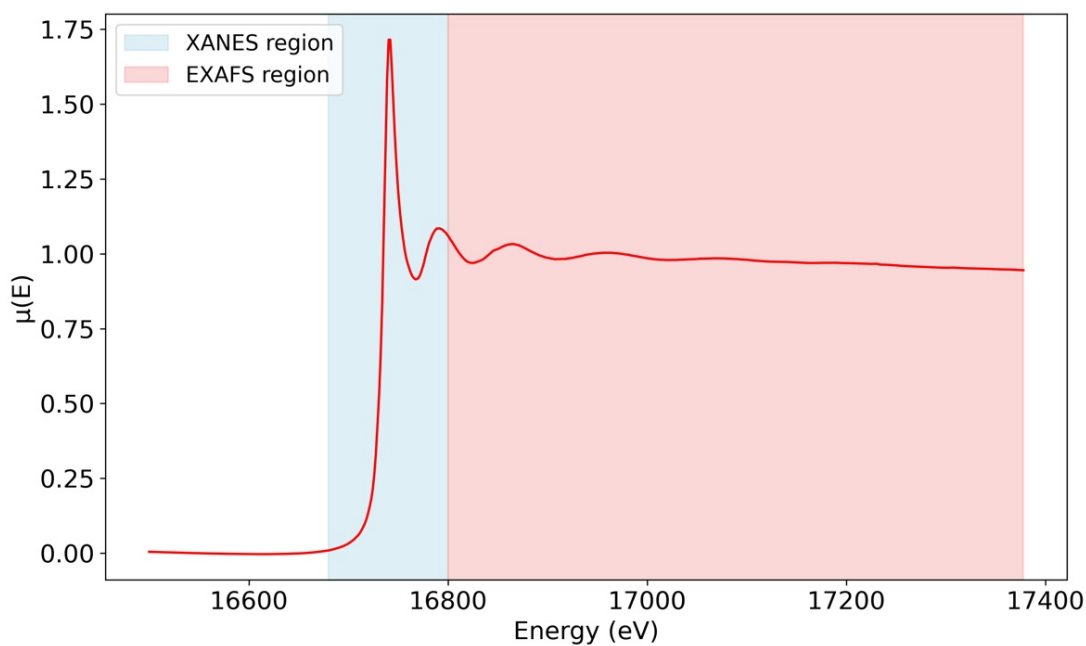


Figure 4.5: XAS spectrum of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L_3 -edge at the MARS beamline of the SOLEIL synchrotron.

that high-energy (short-wavelength) photoelectrons behave differently than low-energy (long-wavelength) ones, particularly in how they interact with surrounding atoms.

4.2.2 X-ray Absorption Near Edge Structure (XANES)

In the XANES region, the photoelectron is excited to unoccupied bound states, or just above the ionization threshold into the continuum, resulting in relatively low kinetic energies (typically a few eV).

As a result, the XANES spectrum can be divided into several characteristic regions based on energy relative to the absorption edge:

- **Absorption Edge (White Line):** sharp rise in absorption that occurs when a core electron absorbs sufficient X-rays energy to be excited out of its bound state. This threshold energy is characteristic of each chemical element and energy state.
- **Pre-edge region:** The region immediately preceding the absorption edge, often containing small peaks or weak features typically attributed to quadrupole-allow nature [6].
- **Post-edge region:** The spectral region extending from just beyond the white line to approximately 50-100 eV higher in energy, where multiple-scattering effects begin to dominate.

Since the photoelectron has a "long" wavelength, comparable to interatomic distances, multiple scattering effects are greatly enhanced and dominate the fine structure in the post-edge region. Consequently, XANES is particularly sensitive to the oxidation state and coordination environment of the absorbing atom.

For actinide elements, particular attention is given to the L_3 - and M_4 -edges, which correspond to electronic transitions from the $2p_{3/2}$ (L_3) and $3d_{3/2}$ (M_4) core orbitals to unoccupied 5f or 6d final states that are directly involved in actinide bonding and reactivity. While the M_4 -edge can provide detailed information on the 5f electronic structure, strong lifetime broadening limits its use in conventional XANES and necessitates high-energy-resolution fluorescence

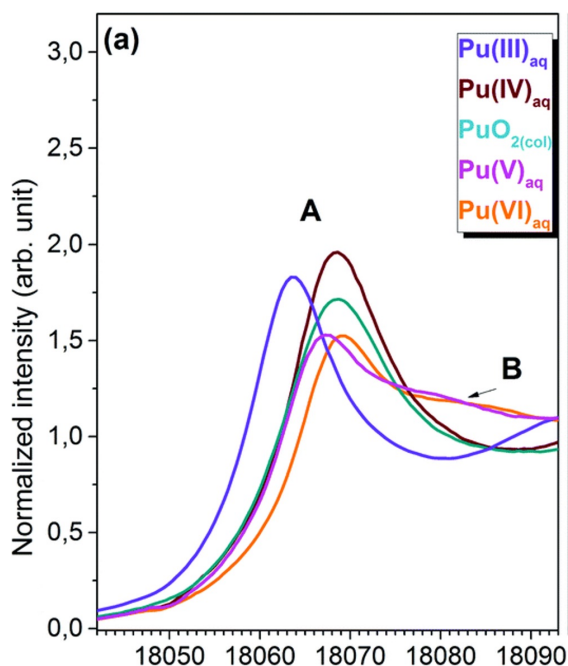


Figure 4.6: Plutonium L_3 -edge XANES spectra for aqueous solution of Pu(III)-Pu(VI) with Pu(IV) colloids [7].

detection (HERFD-XANES), as will be discussed later. In contrast, the L_3 -edge XANES features reflect the oxidation state and coordination environment of the actinide center, as illustrated in the following examples:

Oxidation state: The oxidation state of the absorbing atom can be determined from the energy position of the absorption edge, which varies with the oxidation state. This trend is illustrated in Figure 4.6 [7], where the white line in the L_3 -edge XANES spectra of various plutonium aqueous solutions shifts between Pu(III), Pu(V), Pu(IV), and Pu(VI). In practice, oxidation state determination is commonly performed by comparing the XANES features of unknown samples with those of well characterized reference compounds, a method known as fingerprinting.

Coordination environment of the absorbing atom: XANES is also a powerful tool for probing the coordination environment of the absorbing atom. This is demonstrated in Figure 4.6 [7] where the aqueous solutions of Pu^{V} and Pu^{VI}

exhibit a distinct post-edge shoulder in the XANES spectra compared to Pu^{III} and Pu^{IV} . This shoulder is a spectral fingerprint of actinyl cations (e.g., PuO_2^+ , PuO_2^{2+}), which are defined by linear di-oxo bonds. The feature originates from multiple scattering effects along the axial oxygen atoms of the actinyl moiety. This interpretation was previously supported by Den Auwer et al. [8], who used XANES and theoretical modeling to identify the signatures of oxo groups in actinide complexes.

While conventional XANES provides valuable insights into the oxidation state and coordination environment of the absorbing atom, its resolution is limited by the core-hole lifetime broadening, particularly at the L- (around 8 eV) and M-edges (around 4 eV) [9] of heavy elements like actinides. This intrinsic broadening often prevents the detection of subtle spectral changes or features (See subsection 4.2.4).

To overcome these limitations, high-energy resolution fluorescence detection XANES (HERFD-XANES) has been developed. HERFD-XANES measurements are typically obtained from resonant inelastic X-ray scattering (RIXS) maps by selecting the emission energy that maximizes spectral sharpness. Both techniques will be discussed in the following sections.

4.2.3 Resonant Inelastic X-ray Scattering (RIXS)

Resonant inelastic X-ray scattering (RIXS) is a photon-in/photon-out spectroscopic technique in which an incident photon excites a core electron into an unoccupied electronic state, creating an intermediate core-excited state. The system then relaxes by the emission of a photon, either through a transition from another core level (core-to-core RIXS) or from a valence orbital (core-to-valence RIXS), as illustrated in subfigure (a) of Figure 4.7.

Experimentally, RIXS is performed by scanning the incident photon energy across an absorption edge while detecting the emitted X-ray intensity at specific emission energies. This yields a two-dimensional RIXS map that can be plotted either as emitted photon energy versus incident energy, or more commonly as energy transfer (defined as the difference between incident and emitted energy) versus incident energy. An example is shown in subfigure (b) of Figure 4.7,

which displays a 2D RIXS map acquired at the U L_3 -edge of UO_2 . Core-to-core

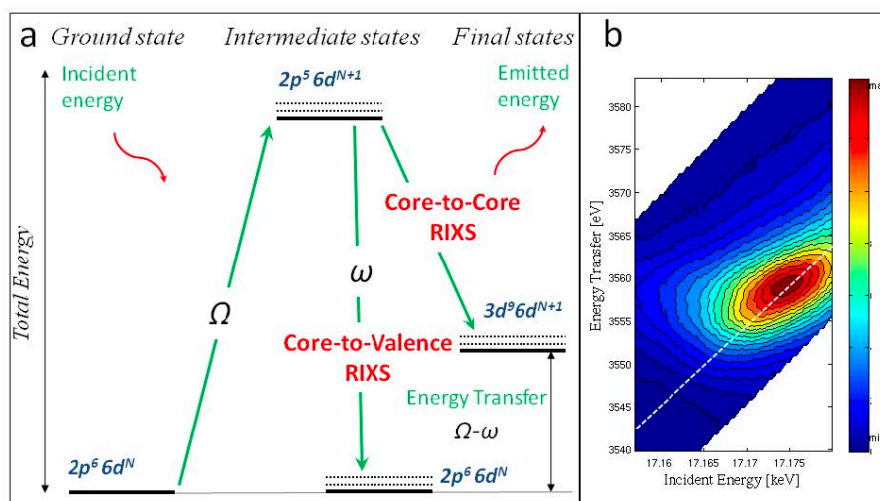


Figure 4.7: (a) Schematic representation of resonant inelastic X-ray scattering (RIXS) processes. An incident photon of energy Ω excites a core electron into an unoccupied state, creating an intermediate state. The system then relaxes either via a core-level transition (core-to-core RIXS) or through a valence electron decay (core-to-valence RIXS), emitting a photon of energy ω . The energy transfer $\Omega - \omega$ corresponds to the energy of the final state excitation. (b) Example of a 2D RIXS map showing emission intensity as a function of incident energy and energy transfer at the U L_3 -edge of UO_2 [10].

RIXS results in a final state with a core hole that has a longer lifetime and thus a narrower natural linewidth than the intermediate state [11, 12]. This feature makes it especially useful for identifying emission lines with minimal broadening. Such emission maxima serve as optimal detection energies for high-resolution spectroscopic techniques. High-energy resolution fluorescence detection XANES (HERFD-XANES), which is derived directly from the RIXS plane by extracting a diagonal cut along the line of maximum emission intensity. This approach is discussed in the following section.

4.2.4 High-Energy Resolution Fluorescence Detection XANES (HERFD-XANES)

HERFD-XANES is an advanced spectroscopic technique developed to overcome the resolution limits of conventional XANES, which are primarily caused by

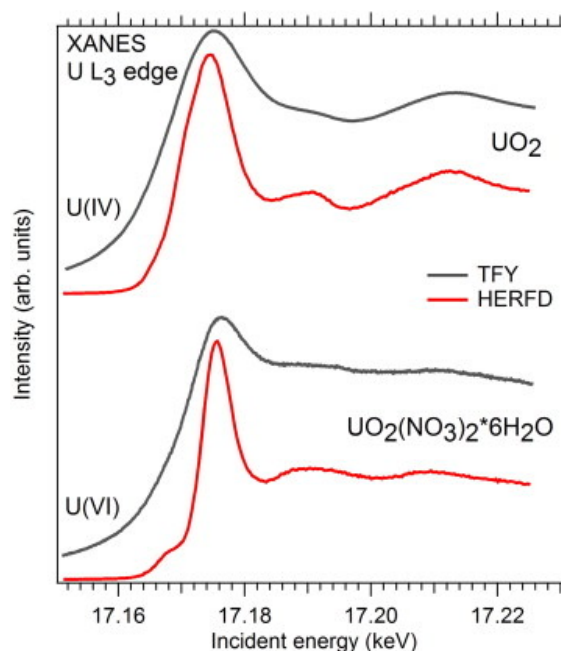


Figure 4.8: U L_3 -edge of UO_2 and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ measured in total fluorescence yield (TFY) and HERFD modes [10].

lifetime broadening of core-excited states. In HERFD-XANES, the fluorescence signal is collected at a fixed emission energy using a crystal analyzer tuned to the maximum of a core-to-core emission line. By constraining the final state to one with a longer lifetime and narrower linewidth, this approach significantly improves the effective energy resolution.

As illustrated in Figure 4.8 [10], the U L_3 -edge XANES spectra of UO_2 and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ show striking differences between the two detection modes. In total fluorescence yield (TFY-XANES) the spectral features appear broadened due to both lifetime and instrumental effects. In contrast, the HERFD-XANES spectrum reveals much sharper and more distinct structures, clearly demonstrating the enhanced resolution of the technique, enabling a more precise characterization of the electronic structure.

A comparable enhancement is observed at the U M_4 -edge, as shown in Figure 4.9 [13] for UO_2 , where HERFD-XANES again provides narrower and well-resolved features relative to TFY detection.

This enhanced resolution enables the identification and analysis of several

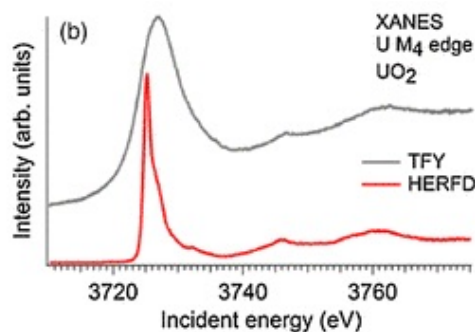


Figure 4.9: U M_4 -edge of UO_2 measured in total fluorescence yield (TFY) and HERFD modes [14].

key aspects of actinide electronic structure, including:

Oxidation state determination: HERFD-XANES enables the determination of oxidation states with high sensitivity and allows for their quantitative analysis in mixed-valence states, which require suitable reference compounds. As an illustrative example, Figure 4.10 illustrates the HERFD-XANES spectra acquired at the uranium M_4 -edge for a series of uranium oxide compounds with mixed valence states: U_4O_9 , U_3O_7 , and U_3O_8 . The solid lines represent the experimental spectra of these compounds, where we can see a shift to the right in the white line as the oxidation state increases. The distinct spectral features labeled 1, 2, and 3 (or 3*) correspond to electronic transitions associated with U(IV), U(V), and U(VI), respectively. These spectral assignments are based on a comparison with reference compounds (UO_2 , KUO_3 and β - UO_3) containing well-defined oxidation states and are further supported by theoretical calculations, enabling the quantification of uranium oxidation states in complex systems [15].

Local symmetry: HERFD-XANES spectra exhibit a strong sensitivity to the local symmetry around actinide centers, making them valuable tools for probing changes in coordination environments. As shown in Figure 4.11, distinct spectral features are observed for four U(VI) compounds, each with different symmetry: Sr_3UO_6 (O_h), $CaUO_4$ (D_{3d}), β - $SrUO_4$ (D_{4h}), and $Cs_2UO_2Cl_4$ (D_{4h}). Subtle differences in peak shapes and positions reflect changes in the crystal field [16].

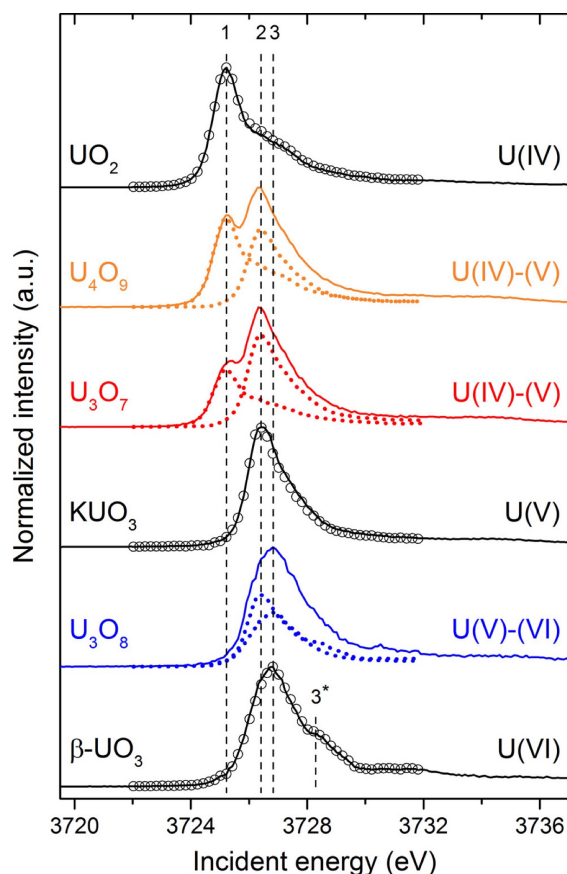


Figure 4.10: HERFD-XANES spectra at the uranium M_4 -edge for various uranium oxide compounds (U_4O_9 , U_3O_7 , U_3O_8). Solid lines represent the experimental spectra, while dotted lines and open circles correspond to component spectra obtained through Iterative Target Transformation (ITT), scaled according to the calculated weight fractions. The labeled spectral features (1, 2, 3/3*) correlate with uranium in formal oxidation states U(IV), U(V), and U(VI), respectively [15].

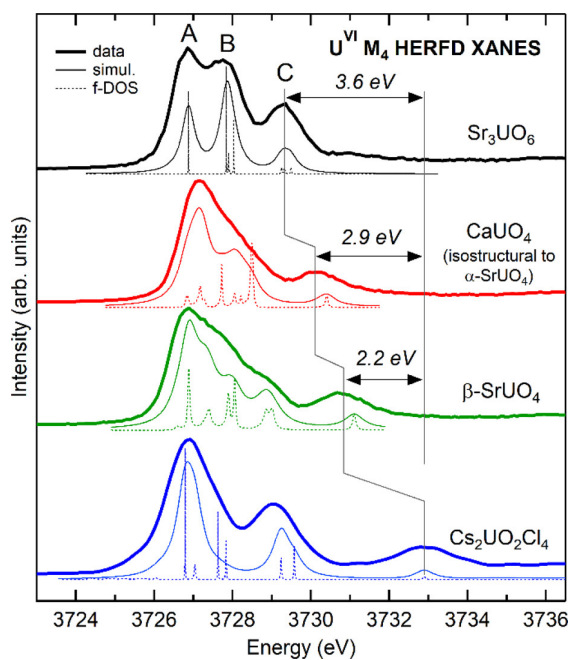


Figure 4.11: Uranium M_4 -edge HERFD-XANES spectra of four U(VI) compounds: Sr_3UO_6 (O_h), CaUO_4 (D_{3d}), $\beta\text{-SrUO}_4$ (D_{4h}), and $\text{Cs}_2\text{UO}_2\text{Cl}_4$ (D_{4h}). Experimental spectra (thick lines), simulated spectra (thin lines), and uranium f -projected DOS (dotted lines) are shown [16].

Although XANES, HERFD-XANES, and RIXS provide valuable information on oxidation states and the coordination environment of actinide compounds [11, 17], they are not sufficient for detailed structural characterization. For this purpose, Extended X-ray Absorption Fine Structure (EXAFS) analysis is required because it enables the quantitative determination of interatomic distances, coordination numbers, and structural disorder. The principles of EXAFS will be discussed in the following section.

4.2.5 Extended X-ray Absorption Fine Structure (EXAFS)

The EXAFS region refers to the post-edge region of the XAS spectrum, which extends approximately from 50-1000 eV above the absorption edge. In this energy range, the incident X-ray photon has enough energy to excite the core electron into the continuum, producing a photoelectron with high kinetic energy and correspondingly a short wavelength compared to interatomic distances.

The ejected photoelectron behaves as a spherical wave propagating outward from the absorbing atom and is elastically scattered by neighboring atoms. The interference between the outgoing and backscattered waves generates oscillations in the X-ray absorption coefficient, known as EXAFS. Constructive interference results in absorption maxima, whereas destructive interference results in minima.

These oscillations encode detailed structural information about the local atomic environment of the absorber. Because the photoelectron has a relatively short mean free path (a few angstroms), the high-energy photoelectron is primarily sensitive to the short-range order within the first few coordination shells around the absorbing atom. Consequently, EXAFS provides a powerful tool for probing the local environment around the absorber, including interatomic distances, coordination numbers, and the identity and disorder of neighboring atoms [18].

For actinides and other heavy elements, EXAFS measurements are most commonly performed at the L_3 -edge, which corresponds to the excitation of a $2p_{3/2}$ core electron. The L_3 -edge lies in the hard X-ray region (between 5 keV-200 keV), where the resulting photoelectrons have sufficiently high energies

and long mean free paths to probe multiple coordination shells. This allows extraction of key structural parameters such as bond distances, coordination numbers, and disorder factors [17, 19].

Interpreting EXAFS data requires theoretical modeling of photoelectron scattering. Fortunately, at the high energies relevant to the EXAFS region, several simplifications become valid: the photoelectron can be treated as a spherical (or plane) wave, and the single-scattering approximation is often sufficient. These approximations make EXAFS analysis relatively straightforward compared to the XANES region, where the lower photoelectron energy leads to stronger multiple scattering effects and necessitates more sophisticated treatments involving full electronic structure calculations. As a result, EXAFS can be quantitatively described using a simplified analytical expression, known as the EXAFS equation, introduced below.

4.2.6 Derivation of the EXAFS Equation

As discussed above, the EXAFS phenomenon arises from the ejection of a core electron, referred to as a photoelectron, upon absorption of an X-ray photon. The photoelectron is described as a spherical wave emanating from the absorbing atom, with a wavevector k given by:

$$k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}, \quad (4.6)$$

where E is the incident photon energy, E_0 is the absorption edge energy, and m_e is the electron mass and $\hbar$ the reduced Planck constant.

As the photoelectron propagates outward, it may be elastically scattered by neighboring atoms. The resulting backscattered waves then interfere with the outgoing wave, leading to modulations in the absorption coefficient $\mu(E)$. The oscillatory component, known as the EXAFS signal $\chi(E)$, is defined as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)}, \quad (4.7)$$

where $\mu_0(E)$ is a smooth background representing the absorption of an isolated

atom, and $\Delta\mu_0$ is the absorption edge step.

The fundamental origin of these oscillations lies in the quantum-mechanical transition probability for X-ray absorption, governed by Fermi's Golden Rule:

$$\mu(E) \propto \sum_f |\langle \psi_f | H_{\text{int}} | \psi_i \rangle|^2 \delta(E_i - E_f + h\nu), \quad (4.8)$$

where ψ_i and ψ_f are the wave functions that describe the atom in its initial and final state, respectively, H_{int} is the Hamiltonian describing the interaction between the radiation field and matter, and δ is the Dirac delta function enforcing energy conservation, i.e. $E_f = E_i + h\nu$.

Under the electric dipole approximation, the interaction Hamiltonian becomes $H_{\text{int}} = \boldsymbol{\varepsilon} \cdot \mathbf{r}$, where $\mathbf{r}$ is the coordinate of the photoelectron and $\boldsymbol{\varepsilon}$ is the polarization vector of the electric field of the incident photon. This approximation is valid because the X-ray wavelength is much larger than the spatial extent of the core orbitals involved in the transition.

This formalism is further simplified by neglecting the angular dependence of the scattering amplitude. The expressions used in this work are thus valid only for isotropic samples, such as powders, liquids, or polycrystalline materials, where the directional effects average out. In this first-order treatment, only simple single-scattering paths are considered, in which the photoelectron travels from the absorber to a neighboring atom and back. This corresponds to backscattering events with an effective scattering angle of π .

The outgoing photoelectron is modeled as a spherical wave emanating from the absorber:

$$\psi(k, r) = \frac{e^{ikr}}{kr}. \quad (4.9)$$

When this wave encounters a neighboring atom at distance R , it is partially backscattered and returns to the absorber as a spherical wave, as well. Assuming that the photoelectron wave is approximately planar in the vicinity of the scatterer, interference between the outgoing and backscattered waves modulates the electron density at the absorber, giving rise to the EXAFS oscillations:

$$\chi(k) \propto \frac{|f(k, \pi)|}{kR^2} \sin(2kR + \delta(k)), \quad (4.10)$$

where $f(k, \pi)$ is the complex backscattering amplitude at angle π , and $\delta(k)$ is the total phase shift between waves representing the ejected photoelectron and the photoelectron after backscattering.

For notational simplicity, and since only backscattering is considered in this approximation, the angular dependence is often omitted for simplicity:

$$\chi(k) \propto \frac{f(k)}{kR^2} \sin(2kR + \delta(k)). \quad (4.11)$$

In real systems, thermal vibrations and static disorder cause fluctuations of the interatomic distances. These effects are accounted for by the Debye-Waller factor σ :

$$e^{-2k^2\sigma^2}, \quad (4.12)$$

where σ^2 is the mean-square relative displacement of the absorber-scatterer pair at distance R .

Inelastic losses and finite core-hole lifetimes are included via the photoelectron mean free path $\lambda(k)$:

$$e^{-2R/\lambda(k)} \quad (4.13)$$

Amplitude Reduction Factor S_0^2 . In the derivation of the EXAFS equation, the single-electron approximation assumes that X-ray absorption results in the excitation of a single photoelectron into the continuum. However, in real systems, the sudden creation of a core hole may also lead to many-body effects at the absorbing atom, such as shake-up (excitation of other bound electrons) or shake-off (ejection of a second electron). While these inelastic processes have little effect on the edge position, they reduce the probability that the final state consists of a single photoelectron.

To account for this intrinsic amplitude loss, an empirical factor S_0^2 is introduced in the EXAFS equation. This factor represents the intrinsic loss of EXAFS amplitude due to many-body effects localized at the absorbing atom. It typically takes values between 0.7 and 1.0, and is either estimated from standard reference compounds or fixed using theoretical calculations (FEFF simulations).

EXAFS equation for multiple shells. When generalized to include multiple coordination shells, the EXAFS equation takes the following form:

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k)}{k R_j^2} e^{-2k^2 \sigma_j^2} e^{-2R_j/\lambda(k)} \sin[2kR_j + \delta_j(k)] \quad (4.14)$$

with the parameters defined as:

- N_j : coordination number of neighboring atoms,
- R_j : distance to neighboring atom,

The functions $f_j(k)$ and $\delta_j(k)$ are not known analytically and must be obtained either from experimental reference compounds with known structure or from theoretical calculations. Nowadays, we can calculate $f_j(k)$ and $\delta_j(k)$ using the computer program FEFF [20, 21]. A structure that is close to the expected structure can be used to generate a FEFF [20, 21] model, and used in the analysis programs to refine distances and coordination numbers. If we know the scattering properties of the neighboring atom, namely $f_j(k)$ and $\delta_j(k)$, as well as the mean-free-path $\lambda_j(k)$ we can determine: R_j , N_j and σ_j^2 .

Note that $f_j(k)$ and $\delta_j(k)$ depend on atomic number Z , meaning that EXAFS is also sensitive to the identity of the neighboring atoms. As a result, EXAFS can distinguish between neighboring atoms with significantly different atomic numbers. However, elements with similar atomic numbers (differing by 1 such as oxygen and fluorine) generally have indistinguishable EXAFS signatures.

4.2.7 EXAFS Data Reduction

A major advantage of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is its ability to provide quantitative information about the local environment surrounding the absorbing atom, including radial distances to neighboring atoms and their coordination numbers. However, accurate interpretation requires rigorous and systematic data processing.

The processing of EXAFS data involves several key steps, which can be carried out using the software ATHENA [22]. The main steps are summarized below:

1. Conversion of measured intensities to $\mu(E)$: Starting from the measured X-ray intensities before and after the sample, the absorption coefficient $\mu(E)$ is calculated using the relation either in Equation 4.3 or Equation 4.4 according to the detection mode used.
2. Selection of edge energy E_0 : The threshold energy E_0 can be determined in many different ways, such as: by locating the maximum of the white line (peak in absorption) or by identifying the inflection point thanks to the first derivative of $\mu(E)$. In this work, the latter method is used.
3. Pre-edge background subtraction: The pre-edge signal is modeled with a polynomial function and subtracted to correct for instrumental baseline effects and contributions from other elements.
4. Post-edge background subtraction: Since the isolated atomic absorption coefficient $\mu_0(E)$, without neighboring atom contributions, is not directly measurable, it is approximated using a smooth spline function fitted to the post-edge region.
5. Normalization of the spectrum: This step scales the absorption edge jump to unity (Figure 4.12).
6. Transformation to k -space: The normalized EXAFS signal $\chi(E)$ is converted to $\chi(k)$ using the relationship between the photoelectron wavevector k and photon energy E (Equation 4.6).
7. Application of k -weighting: Because the EXAFS signal amplitude decreases with increasing k , a k -weighting is commonly applied to emphasize higher k contributions. This is achieved by multiplying the signal by k , k^2 , or k^3 , as illustrated in Figure 4.13, where the signal becomes progressively more pronounced from k^0 to k^3 . For heavy elements such as actinides, k^2 or k^3 weighting is often preferred to enhance the high- k signal. In this work, a k^3 weighting was employed.
8. Fourier Transform (FT): The $\chi(k)$ function is Fourier transformed to real space (R -space), revealing peaks that correspond approximately to distances between the absorbing atom and its neighbors. This representation

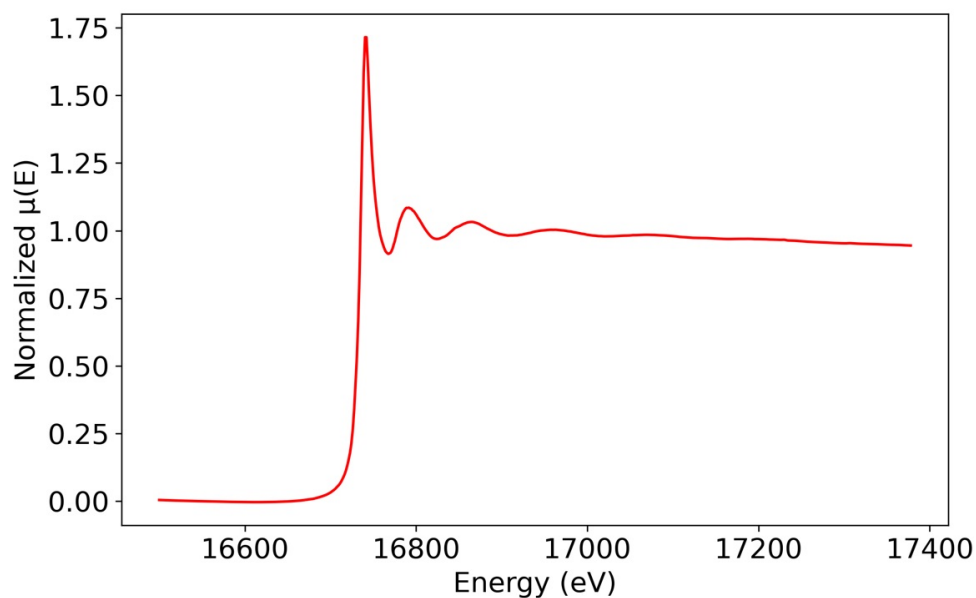


Figure 4.12: Normalized XAS spectrum with subtracted background of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L_3 -edge at the MARS beamline of the SOLEIL synchrotron.

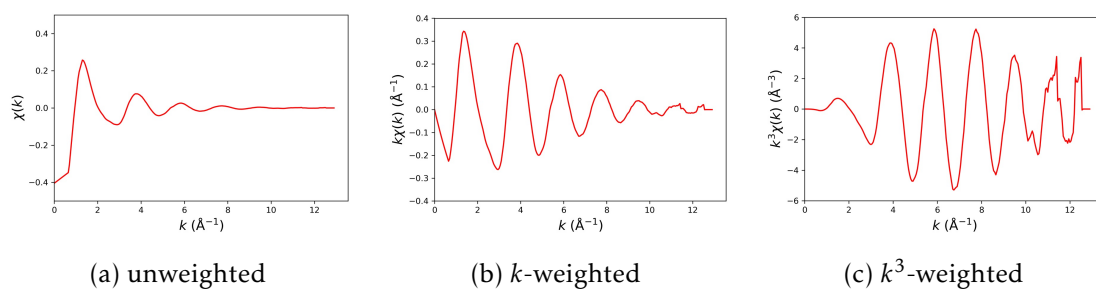


Figure 4.13: The $\chi(k)$ of a Pa(V) sample in concentrated hydrofluoric acid, acquired at the L_3 -edge at the MARS beamline of the SOLEIL synchrotron: (a) unweighted, (b) weighted by k , and (c) weighted by k^3 .

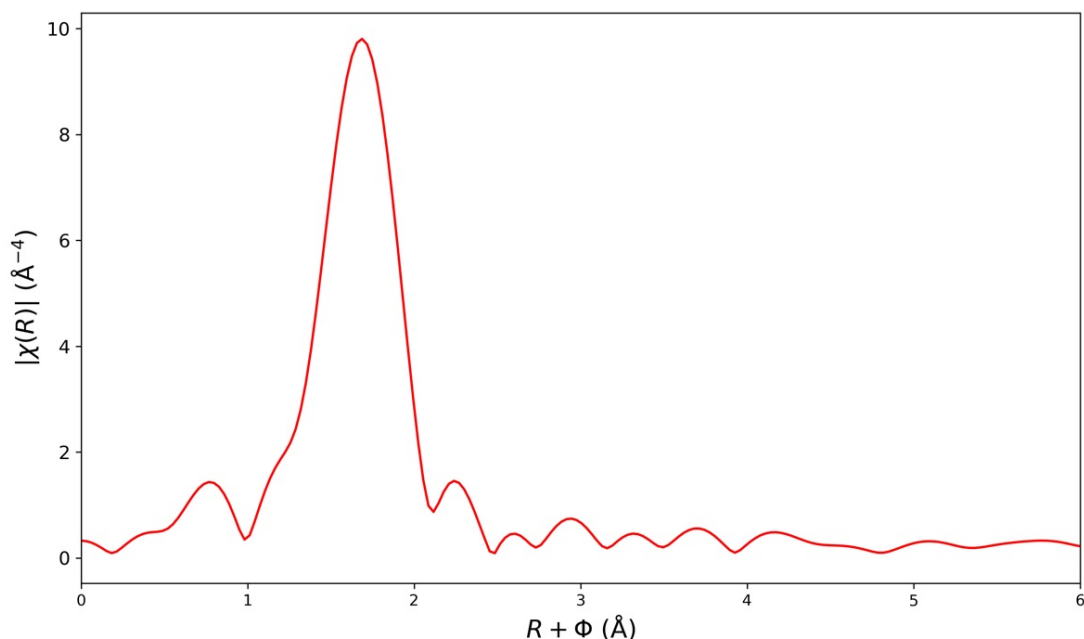


Figure 4.14: Fourier transform (FT) magnitude of EXAFS data from Pa(V) sample in concentrated hydrofluoric acid, acquired at the L_3 -edge at the MARS beamline of the SOLEIL synchrotron.

is analogous to a radial distribution function, helping to identify coordination shells (Figure 4.14). EXAFS data fitting can be performed in both k -space and R -space, the R -space representation is often preferred for its more intuitive correspondence with real-space distances.

To obtain the FT, the fit is typically performed over a selected k -range (the k -space window). This k -range must be chosen carefully to optimize the R -space resolution. A broader selected k -range, Δk improves the distance resolution ΔR , which can be approximated by the relation:

$$\Delta R = \frac{\pi}{2\Delta k}. \quad (4.15)$$

However, extending the k -range must be balanced against the rising noise at higher k values, especially for lighter elements or dilute samples.

EXAFS Data Fitting with ARTEMIS

After data reduction and processing in ATHENA [22], quantitative analysis of the EXAFS signal is performed using the ARTEMIS [22] program. While ATHENA handles data pre-processing (energy calibration, normalization, background subtraction, Fourier transform, etc.), ARTEMIS facilitates the fitting of the experimental EXAFS spectrum using theoretical scattering paths calculated by FEFF.

1. Importing the data: The normalized, background-subtracted EXAFS signal, expressed as $\chi(k)$, is imported.
2. Building the structural model: A structural model of the local atomic environment around the absorber is required to simulate the EXAFS signal. In this work, structural models are obtained from DFT geometry optimizations. These geometries serve as input for FEFF8 (integrated into the ARTEMIS package), which calculates theoretical backscattering phase and amplitude functions for initiating the EXAFS fitting.
3. Selecting relevant paths: FEFF generates a list of all possible scattering paths, including single and multiple scattering contributions. In most cases, only the most significant paths, typically the nearest neighbor single scattering contributions are selected first. These paths are incorporated into the ARTEMIS fitting model.
4. Defining Fitting Parameters: For each selected path, several parameters can be refined or fixed:
 - N_j : coordination number,
 - R_j : interatomic distance,
 - σ_j^2 : Debye-Waller factor,
 - ΔE_0 : edge energy shift,
 - S_0^2 : amplitude reduction factor.

These parameters can be defined as constants or treated as fitting variables. Typical recommended fitting parameter ranges are summarized in Table 4.2.

Table 4.2: Recommended parameter ranges in EXAFS fitting.

Parameter	Recommended Range
S_0^2	0.7-1
E_0	$[-10, 10]$ eV
ΔR	$[-0.1, 0.1]$ Å
σ^2	$[0.002, 0.02]$ (Å ²)

5. Performing the fit: Once the paths and parameters are defined, ARTEMIS performs a fit of the theoretical EXAFS signal to the experimental data. The fitting procedure minimizes the residual between the measured and calculated $\chi(k)$ or $\chi(R)$ spectra.
6. Evaluating fit quality: The quality of the fit is assessed using statistical indicators such as the reduced chi-square (χ_v^2) and R-factor ($\mathcal{R}$). These are defined as follows:

$$\chi_v^2 = \sqrt{\frac{\sum_k k^6 [\chi_{exp}(k) - \chi_{fit}(k)]^2}{N_{independent} - N_{fit}}}, \quad (4.16)$$

$$\mathcal{R} = \sqrt{\frac{\sum_k k^6 (\chi_{exp}(k) - \chi_{fit}(k))^2}{\sum_k k^6 \chi_{exp}^2(k)}}, \quad (4.17)$$

Here, $N_{independent}$ denotes the number of data points in the fit, and N_{fit} is the number of fitted parameters. To ensure a statistically meaningful fit, it is essential that N_{fit} remains lower than the number of independent data

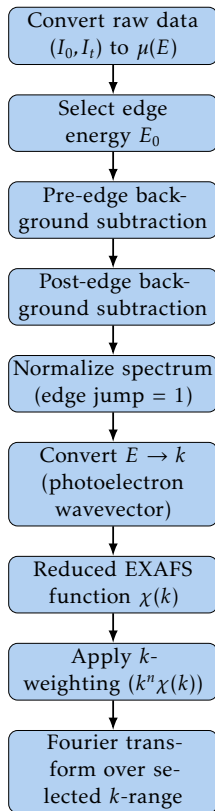
points $N_{independent}$, given by:

$$N_{independent} = \frac{2\Delta k \Delta R}{\pi}. \quad (4.18)$$

where Δk is the fitting window in k -space and ΔR refers here to the window in R -space.

The fitted structural parameters are then interpreted to provide information on local atomic distances, coordination numbers, and structural disorder around the absorbing atom. If necessary, the model can be iteratively refined by adjusting path selection, adding multiple-scattering contributions, or modifying parameter constraints.

EXAFS Data Reduction (ATHENA)



EXAFS Data Fitting (ARTEMIS)

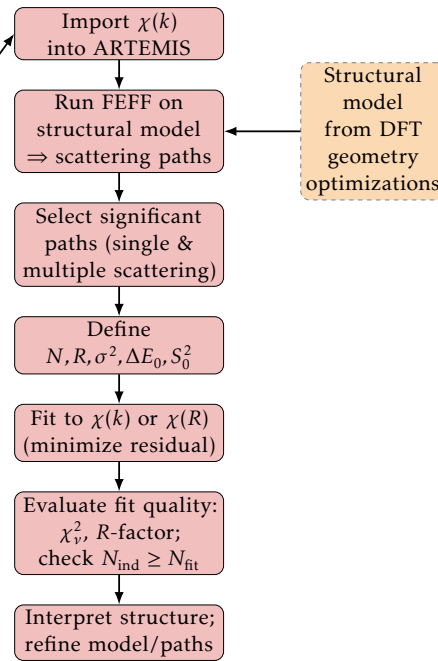


Figure 4.15: Workflow for EXAFS data reduction and fitting.

4.2.8 EXAFS limitations

While EXAFS is a powerful tool for probing the local structural environment of atoms, its application involves several limitations and challenges that must be carefully considered during experimental design and data analysis.

Sensitivity to similar atoms

A key limitation is the inability of EXAFS to distinguish between atoms with similar atomic numbers. Because the technique depends on differences in the backscattering amplitude and phase shift of neighboring atoms, light elements such as carbon, nitrogen, oxygen, and fluorine produce nearly indistinguishable signals. This causes uncertainty when assigning atom identities purely based solely on EXAFS data.

An illustration of this statement can be taken from the work of Giandomenico et al. [23]. It focused on the case of Pa^V studied in 0.5 M and 0.05 M hydrofluoric acid. The presence of water molecules or fluoride ions in the first coordination sphere could not be ruled out since fluorine and oxygen have very similar backscattering amplitudes and phase shifts.

Similarly, Denecke et al. [24] demonstrated that C and N cannot be distinguished by EXAFS in the Cm(III) and Eu(III) complexes with (n-C₃H₇)₄-BTP) second coordination shell because they are $Z + 1$ elements.

Limited k -range and spatial resolution

Another major consideration is the restricted k -range of the data. The resolution in real space (R -space) is inversely related to the width of the k -range used in the analysis, as expressed by the relation:

$$\Delta R \approx \frac{\pi}{2\Delta k} \quad (4.19)$$

A restricted k -range due to instrumental constraints, overlapping absorption edges, or noise at high k broadens Fourier peaks and reduces the ability to resolve neighboring coordination shells or distinguish between similar bond distances. In the study by Giandomenico et al. [23], the available k -range was between

$2\text{--}10\text{ \AA}^{-1}$, corresponding to a resolution of less than $0.2\text{ \AA}$. This limitation prevented the distinction between oxygen and fluorine ligands in the coordination sphere, whose EXAFS signatures are very similar and whose Pa–O and Pa–F distances differ by only $\sim 0.1\text{ \AA}$.

Denecke et al. [25] demonstrated that the extended k -range (exceeding $10\text{ \AA}^{-1}$) enabled resolution of the second coordination shell, thereby allowing the identification of phosphate groups in the inner coordination environment. This was crucial because the U–O bond distance alone could not provide sufficient structural information.

Model Dependence

EXAFS analysis is inherently model dependent, posing significant challenges for structural interpretation. A reliable fit requires an initial structural model of the local environment around the absorber, including key parameters such as coordination numbers, interatomic distances, and atomic disorder. The accuracy of the EXAFS-derived structural parameters is only as good as the quality and realism of the model used.

Two main approaches are commonly used to construct such models:

- **Crystallographic data** from known or structurally related compounds provides a common starting point. In actinide chemistry, for example, uranium oxo complexes with well-characterized crystal structures have served as surrogates for analyzing unknown protactinium species [26].
- **Theoretical models** derived from *ab initio* or density functional theory (DFT) geometry optimizations are increasingly preferred, especially when no suitable experimental structures exist [21]. Unlike static crystallographic models, DFT-optimized structures can account for solvation effects, ligand flexibility, and oxidation state variations, factors that are particularly relevant in solution-phase systems.

The advantage of theoretical models becomes evident beyond the first coordination shell [19], where experimental crystallography often fails due to thermal

motion or insufficient resolution. However, regardless of the model's origin, inaccurate or oversimplified models can yield misleading EXAFS fits.

A particular challenge is determining coordination numbers, which are strongly correlated with the Debye-Waller factor (σ^2). Both parameters affect the amplitude of the EXAFS oscillations, making it difficult to disentangle their contributions. For example, underestimating σ^2 may result in an overestimated coordination number. To mitigate such ambiguities, constraints from complementary techniques such as XANES, NMR spectroscopy, IR-Raman spectroscopy, or computational chemistry are often essential.

Having introduced the fundamentals of synchrotron radiation and describing the principles of X-ray absorption (XANES, EXAFS) and emission techniques (RIXS, HERFD-XANES), the following sections present the experimental results. The first part focuses on the EXAFS analysis of Pa(V) samples in both concentrated and diluted hydrochloric acid (section 4.3). The second part discusses the RIXS maps and HERFD-XANES spectra of Pa(V) solutions in concentrated HF and in $\text{H}_2\text{C}_2\text{O}_4$ measured at the Pa L_3 - and M_4 -edges.

4.3 EXAFS analysis of Pa(V) in hydrochloric acid

The material presented in this section corresponds to a published article, for which I am the second author and the primary theoretician:

- M. Maloubier et al., “Persistent Mono-oxo Bonding With Protactinium(V) Revealed in Highly Acidic Chloride Solutions”, *Angewandte Chemie International Edition*, 2025, e18403, DOI: 10.1002/anie.202518403

All quantum-mechanical (QM) data, including the optimized geometries of all species, are available in the open-access Zenodo repository under the following DOI: 10.5281/zenodo.15863727. Additional results and details are provided in the Supporting Information.

In this work, I performed the EXAFS fitting under the guidance of Melody Maloubier. I also carried out all the QM calculations under the supervision of Valérie Vallet and Florent Réal, and I contributed to the writing of the computational details section of the manuscript.

Before presenting the article, I briefly introduce the objectives of this work and highlight its main results and conclusions.

As discussed in chapter 1 and chapter 3 protactinium (Pa) occupies a unique position in the actinide series, as it is the first element where both 5f and 6d orbitals contribute significantly to chemical bonding. Understanding its coordination chemistry is therefore essential to gain insight into the broader behavior of early actinides. Despite its chemical significance, Pa in its pentavalent oxidation state, the most stable in aqueous media, remains poorly characterized. This is primarily due to its strong tendency to hydrolyze and form insoluble polymeric species or precipitates unless stabilized by strong complexing ligands [28, 29]. Such instability, especially at elevated pH or concentrations, has long hindered detailed investigations in the solution phase [3].

Unlike heavier actinides such as uranium and neptunium, which form linear actinyl ions ($[\text{An}^{\text{V}}\text{O}_2]^+$ or $[\text{An}^{\text{IV}}\text{O}_2]^{2+}$) in their oxidation states +V and +VI, Pa(V) does not adopt this structure. Instead, it has been reported to exhibit a short Pa–O bond in specific highly acidic environments, such as concentrated sulfuric acid (12 M) and oxalic acid [26, 30]. In contrast, in hydrofluoric acid, this mono-oxo bond disappears when the F/Pa ratios exceed 5, leading to the formation of stable non-oxo fluoro-complexes such as PaF_6^- to PaF_8^{3-} [23, 31].

Despite these observations, the nature of the mono-oxo bond remains debated. In particular, as discussed in chapter 3, section 3.2, quantum chemical calculations have not been able to reproduce the experimental EXAFS data for oxalate and sulfate complexes [2], suggesting that solution speciation may be more complex than previously assumed. These inconsistencies have motivated new investigations under different chemical conditions most notably in hydrochloric acid. This shift in focus aims to clarify whether the mono-oxo Pa–O bond exists in chloride medium and to resolve the contradictions between experimental observations and theoretical predictions.

In addition, as presented in chapter 3, section 3.1, theoretical simulations have shown that chloride (Cl^-) stabilizes the mono-oxo complex $\text{PaO}(\text{OH})_2(\text{Cl})(\text{H}_2\text{O})$ over the fully hydrolyzed form $\text{Pa}(\text{OH})_4(\text{Cl})$ [1]. This suggests that hydrochloric acid may offer a promising medium to probe the presence of a persistent Pa–O bond.

Unlike fluoride or oxalate, chloride is a weaker ligand and may thus allow the oxo bond to remain intact under acidic conditions. However, previous studies using solvent extraction, partitioning, or UV-Vis spectroscopy have yielded conflicting interpretations, and no direct structural characterization of Pa(V) species in hydrochloric acid has been reported yet. Tracer-level experiments ($C_{\text{Pa}} \leq 10^{-10} \text{ M}$), such as partition and diffusion methods, have suggested that $[\text{PaO}(\text{OH})\text{Cl}]^+$ predominates in 3 M HCl, although other hydroxo-oxo-chloro and fully chlorinated species have also been proposed depending on the chloride and proton concentrations (See Figure 1 in the paper).

At millimolar concentrations, UV-Vis absorption spectra exhibit strong dependence on acid concentration, sample preparation, and aging. A distinct absorption band near 210 nm observed in freshly prepared solutions by dissolving Pa(V) hydroxide or peroxide in 1–11 M HCl [32, 33] has been attributed to the presence of a Pa–O bond. This feature also appears in sulfuric acid but is absent in hydrofluoric acid, further supporting the oxo-bond hypothesis [33]. However, other studies have challenged this interpretation, proposing that only fully chlorinated Pa(V) complexes form in concentrated HCl [34–37].

These discrepancies raise a central question: Can the mono-oxo Pa–O bond persist in highly acidic chloride medium, despite its apparent instability in similarly acidic fluoride environments?

To address this question, two samples were prepared (see Table 4.1): one in 3 M HCl with 60 μM ^{231}Pa , where $[\text{PaO}(\text{OH})\text{Cl}]^+$ is expected to dominate, and a second in 12 M HCl with 200 μM ^{231}Pa , to test the oxo-bond stability at higher chloride concentration.

Our approach combines experimental X-ray absorption spectroscopy, specifically EXAFS and XANES, with relativistic *ab initio* calculations to gain insight into both the coordination geometry and electronic structure of Pa(V) in hydrochloric acid. This study represents the first such investigation in this medium. As discussed in subsection 4.2.5, EXAFS provides measurements of bond distances and coordination numbers, while XANES (subsection 4.2.2) is particularly useful in systems lacking crystallographic data. It is sensitive to both the oxidation state and local symmetry around the absorbing atom, and can detect subtle changes in the electronic structure associated with the presence of a Pa–O bond.

The complete EXAFS analysis, XANES interpretation, and theoretical calculations are detailed in the associated manuscript. In summary, we conclude that oxo-chloro complexes with a coordination number of seven are the predominant species in both 3 M and 12 M HCl. This behavior is in contrast to what is observed in hydrofluoric acid, where oxo species are destabilized. In highly acidic chloride medium (12 Molar), the species $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ is identified, while in (3 Molar) HCl, both $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and $\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3$ complexes are suggested and may even coexist (Figure 4.16). These findings are in good agreement with the predictions made chapter 3, where chloride was shown to stabilize the mono-oxo complex. Moreover, this study reports the first experimental observation of a mono-oxo bond in Pa(V), with a bond length of 1.83 Å, consistent with theoretical predictions.

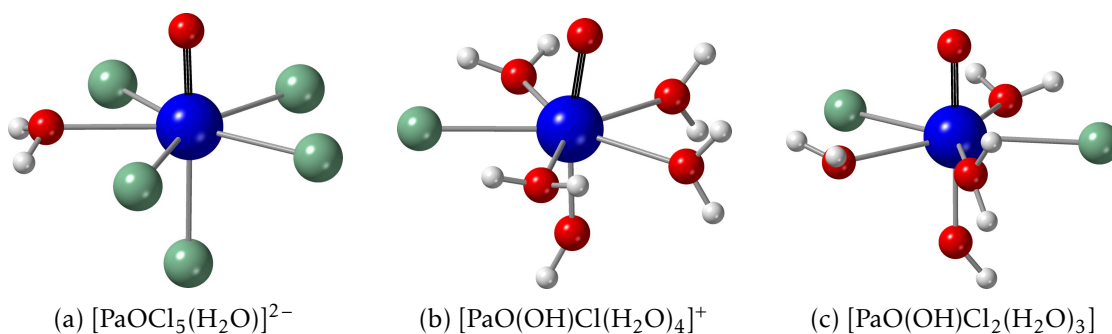


Figure 4.16: Optimized geometries of the complexes: (a) $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ identified in 12 M HCl, and (b) $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and (c) $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ identified in 3 M HCl. All geometries were optimized in the COSMO solvent model at the scalar relativistic (SR-ZORA) level using the PBE0 functional, and were used for EXAFS fitting.



Persistent Mono-Oxo Bonding with Protactinium(V) Revealed in Highly Acidic Chloride Solutions

Melody Maloubier,* Tamara Shaaban, Florent Réal, Claire Le Naour, Hanna Oher, Titouan Aubert, Pier Lorenzo Solari, Bruno Siberchicot, Rémi Maurice,* and Valérie Vallet*

Abstract: Protactinium is one of those long discovered elements with poorly known physico-chemical properties. In aqueous solution, protactinium(V), highly prone to hydrolysis, may or may not display oxo bonding, depending on the medium, in a way that still appears unpredictable due to a critical lack of data. Here, we probe the stability of this bond in hydrochloric acid solutions. Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy, complemented by ab initio calculations, reveal that a short Pa–O_{oxo} bond indeed exists at moderate hydrochloric acid concentration 3 M and unexpectedly persists even in highly acidic conditions (12 M). Our analysis identifies the coexistence of PaO(OH)Cl_{1.2} species at moderate acidity and PaOCl_{4.5} species at high acidity, with both pairs unambiguously displaying the characteristic mono-oxo bond, with a total coordination number of seven. Notably, EXAFS spectral fitting using geometries obtained from relativistic quantum calculations reveals a Pa–O_{oxo} bond length of approximately 1.83 Å, in excellent agreement with computational predictions. This finding overturns expectations and provides new insight into early actinide bonding behavior in extreme chemical conditions. Understanding such coordination chemistry is critical for advancing nuclear fuel management and more broadly actinide science.

Introduction

Understanding the behavior of protactinium (Pa), the first actinide in which the interplay between 5f and 6d orbitals play a significant role in bonding, is essential for deciphering

the broader chemistry of early actinides. Yet, Pa(V), with protactinium in its most common oxidation state in aqueous systems, presents a formidable challenge: it hydrolyzes readily, forming polymers or precipitates unless stabilized by strong ligands.^[1,2] This intrinsic instability, especially under increasing pH or concentration, has long hindered detailed solution-phase characterization.^[3]

Unlike its heavier actinide neighbors, Pa(V) does not form the canonical actinyl ion (linear [An^VO₂]⁺ or [An^{VI}O₂]²⁺), which is characteristic of +V and +VI oxidation states from U to Am. Instead, its aqueous chemistry involves a short mono-oxo bond in certain media such as oxalic or highly concentrated sulfuric acids (12 M).^[4,5] In contrast, in fluoride-rich environments, the oxo bond vanishes for F/Pa ratios higher than 5, yielding stable fluoro-complexes such as [PaF₆][−] to [PaF₈]^{3−}.^[6,7] It should be noted, however, that the actinyl form of protactinium (PaO₂⁺) is stable in the gas phase and has been characterized both experimentally and theoretically.^[8,9] These studies confirm that the linear actinyl geometry can exist under isolated conditions, although it is not retained in solution due to solvation and ligand-field effects.^[10] In addition, ambiguities persist in existing characterizations of the mono-oxo bond in the sense that quantum chemical calculations never reached good agreement with the experimental fits for oxalic and sulfuric acids.^[11] This discrepancy may point to a more complex speciation than previously anticipated and has motivated us to undertake new, independent investigations.

We chose hydrochloric acid as the medium for this investigation, as chloride is known to be a weaker binding ligand than fluoride, which may allow the mono-oxo bond to be stable in highly acidic concentrations. Indeed, there are

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Additional supporting information can be found online in the Supporting Information section

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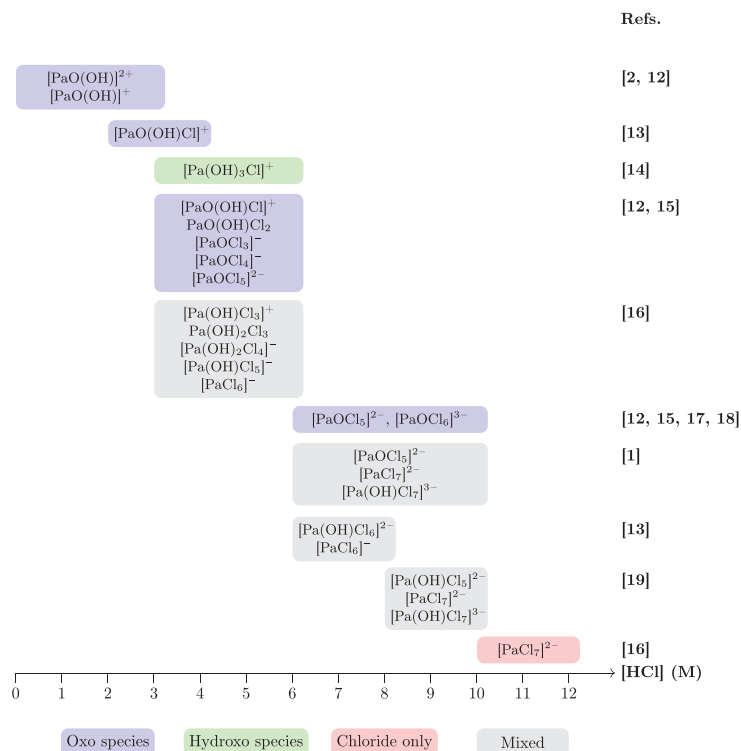


Figure 1. Proposed chloro, hydroxo, and oxo complexes of Pa(V) as a function of HCl concentration. Each colored box spans the reported stability range for the corresponding species, with colors indicating the dominant ligand type (See Table S6 for more detailed correspondence to the references).

conflicting reports on Pa(V) speciation in this medium and no structural characterization has been reported so far. Partition and diffusion methods studies at tracer concentrations ($C_{\text{Pa}} \leq 10^{-10}$ M) have explored the influence of HCl, proton, and chloride concentrations on complex formation (See Figure 1). These studies suggest that the $[\text{PaO}(\text{OH})\text{Cl}]^+$ species predominates in 3 M HCl. Depending on chloride and proton concentrations, a variety of hydroxo-oxo-chloro complexes and fully chlorinated complexes have also been proposed. At the millimolar scale, the shapes of the UV-vis absorption spectra vary not only with medium composition, but also with preparation method and sample age. An absorption band near 210 nm has been observed in freshly prepared solution by dissolution of hydroxide or peroxide of Pa(V) in 1–11 M HCl.^[16,20] This intense band with high extinction coefficient, also observed in sulfuric acid but not in HF, has been associated to the mono-oxo bond $\text{Pa}-\text{O}_{\text{oxo}}$.^[20] However, this interpretation contradicts other studies, which suggest that the Pa(V) forms only pure chloro-complexes in concentrated HCl.^[13,14,19,21]

These discrepancies raise a fundamental question: Can the mono-oxo bond in Pa(V) survive in highly acidic chloride

media, unlike highly acidic fluoride media? To address this, we report the first X-ray absorption spectroscopy (XAS) study of Pa(V) in hydrochloric acid, directly probing the presence and stability of the $\text{Pa}-\text{O}_{\text{oxo}}$ bond over a wide acidity range. Because only a single Pa(V) crystal structure has been reported to date,^[22] quantum chemical calculations are essential to guide the interpretation of experimental data. Our approach integrates extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) spectroscopy with ab initio calculations to characterize both the coordination geometry and electronic structure of Pa(V) in solution.

While the use of the EXAFS spectroscopy may seem obvious in this context, it is important to recall that the XANES spectroscopy can offer a powerful means to resolve speciation ambiguities, especially for systems where crystallographic data are lacking. Indeed, XANES is sensitive to both oxidation state and local symmetry of the absorbing atom, and may detect subtle variations in the electronic structure associated with the presence of a $\text{Pa}-\text{O}_{\text{oxo}}$ bond. In early actinides, including uranium and neptunium, characteristic shifts in the edge position and distinct edge features have

been correlated with actinyl formation. While Pa(V) lacks the classical actinyl ion, the presence of a mono-oxo bond may still produce spectroscopic signatures reflecting a highly anisotropic coordination environment. XANES may thus provide a rare opportunity to assess whether the Pa–O_{oxo} bond persists in chloride-rich solutions and to differentiate oxo-chloro species from fully chlorinated complexes, hence its inclusion in the present study.

To favor the formation of monomeric oxo-chloro species, we worked with Pa concentrations at or below 1×10^{-4} M, given the weak complexing ability of chloride ions, and with relatively low HCl concentration (around 3 M).^[2] A recent theoretical study predicted the existence of a stable mono-oxo bond in a monochloride Pa(V) complex,^[23] motivating our choice of conditions. For XAS measurements, we prepared two samples: one in 3 M with ²³¹Pa (60 μM) expecting [PaO(OH)Cl]⁺ to form. Additionally, a high chloride ion concentration of 12 M was used to test the stability of the mono-oxo bond with ²³¹Pa at 200 μM. As with all radioactive samples, the two solutions were doubly contained in the specific sample holder. L₃ edge spectra were collected at room temperature in fluorescence mode using a 13 element MIRION silicon drift detector on the MARS beamline at the SOLEIL synchrotron. Details on the sample preparation and XAS data collection are given in the Supporting Information (Section 1.1 and Section 1.2).

Results and Discussion

Methodology Overview

A brief overview of the experimental and computational methods is given here; full details and appropriate references are provided in the Supporting Information (Section 1.3). Protactinium(V) solutions in 3 and 12 M HCl were prepared and handled in dedicated radiochemical facilities designed for α-emitters, due to the radiological risk associated with Pa (Section 1 in the Supporting Information). Pa L₃-edge X-ray absorption spectra were collected on the MARS beamline at the SOLEIL synchrotron and analyzed using the Demeter package (ATHENA/ARTEMIS) with theoretical paths generated by FEFF8.^[24] All quantum-chemical calculations follow the approach adopted in recent studies on Pa(V) complexes.^[23] These were performed with the ADF program^[25,26] using the PBE0 hybrid functional^[27] and a triple-ζ plus polarization (TZ2P) basis sets^[28] within the scalar-relativistic (SR-ZORA) approximation.^[29] Thermodynamic corrections, Δ*G*_{corr} were derived from vibrational analyses, and solvation effects were included using the COSMO model.^[30–32] Composite Gibbs free energies of reaction were computed as:^[23]

$$\Delta G_r = \Delta E_{\text{CCSD(T)}} + \Delta E_{\text{SOC}} + \Delta G_{\text{corr}} + \Delta G_{\text{sol}}. \quad (1)$$

All gas-phase CCSD(T) calculations, spin-orbit (Δ*E*_{SOC}) and solvent corrections Δ*G*_{sol} computed with the COSMO-RS

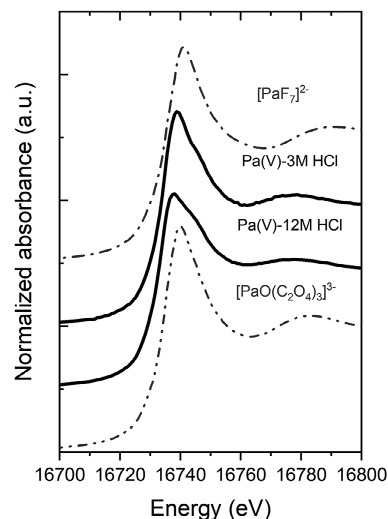


Figure 2. Pa L₃ edge XANES spectra of Pa(V) solutions in 3 and 12 M HCl (solid lines) compared to Pa(V) in a HF solution and in a 1 M oxalic acid solution (dashed lines).^[4,5]

model^[33,34] are described in more details in the Supporting Information (Section 1.3).

XANES Spectra

The Pa L₃ edge XANES spectra of the two solutions do not exhibit the same shape as the only two other known Pa(V) spectra (Figure 2). The white line position (absorption peak maximum) is shifted to lower energy and is identified at 16738.4 eV (calibrated to the K-edge of a Y foil at 17038 eV) compared to 16741.8 eV for [PaF₇]²⁻^[35] and 16740.0 eV for [PaO(C₂O₄)₃]³⁻.^[4] Moreover, in chloride medium, the XANES spectra exhibit a shoulder approximately 10 eV above the edge. While this feature is attributed to resonant scattering along the linear transdioxo cation for other pentavalent and hexavalent actinides,^[36] the occurrence of this transdioxo unit is precluded for Pa(V). Thus, by analogy, this shoulder could be due to the presence of a ligand in the trans position of the mono-oxo, forming a quasi-linear unit, which requires confirmation through the structural elucidation of the complexes formed. If true, this would thus correspond to an indirect signature of the mono-oxo bond.

Analysis of the 3 M HCl Solution

The local structure around the Pa(V) cation in a 3 M HCl solution was characterized using the L₃ edge extended X-ray absorption fine structure (EXAFS). Figure 3a displays the Pa L₃ edge EXAFS spectrum and its corresponding Fourier transform (FT). The FT reveals two primary features at

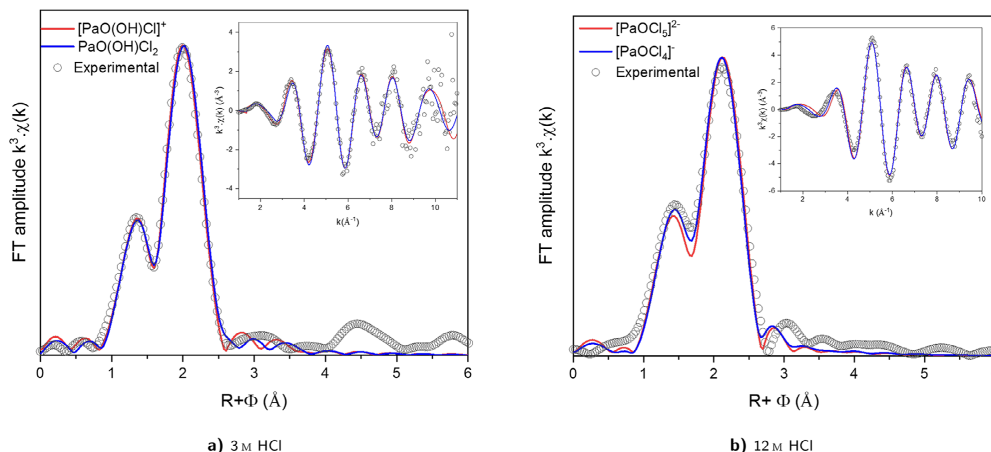


Figure 3. Fourier transform of the k^3 -weighted Pa L_3 -edge EXAFS spectrum and in the right top inset the k^3 -weighted EXAFS functions for a) the 3 M HCl solution; b) for the 12 M HCl Pa solution.

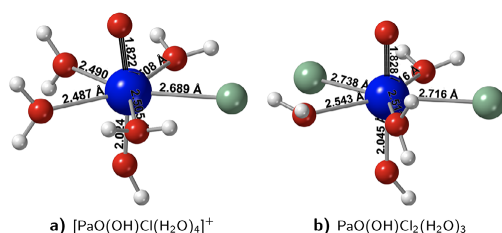


Figure 4. DFT-optimized geometries of the main Pa(V) species in 3 M HCl that best reproduce the EXAFS spectra: a) $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and b) $\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3$.

approximately $R + \phi = 1.4$ and $2.0 \text{ \AA}$ (distances not corrected for phase shift). The first peak is attributed to a short Pa – O interaction, assigned to the mono-oxo bond ($\text{Pa} - \text{O}_{\text{oxo}}$),^[4,5] while the second peak arises from longer-range interactions, such as water molecules and chloride ligands. The presence of the short Pa – O contribution supports the formation of a mono-oxo species in solution.

Based on the work of Muxart et al.,^[2] who suggested that $[\text{PaO}(\text{OH})\text{Cl}]^+$ is the predominant species in 3 M HCl formed from $[\text{PaO}(\text{OH})]^{2+}$, EXAFS fitting was initiated using the density functional theory (DFT)-optimized structure of $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ in which the OH group is in trans position of the oxo bond, as displayed in Figure 4a. The best fit EXAFS parameters are reported in Table 1, with additional fit statistics provided in the Supporting Information (Table S7). For all fit performed in this study, the total coordination number of Pa(V) was fixed to 7 by including water molecules in the inner sphere, in line with previous studies.^[4,5,7,37,38] Even if protactinium is able to form also eight-coordinate complexes, the impact of this variation on the fit is expected to be minor.^[5,39] Fitting the

EXAFS data with the DFT-optimized $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ structure yielded the following bond distances: a Pa – O_{oxo} distance of $1.83 \text{ \AA}$, a Pa – OH distance of $2.12 \text{ \AA}$, an average Pa – OH_2 distance of $2.42 \text{ \AA}$, and a Pa – Cl distance of $2.73 \text{ \AA}$ (Table 1). These values fall within the range of DFT-calculated values and literature data,^[11,40] particularly for the oxo and chloride bonds. Notably, this is the first time that the experimental Pa – O_{oxo} distance aligns closely with quantum chemical prediction, while two earlier studies have reported shorter experimental Pa – O_{oxo} distances ($\sim 1.75 \text{ \AA}$) than the theoretical one ($\sim 1.85 \text{ \AA}$).^[4,5,11]

Attempting to model the EXAFS spectrum without including a hydroxyl ligand (i.e., without considering a Pa – OH path), resulted in an elevated Debye – Waller factor, ($\sigma^2 > 0.01 \text{ \AA}^2$) for the mono-oxo bond (Table S7 in the Supporting Information). In general, this value is expected to be lower, especially for the first contribution and this type of bond. Moreover, the region between $R + \phi = 1$ to $2 \text{ \AA}$ is not adequately reproduced, highlighting the need for another contribution (mainly destructive), as shown in the Supporting Information (Figure S3) with the real part of the FT. This region could only be correctly reproduced if both the mono-oxo bond and the hydroxyl group were considered, resulting in a better fit.

Noticing that the QM Pa – OH distance is shorter by $0.1 \text{ \AA}$ than the EXAFS one ($2.15 \text{ \AA}$), we explored a complex with two hydroxyl groups, $\text{PaO}(\text{OH})_2\text{Cl}(\text{H}_2\text{O})_3$, in which there are two Pa – OH bond lengths: a shorter one at $2.07 \text{ \AA}$, trans to the oxo bond, and a longer one at $2.17 \text{ \AA}$. However, such species (e.g., $\text{PaO}(\text{OH})_2\text{Cl}$) have not been previously proposed, as only the first hydrolyzed form of Pa(V), $[\text{PaO}(\text{OH})]^{2+}$, is typically expected under highly acidic conditions.^[2,21] Furthermore, this optimized structure yields a poor fit (See both R_f and the Debye – Waller factor in the Supporting Information (Table S7). For these reasons, this complex is not considered further.

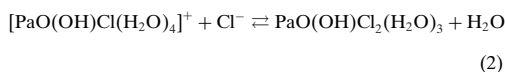
Table 1: Parameters from the best EXAFS fitting models for the Pa L₃ edge spectra in Pa(V) solutions at 3 and 12 M HCl, including coordination numbers (N), interatomic distances (*r* in Å), Debye–Waller factors (σ^2 in Å²), and fit quality metrics (ϵ_k , R_f , and $\Delta\chi^2$).

Model	Shell	$N^a)$	$r^b)$	$\sigma^{2c)}$	$E_0^d)$	$S_0^{2a)}$	ϵ_k	R_f	$\Delta\chi^2$						
HCl-3M sample															
[PaO(OH)Cl(H ₂ O) ₄] ⁺	Pa—O _{oxo}	1.00	1.83(1)	0.006(1)	7.0(2)	1	0.00075	0.5	0.9						
	Pa — OH	1	2.12(1)	0.005(1)											
	Pa — OH ₂	4	2.42(1)	0.005(1)											
	Pa — Cl	1	2.73(1)	0.003(1)											
	Pa—O _{oxo}	1.00	1.82(1)	0.007(1)											
PaO(OH)Cl ₂ (H ₂ O) ₃	Pa — OH	1	2.14(2)	0.013(2)	7.0(2)	1	0.00075	1.1	1.8						
	Pa — OH ₂	3	2.44(1)	0.004(1)											
	Pa — Cl	2	2.73(1)	0.010(1)											
	HCl-12M sample														
	[PaOCl ₅ (H ₂ O)] ^{2−}	Pa—O _{oxo}	1.00	1.83(1)						0.004(1)	5.1(7)	1	0.00032	1.8	84
Pa — OH ₂		1	2.44(2)	0.003 ^{a)}											
Pa — Cl		5	2.69(1)	0.010(1)											
Pa—O _{oxo}		1.00	1.83(1)	0.004(1)											
[PaOCl ₄ (H ₂ O) ₂] [−]	Pa — OH ₂	2	2.42(1)	0.007(2)	5.1(7)	1	0.00032	1.4	65						
	Pa — Cl	4	2.69(1)	0.008(1)											
	Pa—O _{oxo}	1.00	1.83(1)	0.004(1)											

^{a)} Fixed parameters. ^{b)} Interatomic distance in Å. ^{c)} Debye–Waller factor in Å². ^{d)} Threshold energy shift in eV.

Using a [PaO(OH)Cl]⁺ structure requires fixing the Debye–Waller factor at 0.003 Å² for the Cl contribution, despite expectations that this value should increase at longer distances. In the EXAFS equation, the Debye–Waller factor and the coordination number are often correlated. A low σ^2 value may suggest an underestimated Cl coordination number, indicating that the number of chlorine atoms warrants further investigation. Including two chlorides, as in PaO(OH)Cl₂(H₂O)₃, does not improve the fit and results in a substantial increase in the Debye–Waller factor (≥ 0.01 Å²), also affecting other fitting parameters. Based on the quality factor, the [PaO(OH)Cl(H₂O)₄]⁺ structure yields a slightly better fit; however, the improvement is not sufficient to definitively distinguish between the complexes. Coordination numbers derived from EXAFS are known to carry significant uncertainty (typically at least 20%), and a difference of one ligand in the first coordination sphere may not strongly affect the fit, though it can influence the Debye–Waller factor. Given this uncertainty, EXAFS data alone cannot clearly differentiate between the [PaO(OH)Cl]⁺ and PaO(OH)Cl₂.

Therefore, the stability of these two complexes were assessed by calculating the Gibbs free energy of reaction, ΔG_r , for the equilibrium (see Table S3 in the Supporting Information)



The computed Gibbs free energy difference, -10.4 kJ mol^{–1}, indicates that PaO(OH)Cl₂(H₂O)₃ complex is slightly more stable, though not decisively so given the inherent uncertainty of such calculations. Thus, in 3 M HCl, both [PaO(OH)Cl]⁺ and PaO(OH)Cl₂ complexes are suggested and may even coexist. The presence of the OH group in trans position of the

mono-oxo comfort our hypothesis concerning the shoulder in the XANES spectrum.

For these two species, we underline that there is a good agreement between the DFT and EXAFS distances for the bonds to the oxo and chloride ligands, while the distances to the water molecules and hydroxyl groups deviate from the EXAFS ones by ± 0.1 Å. This discrepancy is even more surprising that the chosen QM level (SR-ZORA/PBE0/COSMO) yields accurate distances for both the uranyl aqua ion and the uranyl tetrahydroxide ion (See Table S5 in the Supporting Information).^[41] The reason for this deviation remains unclear at this stage. However, the excellent agreement for the Pa–O_{oxo} bond is not the result of a fortuitous choice of the QM methodology, as we have already demonstrated that i) good DFT calculations are in excellent accord with correlated wave-function calculations and that ii) static calculations are in excellent accord with molecular dynamics simulations, for a given DFT level.^[11,37]

Analysis of the 12 M HCl Solution

At 12 M, chloride ligands are expected to dominate the coordination environment. Indeed, above 10 M, literature reports suggest that Pa(V) could exist either as the fully chlorinated species [PaCl₇]^{2–} (Figure 1 and Table S6 in the Supporting Information). However, direct structural evidence has so far been lacking, and the stability of a mono-oxo bond in highly acidic media remains controversial.

The Fourier transform of the EXAFS spectrum (Figure 3b) reveals a pronounced short-range contribution at 1.8 Å, consistent with a Pa–O_{oxo} bond. This observation alone is significant: fully chlorinated species, which would produce a single-shell EXAFS oscillation pattern, are clearly incompatible with the multiplet signal observed here. These

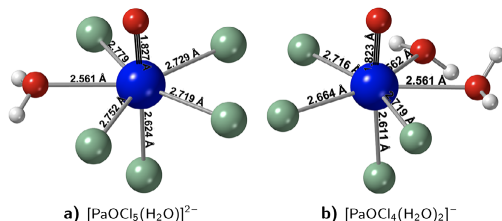
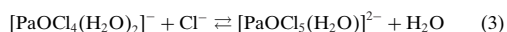


Figure 5. DFT-optimized geometries of the main Pa(V) species in 12 M HCl that best reproduce the EXAFS spectra: a) $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ and b) $[\text{PaOCl}_4(\text{H}_2\text{O})_2]^-$.

data immediately suggest that the oxo bond is retained despite the high chloride concentration.

We tested several coordination models to fit the EXAFS data. Complexes such as $[\text{Pa}(\text{OH})\text{Cl}_6]^{2-}$ and $[\text{PaOCl}_6]^{3-}$ yielded unsatisfactory fits, with *R*-factors exceeding 3.5% and bond distances inconsistent with theoretical expectations. Significantly better fits were obtained using the structures $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ and $[\text{PaOCl}_4(\text{H}_2\text{O})_2]^-$ displayed in Figure 5, both of which feature a short Pa–O_{oxo} bond alongside a mix of chloride and aquo ligands, one chloride being in trans position of the oxo ligand. In both models, the fitted bond distances include a Pa–O_{oxo} bond at (1.83 ± 0.01) Å, Pa–Cl distances of 2.69 Å, and Pa–OH₂ bonds near 2.43 Å. These values are in excellent agreement with optimized geometries from DFT, and the respective *R*-factors (1.8 % and 1.5 %) indicate robust model fidelity. This reinforces the hypothesis that Pa(V) in 12 M HCl does not exist solely as a fully chlorinated species.

Though EXAFS alone does not distinguish between the two species, complementary theoretical analysis largely lends weight to $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ as the predominant form. Gibbs free energy calculations for the reaction (See Table S3 in the Supporting Information):



favor this species over the $[\text{PaOCl}_4(\text{H}_2\text{O})_2]^-$ alternative by 27 kJ mol⁻¹. This relative Gibbs free energy difference is quite significant and expected to be larger than our computational accuracy, unlike the previous case (3 M).

To test the lability of the coordinated water molecule in $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$, ab initio molecular dynamics (AIMD) trajectories in explicit solvent were conducted and showed that the water ligand remains coordinated over time (few ps) (See details in Section 1.3 and Table S1 in the Supporting Information). This is in line with the poor EXAFS fit obtained using the non-hydrated $[\text{PaOCl}_5]^{2-}$ structure (See Table S8 in the Supporting Information). Therefore, the coordination number of seven is maintained from 3 to 12 M. In conclusion, the 12 M solution seems to be mainly composed of the $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ species displayed in Figure 5a, in which a chloride sits opposite of the mono-oxo, in agreement with the XANES spectrum.

Notably, the DFT-optimized geometries of PaOCl_5 (See Figure S2d in the Supporting Information) and $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ (Figure 5a) display a clear, though moderate, shortening of the Pa–Cl bond located trans to the oxo group (2.63–2.64 Å) compared to the cis chlorides (2.67–2.77 Å) (See Figure 5a). This systematic difference supports the presence of the *inverse trans influence* (ITI), a well-established feature of high-oxidation-state early actinide oxo complexes. The ITI has been thoroughly analyzed in both theoretical and experimental studies, including gas-phase calculations on $[\text{MOX}_5]^n$ (*M* = Pa, U, Np),^[42] the $[\text{C}_8\text{H}_{20}\text{N}]_2[\text{PaOCl}_5]$ solid-state structure,^[11] and comparative analyses of actinide halide and oxo systems.^[43–46] In all cases, shorter trans bonds arise from enhanced covalency along the actinide–oxo axis. Here, the magnitude of the contraction (0.04–0.08 Å) lies within the typical uncertainty of EXAFS fitting and thus cannot be resolved experimentally, although our quantum chemical calculations clearly point this effect out.

Conclusion

This study provides the first direct structural evidence that the mono-oxo bond in Pa(V) persists across a wide range of chloride-rich acidic conditions, from moderate to highly concentrated HCl. Through the integration of EXAFS and XANES spectroscopy with ab initio calculations, we identified oxo–chloro complexes with a coordination number of seven as the dominant solution species in both 3 and 12 M HCl, unlike what was observed in hydrofluoric acid. The proposed species exhibit a short Pa–O_{oxo} bond length (1.83 Å) with, in trans position either an hydroxide ligand (3 M) or a chloride ligand (12 M), responsible for the multiple-scattering feature visible in the XANES spectra, which unambiguously evidences the mono-oxo bond.

These findings demonstrate the stability of the mono-oxo bond in another highly acidic medium, beyond sulfuric acid. This raises new questions about whether similar stability holds in the presence of other acidic and/or competitive ligands, thus renewing the interest for establishing a more detailed speciation of protactinium in varying media.

Supporting Information

Experimental and computational details; XAS acquisition and analysis parameters; complete EXAFS fitting models for Pa(V) in 3 and 12 M HCl; AIMD setup and averaged structural data; computed Gibbs free energies and isomer stabilities; benchmarking on uranyl reference systems; optimized DFT geometries and representative spectra.

Author Contributions

M.M. is the primary experimentalist and T.S. is the primary theoretician.



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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

All quantum mechanics (QM) data, including the optimized coordinates for all species, are accessible on the open-access Zenodo repository with the following DOI: <https://doi.org/10.5281/zenodo.15863727>. Any raw data files corresponding to the XAS spectra are available upon reasonable request from the corresponding author M.M.

Keywords: Ab initio calculations • EXAFS spectroscopy • Mono-oxo bond • Protactinium • XANES

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Supporting Information:
Persistent mono-oxo Bonding in Protactinium(V)
Revealed in Highly Acidic Chloride Solutions

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Contents

List of Figures	S-2
List of Tables	S-3
1 Methods	S-5
1.1 Pa ^(V) sample preparation	S-5
1.2 XAS data collection and analysis	S-5
1.3 Quantum Chemical simulations	S-6
1.4 Ab initio molecular dynamics simulations	S-7
2 Results of AIMD and QM simulations	S-8
3 Literature review of Pa(V) complexation in HCl solutions	S-10
4 List of complexes for the EXAFS fitting	S-11
5 EXAFS spectra	S-15
References	S-16

List of Figures

S1 Geometries of all the complexes optimized in the COSMO solvent, at the scalar relativistic (SR-ZORA) level of theory with the PBE0 functional and used to fit the EXAFS data of the HCl-3 M sample.	S-13
S2 Geometries of all the complexes optimized in the COSMO solvent, at the scalar relativistic (SR-ZORA) level of theory with the PBE0 functional and used to fit the EXAFS data of the HCl-12 M sample.	S-14

- S3 Real part of the Fourier transform of the EXAFS spectrum for the Pa(V) solution in 3 M HCl. Experimental data are shown as black circles; the fit using the $[\text{PaO}(\text{OH})\text{Cl}]^+$ structure is shown in red, and the fit using the PaOCl_3 structure in blue. S-15

List of Tables

- S1 Average bond distances obtained from a 6 ps trajectory for $[\text{PaOCl}_5(\text{H}_2\text{O})]^+$ surrounded by 128 water molecules. S-8
- S2 Composite Gibbs free energies of reaction in the aqueous solvent (COSMO-RS), ΔG_r , with the different contributions to it ($\Delta E_{\text{CCSD(T)}}$, ΔG_{corr} , ΔE_{SOC} and ΔG_{sol}) (all values are in kJ mol^{-1}) of the reactions. The geometries of all complexes were optimized in the COSMO solvent, at the scalar relativistic (SR-ZORA) level of theory with the PBE0 functional. S-8
- S3 Composite Gibbs free energies of reaction, ΔG_r (in kJ mol^{-1}), for two chloride substitution reactions of protactinium(V) complexes in the 3 M and 12 M HCl samples. S-8
- S4 Relative Gibbs free energies (in kJ mol^{-1}) of isomers of $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and $\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3$, with different ligands positioned trans to the O_{oxo} group. The reported values correspond to composite Gibbs free energies of reaction in aqueous solution (COSMO-RS), ΔG_r , including contributions from $\Delta E_{\text{CCSD(T)}}$, ΔG_{corr} , ΔE_{SOC} , and ΔG_{sol} . Geometries were optimized in the COSMO solvent at the scalar relativistic (SR-ZORA) level of theory using the PBE0 functional. S-9

S5	EXAFS structure results measured UO_2^{2+} in acidic solution, $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, and in highly alkaline solutions, $[\text{UO}_2(\text{OH})_4]^{2-}$ compared with structural parameters determined by quantum chemical calculations, either using Hartree-Fock method in the gas phase (GP) or PBE0 functional with the COSMO solvation model.	S-9
S6	Suggested chloro complexes of Pa(V) as a function of HCl concentration and at Pa trace-level concentrations.	S-10
S7	Parameters from the different EXAFS fitting models for the Pa L_3 edge spectra in Pa(V) solution at 3 M.	S-11
S8	Parameters of the different EXAFS fitting models for the Pa L_3 edge spectra of the 12 M HCl Pa(V) solution.	S-12

1 Methods

Caution : ^{231}Pa is a naturally occurring α - and γ -emitting radionuclide ($t_{1/2}=32\,800\text{ yr}$, 1.74 GBq g^{-1}). With its daughters, this isotope presents a radiological risk. All experiments were performed in specific laboratories designed for the safe handling of radioactive materials.

1.1 $\text{Pa}^{(\text{V})}$ sample preparation

The ^{231}Pa solution was initially purified from its decay products (especially ^{227}Th , and ^{223}Ra) by anion-exchange resin (AG-MP1, Bio-Rad, 100-200 mesh), monitored by gamma spectrometry.^{S1} The collected Pa fractions were evaporated to dryness in a Teflon crucible. To remove any traces of HF, the residue was taken up in 5 M HClO_4 , the appearance of white fumes during evaporation attesting its absence. The final residue was then taken up in 9 M HCl to form the stock solution at $4\times 10^{-3}\text{ M }^{231}\text{Pa}$. For the 3 M HCl sample, a 50 μL of the stock solution was diluted in a 1.8 M HCl / 3.5 M HClO_4 mixture, resulting in a ^{231}Pa concentration of $0.6\times 10^{-4}\text{ M}$, as estimated by gamma spectrometry. The 12 M HCl sample was prepared by diluting 50 μL of the stock solution into 250 μL of concentrated HCl, yielding a final ^{231}Pa concentration of $2\times 10^{-4}\text{ M}$.

1.2 XAS data collection and analysis

XAS measurements at the protactinium L_3 edge (16 733 eV) were performed on the MARS beamline at SOLEIL synchrotron.^{S2,S3} The optical setup featured a water-cooled double-crystal monochromator (FMB Oxford), used to select the incident energy of the X-ray beam and for horizontal focusing, and two large water-cooled reflecting mirrors (IRELEC/SESO) that are used for rejecting the harmonics at high energy and vertical collimation and focusing. The monochromator was set with the Si(220) crystal and the mirrors with the Pt strips. Energy calibrations were conducted at the Yttrium K edge (17 038 eV). EXAFS spectra were collected in fluorescence mode with a multi-element silicon drift detector (MIRION).

Data analysis was performed with ATHENA and ARTEMIS codes from the Demeter 0.9.26 package.^{S4} The edge energy (E_0) was defined as the first inflection point of the absorption edge. Fourier transforms (FT) of k^3 -weighted EXAFS data were performed over the 2.2 to $10 \text{ \AA}^{-1}$ range with Hanning windows (maximum value limited by a glitch in the spectra). This restricts the number of parameters that can be reliably fitted. For this reason, the coordination numbers (N) for each path were fixed according to the proposed structures. EXAFS data were adjusted using phases and amplitudes determined with FEFF8 code^{S5} within ARTEMIS software using the DFT-optimized structures as starting points (See section 1.3). Fit quality was assessed using the reduced χ^2 and R -factor metrics provided by ARTEMIS.

1.3 Quantum Chemical simulations

To compute theoretical backscattering phase and amplitude functions with the FEFF8,^{S5} candidate structures with relevant stoichiometries were optimized with the ADF^{S6,S7} software (See Table 1 and Table S8). Geometry optimizations employed the PBE0 exchange-correlation functional,^{S8} incorporating solvent effects via the Conductor-like Screening Model (COSMO).^{S9-S11} A triple-zeta plus polarization (TZ2P) basis set^{S12} was used for all atoms and no core orbitals were frozen. Scalar relativistic (SR) effects were accounted for with zeroth-order regular approximation (ZORA) Hamiltonian.^{S13-S16} Harmonic vibrational frequency calculations were performed to confirm that the optimized structures correspond to true local minima and to obtain thermodynamic corrections to the Gibbs free energy (ΔG_{corr}). Spin-orbit coupling was not included in the geometry optimization since it was proved to have a small influence on the structures of Pa(V) complexes^{S17}. Different isomers were explored and their relative stability is reported in Table S4. The geometry of the most stable isomer within a given stoichiometry was used as input for FEFF8 calculations^{S5} to generate theoretical scattering paths for subsequent EXAFS fitting.

The relative stability of complexes with different stoichiometries were compared by cal-

culating the Gibbs free energy change, ΔG_r , at standard conditions ($T = 298\text{ K}$ and $P = 1\text{ bar}$). Following the approach adopted in recent studies on Pa(V) complexes,^{S17} ΔG_r was constructed from four additive components: the scalar relativistic reaction energy at the CCSD(T) level ($\Delta E_{CCSD(T)}$), the spin-orbit correction (ΔE_{SOC}), the thermodynamic correction (ΔG_{corr}), and the solvation free energy (ΔG_{sol}) obtained using the COSMO-RS model with BP-TZVP-25 parametrization of the COSMOtherm package:^{S18,S19}

$$\Delta G_r = \Delta E_{CCSD(T)} + \Delta E_{SOC} + \Delta G_{corr} + \Delta G_{sol}. \quad (1)$$

1.4 Ab initio molecular dynamics simulations

Ab initio molecular dynamics (AIMD) simulations of $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ hydrated by 128 water molecule in cubic box replicated periodically were performed with the ABINIT software package^{S20} and the projector augmented-wave (PAW) formalism.^{S21} The pseudopotentials of protactinium, oxygen and chlorine were generated for the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional^{S22} using the ATOMPAW code.^{S23} The AIMD simulations use the PBE functional with dispersion corrections.^{S24} Scalar relativistic effects have been included. Note that it was proven in an earlier study on the closed-shell Pa(V) that spin-orbit coupling marginally affects the structural and energetical properties.^{S25} An adequately kinetic energy cutoff of 762 eV was chosen to ensure fully converged total energies for all systems. Calculations on periodic systems of charged ions involve electrostatic interactions between images. The total energies were corrected and only the first order corrections were taken into account. First of all, atomic relaxations at 0 K without water molecules were performed in the gas phase. Next, AIMD simulations were performed using 128 water molecules in a cubic simulation box with periodic boundary conditions. All simulations were carried out in the isokinetic ensemble at 298 K at the density of water, i.e., 1 g cm^{-3} . The ionic temperature was controlled during the AIMD simulations using a velocity scaling procedure. All simulations were carried out at the Γ point of the Brillouin zone. In the first

4.4 RIXS maps and HERFD-XANES of Pa(V) solutions in HF and H₂C₂O₄

Two of the solutions listed in Table 4.1 were measured at the Pa L₃-edge using $2p3d$ RIXS (Figure 4.17a) and HERFD-XANES: Pa(V) in 0.5 M HF, which stabilizes the non-oxo species [PaF₇]²⁻, and in 1 M H₂C₂O₄, which stabilizes the oxo species [PaO(C₂O₄)₃]³⁻. These assignments are based on previous studies: [PaF₇]²⁻ was proposed by Le Naour et al. [30], and [PaO(C₂O₄)₃]³⁻ by Mendes et al. [26], with their structures confirmed by theoretical calculations and EXAFS (see Figure 4.18).

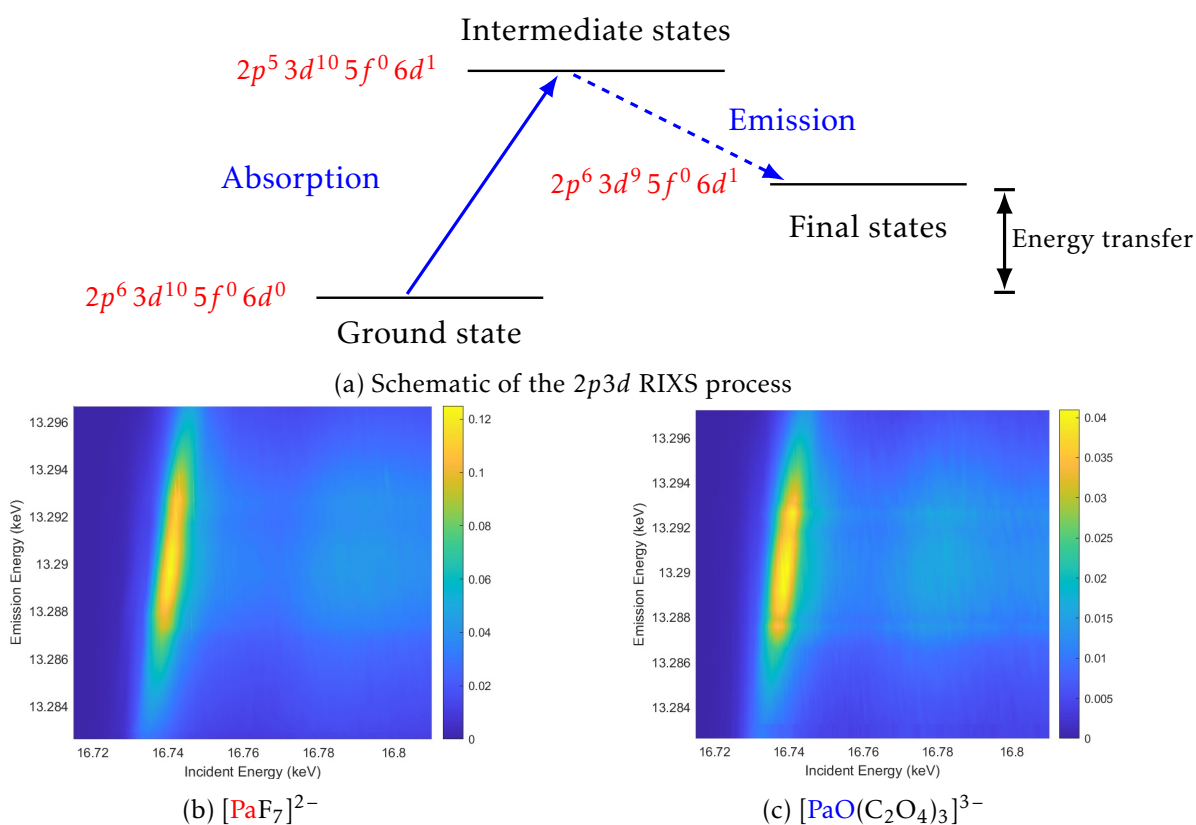


Figure 4.17: (a) $2p3d$ RIXS schematic at the Pa L₃-edge; (b-c) experimental RIXS maps of [PaF₇]²⁻ and [PaO(C₂O₄)₃]³⁻, performed at the MARS beamline of the SOLEIL synchrotron at the Pa L₃-edge during the experimental campaign conducted from February 14th to 19th, 2024.

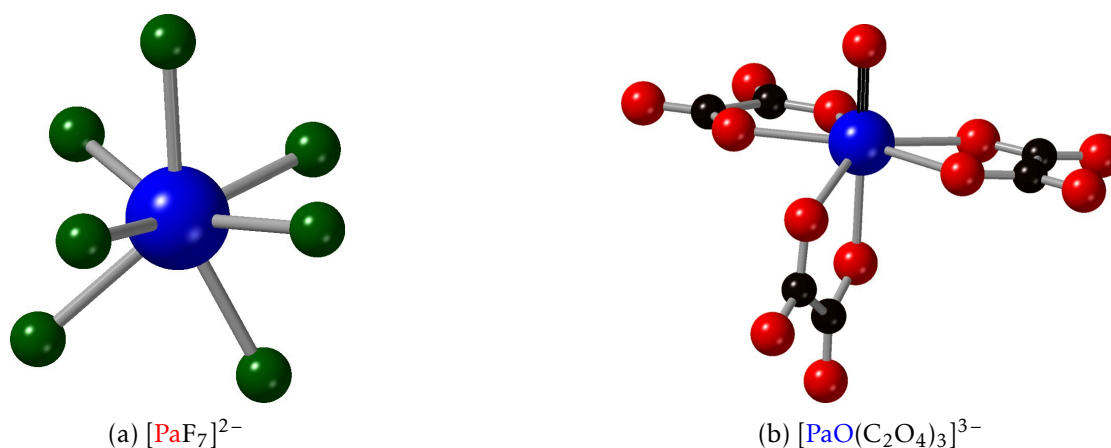


Figure 4.18: Optimized geometries of (a) $[\text{PaF}_7]^{2-}$ and (b) $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. The geometries were optimized in the COSMO solvent model at the scalar relativistic (SR-ZORA) level using the PBE0 functional.

The resulting $2p3d$ RIXS maps (see Figure 4.17b and Figure 4.17c) are very similar for the two complexes, indicating that the spectral response at the L_3 -edge is not strongly sensitive to the presence or absence of the $\text{Pa}\equiv\text{O}$ bond. In both cases, the main features appear at comparable incident and emission energies, and no distinctive signatures that could be attributed to the $\text{Pa}\equiv\text{O}$ bond are observed. This confirms that the information obtainable from RIXS at the L_3 -edge is limited for distinguishing between oxo and non-oxo Pa(V) species.

The HERFD-XANES spectra extracted at the maximum of the emission line (Figure 4.19) show, for both complexes, a sharp white line with a separation of about 1 eV, along with an additional weaker contribution separated by approximately 12 eV. The spectrum of $[\text{PaF}_7]^{2-}$ exhibits a weak pre-edge feature, which can be attributed to quadrupole transitions [6]. However, when examining the overall spectral profiles, no distinct signatures can be unambiguously assigned to the presence of a mono-oxo bond.

At the M_4 -edge, however, Luo [4] reported the first measurements of the same two Pa(V) complexes using $3d4f$ RIXS (Figure 4.20a) and HERFD-XANES. The $3d4f$ RIXS maps (see Figure 4.20b and Figure 4.20c in Figure 4.20) again show two features at the same incident energy (~ 3610 eV), separated by about 1 eV. HERFD-XANES spectra (see Figure 4.21) display a sharp white line near 3610 eV, with a shoulder about 1 eV above and a weaker feature near 3619 eV.

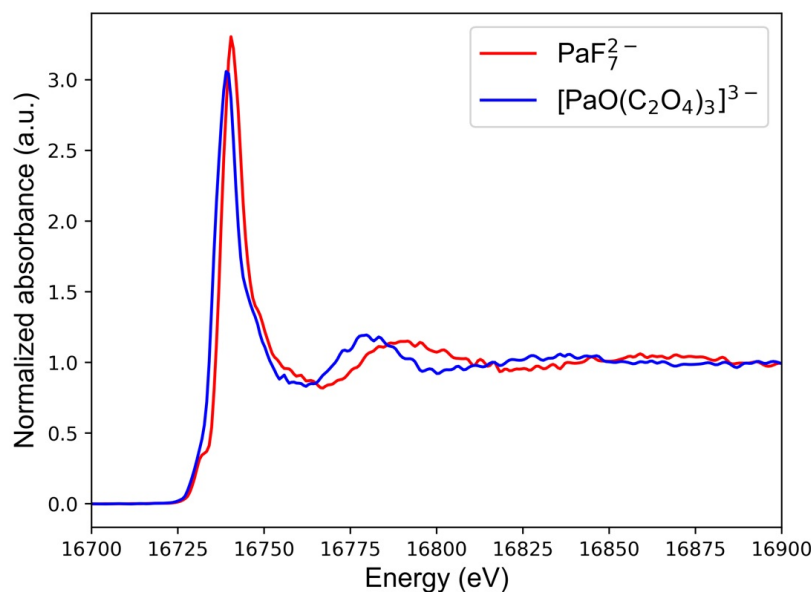


Figure 4.19: Pa L_3 -edge HERFD-XANES of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$.

At both the L_3 - and M_4 -edges, the experimental spectra do not reveal clear differences between the oxo and non-oxo complexes. Without the structural information provided by EXAFS, HERFD-XANES alone does not demonstrate the presence of the mono-oxo bond. This raises the question: if the mono-oxo bond is known to exist in oxalate complexes, why does no difference emerge in the XANES spectra, and can quantum-chemical methods account for this apparent similarity?

In this thesis, attention is therefore focused on the M_4 -edge, due to its well-resolved spectral features that are particularly sensitive to the 5f electronic configuration of Pa(V), thereby providing detailed insight into the nature of its valence orbitals. To address these questions, complementary simulations of XANES spectra are performed, using theoretical approaches such as TD-DFT and RASSCF, which have already proven successful in reproducing the spectral features of uranyl and plutonyl compounds [38–42]. In the same way, the combination of experimental data and theoretical simulations provides valuable information on the electronic structure and coordination environment of Pa(V),

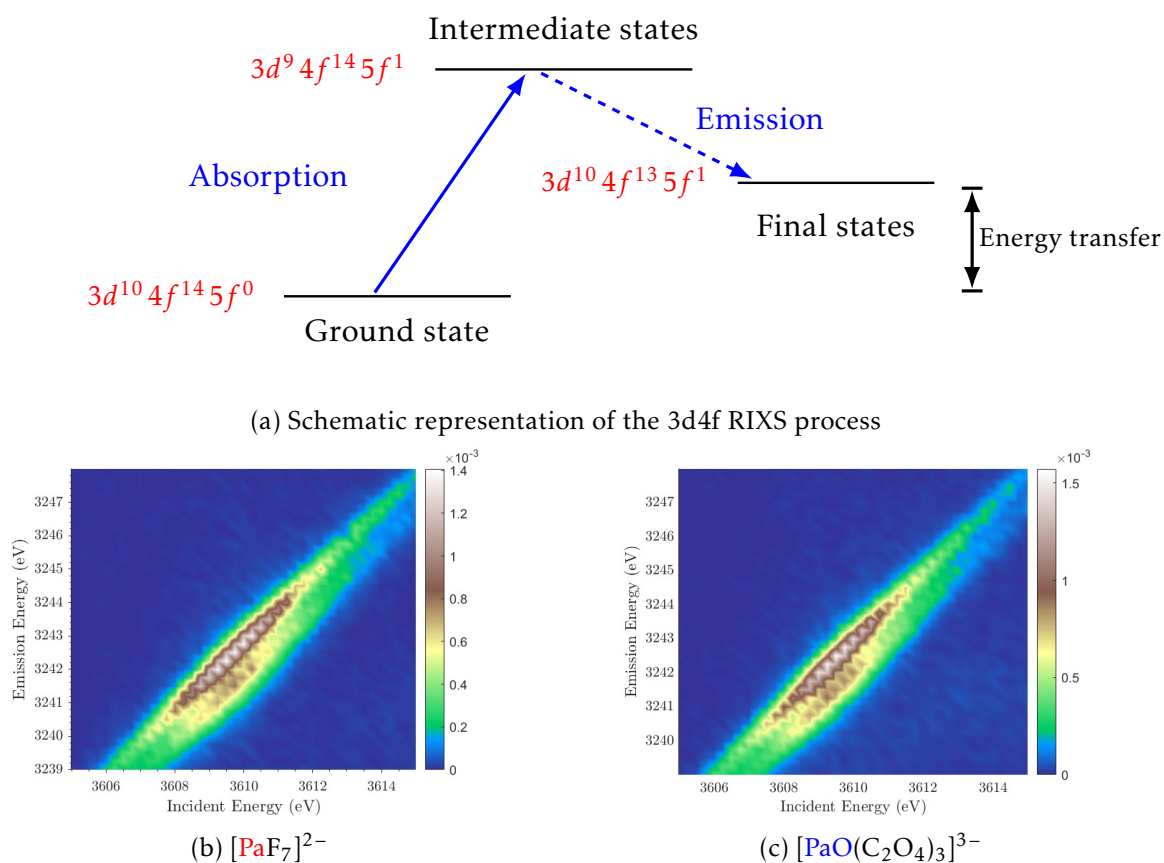


Figure 4.20: (a) Schematic illustration of the 3d4f RIXS process at the Pa M₄-edge. (b) and (c) Experimental RIXS maps of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, respectively, measured at the MARS beamline of the SOLEIL synchrotron in 2022 [4].

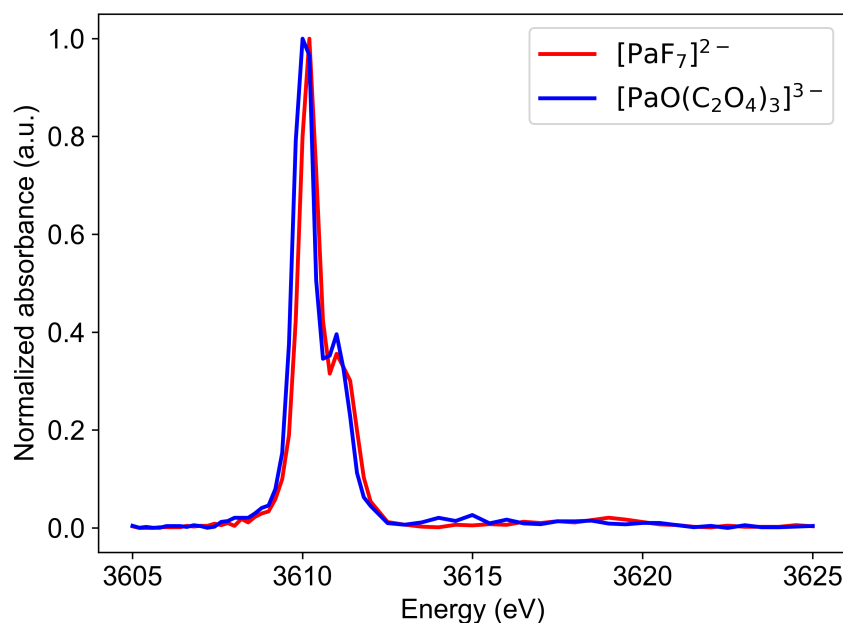


Figure 4.21: Pa M₄-edge HERFD-XANES of [PaF₇]²⁻ and [PaO(C₂O₄)₃]³⁻ [4].

thus contributing to a more comprehensive understanding of its chemical behavior. The following chapter presents these simulations of Pa(V) spectra and discusses their implications in detail (chapter 5).

4.5 Conclusion

In this chapter, the efficiency of X-ray absorption and emission spectroscopy for the characterization of actinide species is demonstrated. EXAFS measurements at Pa L₃-edge were effective for analyzing Pa(V) solutions in 3 M and 12 M HCl, revealing that oxo-chloro complexes with a coordination number of seven are the predominant species in both media. These results represent the first experimental observation of such complexes and are in excellent agreement with the predictions presented in chapter 3, where chloride was shown to stabilize the mono-oxo complex. Furthermore, this work provides the first instance where the experimentally determined Pa(V) mono-oxo bond length (1.83 Å) is in excellent agreement with theoretical modeling.

The combined RIXS and HERFD-XANES investigations at the L_3 - and M_4 -edges did not reveal significant experimental differences between oxo and non-oxo complexes. However, the M_4 -edge provides sharper and better resolved spectral features that are directly sensitive to the unoccupied 5f states of Pa(V). Building on this, the next chapter turns to theoretical simulations of M_4 -edge XANES spectra using advanced electronic-structure methods. By complementing the experimental data with theory, these simulations provide a deeper understanding of the electronic structure, bonding, and transition character of Pa(V) complexes, thereby advancing our overall insight into the chemical behavior of this elusive actinide.

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The core-excited states of protactinium(V) complexes

5.0.1 Introduction

In chapter 4, section 4.4, we presented the HERFD-XANES spectra at the Pa L_3 - and M_4 -edges, together with the corresponding RIXS maps, for $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. As discussed, the combined RIXS and HERFD-XANES investigations at both edges did not reveal significant experimental differences between oxo and non-oxo complexes. We therefore proceed here to simulate their XANES spectra at the M_4 edge and analyze the nature of the electronic transitions involved, with the aim of rationalizing the experimental spectral profiles.

Theoretical simulations played an important role in unraveling the actinides complexes spectra. Tamm-Dancoff approximation within the Time-Dependent Density Functional Theory (TDA-TDDFT), when combined with a two-component Hamiltonian accounting for both scalar and spin-orbit relativistic effects, has been shown to reproduce the gross features of the M_4 -edge in uranyl and related systems [1, 2]. In such TDDFT calculations, the choice of functional is crucial for correctly placing the spectral features. In this respect, the CAM-B3LYP functional has been proven, through comparison with four-component damped response theory, to provide reliable relative peak positions while requiring con-

siderably fewer computational resources. Its performance is often comparable to that of more sophisticated multireference approaches such as RASSCF [3, 4]. However, the latter are needed for a detailed treatment of many-body effects, since spin-orbit-coupled CASSCF can capture excitations beyond the single-excitation manifold accessible to DFT, such as shake-up processes and changes in orbital hybridization between actinide 5f and ligand orbitals. Indeed, studies employing spin-orbit-coupled CASSCF with perturbative correlation treatments (CASPT2) have enabled clear assignments of spectral components to specific 5f-derived molecular orbitals. For example, the pioneering work of Sergentu et al. reproduced the HERFD-XANES spectra reported by Vitova et al. [6] with high accuracy. More recently, Polly et al. [7] and Stanistreet-Welsh and Keridge [3] confirmed the robustness of such multireference simulations, with Polly et al. [7] further extending the methodology to compute complete UO_2^{2+} 3d4f RIXS maps in excellent agreement with experiment [6]. Remembering that no significant difference was observed experimentally in the XANES spectra and that system with a unique oxo-bond was not studied so far, we propose here to investigate the Pa M_4 -edge theoretical XANES spectrum using both relativistic TDDFT and multireference methods. As a first step, we consider the bare ions $[\text{Pa}]^{5+}$ and $[\text{PaO}]^{3+}$, and compare the latter with the UO_2^{2+} cation. We then extend our analysis to the complexes $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$.

Before discussing the results, we first describe the computational protocols adopted in the TDDFT and multireference (RASSCF and RASPT2) approaches.

5.0.2 Computational Modeling

Structures

As stated in the introduction, the main objective of this work is to evaluate the XANES spectra of the bare ions Pa^{5+} and PaO^{3+} , as well as a set of complexes that either contain a $\text{Pa}\equiv\text{O}$ unit or do not, which include $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. The complexes are shown in Figure 5.1 and their geometries were optimized at the SR-ZORA/PBE0 level with TZ2P basis set representing the water solvent with the COSMO implicit model.

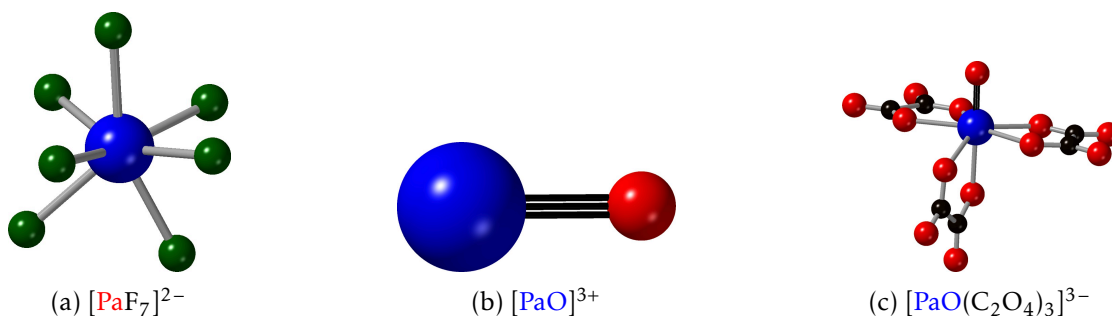


Figure 5.1: Optimized geometries of selected **Pa** and **PaO** complexes, computed at the SR-ZORA/PBE0/TZ2P level in the COSMO solvent model. Color code: navy blue (Pa), dark green (F), red (O), black (C), white (H).

5.0.3 TD-DFT Calculations

Using the TDA-TDDFT, we applied the computational protocol developed by Misael et al. [2]. In this approach, the long-range corrected CAM-B3LYP functional was used. Slater-type basis sets of triple zeta quality (TZ2P) were used for all atoms, guided by a benchmarking of various basis sets, which will be discussed separately in subsubsection 5.0.3. Relativistic effects were accounted for using the exact two-component (X2C) Hamiltonian, which provides core orbital energetics in very close agreement with those obtained from the four-component Dirac-Coulomb Hamiltonian [8]. Throughout this work, we refer to this protocol as 2c-TDA-CAMB3LYP. A Gaussian nuclear model was adopted in all calculations. All simulations were performed with the Amsterdam Density Functional (ADF) package [9].

The Pa M_4 -edge excitations were accessed using the restricted energy window (REW) projection, restricting excitations to those originating from the Pa $3d_{3/2}$ core orbitals. Further details of this protocol are discussed in the following section. The orbital character of the transitions was determined by analyzing the corresponding Natural Transition Orbitals (NTOs) [10] and plotting them using ADFView. Spectral profiles were obtained by convolving the computed energies and oscillator strengths with a Lorentzian function with a full width at half maximum (FWHM) of 0.3 eV and 1.5 eV.

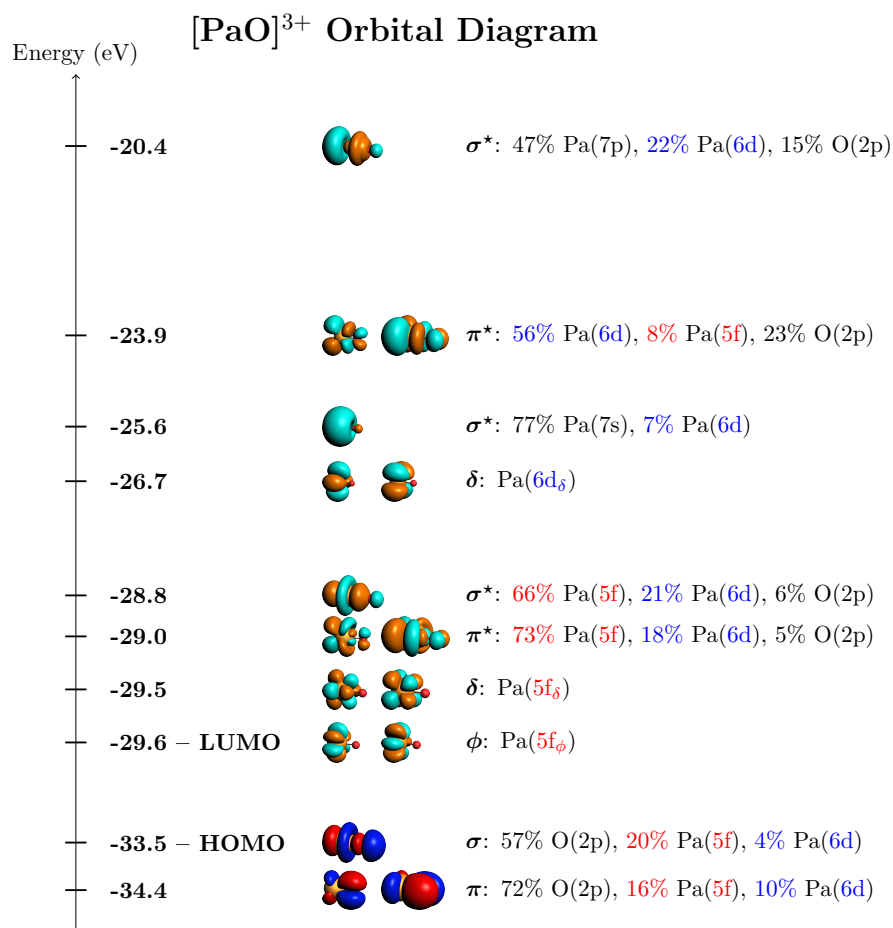


Figure 5.2: Schematic orbital diagram of $[\text{PaO}]^{3+}$, computed at the scalar relativistic level with the SAOP functional. The atomic contributions (weight in %) are highlighted in red for Pa(5f), blue for Pa(6d) and black for other orbitals (Pa(7s), Pa(7p), O(2p)).

Computational protocol

To obtain a representative spectrum, a large number of excited states (typically more than 200 states) must be computed, which poses a significant challenge due to the high computational cost. To make these calculations feasible, approximations previously applied by Misael et al. [2] were adopted. These include selecting the single-orbital transitions with oscillator strengths larger than a cutoff value and reducing the number of virtual orbitals considered in the calculations. The impact of these approximations was first assessed using the TZ2P basis set, and the influence of the basis set itself is discussed in the following sections.

Oscillator strength cutoff

Following the approach previously employed by Misael et al. [2], single-orbital transitions with oscillator strengths larger than the cutoff value of 10^{-5} was therefore applied in the present work. The idea is to reduce the computational effort by decreasing the number single-orbital transitions considered in the Davidson diagonalization without compromising the reliability of the spectral features. Comparison of the spectra generated with and without this threshold with TZ2P basis sets confirmed that the cutoff had no noticeable effect on the resulting profiles for $[\text{PaO}]^{3+}$ and $[\text{PaF}_7]^{2-}$, (see Figure 5.6c and Figure 5.8c). In both cases, the spectra labeled OS-5 (the cutoff value of 10^{-5}) are identical to those without any oscillator strength restriction, labeled *Full VS* (neither oscillator strength cutoff nor virtual space restriction applied), validating the use of this cutoff. The same cutoff was therefore applied to all other complexes studied in this work.

Restriction of virtual orbitals

A cutoff of $10 E_h$ (≈ 272 eV) was imposed on the virtual orbital space, thus excluding very high-energy virtual orbitals that do not contribute significantly to the low-energy excitations of interest. The validity of this approximation was verified for $[\text{PaO}]^{3+}$, where the analysis of the LUMOs (see Figure 5.2) considering that the orbitals involved in the Pa M_4 -edge XAS transitions are

essentially those near the Fermi level. Further evidence is provided by the spectra shown in Figure 5.6c and Figure 5.8c, where the spectra labeled *Full VS* (neither oscillator strength cutoff nor virtual space restriction applied) and *OS-5-VS* (oscillator strength cutoff (10^{-5}) and virtual-space restriction up to 10 Ha) are essentially identical for both $[\text{PaO}]^{3+}$ and $[\text{PaF}_7]^{2-}$. These results demonstrate that restricting the virtual space is a valid approximation, which was therefore applied to all other complexes considered in this study.

Basis set effect

After confirming that the oscillator strength cutoff and virtual space restriction do not affect the computed spectral profiles, we next examined the influence of the atomic basis set quality. Calculations were carried out with increasingly large DZP, TZP, TZ2P, and QZ4P basis sets on the bare ions $[\text{Pa}]^{5+}$ and $[\text{PaO}]^{3+}$ (see Figure 5.3a and Figure 5.6a). We found that DZP, TZP, and TZ2P yield identical excitation energies, while QZ4P produces a systematic shift of approximately 0.7 eV to lower energies. When the spectra are aligned by shifting the peak positions relative to the QZ4P reference (see Figure 5.3b and Figure 5.6b), the resulting spectral profiles are essentially identical regardless of the basis set employed. The same trend is observed for $[\text{PaF}_7]^{2-}$.

In terms of computational cost, however, the QZ4P basis set is significantly more demanding, particularly for complexes (the calculation for $[\text{PaF}_7]^{2-}$ required 42 hours on 32 cores, compared to 7 hours for TZ2P). Therefore, TZ2P was selected for all subsequent calculations on the complexes, as it provides an excellent balance between accuracy and efficiency. Furthermore, since the absolute excitation energies require an empirical alignment with experiment (as is also the case for uranyl), the relative spectral features obtained with TZ2P are fully reliable for the purposes of this study.

5.0.4 RASSCF Calculations

Multiconfigurational wavefunction calculations were performed using the restricted active space self-consistent field (RASSCF) method. Dynamical correlation was subsequently included through second-order perturbation theory

(RASPT2) with an IPEA shift of 0.0 and an imaginary shift of $0.2 E_h$. The second-order Douglas-Kroll-Hess Hamiltonian (DKH2) was employed together with all-electron ANO-RCC-VTZP basis sets of triple-zeta quality for all atoms.

Both scalar relativistic effects and spin-orbit coupling were taken into account. Spin-orbit interactions were evaluated within the restricted active space state interaction (RASSI) framework, including all relevant spin states in the interaction. All calculations were performed in C_1 symmetry (without symmetry restrictions), and supersymmetry was employed to allow orbital rotations. All calculations were carried out using the OpenMolcas package, version 25.02 [11–13]. The choice of active spaces is discussed below.

Finally, spin-orbit natural orbitals were calculated for all the core excited states in order to characterize the nature of the electronic transitions [14, 15].

Choice of active space

As discussed in section 2.13, within RASSCF the complete active space (CAS) is divided into three restricted active spaces (RAS), called RAS1, RAS2, and RAS3. For the XANES simulations, the core orbitals were defined in RAS1 and the valence virtual orbitals in RAS3. One hole was allowed in RAS1 and one electron in RAS3, restricting the wavefunction to include only single excitations. Since RAS1 contains the spin-orbit free 3d core orbitals, both the M_4 and M_5 edges are formally computed, but our analysis was limited to the high-energy M_4 edge manifold.

When defining the active spaces for the different complexes, it is essential to assess the consistency between RASSCF and RASPT2. RASPT2 requires a well-defined reference at the RASSCF level, and significant discrepancies between the two indicate that PT2 corrections affect different states unevenly.

For the $[\text{Pa}]^{5+}$ M_4 -edge calculations, the 5f orbitals were placed in RAS3.

For the $[\text{PaO}]^{3+}$ M_4 -edge calculations, both the 5f and 6d orbitals were included in RAS3. Due to the absence of inversion symmetry, the anti-bonding orbitals exhibit mixing of 5f and 6d character (see Figure 5.2). A comparison between the RASSCF and RASPT2 results revealed a splitting of the first absorption peak at the RASPT2 level (Figure 5.10a), a sign of an unbalanced choice of

the active space. Indeed, analysis of the character of the computed transitions indicated contributions from Pa 7s orbitals. However, including the 7s orbitals in RAS3 did not resolve the discrepancy between the RASSCF and RASPT2 spectra (Figure 5.10b). By contrast, including the bonding σ and π orbitals (formed from the combination of Pa 5f/6d and O 2p orbitals) in RAS2, allowed us to reach the expected overall agreement between RASSCF and RASPT2 (Figure 5.10c).

For the $[\text{PaF}_7]^{2-}$ complex, both the 5f and 6d orbitals were included in RAS3.

In our calculations, the RASPT2 excitation energies are systematically shifted to lower values relative to RASSCF, reflecting the importance of dynamical correlation, an effect also reported in uranyl simulations [7]. Therefore, in the following discussion, we focus exclusively on the RASPT2 results.

The following table summarizes the active spaces defined and the number of roots calculated for each system.

System	RAS1	RAS2	RAS3	Number of roots	
				Singlets	Triplets
$[\text{Pa}]^{5+}$	3d	–	5f	60	60
$[\text{PaO}]^{3+}$	3d	Pa 5f/6d, O 2p (σ and π bonding)	5f, 6d	60	60
$[\text{PaF}_7]^{2-}$	3d	–	5f, 6d	60	60

Table 5.1: Summary of the active spaces defined and the number of roots (singlets and triplets) calculated for each system.

5.1 Results

5.1.1 M_4 - edge of $[\text{Pa}]^{5+}$

As discussed above, before simulating the XANES spectra of the protactinium complexes, we first simulate the bare ions $[\text{Pa}]^{5+}$ and $[\text{PaO}]^{3+}$.

Looking at the M_4 -edge spectrum of $[\text{Pa}]^{5+}$ simulated using SO-RASPT2 (Figure 5.4), we observe a single peak around 3632.3 eV, corresponding to the transition from the $3d_{3/2}$ core orbitals to the 5f orbitals. A similar result is obtained with 2c-TDA-CAMB3LYP, where only one peak is observed (Figure 5.3a,

values are reported in 5.2). This consistency between multireference and TDDFT approaches indicates that the spectral profile of $[\text{Pa}]^{5+}$ is dominated by a well-defined $3d_{3/2} \rightarrow 5f$ transition.

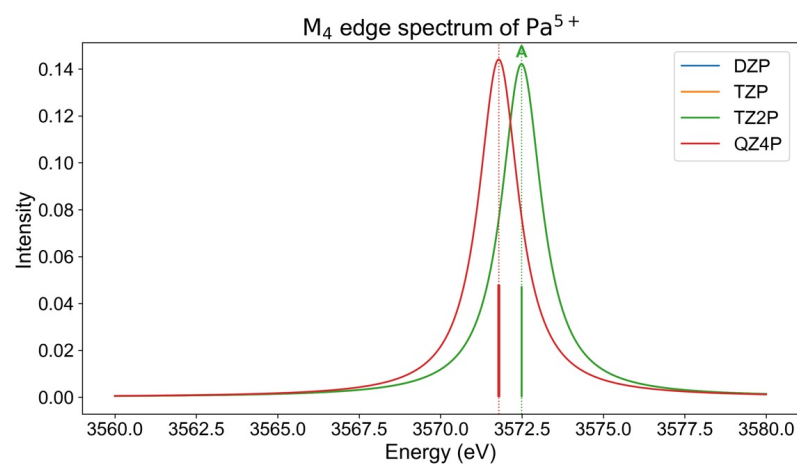
Method	Basis set	$[\text{Pa}]^{5+}$	$[\text{PaF}_7]^{2-}$
		A	A
2c-TDA-CAMB3LYP	DZP	3570.4	3570.4
	TZP	3572.5	3570.4
	TZ2P	3572.5	3570.4
	QZ4P	3571.8	3569.8
SO-RASSCF	VTZP	3633.6	3631.4
SO-RASPT2 ¹	VTZP	3632.3	3627.8

Table 5.2: Absolute energies in eV of the main peak A in the Pa M_4 -edge of $[\text{Pa}]^{5+}$ and $[\text{PaF}_7]^{2-}$. Comparison for DZ, TZP, TZ2P and QZ4P basis sets in TDA-CAMB3LYP calculations and for VTZP basis sets at the SO-RASSCF and SO-RASPT2 levels

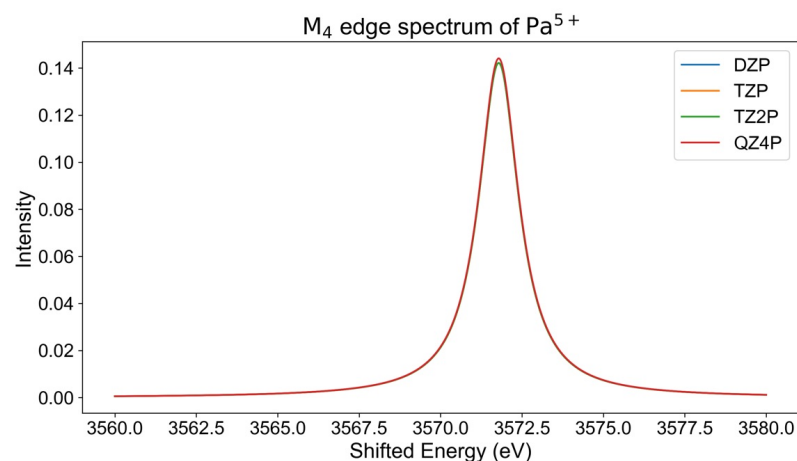
5.1.2 M_4 -edge of $[\text{PaO}]^{3+}$

For $[\text{PaO}]^{3+}$, the SO-RASPT2 calculations predict one strong peak around 3630 eV, denoted peak A, and a weaker one around 3640 eV, denoted peak B (Figure 5.7a). By examining the stick spectrum, peak A can be resolved into three components when convoluted with a FWHM of 0.3 eV (Figure 5.7b). These sub-peaks are labeled A_1 , A_2 , and A_3 .

- Peak A_1 corresponds mainly to transitions into the Pa non-bonding $5f_\delta$ and $5f_\phi$ orbitals.
- Peak A_2 corresponds to the antibonding π^* with highest contribution from Pa 5f orbital (84 %), and a smaller contribution from Pa 6d orbitals (8 %) and O 2p (8 %).
- Peak A_3 corresponds to the antibonding σ^* with highest contribution from Pa 5f orbital (62 %), again with small contributions from Pa 6d orbitals (24 %) and O 2p (12 %).



(a) Basis set convergence



(b) Basis set convergence, peak position shifted with respect to the QZ4P basis set

Figure 5.3: 2c-TDA-CAM-B3LYP Pa M_4 -edge XAS of $[\text{Pa}]^{5+}$ with DZP, TZP, TZ2P, and QZ4P (full virtual orbital space; no oscillator strength cutoff). A Lorentzian broadening with FWHM 1.5 eV is applied. **(a)** Basis set convergence. **(b)** DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions.

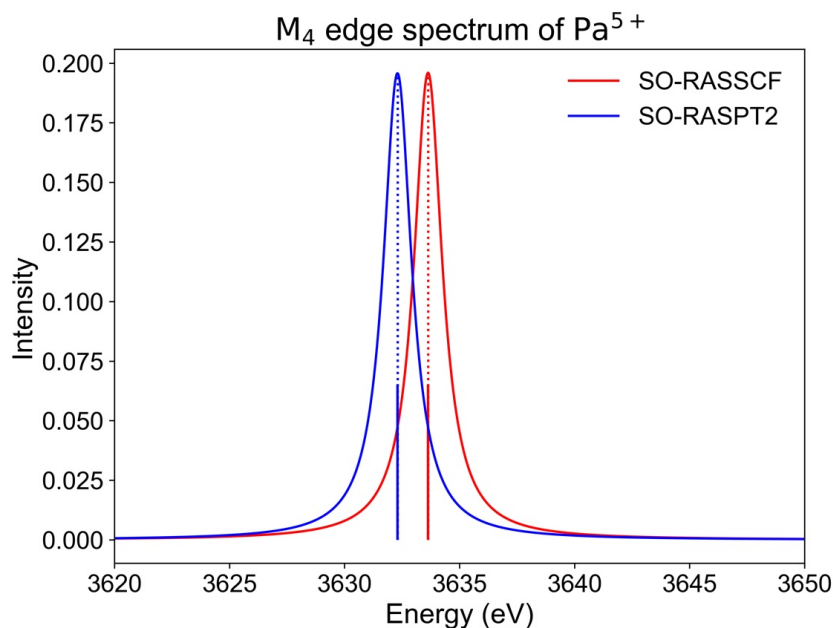


Figure 5.4: M_4 -edge spectrum of $[\text{Pa}]^{5+}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.

Peak B is assigned to transitions into a higher-lying π^* orbital with the highest contribution from Pa 6d orbitals (71 %) with small contributions from Pa 5f orbitals (5 %) and O 2p (23 %). The reduced Pa 5f contribution compared to that of peak A accounts for its weaker intensity. A summary of the SO-RASPT2 assignments is provided in Table 5.3.

Similar results are obtained with 2c-TDA-CAMB3LYP, as shown in Figure 5.5 and summarized in Table 5.4.

5.1.3 M_4 -edge of $[\text{PaF}_7]^{2-}$

For the M_4 -edge spectrum of $[\text{PaF}_7]^{2-}$ calculated at the SO-RASPT2 level (Figure 5.9), a single peak is observed at 3627.8 eV. This peak corresponds to transitions into the Pa-centered 5f orbitals, with only a minor contribution (about 6 % from the F 2p orbitals (Table 5.6).

These results indicate a negligible degree of charge transfer, and essentially no ligand effect, since the spectra of $[\text{PaF}_7]^{2-}$ and $[\text{Pa}]^{5+}$ display the same profile.

Peak	E [eV]	f_{osc}	Contribution	Orbital(s)
A ₁	3628.7	0.017	NB: Pa(5f _{ϕ})	
A ₁	3628.8	0.009	NB: Pa(5f _{δ})	
A ₂	3629.3	0.005	π^* : 8% Pa(6d), 84% Pa(5f), 8% O(2p)	
A ₂	3629.6	0.020	π^* : 8% Pa(6d); 84% Pa(5f); 8% O(2p)	
A ₃	3630.4	0.012	σ^* : 24% Pa(6d), 62% Pa(5f), 12% O	
B	3637.8	0.001	π^* : 71% Pa(6d), 5% Pa(5f), 23% O(2p)	

Table 5.3: Summary of electronic transitions contributing to the M₄-edge of PaO³⁺, computed at the SO-RASPT2 level. Dominant orbital characters (5f, 6d, and O 2p) and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the 3d_{3/2} electron is excited into. The peak labels correspond to Figure 5.7b.

Peak	E [eV]	f_{osc}	Contribution	Orbital(s)
A ₁	3568.1	0.001	51% NB Pa(5f _δ)	
			46% NB Pa(5f _φ)	
A ₁	3568.6	0.022	36% NB Pa(5f _φ)	
			30% NB Pa(5f _δ)	
			21% σ* [63% Pa(5f); 18% Pa(6d); 10% O(2p)]	
A ₁	3568.6	0.004	NB Pa(5f _δ)	
A ₂	3569.5	0.014	58% σ* [63% Pa(5f); 18% Pa(6d); 10% O(2p)]	
			34% π* [71% Pa(5f); 16% Pa(6d); 10% O(2p)]	
A ₂	3569.7	0.036	51% π* [71% Pa(5f); 16% Pa(6d); 6% O(2p)]	
			17% σ* [63% Pa(5f); 18% Pa(6d); 10% O(2p)]	
			13% NB Pa(5f _δ)	
A ₃	3570.0	0.024	48% σ* [63% Pa(5f); 18% Pa(6d); 10% O(2p)]	
			34% π* [71% Pa(5f); 16% Pa(6d); 6% O(2p)]	
B	3576.5	0.003	π* [56% Pa(6d); 8% O(2p)]	

Table 5.4: Summary of electronic transitions contributing to the M₄-edge of [PaO]³⁺, computed at the SO-CAM-B3LYP level with TZ2P basis set. Dominant orbital characters (5f, 6d, and O 2p) and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the 3d_{3/2} electron is excited into. The peak labels correspond to Figure 5.5.

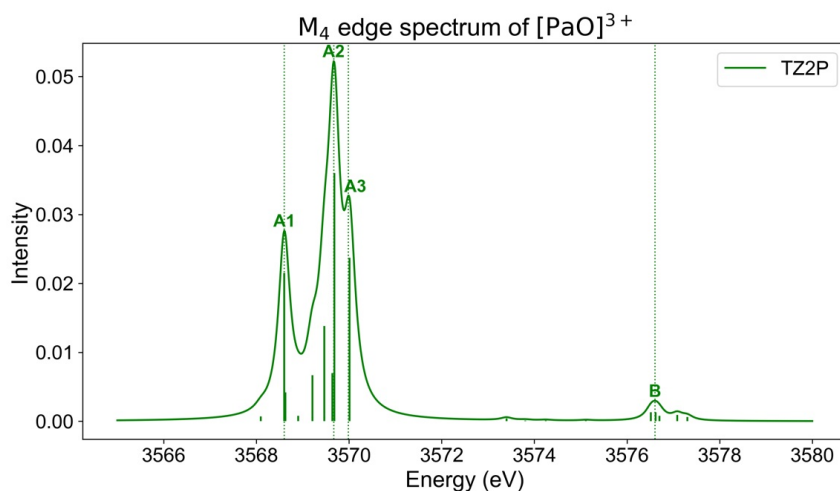
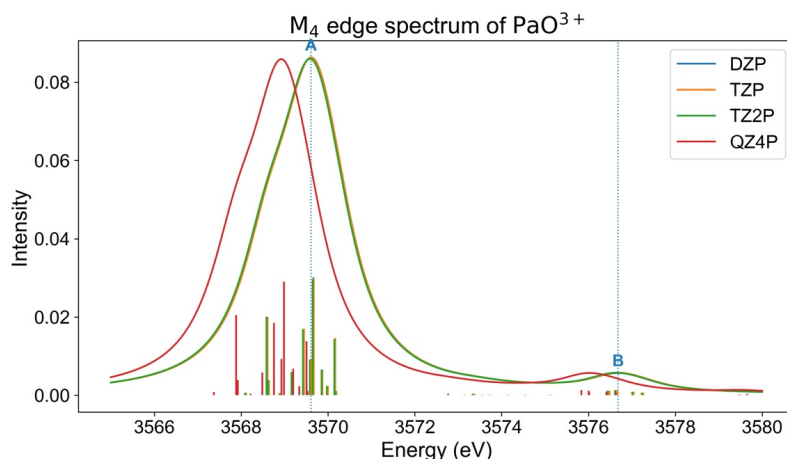


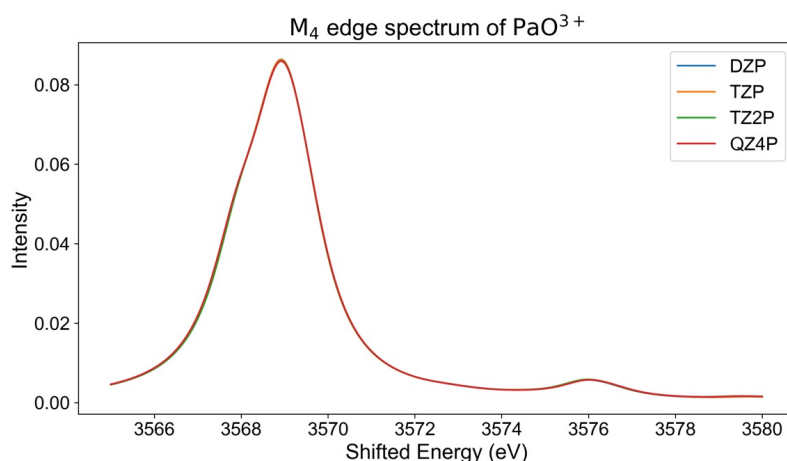
Figure 5.5: M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the 2c-TDA-CAMB3LYP level of theory with TZ2P basis set, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 0.3 eV.

Method	Basis set	$[\text{PaO}]^{3+}$ $r(\text{Pa}-\text{O}_{\text{oxo}})=1.710 \text{ \AA}$			$[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ $r(\text{Pa}-\text{O}_{\text{oxo}})=1.858 \text{ \AA}$
		A	B	B-A	A
TDA-CAMB3LYP	DZP	3569.6	3576.7	7.1	3569.7
	TZP	3569.6	3576.7	7.1	
	TZ2P	3569.6	3576.6	7.0	
	QZ4P	3568.9	3576.0	7.1	
SO-RASSCF	VTZP	3631.1	3639.8	8.6	
SO-RASPT2 ¹	VTZP	3629.5	3638.0	8.5	

Table 5.5: Absolute energies in eV of the main peaks A and B in the Pa M_4 -edge of $[\text{PaO}]^{3+}$ and of the main peak A in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. The B peak is barely visible in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. Comparison for DZP, TZP, TZ2P and QZ4P basis sets in 2c-TDA-CAMB3LYP calculations and for VTZP basis sets at the SO-RASSCF and SO-RASPT2 levels.



(a) Basis set convergence



(b) Basis set convergence, peak position shifted with respect to the QZ4P basis set

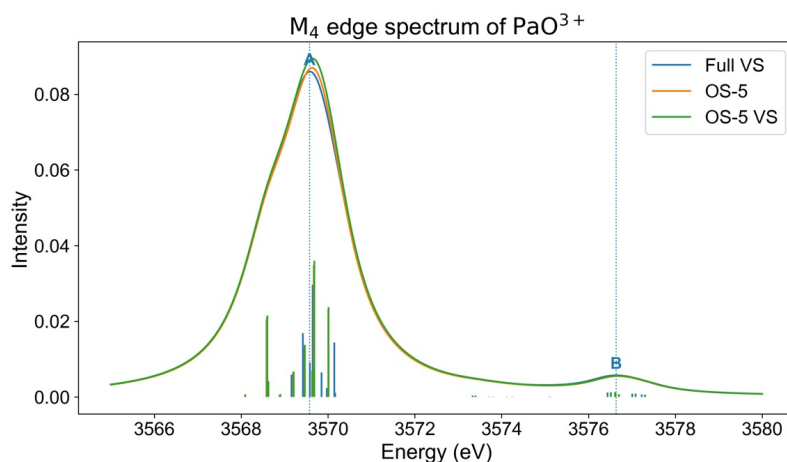
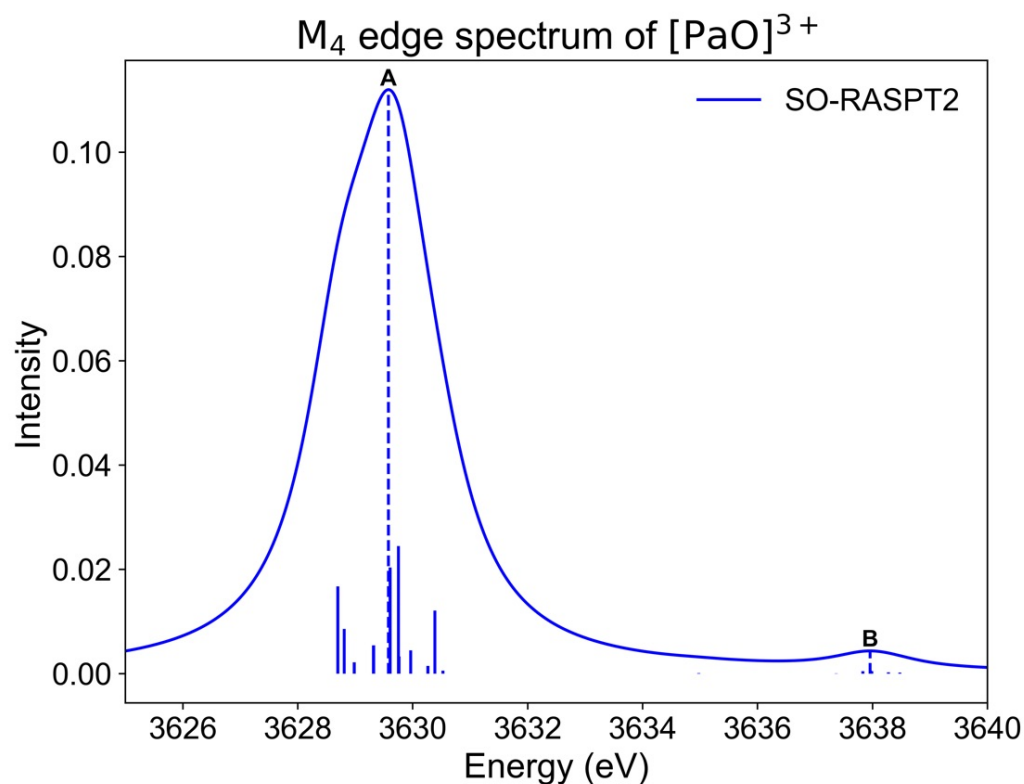
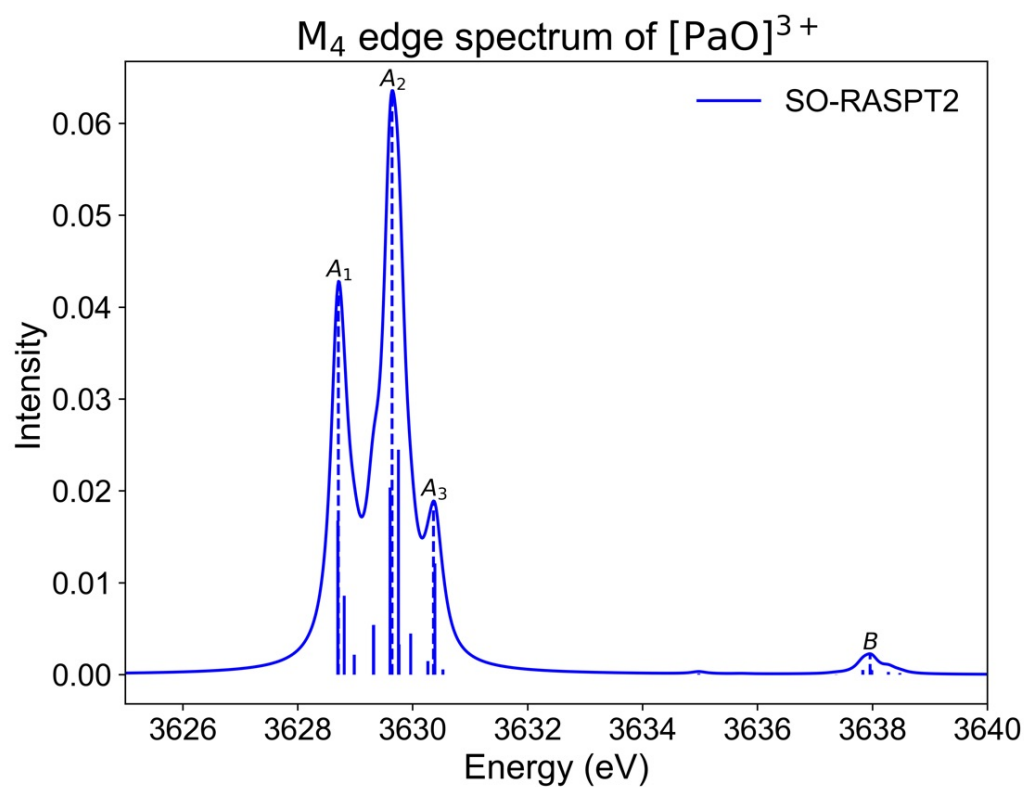
(c) Effect of the $\tau_{osc} > 1e^{-5}$ selection for TZ2P basis sets

Figure 5.6: Comparison of 2c-TDA-CAMB3LYP XAS at the Pa M_4 -edge of $[\text{PaO}]^{3+}$ for DZP, TZP, TZ2P, and QZ4P basis sets, using virtual space restrictions and an oscillator strength cutoff. A Lorentzian broadening with FWHM 1.5 eV is applied. **(a)** Basis set convergence. **(b)** DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions. **(c)** Effect of the selection $\tau_{osc} > 10^{-5}$ (OS-5) and the virtual space restriction (OS-5-VS), compared to neither oscillator strength cutoff nor virtual space restriction (Full-VS), for the TZ2P basis set.



(a) FWHM = 1.5 eV



(b) FWHM = 0.3 eV

Figure 5.7: M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the SO-RASPT2 level of theory. Lorentzian broadening parameter is set to a FWHM of either 1.5 eV or 0.3 eV.

Even in terms of absolute energies, the values are very close, as summarized in Table 5.2. Importantly, the M_4 -edge spectrum of $[\text{PaF}_7]^{2-}$ exhibits the same profile when computed with both TD-DFT and SO-RASPT2, further reinforcing our confidence in these results.

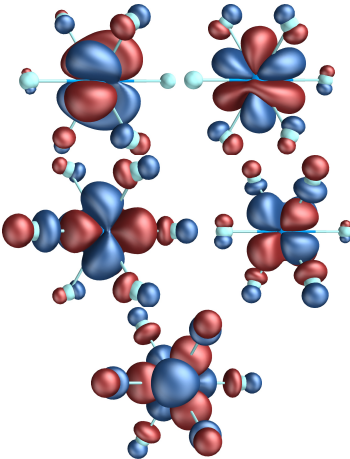
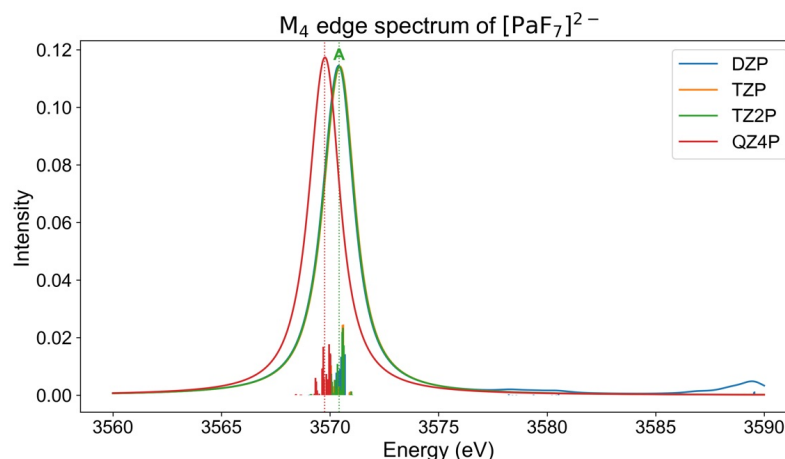
E [eV]	f_{osc}	Assignment	Orbital(s)
3627.6	0.025	98% Pa(5f); 2% F(2p)	
3628.0	0.016	98% Pa(5f); 2% F(2p)	
3628.3	0.012	94% Pa(5f); 6% F(2p)	

Table 5.6: Summary of electronic transitions contributing to the M_4 -edge of $[\text{PaF}_7]^{2-}$, computed at the SO-RASPT2 level. Pa and fluoride contributions and dipole transition strengths (f_{osc}) are listed alongside visualizations of the corresponding virtual orbitals the $3d_{3/2}$ electron is excited into.

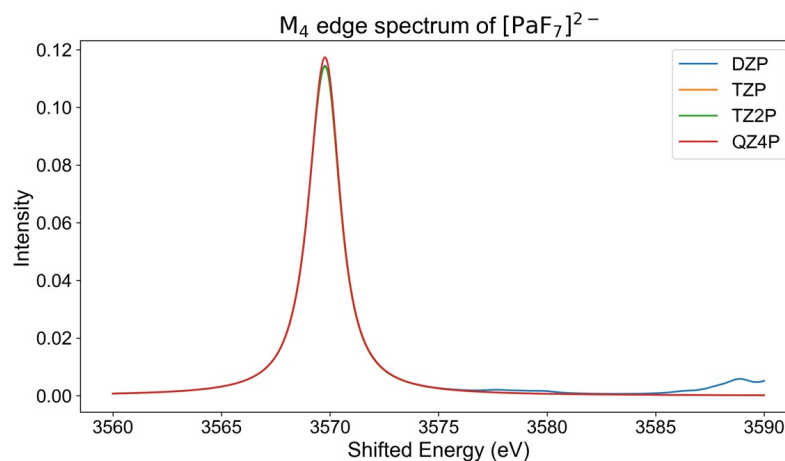
5.1.4 M_4 -edge of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$

Before discussing the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ M_4 -edge spectrum, it is important to note, as discussed in chapter 3, that there is a discrepancy between the calculated mono-oxo bond distance (1.858 Å) and the experimental value (1.75 Å). Since such a difference can affect the M_4 -edge spectral profile of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, we tested the influence of the mono-oxo bond distance on the M_4 -edge spectrum of $[\text{PaO}]^{3+}$. Three distances were tested: 1.710 Å, corresponding to the mono-oxo bond in the bare ion $[\text{PaO}]^{3+}$; 1.858 Å, corresponding to the bond in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$; and an intermediate value of 1.780 Å. These tests were performed using the 2c-TDA-CAMB3LYP protocol.

As shown in Figure 5.11, the spectral profiles obtained with these three



(a) Basis set convergence



(b) Basis set convergence, peak position shifted with respect to the QZ4P basis set

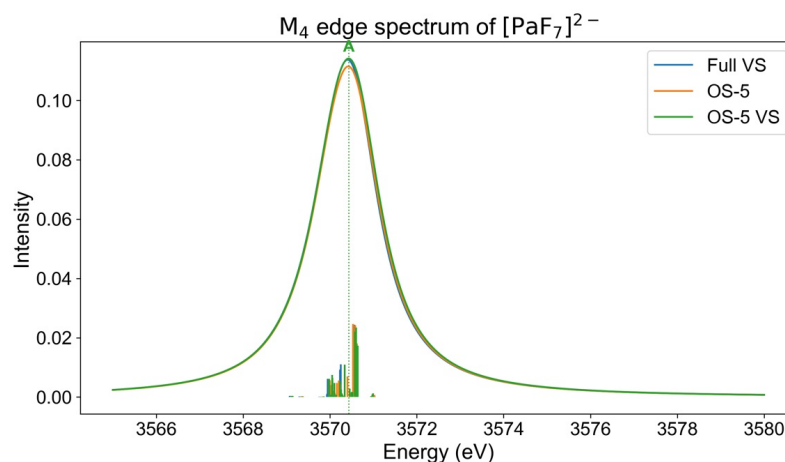
(c) Effect of the $\tau_{osc} > 10^{-5}$ selection for TZ2P basis sets

Figure 5.8: Comparison of 2c-TDA-CAMB3LYP XAS at the Pa M_4 -edge of $[\text{PaF}_7]^{2-}$ for DZP, TZP, TZ2P, and QZ4P basis sets, using virtual space restrictions and an oscillator strength cutoff. A Lorentzian broadening with FWHM 1.5 eV is applied. **(a)** Basis set convergence. **(b)** DZP, TZP, and TZ2P spectra are shifted with respect to QZ4P (reference) to compare peak positions. **(c)** Effect of the selection $\tau_{osc} > 10^{-5}$ (OS-5) and the virtual space restriction (OS-5-VS), compared to neither oscillator strength cutoff nor virtual space restriction (Full-VS), for the TZ2P basis set.

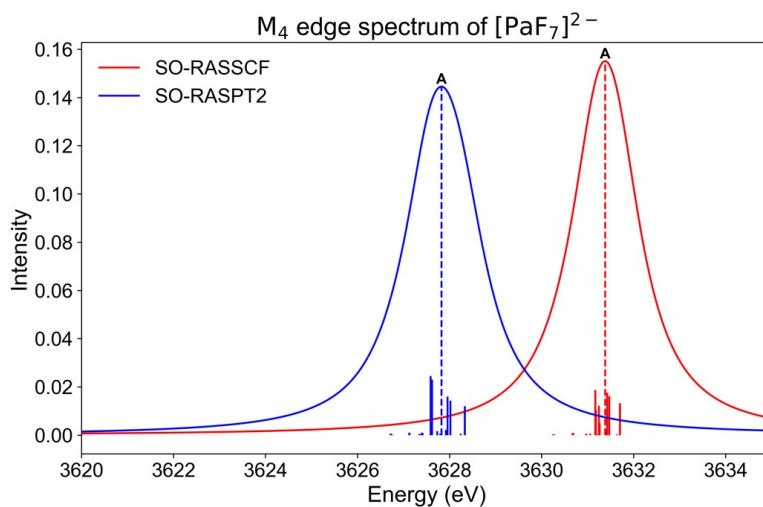


Figure 5.9: M_4 -edge spectrum of $[\text{PaF}_7]^{2-}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.

distances are nearly identical. Only a slight shift of peak B is observed at 1.858 Å, but the overall spectral features remain unchanged. Therefore, the 2c-TDA-CAMB3LYP calculations of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ are carried out with the optimized geometry, where the mono-oxo bond distance is 1.858 Å.

We have also shown that the M_4 -edge spectrum of $[\text{PaF}_7]^{2-}$ exhibits the same profile when computed with both TD-DFT and SO-RASPT2. Since TD-DFT is computationally less demanding than RASSCF and RASPT2, we therefore employ the 2c-TDA-CAMB3LYP protocol for the $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ calculation.

Now, looking at the Pa M_4 -edge spectrum of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ (Figure 5.12), we observe that it exhibits a similar profile to that of $[\text{PaO}]^{3+}$ (Figure 5.6). The A peak is shifted by 0.1 eV in $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ with respect to $[\text{PaO}]^{3+}$ (Table 5.5), whereas the B peak shows almost negligible intensity. From this comparison, we can conclude that the spectral profile of $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$ closely resembles that of the bare ion $[\text{PaO}]^{3+}$, indicating that the ligand field effect of the coordinated oxalate groups is negligible.

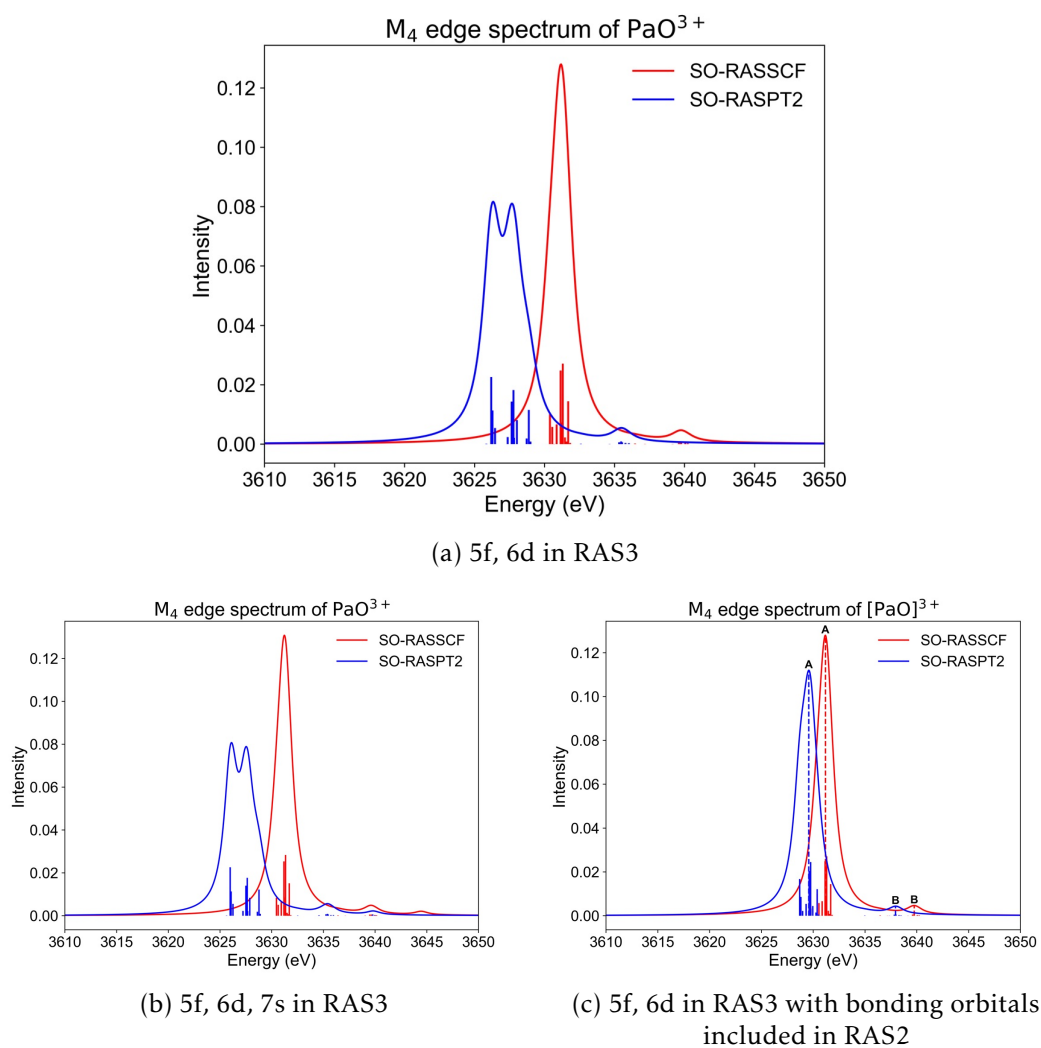


Figure 5.10: M_4 -edge spectrum of $[\text{PaO}]^{3+}$ computed at the SO-RASSCF and SO-RASPT2 levels of theory with different choices of active spaces, (a) 5f, 6d in RAS3; (b) 5f, 6d, 7s in RAS3; and (c) 5f, 6d in RAS3 with bonding orbitals included in RAS2. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.

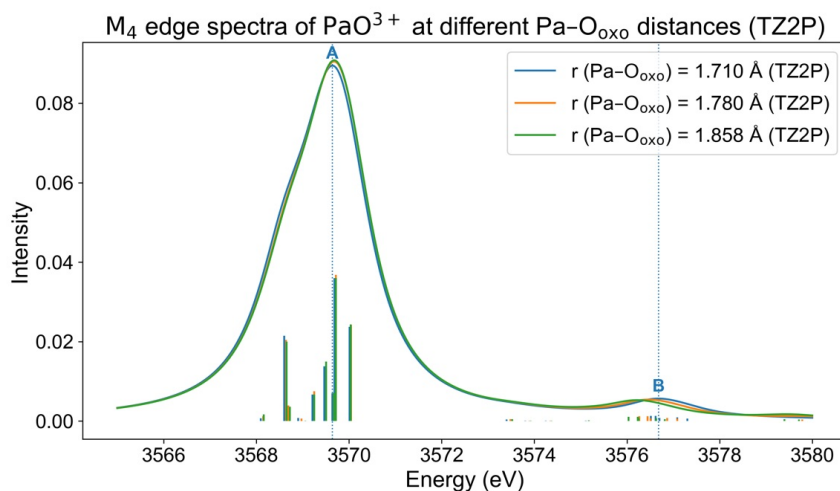


Figure 5.11: 2c-TDA-CAMB3LYP spectra with TZ2P basis set at the Pa M₄-edge of [PaO]³⁺ for different Pa–O_{oxo} distances, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.

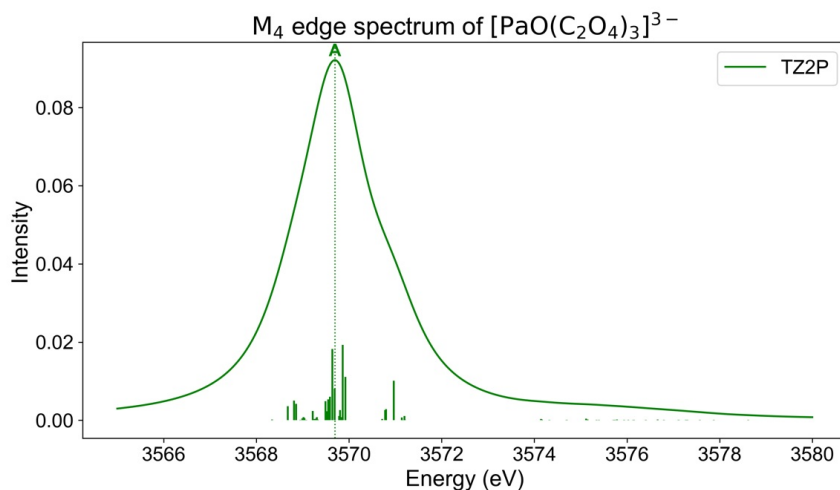


Figure 5.12: 2c-TDA-CAMB3LYP spectra with TZ2P basis sets at the Pa M₄-edge of [PaO(C₂O₄)₃]³⁻, using an oscillator strength cutoff ($\tau_{\text{osc}} > 10^{-5}$) and a virtual space restriction. Lorentzian broadening parameter is set to a FWHM of 1.5 eV.

5.1.5 Comparison of the M_4 -edge of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$

Looking at the spectral profiles of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, no significant differences are observed: both exhibit a single broad peak, with a relative energy shift of about 0.7 eV at the 2c-TDA-CAMB3LYP level with the TZ2P basis set. The distinction lies in the nature of the NTOs. For $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$, in addition to the $5f_\delta$ and $5f_\phi$ orbitals, the antibonding π^* and σ^* orbitals also contribute, as expected from the $[\text{PaO}]^{3+}$ unit.

To reliably distinguish between a complex containing an oxo bond and one without, highly resolved M_4 -edge measurements will be required, as the present spectral profiles alone do not provide sufficient differentiation. On the theoretical side, complementary RIXS simulations would be necessary, since they can explicitly capture the final-state effects underlying the subtle spectral shoulders that absorption-based calculations miss.

When both theoretical spectra are compared to the experimental data (Figure 4.21), we reproduce the main first peak well, but not the shoulder feature. The latter is likely due to final-state effects, which cannot be described within our present absorption-based simulations, whereas the experiment probes emission. High-resolution experiments, combined with RIXS calculations, would therefore provide a more complete picture.

5.2 Conclusion

In this chapter, we have shown that both the 2c-TDA-CAM-B3LYP and SO-RASSCF/RASPT2 approaches provide a reliable description of the Pa M_4 -edge spectra of Pa complexes. We have also demonstrated that there is no significant difference between the $[\text{Pa}]^{5+}$ and $[\text{PaO}]^{3+}$ M_4 -edge spectral profiles, which are themselves very similar to those of $[\text{PaF}_7]^{2-}$ and $[\text{PaO}(\text{C}_2\text{O}_4)_3]^{3-}$. This indicates that the transitions are predominantly localized on the Pa center and, when applicable, on the oxo group, with only negligible charge-transfer contributions.

The remaining discrepancies with respect to the experimental data highlight two complementary directions: on the experimental side, the need for higher-resolution M_4 -edge measurements; and on the theoretical side, the necessity of

RIXS simulations to account for final-state effects. These aspects, together with possible strategies to refine the theoretical description, will be discussed in the perspectives section 6.4.

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Conclusions and Perspectives

The study of protactinium in its predominant +V oxidation state is uncommon because of its rarity and the experimental challenges associated with its manipulation. This research has expanded the understanding of protactinium chemistry from both experimental and theoretical perspectives by answering three central questions:

- Which types of ligands are capable of stabilizing the mono-oxo bond of Pa(V)?
- What is the nature of the Pa–O bond in these complexes?
- Why do experimental Pa–O bond distances (1.72–1.75 Å) differ from theoretical predictions (1.86 Å)? Does this discrepancy arise from theoretical limitations or experimental uncertainties?
- Does the Pa–O bond persist in concentrated HCl medium, despite previous diffusion and partition studies suggesting otherwise?
- Is there agreement between theoretical and the new experimental results regarding the stability of the Pa–O bond in HCl?
- Are the experimentally determined Pa–O bond distances consistent with theoretical predictions?

- Can the L_3 -edge High Energy Resolution Fluorescence Detection (HERFD) and Resonant Inelastic X-ray Scattering (RIXS) techniques provide clearer spectroscopic signatures of the Pa–O bond compared to previous M_4 -edge studies?
- How accurately do the theoretical core-excitation simulations reproduce the experimental spectra, what insights do they provide into the nature of the electronic transitions?

The main findings obtained from this work, along with perspectives for future research, are summarized below.

6.1 Theoretical insights into the stabilization of the mono-oxo bond

The theoretical protocol developed in chapter 3 was used to compute the Gibbs free energy (ΔG_r) of the reaction $\text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O}) \longrightarrow \text{Pa}(\text{OH})_4(\text{X})$, where X represents either monodentate ligands, hydroxide (OH^-), halides (F^- , Cl^- , Br^- , I^-), and thiocyanate (SCN^-) or bidentate ligands such as nitrate (NO_3^-), sulfate (SO_4^{2-}), and the organic oxalate ($\text{C}_2\text{O}_4^{2-}$).

This approach proved sufficiently accurate to determine their relative stabilities. The calculations demonstrated that the Pa–O bond has triple-bond character and that several ligands, including Cl^- , Br^- , I^- , SCN^- , NO_3^- , and SO_4^{2-} , can effectively stabilize the mono-oxo bond [1]. These theoretical findings provided strong motivation for new experimental investigations, especially in chloride media, where no structural data had previously been reported.

6.2 Experimental validation in hydrochloric acid media

The existence of a mono-oxo bond in concentrated hydrochloric acid was predicted theoretically and subsequently confirmed experimentally using XANES

and EXAFS measurements. These results demonstrated the persistence of the Pa–O bond in highly concentrated 12 M HCl where $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ is formed, contrary to earlier reports suggesting the exclusive formation of chlorinated species. Importantly, the experimental Pa–O bond distance of approximately 1.83 Å is in excellent agreement with theoretical predictions marking the first such consistency achieved for Pa(V) in solution. At lower acidities (3 M HCl), the coexistence of hydroxo and oxo species was observed, with $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ identified as the most probable configurations [2].

The strong agreement between experimental and theoretical results confirms that the developed computational approach is reliable for predicting Pa(V) speciation and evaluating the stability of Pa(V) complexes before conducting future XAS measurements.

6.3 Perspectives for ligand chemistry

The predictive power of the present theoretical framework opens promising directions for future work. A logical next step would be to examine the effect of heavier halides, particularly bromide and iodide [1], as there is no structural data about the speciation of Pa(V) with HBr and HI.

Beyond halides, oxygenated ligands such as peroxo ligands, citric acid, and mellitic acid represent ideal candidates for exploring ligand-dependent modulation of the Pa–O bond. These systems would also provide a basis for comparing protactinium's coordination behavior with that of uranium and neptunium analogues.

In the specific case of oxalate complexes, the discrepancy between experimental (1.72–1.75 Å) and theoretical (1.86 Å) Pa–O bond lengths remains unresolved [3]. Preliminary theoretical results suggest that protonation of the oxalate ligand shortens the Pa–O bond. Experimental confirmation of this hypothesis would be highly valuable. Complementary capillary electrophoresis-ICP-MS measurements could provide information on the charge and composition of the dominant species in solution, while infrared and Raman spectroscopies could directly probe the presence or absence of the Pa–O stretch and confirm protonation effects through observing the Pa–O and O–H stretches in the Raman and

IR spectra.

6.4 Advances in X-ray spectroscopy and theoretical interpretation

From a spectroscopic perspective, the results presented in chapter 5, demonstrated that the two-component TDA-CAM-B3LYP approach provides a reliable description of the Pa M_4 -edge spectra of Pa(V) complexes, in good agreement with multi-reference method based calculations, namely RASPT2. Both approaches yield nearly identical spectral profiles for Pa(V) and PaO^{3+} , as well as for PaF_7^{2-} and $\text{PaO}(\text{C}_2\text{O}_4)_3^{3-}$.

This similarity indicates that the main transitions are largely localized on the Pa center and the oxo group, with only minor ligand-to-metal charge-transfer contributions. Consequently, XAS at the M_4 -edge alone is not sufficient to distinguish the mono-oxo bond unambiguously.

Future experimental efforts should therefore focus on high-resolution measurements at both the M_4 - and L_3 -edges using HERFD and RIXS techniques. These methods are expected to provide enhanced sensitivity to the local electronic environment and to reveal subtle spectral signatures associated with the mono-oxo bond. Such measurements should be extended to the newly identified protactinium complexes in hydrochloric acid solution, particularly those featuring a hydroxide ligand in the trans position to the oxo group, as they are expected to yield more resolved spectral features that could serve as a distinctive fingerprint of the Pa–O bond.

On the theoretical side, further work should extend beyond static excitation calculations to include RIXS mapping, thereby accounting for final-state effects and vibronic coupling. Such simulations would enable a more direct comparison with HERFD-RIXS experiments and improve the interpretation of the experimental spectra.

6.5 Broader outlook and long-term perspectives

If this research were to be extended in the future through a new PhD project or a collaborative program the following directions would be particularly valuable:

1. Comprehensive ligand series: Systematically study halide, peroxo, and organic ligands to establish a unified understanding of ligand effects on the stabilization and electronic structure of the Pa–O bond.
2. Comparative actinide analysis: Extend the developed computational and spectroscopic framework to neighboring actinides (Th, U, Np) to identify periodic trends in 5f-6d hybridization and bonding.
3. Environmental relevance: Explore Pa(V) interaction with mineral and organic surfaces to assess its potential mobility and retention mechanisms in natural systems.

In conclusion, this thesis provides the first consistent theoretical and experimental description of the mono-oxo bond in Pa(V) complexes in solution. It establishes a robust framework for predicting and characterizing protactinium speciation across diverse chemical environments. Beyond its intrinsic scientific value, this work contributes to the broader understanding of early actinide chemistry, bridging the gap between transition-metal and 5f-element behavior.

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Scientific contributions

Publications

- T. Shaaban et al., “Stability of the Protactinium(V) Mono-Oxo Cation Probed by First-Principle Calculations”, *Chemistry – A European Journal*, 2024, **30**, e202304068, DOI: 10.1002/chem.202304068
- T. Shaaban et al., “Is the protactinium(V) mono-oxo bond weaker than what we thought?”, *Chemical Communications*, 2024, **60**, 14376–14379, DOI: 10.1039/D4CC04522J
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Oral presentations (first author was the presenter)

- V. Vallet et al., Migration’25, New Orleans, Louisiana, USA, 2025
- T. Shaaban et al., *Experimental Characterization and Theoretical Modelling of X-Ray Absorption Spectra of Protactinium(V) Complexes*, RCP2025 : Rencontres de Chimie Physique 2025, Aussois, France, 2025
- M. Maloubier et al., *Complexation of Protactinium(V) with Chlorides in Aqueous Solution: Thermodynamic and Structural Insights*, 54èmes Journées Des Actinides, Annecy, France, 2025

- T. Shaaban et al., *Experimental Characterization and Theoretical Modelling of X-Ray Absorption Spectra of Protactinium(V) Complexes*, 54èmes Journées Des Actinides, Annecy, France, 2025
- T. Shaaban et al., *Experimental Characterization and Theoretical Modelling of X-Ray Absorption Spectra of Protactinium(V) Complexes*, Journées de l'association CenTRA, Lille, France, 2025
- M. Maloubier et al., *Complexation of Protactinium(V) with Chlorides in Aqueous Solution: Thermodynamic and Structural Insights*, ATAS – AnXAS 2024 - Joint Workshop, Karlsruhe, Germany, 2024
- T. Shaaban et al., *Effect of Ligands on Pa^{5+} and PaO^{3+} Relative Stabilities: A Computational Study*, 53rd Journées Des Actinides International Conference, Lille, France, 2024
- T. Shaaban et al., *Effect of Inorganic Ligands on Pa^{5+} and PaO^{3+} Relative Stabilities: A Computational Study*, 11th International Conference on f Elements (ICFE-11), Strasbourg, France, 2023

Poster presentations

- T. Shaaban et al., *Experimental Characterization and Theoretical Modelling of X-Ray Absorption Spectra of Protactinium(V) Complexes*, ATAS – AnXAS 2024 - Joint Workshop, Karlsruhe, Germany, 2024
- T. Shaaban et al., *Influence of Inorganic Ligands on the Relative Stabilities of Pa^{5+} and PaO^{3+} Complexes: A Computational Study*, JTMS 2023 : Journées "Théorie, Modélisation et Simulation", Strasbourg, France, 2023

THEORETICAL AND EXPERIMENTAL EXPLORATION OF THE PHYSICO-CHEMICAL AND SPECTROSCOPIC PROPERTIES OF PROTACTINIUM(V)

Abstract

Protactinium (Pa, $Z = 91$) occupies a unique position between transition metals and the heavier actinides, as both its 5f and 6d orbitals contribute to the ground-state electronic configuration. In aqueous solution, protactinium exists mainly in the +V oxidation state; however, unlike uranium or neptunium, it does not form a stable di-oxo cation (PaO_2^+). Instead, it can form a mono-oxo bond (Pa–O) in solution, for which only limited experimental information exists. Because of its scarcity, strong radioactivity, and marked tendency toward hydrolysis, polymerization, and sorption onto solids, experimental investigations of protactinium chemistry remain highly challenging. This thesis therefore combines advanced quantum-chemical modeling and high-resolution X-ray spectroscopy to elucidate the stability, structure, and spectroscopic signatures of Pa(V) mono-oxo complexes.

A theoretical framework was developed to evaluate the thermodynamics of oxo-bond formation and ligand-dependent stabilization in aqueous media using relativistic density functional theory (DFT) and correlated wave-function methods. The Gibbs free energy of the reaction $\text{Pa}(\text{OH})_4(\text{X}) \longrightarrow \text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$ was computed for a series of monodentate ligands, hydroxide (OH^-), halides (F^- , Cl^- , Br^- , I^-), and thiocyanate (SCN^-) as well as for bidentate ligands such as nitrate (NO_3^-), sulfate (SO_4^{2-}), and oxalate ($\text{C}_2\text{O}_4^{2-}$). These calculations showed that Cl^- , Br^- , I^- , SO_4^{2-} , SCN^- , and NO_3^- effectively stabilize the mono-oxo bond and that the Pa–O interaction exhibits triple-bond character. The derived thermodynamic trends provided quantitative guidance for subsequent experimental work.

These predictions were validated by X-ray Absorption Spectroscopy (XANES and EXAFS) measurements performed at the SOLEIL synchrotron within the ANR-CHESS project. For the first time, a persistent Pa–O bond was observed in concentrated hydrochloric acid, revealing the formation of $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ even in 12 M HCl. The experimental Pa–O bond length of 1.83 Å agrees remarkably well with theoretical predictions, resolving a discrepancy between theory and experiment. At lower acidities (3 M HCl), mixed hydroxo–oxo species such as $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ and $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ were identified, confirming the coexistence of multiple Pa(V) species depending on acidity.

To interpret the HERFD-XANES spectra at the M_4 -edge of PaF_7^{2-} and $\text{PaO}(\text{C}_2\text{O}_4)_3^{3-}$, core-excited states were modeled using two-component relativistic TD-DFT (2c-TDA-CAM-B3LYP) and multireference RASPT2 methods. Both approaches gave consistent results, indicating that the main transitions are localized on the Pa and Pa–O fragments of the respective complexes, with minimal ligand-to-metal charge transfer.

Overall, this work provides the first coherent theoretical–experimental description of Pa(V) speciation in aqueous media. It establishes a predictive computational framework for anticipating complex stability and guiding synchrotron experiments. The results demonstrate that the mono-oxo Pa–O bond can persist in highly acidic environments and that theoretical models can now reproduce experimental bond distances and spectral features with good accuracy.

Keywords: actinide, protactinium, x-ray absorption spectroscopy, quantum chemistry

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EXPLORATION THÉORIQUE ET EXPÉRIMENTALE DES PROPRIÉTÉS PHYSICO-CHIMIQUES ET SPECTROSCOPIQUES DU PROTACTINIUM(V)

Résumé

Le protactinium (Pa, $Z = 91$) occupe une position unique entre les métaux de transition et les actinides lourds, car ses orbitales 5f et 6d contribuent toutes deux à sa configuration électronique à l'état fondamental. En solution aqueuse, il se trouve principalement à l'état d'oxydation +V ; toutefois, contrairement à l'uranium ou au neptunium, il ne forme pas de cation dioxo stable (PaO_2^+), mais peut établir une liaison mono-oxo (Pa–O), encore peu caractérisée expérimentalement. La rareté, la radioactivité et la forte réactivité du protactinium compliquent considérablement son étude.

Cette thèse combine modélisation quantique avancée et spectroscopie X à haute résolution pour étudier la stabilité, la structure et les signatures spectroscopiques des complexes mono-oxo de Pa(V). À l'aide de DFT relativiste et de méthodes à fonction d'onde corrélée, un protocole théorique a été développé pour évaluer la thermodynamique de formation des liaisons oxo $\text{Pa}(\text{OH})_4(\text{X}) \longrightarrow \text{PaO}(\text{OH})_2(\text{X})(\text{H}_2\text{O})$, notamment pour des ligands monodentés (hydroxyde, halogénures, thiocyanate) et bidentés (nitrate, sulfate, oxalate). Les résultats montrent que plusieurs de ces ligands stabilisent efficacement la liaison Pa–O, qui présente un caractère de triple liaison. Ces tendances ont guidé les investigations expérimentales.

Les prédictions théoriques ont été validées par des mesures XANES et EXAFS réalisées au synchrotron SOLEIL (projet ANR-CHESS). Une liaison Pa–O persistante a été observée pour la première fois en milieu fortement acide, confirmant la formation de $[\text{PaOCl}_5(\text{H}_2\text{O})]^{2-}$ dans une solution concentrée, 12 M HCl, avec une longueur de liaison expérimentale (1.83 Å) en excellent accord avec les valeurs théoriques. À plus faible acidité, des espèces mixtes hydroxo–oxo, telles que $[\text{PaO}(\text{OH})\text{Cl}(\text{H}_2\text{O})_4]^+$ ou $[\text{PaO}(\text{OH})\text{Cl}_2(\text{H}_2\text{O})_3]$ ont également été identifiées, confirmant la coexistence de plusieurs espèces de Pa(V) en fonction de l'acidité.

Enfin, les spectres HERFD-XANES au seuil M_4 de complexes modèles ont été interprétés par modélisation des états excités à l'aide de la méthode TD-DFT relativiste à deux composantes (2c-TDA-CAM-B3LYP) ainsi que par la méthode multiréférence RASPT2. Les deux approches ont donné des résultats cohérents, indiquant que les principales transitions sont localisées sur les fragments Pa et Pa–O des complexes respectifs, avec un transfert de charge ligand-métal négligeable.

Ce travail fournit la première description intégrée, à la fois théorique et expérimentale, de la spéciation du Pa(V) en solution aqueuse. Il démontre la stabilité de la liaison mono-oxo en milieu acide et confirme la capacité des modèles quantiques modernes à prédire avec fiabilité les propriétés structurales et spectrales du protactinium.

Mots clés : actinides, protactinium, spectroscopie d'absorption de rayons x, chimie quantique
