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# Computational Actinide Chemistry: Structure, Bonding and Thermodynamics

Sophie Kervazo

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UNIVERSITÉ DE LILLE

MCMASTER UNIVERSITY

CO-TUTORIAL DOCTORAL THESIS

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# Computational Actinide Chemistry: Structure, Bonding and Thermodynamics

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Author:

Sophie KERVAZO

*A thesis submitted in fulfillment of the requirements  
for the degree of Doctor of Philosophy*

*in:*

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*in the doctoral school*

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*in:*

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Department of Chemistry and Chemical Biology

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THÈSE EN COTUTELLE

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## Computational Actinide Chemistry: Structure, Bonding and Thermodynamics

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Auteur:

Sophie KERVAZO

*En vue de l'obtention du*

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Department of Chemistry and Chemical Biology

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# ABSTRACT

The main question of this thesis is: do we have today the tools to efficiently describe the structure, the bonding and the thermodynamics of actinide systems? This broad question is answered thanks to three studies. The first two are directly applied to the plastic industry and the nuclear plant safety. The last one, more fundamental, concerns the benchmarking of newly developed theoretical approach on f-element systems.

First, actinides and transition metal arene-coordinated alkyl cations have been recently proven to be efficient catalysts for ethylene polymerizations. Interestingly, thorium, uranium and zirconium alkyl cations catalytic activity depends on the solvent. To understand these behaviours and to confirm the tendency of these complexes to engage in unusual-arene coordination, relativistic DFT calculations combined with a characterization of the interaction thanks to the ETS-NOCV method are used.

Second, in accident scenario along the reprocessing of spent nuclear fuel, plutonium can be released in various volatile forms ( $\text{PuO}_2$ ,  $\text{PuO}_3$  or  $\text{PuO}_2(\text{OH})_2$ , ...). The exploration of these scenarios by the use of simulations requires, among the various parameters, the knowledge of the thermodynamic properties of the possibly formed elements. Our in-silico study focusses on the determination of the enthalpies of formation of the former two species for which experimental uncertainties remain, using multi-configurational relativistic wavefunction method.

The last part of the thesis focusses on the benchmark of the B2-PLYP functional for f-element systems, which turns out quite accurate with respect to the experimental data and the gold-standard CCSD(T) method.

## ABSTRACT

La question générale traitée dans cette thèse est de déterminer si, aujourd'hui, nous disposons d'outils théoriques efficaces pour d'écrire la structure, la liaison et les propriétés thermodynamiques de système comprenant un actinide. Cette large question va être abordée à l'aide de trois études différentes. Les deux premières sont directement liées à l'industrie plastique et à la sûreté nucléaire. La dernière, plus fondamentale concerne une analyse comparative d'une approche théorique nouvellement développée sur des systèmes comprenant des éléments f.

Tout d'abord, les cations alkyles contenant un actinide (Th, U) ou un métal de transition (Zr) coordonné à un arène se sont révélés efficaces pour la catalyse de la synthèse du polyéthylène. Étonnamment, les activités catalytiques des cations alkyles dépendent du solvant. Pour comprendre cela et confirmer la tendance qu'ont ces complexes à se lier à l'arène, une étude en DFT dans un contexte relativiste combinée à une caractérisation de liaison avec la méthode ETS-NOCV fut faite.

La deuxième étude vise à étoffer les bases de données thermodynamiques qui servent à explorer numériquement les scénarios d'accidents. Notre étude *in silico* porte sur la détermination des enthalpies de formation des deux espèces pour lesquelles des incertitudes expérimentales subsistent ( $\text{PuO}_3$  ou  $\text{PuO}_2(\text{OH})_2$ , ...), en utilisant une méthode quantique multiconfigurationnelle et relativiste.

La dernière partie de la théorie se concentre sur l'estimation de la précision de la fonctionnelle B2-PLYP pour les éléments f, qui s'avère assez précise en comparaison aux données expérimentales et à la méthode de référence CCSD(T).

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A french comedian Pierre Desproges in one of his chronicles of ordinary hatred said the humanity is divided in four categories: relations, friends, close friends and people you do not know. The the people I do not know, thank you for reading this lines. I hope it can help for your project or to fight insomnia.

Friends/ colleagues: during a PhD, the time spend with friends being inversely proportional to that spend with the colleagues so I thank you all for enlightening scientific conversions, nice beers or a nice scientific conversions with enlightening beers. Family (not describe by Desproges): I have the luck to have a great family, always there when needed or just to share a slice of pizza. Thank you for being here, it is also a pleasure to go home thanks to you all. Close friend: Desproges said that you can count them on the Baron Empain's hand or Django Reihart's for the most misanthrope of us. Nonetheless, you are still being here, thank you !

Desproges was then adding the woman he loved. I will just change the gender to thank to man who is here for me day after day. Finally I think Desproges forget another type of people: the mothers. I thank mine for always supporting me and being there.

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# List of Abbreviations

AMFI	Average Mean Field Integrals
ANO	Atomic Natural Orbitals
ASTEC	Accident Source Term Evaluation Code
BSSE	Basis Sets Superposition Error
CASSCF	Complete <b>Actif</b> Space Self Consistent Field
CASPT2	Complete <b>Actif</b> Space Perturbation Theory at the 2 <sup>nd</sup> order
CBS	Complete Basis Set
CC	Coupled Cluster
CCSD(T)	Coupled Cluster with Singles and Double and Triple
CI	Configuration Interaction
CPP	Core Polarisation Potential
CSF	Configuration State Function
DFT	Density Functional Theory
DKH	Douglas Kroll Hess
DMRG	Density Matrix Renormalisation Group
EA	Electronic Afinity
ECP	Effective Core Potential
EOM	Equation Of Motion
ETS	Extended Transition State
FCI	Full Configuration Interaction
FORA	First Order Regular Approximation
GGA	Generalized Gradient Approximation
HF	Hartree Fock
IP	Ionisation <b>Potential</b>
IRSN	Institut Radioprotection et de Sureté Nucléaire
KS	Kohn Sham
GTO	Gaussian Type Orbitals
LCAO	Linear Combimaison of Atomic Orbitals
LDA	Local Density Approximation
MAD	Mean Average Deviation
MO	Molecular Orbital



<b>MP</b>	<b>M</b> øller- <b>P</b> lesset
<b>MP2</b>	<b>M</b> øller- <b>P</b> lesset at the 2 <sup>nd</sup> order
<b>NEVPT2</b>	<b>N</b> - <b>E</b> lectron <b>V</b> alence state <b>P</b> erturbation <b>T</b> heory at the 2 <sup>nd</sup> order
<b>NOCV</b>	<b>N</b> atural <b>O</b> rital for <b>C</b> hemical <b>V</b> alence
<b>PE</b>	<b>P</b> oly <b>E</b> thylene
<b>PT</b>	<b>P</b> erturbation <b>T</b> heory
<b>PUREX</b>	<b>P</b> lutonium <b>U</b> ranium <b>R</b> edox <b>E</b> Xtraction
<b>RASSI</b>	<b>R</b> estricted <b>A</b> ctif <b>S</b> pace <b>S</b> tate <b>I</b> nteraction
<b>RECP</b>	<b>R</b> elativistic <b>E</b> ffective <b>C</b> ore <b>P</b> otential
<b>RHF</b>	<b>R</b> estricted <b>H</b> artree <b>F</b> ock
<b>SA</b>	<b>S</b> tate <b>A</b> verage
<b>SCF</b>	<b>S</b> elf <b>C</b> onsistent <b>F</b> ield
<b>SF</b>	<b>S</b> pin <b>F</b> ree
<b>SO</b>	<b>S</b> pin <b>O</b> rbital
<b>SOC</b>	<b>S</b> pin <b>O</b> rbital <b>C</b> oupling
<b>SR</b>	<b>S</b> calar <b>R</b> elativistic
<b>SS</b>	<b>S</b> tate <b>S</b> pecific
<b>STO</b>	<b>S</b> later <b>T</b> ype <b>O</b> rbital
<b>TDDFT</b>	<b>T</b> ime <b>D</b> ependent <b>D</b> ensity <b>F</b> unctional <b>T</b> heory
<b>TPH</b>	<b>T</b> etra- <b>P</b> ropylene
<b>UCCSD(T)</b>	<b>U</b> nrestricted <b>C</b> oupled <b>C</b> luster with <b>S</b> ingle <b>D</b> ouble and ( <b>T</b> riple)
<b>UHF</b>	<b>U</b> nrestricted <b>H</b> artree <b>F</b> ock
<b>ZORA</b>	<b>Z</b> eroth <b>O</b> rders <b>R</b> egular <b>A</b> pproximation
<b>ZPE</b>	<b>Z</b> ero <b>P</b> otential <b>E</b> nergy

## Chapter 1

# General Introduction

Actinides are located in the last row of the periodic table, with an atomic number of 89 to 103 and even if they are large atoms with limited natural availability, for some of them, their use are present in our daily life. The plastic piece holding this pages together and the electric power used to write them do not contain actinides but could be the result of the daily exploitation of actinides complexes.

As quantum chemist, the modelling actinides can be a challenge for two main reasons. The first is the inclusion of relativistic effects, the second is how to properly take into account the electronic correlation within the partially occupied 7s, 5f and 6d valence orbitals of actinides. The main question of this thesis is: do we have today the tools to efficiently describe the structure, the bonding and the thermodynamics of actinide systems ?

This broad question is answered thanks to three studies. The two first are directly applied to the plastic industry and the nuclear plant safety. The last one, more fundamental, concerns the benchmarking of double hybrid functional on f-element systems.

The first applied use of actinides we are interested in is the use of actinides complexes as catalyst for the ethylene polymerisation. As with many great discoveries in chemistry, and sciences in general, polyethylene (PE) was first synthesised in Germany by accident in 1898 by Hans von Pechmann. It has now an important position in our daily life since it is used in many plastic items such as plastic bags, bottles, etc...

The most widely used ethylene polymerisation catalysis process is the Ziegler-Natta that allows an ethylene coordination and 1,2 insertion [1] in arene solvent in industry [2] or alkane one in academic laboratory [3]. Many patents are filled as the industrial application of new and better catalysts for ethylene polymerisation could really

be lucrative. The most interesting patent here was filled by Dow Chemical Company in 1987 in order to base, for the first time, the polymerisation of ethylene on actinides and more precisely on a mixture of bis(metallocene) precursor  $[\text{Cp}^*_2\text{AnX}_2]$  and  $[\text{Cp}^*\text{AnX}_3]$  ( $\text{An} = \text{Th}, \text{U}$  and  $\text{X} = \text{Cl}, \text{Me}, \text{CH}_2\text{SiMe}_3$ ) with different activating agents.

With the goal of improving the polymerisation of polyethylene, Pr David Emslie and his former PhD student Nicholas R. Andreychuk at McMaster University worked on new compounds based on actinides as catalysts. They could obtain the arene-coordinated alkyl cations  $[(\text{XA}_2)\text{An}(\text{CH}_2\text{SiMe}_3)(\text{arene})]^+$  with ( $\text{An} = \text{Th}, \text{U}$ ;  $\text{XA}_2 = 4,5\text{-bis}(2,6\text{-diisopropylanilido})\text{-}2,7\text{-di-}t\text{-tert-butyl-}9,9\text{-dimethylxanthene}$ ); arene = benzene, toluene, bromobenzene or fluorobenzene) (Figure 1.1) and  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  as counter ion and the close equivalent  $[(\text{XN}_2)\text{Zr}(\text{CH}_2\text{SiMe}_3)(\text{arene})]^+$  with the same arenes and ( $\text{XN}_2$ ) being the 4,5-bis(2,4,6-triisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene.

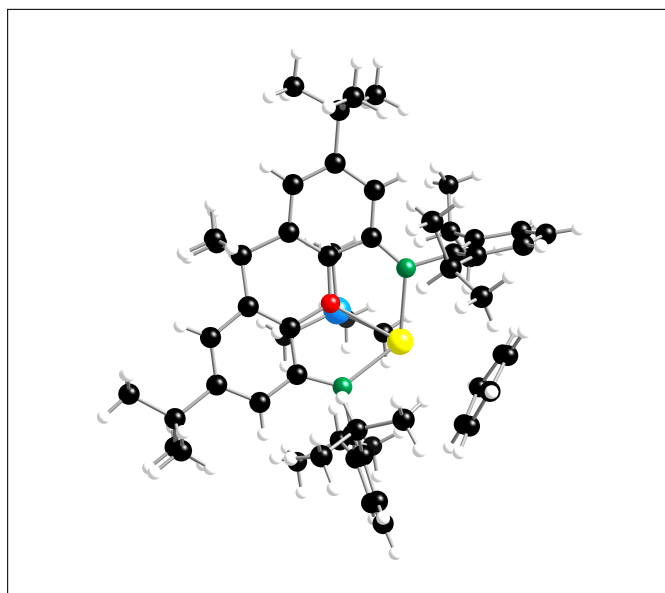


FIGURE 1.1:  $(\text{XA}_2)\text{U}(\text{CH}_2\text{SiMe}_3)(\text{benzene})^+$

The activity of the catalyst does not only depend on the arene but also of the metallic center. Our theoretical contribution, presented in Chapter 3 aims at understanding the mechanism of the catalysis by an in-depth study of the bond between the arene and the transition metal Zr or an actinide (Th or U) center

As second study, we worked with the French Radioprotection and Nuclear Safety agency (IRSN). While in the past decades the climate change and the future nuclear plants are at the heart of political debate, it is important to recall that no matter the prospective political decisions, nuclear safety must be addressed now. One of the challenges of nuclear power plants is the recycling of the nuclear fuel. Worldwide

the chosen recycling process is the PUREX (Plutonium Uranium Redox EXtraction) one. It uses a liquid-liquid extraction in order to separate the fission products from Plutonium and Uranium in order to reinject the former in the nuclear cycle. The problem with PUREX process is that the solvent tetra-propylene (TPH) could ignite itself and lead to a release, among numerous species, of gaseous plutonium in the atmosphere. This actually happened three times, twice at Savannah River (USA) in 1953 and 1975 and at Tomsk (Russia) in 1993. Even if the plutonium species only represents 0.9% of the fission products it is still responsible for 50% of the radiotoxicity after 100 years (see Figure 1.2).

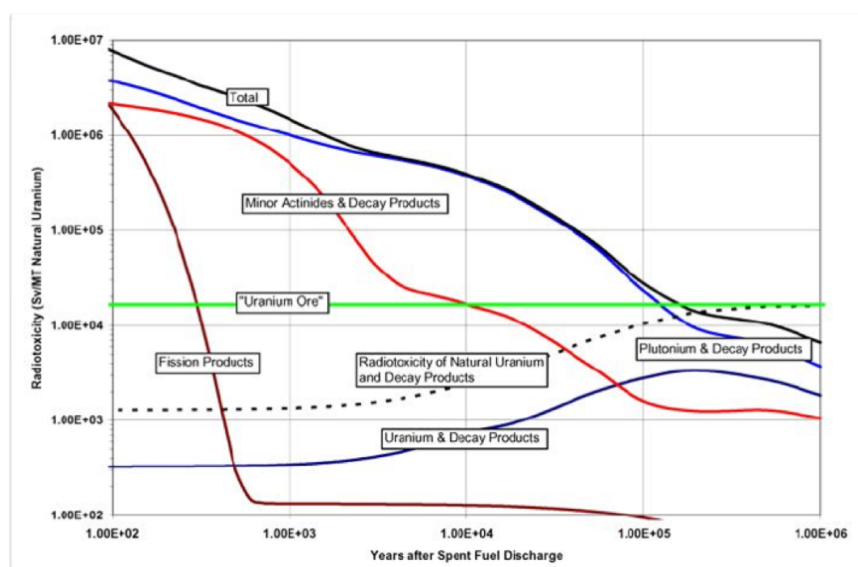


FIGURE 1.2: Radiotoxicity of spent nuclear fuel [4]

To perform nuclear safety analysis, the chemical behaviour of the Pu species need to be known. Experimental studies are complicated to pursue for safety reason. Since Pu can have multiple degrees of oxidation including (VI) it cannot be replaced by the less radioactive Th or Ce for the experiments. The volatile species expected to be formed in the contact with oxygen are the dioxide  $\text{PuO}_2$ , trioxide  $\text{PuO}_3$  and oxy-hydroxide ( $\text{PuO}_2(\text{OH})_2$ ) of plutonium. However, the experiments conducted in the past 30 years disagree on the formation of  $\text{PuO}_3$  *i.e.* some analysis of experimental data proposed that  $\text{PuO}_3$  could be formed along the chemical processes, while others do not. Thus theoretical simulations of an accident is the best solution to answer this question. The ASTEC (Accident Source Term Evaluation Code) simulator code, developed by the IRSN, can simulate the accident condition of pression and temperature but precise thermodynamic data such as heat capacities, entropies and enthalpies of formation of the different species involved are needed as input parameters. This study will limit itself to the plutonium oxides  $\text{PuO}_2$  and  $\text{PuO}_3$  and the

oxyhydroxide  $\text{PuO}_2(\text{OH})_2$ . Those thermodynamic values can be obtained computationally thanks to a detailed knowledge of their electronic structure which implies to take into account thoroughly relativistic effects and electronic correlation. The challenging aspect of this work as detailed in Chapter 4, is the multiconfigurational character of the ground-state wave function.

The treatment of electronic correlation is still source of new developments in quantum chemistry. For the past 10 years, the DFT community tried to better account for electronic correlation in the functionals by proposing new approaches. One of them is the so-called double-hybrid method, which is based on the use of a hybrid functional combined with the MP2 correlated method. This family of functionals has proven its efficiency for a lot of system but so far it was never applied to f-elements. During this thesis, one double hybrid (B2-PLYP) was tested for f-elements systems and representative chemical reaction in Chapter 5

In this thesis the general methods of quantum chemistry are first presented in Chapter 2. These will be followed in Chapter 3 by the exploration of the bonding between alkyl cations and arenes to rationalise the catalytic process of polyethylen. A third part (Chapter 4) will be devoted to the determination of thermodynamic properties of plutonium oxides and oxyhydroxide. The last chapter (Chapter 5) will evaluate the performances of double hybrid functional B2-PLYP for the determination of thermodynamic properties of f-elements containing systems. We will close this manuscript with general conclusions and perspectives.

## Chapter 2

# Methods

### 2.1 Introduction to Quantum Chemistry

As discussed in the introduction, the experimental expertise is complementary to theoretical studies. In this chapter, I will define all the necessary tools to understand what is solved from a computational point of view and all the important concepts that were used during my PhD work. As we already mentioned, the context of this study implies accounting for relativistic effects due to the presence of actinides. However, for the sake of clarity, we will start with the presentation of quantum chemical mechanics notions in a non-relativistic framework before introducing the relativistic Dirac equation and the other flavors of relativistic approximate Hamiltonians. Last but not least the concept of basis sets will be presented.

#### 2.1.1 Schrödinger equation

The time-dependent Schrödinger equation describes the physics of a molecular system with respect to time [5]:

$$\hat{H}\psi = i\hbar\frac{\partial\psi}{\partial t} \quad (2.1)$$

Where  $\psi(t)$  is the wave function of the state under consideration, in general the ground state (or an excited state),  $\hat{H}$  the Hamiltonian operator,  $i$  the imaginary number and  $\hbar$  the Planck constants divided by  $2\pi$ . The first approximation is to consider the system as stationary at a moment  $t$  [6] and thus the equation becomes an eigenvalue equation, independent of time:

$$\hat{H}(\mathbf{r}, \mathbf{R})\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R}) \quad (2.2)$$

with  $\psi(\mathbf{r}, \mathbf{R})$  the wave function of the system made on our case of electrons at positions  $\{\mathbf{r} = r_1, \dots, r_n\}$  and nuclei at the positions  $\{\mathbf{R} = R_1, \dots, R_N\}$  and  $E$  being the total energy.  $\hat{H}$  is written for a molecule, in atomic units as:

$$\hat{H} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \quad (2.3)$$

$i$  and  $j$  are indices running over the electrons while  $A$  and  $B$  indices are related to the nuclei.  $r_{ij}$  is the distance between the electron  $i$  and  $j$ ,  $r_{iA}$  the one between an electron  $i$  and a nucleus  $A$  and  $R_{AB}$  is the distance between two nuclei. Finally,  $Z_A$  is the atomic number of nucleus  $A$ . The two-first terms of equation 2.3 represent the kinetic energies terms of the electrons and the nuclei, respectively. The last three terms are the standard Coulomb interaction potential terms for electron-nucleus, electron-electron and nucleus-nucleus interactions.

### 2.1.2 Born-Oppenheimer approximation

As a proton is heavier than an electron (mass ratio of 1 836) the velocity of the nucleus considered to be negligible. Thus, it is possible to decouple the Hamiltonian as a sum of the electronic Hamiltonian  $\hat{H}^{el}$  and the nuclear one  $\hat{H}^{nuc}$

$$\hat{H} = \hat{H}^{el} + \hat{H}^{nuc} \quad (2.4)$$

In the adiabatic approximation [7] or Born-Oppenheimer approximation, the wave function  $\psi(\mathbf{r}, \mathbf{R})$  can be written as a product of the electronic contribution,  $\psi^{el}$ , and the nuclear one  $\psi^{nuc}$ :

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_{\mathbf{R}}^{el}(\mathbf{r}) \psi^{nuc}(\mathbf{R}) \quad (2.5)$$

The electronic Hamiltonian operator is define as:

$$\hat{H}^{el} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_{i,A} \frac{Z_A}{r_{iA}} + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \frac{1}{2} \sum_{A \neq B} \frac{Z_A Z_B}{R_{AB}} \quad (2.6)$$

It can be shown that the contribution of the nucleus-nucleus interaction term is just a constant in the total energy calculation. The eigenvectors are the electronic wave functions  $\psi_{\mathbf{R}}^{el}(\mathbf{r})$  that depend parametrically on  $\mathbf{R}$ . Therefore, the electrons move on a potential energy surface (PES),  $E_{\mathbf{R}}^{el}$ , that can be obtained by solving the following:

$$\hat{H}^{el}\psi_{\mathbf{R}}^{el} = E_{\mathbf{R}}^{el}\psi_{\mathbf{R}}^{el} \quad (2.7)$$

The methods presented in the following pages have for purpose to solve this eigenvalue problem.

### 2.1.3 Constraints on the wave-function

The first hypothesis is to consider the electrons as independent particules. Thus the n-particle wave function can be written as the product of N one-particle orbitals  $\phi$  (see Section 2.5.1).

$$\psi(r_1, r_2, \dots, r_N) = \phi_1(r_1)\dots\phi_N(r_N) \quad (2.8)$$

A prerequisite for the form of the electronic wave function (now written as  $\psi$ ), because it characterises fermion particules, is its anti-symmetric character with respect to the particle exchange:

$$\psi(i, j) = -\psi(j, i) \quad (2.9)$$

A manifestation of the Pauli exclusion principle [8], which states that two fermions cannot occupied the same quantum state, *i.e.* they cannot have the same four quantum numbers (n, l, m and s).

A trial wave function that satisfies both criteria is the Slater determinant [9] composed of orthonormal spin orbitals.

$$\psi(r_1, r_2, \dots, r_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \dots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \dots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \dots & \phi_N(r_N) \end{vmatrix} \quad (2.10)$$

with the spin orbitals in column and the electron coordinates in row. From now on,  $\psi$  will denote Slater determinants.

One can notice:

- The anti-symmetry of the wave-function is present since the exchange of two rows changes the sign of the determinant.



- The Pauli principle and the indiscernibility of the electrons remains. Indeed, having two electrons in the same state will give a determinant equals to zero since two columns will be equal.
- The normalisation constant is  $\frac{1}{\sqrt{N!}}$ .

## 2.2 Single-Reference Methods

In this section, the methods common to the three thesis projects using the single-reference approximation will be presented. The specific methods proper to each of them are introduced in the chapter in question.

### 2.2.1 Hartree-Fock method

In the context of Wave Function Theory, equation 2.10 can be solved thanks to different approximations. The Hartree-Fock approach [10] is the foundation of many other methods and more specifically the so-called *post* Hartree-Fock methods, presented later. It rests on the mean-field approximation which assumes that a given electron is subjected to the average potential (which as discussed below, consists of a classical (electrostatic) and a non-classical (exchange) interaction) of the other electrons, rather than the individual electron-electron interactions. The Hartree-Fock wave function is determined by the variation principle by minimising the energy of the system:

$$E_{HF} = \frac{\langle \Phi | H^{el} | \Phi \rangle}{\langle \Phi | \Phi \rangle} \geq E \quad (2.11)$$

$E_{HF}$  being the HF energy and  $E$  the exact total energy of the system. Since the N-electrons problem can be decomposed in N one-electron problems, the solution  $\Phi$  can be described by a Slater determinant built from the orbitals  $\phi_i$ . The variational conditions on the orbitals lead to a new effective one-electron operator, the Fock operator [6]  $\hat{F}_i$ .

$$\hat{F}_i \phi_i = \epsilon_i \phi_i \quad (2.12)$$

Its eigenvector,  $\phi_i$  is the molecular spin-orbital of the electron i and its eigenvalue  $\epsilon_i$  the corresponding orbital energy. The Fock operator can be written as:

$$\hat{F}_i(\mathbf{r}) = \hat{h}_i(\mathbf{r}) + \sum_{j=1}^N |\hat{J}_j(\mathbf{r}) - \hat{K}_j(\mathbf{r})| \quad (2.13)$$

The one-electron core Hamiltonian  $\hat{h}_i(\mathbf{r})$  is composed of the kinetic energy of the electron  $i$  and the nucleus-electron potential energy:

$$\hat{h}_i(\mathbf{r}) = -\frac{1}{2} \nabla_i^2 - \sum_{K=1}^N \frac{Z_K}{r_{iK}} \quad (2.14)$$

The second part of the equation 2.13 is composed by the two one-electron operators. The Coulomb operator  $J_j$ , corresponds to the classic representation of the repulsion between two electrons ( $i$  and  $j$ ). The second operator is the non-classical exchange operator and arises from the indiscernability of the electrons and the anti-symmetry of the wave-function. It forbids electrons with identical spins to occupy the same spatial position. Applying the exchange and Coulomb operators on  $\phi_j$  gives:

$$\hat{J}_j \phi_i(\mathbf{r}_i) = \left[ \int \frac{\phi_j^*(\mathbf{r}_j) \phi_j(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j \right] \phi_i(\mathbf{r}_i) \quad (2.15)$$

$$\hat{K}_j \phi_i(\mathbf{r}_i) = \left[ \int \frac{\phi_j^*(\mathbf{r}_j) \phi_i(\mathbf{r}_j)}{r_{ij}} d\mathbf{r}_j \right] \phi_j(\mathbf{r}_i) \quad (2.16)$$

Thus the eigenvalue  $\epsilon_i$  of the eigenfunction  $\phi_i$  in the equation 2.12 is:

$$\epsilon_i = \langle \phi_i | \hat{F}_i | \phi_i \rangle = \langle \phi_i | \hat{h}_i | \phi_i \rangle + \langle \phi_i | \sum_{j=1}^N (\hat{J}_j - \hat{K}_j) | \phi_i \rangle \quad (2.17)$$

Finally, the whole energy Hartree-Fock is:

$$E_{HF} = \sum_{i=1}^N h_{ii} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N (J_{ij} - K_{ij}) = \sum_{i=1}^N [\epsilon_i - \frac{1}{2} \sum_{j=1}^N (J_{ij} - K_{ij})] \quad (2.18)$$

Where  $N$  remains the number of electrons and  $\epsilon_i$ ,  $J_{ij}$  and  $K_{ij}$  follow the description of the equations 2.17 and:

$$J_{ij} = \int \phi_i^* \hat{J}_i \phi_i; K_{ij} = \int \phi_i^* \hat{K}_i \phi_i \quad (2.19)$$

One can note that the total energy Hartree-Fock is not the sum or the energy of the spin-orbitals of the equation 2.17 otherwise the electronic repulsion would be counted twice for each electron.

## 2.2.2 The problem of Electron Correlation

### Definition

As mentioned above, in the HF approximation, the instantaneous electron-electron interaction was replaced by an average potential while this approximation can yield to a fairly good representation of the physical systems. It is, nevertheless, still far from the exact solution as far as physico-chemical process are concerned. The missing interactions are what is referred as electronic correlation  $E_{corr}$  [11] which is defined as the difference between the total exact non relativistic energy of the system  $E_{tot}$  and the Hartree-Fock one  $E_{HF}$  (for a given basis set limit, see Section 2.5):

$$E_{corr} = E_{tot} - E_{HF} \quad (2.20)$$

Though electron correlation represents only 5 to 10% of the total energy of the system it can change the whole picture of the wave function and impact molecular properties and thus cannot be neglected [12]. From a physical point of view, electronic correlation is due to two types of instantaneous repulsions. The first one is the repulsion between the two negative charges, leading to the Coulomb hole. The second type of repulsion prevents two particles with the same spin to be at the same position corresponding to the Fermi hole.

One can distinguish between the dynamical and non-dynamical (or static) electronic correlation. The static correlation, occurring in case of near orbitals degeneracy, implies that the wave function has to be described by more than one Slater determinant. The dynamical correlation, is connected to the instantaneous correlation of the electron motions and is accounted for by post-Hartree-Fock methods discussed after.

### Møller-Plesset Perturbation Theory

In order to include dynamical correlation into a single reference wavefunction, Perturbation Theory (PT) [13] can be used. One can rewrite the Schrödinger equation as:

$$\hat{H}\psi = E\psi \quad (2.21)$$

with :

$$\hat{H} = \hat{H}_0 + \hat{H}' \quad (2.22)$$

where  $\hat{H}_0$  is the HF Hamiltonian and  $\hat{H}'$  the perturbation one defined in the equation 2.26.

The energy and the wave function can be written as Taylor expansion of  $\lambda$  (being the strength of the perturbation) since  $E_{PT}$  and  $\psi$  are continuous functions between zero and infinity:

$$E_{PT} = \lambda^{(0)}E_0 + \lambda^{(1)}E_1 + \lambda^{(2)}E_2 + \dots \quad (2.23)$$

$$\psi = \lambda^{(0)}\psi_0 + \lambda^{(1)}\psi_1 + \lambda^{(2)}\psi_2 + \dots \quad (2.24)$$

If  $\lambda = 1$ , the  $n$ -th order energy and wavefunction are of all the terms with indices  $\leq n$ .

In the Møller-Plesser (MP) Perturbation Theory,  $\hat{H}_0 = \hat{H}_{HF}$  thus it consists in the introduction of a perturbation to a reference (HF) wave function. In other words, excited Slater determinants are included.

We will focus on Møller-Plesset to the 2<sup>nd</sup> order (MP2), for which double excitations are included. Since it is easily proven that MP1 (Møller-Plesser to the 1<sup>st</sup> order) is actually equivalent to HF [10] with the Brillouin theorem. The Brillouin theorem stating that the singly excited configurations do not contribute to the 1<sup>st</sup> order correction to the wave function. By single excitation, one has to understand the promotion of one electron to an unoccupied orbital is allowed (see Figure 2.1), for double excitations, it is two electrons. The number of excited determinants is directly linked to the size of the basis set implying that, the computational cost will be also dependent on it (see Table 2.1 and Section 2.5.1 for the definition of a basis set). Let us have a look at  $E_{MP2}$  starting from  $\lambda = 1$  and equation 2.23 .

$$E_{MP2} = E_0 + E_1 + E_2 = \sum_i \epsilon_i - \frac{1}{2} \sum_{ij} \langle ij | |ij \rangle \quad (2.25)$$

As mentioned before, MP2 includes single and double excitations (if non-canonical/open-shell orbitals are used). The matrix elements with singly excited determinants  $\Phi_i^a$  are:

$$\begin{aligned} \langle \Phi_0 | \hat{H}' | \Phi_i^a \rangle &= \langle \Phi_0 | \hat{H}_0 - \sum_j^{N_{elec}} \hat{F}_j | \Phi_i^a \rangle \\ &= \langle \Phi_0 | \hat{H}_0 | \Phi_i^a \rangle - \langle \Phi_0 | \sum_j^{N_{elec}} \hat{F}_j | \Phi_i^a \rangle \\ &= \langle \Phi_0 | \hat{H}_0 | \Phi_i^a \rangle - \left( \sum_j^{N_{elec}} \epsilon_j \right) \langle \Phi_0 | \Phi_i^a \rangle \end{aligned} \quad (2.26)$$

Where the subscript of  $\Phi$ ,  $i, j, \dots$  are the occupied orbitals the electron is promoted from and  $a, b, \dots$  the virtual orbitals.  $\Phi_0$  and  $\Phi_i^a$  are two orthogonal states so the

second term is equals to zero. For the first term, the Brillouin theorem [14] states that (for closed shell systems) if two orthogonal states satisfying HF equation are different by only one orbital then:  $\langle \Phi_0 | \hat{H}_0 | \Phi_i^a \rangle = 0$ , so that  $\langle \Phi_0 | \hat{H}' | \Phi_i^a \rangle = 0$ . Thus,  $E_2$  only involves doubly excited determinants:

$$E_2 = \sum_{i < j} \sum_{a < b}^{occ \ vir} \frac{\langle \Phi_0 | \hat{H}' | \Phi_{ij}^{ab} \rangle \langle \Phi_{ij}^{ab} | \hat{H}' | \Phi_0 \rangle}{E_0 - \epsilon_{ij}^{ab}} \quad (2.27)$$

Because of the Koopmans' Theorem [15] the difference in total energy between two Slater determinants is the difference in Molecular Orbitals (MO) energies thus the second-order energy for a closed-shell system can be written with a sum over the spatial orbitals a, b, r and s as:

$$E(\text{MP2}) = 2 \sum_{abrs}^{N/2} \frac{\langle ab | rs \rangle - \langle rs | ab \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} - \sum_{abrs}^{N/2} \frac{\langle ab | rs \rangle - \langle rs | ba \rangle}{\epsilon_a + \epsilon_b - \epsilon_r - \epsilon_s} \quad (2.28)$$

The two main advantages of MP2 are the low computational cost compared to variational methods (such as CI see Section 4.2.1) and its size extensivity<sup>1</sup>.

Higher orders of perturbation such as MP3 (with the third order energy) or MP4 (with the fourth order energy) allow to include more dynamical correlation but at a greater cost. However, it has been shown that MP perturbation theory may not always converge [17], converge slowly or even oscillate. The issue of convergence, as well as the fact that other approaches such as coupled cluster have a similar cost than MP3, MP4 etc... but are more reliable, means that these approaches are now seldom used.

TABLE 2.1: Computational Cost and Amount of Correlation Included In the different Møller-Plesser Perturbation Theories. (see section 2.5.1 for the definition of  $M_{basis}$ )

Method	Computational Cost	Amount of Correlation Included
MP2	$M_{basis}^5$	80 - 90 %
MP3	$M_{basis}^6$	90 - 95 %
MP4	$M_{basis}^7$	95 - 97 %

<sup>1</sup>Size-extensivity is a mathematical concept introduced by Bartlett [16] to characterised a method with a linear scaling between the energy and the number of electrons. The size consistency is also a property of a method, referring to the fact that if A and B are two subsystems sharing no electrons the following equality is true:  $E(A + B) = E(A) + E(B)$ . This property is particularly important when a dissociation curve is explored.

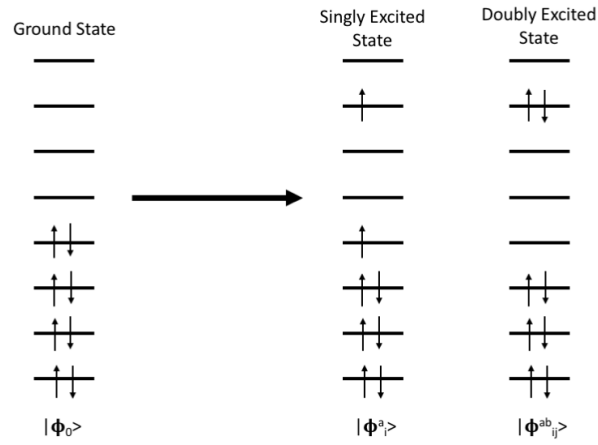


FIGURE 2.1: Single Excitation from a Ground State [17]

### Coupled Cluster Method

The coupled cluster (CC) method [18–21] is an approach based on the Many-Body Perturbation Theory where high-order excitations are included efficiently. Thus, the Schrödinger equation can be written as:

$$\hat{H}\Psi_{CC} = E\Psi_{CC} \quad (2.29)$$

$\Psi_{CC}$  is defined with an excitation operator  $\hat{T}$  acting on a reference wave function:

$$\Psi_{CC} = e^{\hat{T}}\Psi_0 \quad (2.30)$$

The exponential term can be expanded as:

$$e^{\hat{T}} = 1 + \hat{T} + \frac{1}{2!}\hat{T}^2 + \frac{1}{3!}\hat{T}^3 + \dots = \sum_{k=0}^{\infty} \frac{1}{k!}\hat{T}^k \quad (2.31)$$

the excitation operator  $\hat{T}$  is the sum:

$$\hat{T} = \sum_{i=1}^N \hat{T}_i \quad (2.32)$$

the subscript being the excitation order and  $N$  the number of electrons in the system. The excitation order corresponds to the number of electrons excited from an

occupied to an unoccupied orbital, for example:

$$\hat{T}_1 \Psi_0 = \sum_i^{\text{occ}} \sum_a^{\text{virtual}} t_i^a \Phi_i^a \quad (2.33)$$

and

$$\hat{T}_2 \Psi_0 = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{virtual}} t_{ij}^{ab} \Phi_{ij}^{ab} \quad (2.34)$$

represent single and double excitations, where  $t_i^a$  and  $t_{ij}^{ab}$  are the amplitudes of the excitations and so on. Here, the variational principle generally used to find the energy cannot be applied. Indeed, non-vanishing terms all the way up to the order of  $N$  arise because of the expansion in equation 2.31. Therefore, the energy is determined by projecting equation 2.29 onto the reference wave function  $\Phi_0$ . The coupled-cluster  $E_{CC}$  energy is then expressed as:

$$E_{CC} = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle \quad (2.35)$$

This method, similar to MP2 in the idea, retrieves the dynamical correlation of the system but still describes it with a single reference determinant. However, in contrast to MP2, the single excited  $T_1$  operators are known to introduce orbital relaxation [22] and make CC method more reliable than MP2 in cases the HF orbitals are not optimal

If no constraints on the excitation order are put in place, one would arrive at the FCI calculation and the method 4.2.1 would only be applicable for very small systems, so a truncated form was developed including only the single and double electrons excitations [23]. This truncated CC, called CCSD, remains size extensive and affordable for medium systems. Higher-order truncations are available such as CCSDT[24] including explicitly the triple excitations or CCSDTQ adding the quadruple ones, but they are too expensive for the gain in electronic correlation retrieved. The triple excitations, that might be important for the description of some wave functions, are then included perturbatively, leading to CCSD(T) being the most wisely used triple variant [25]<sup>2</sup>.

Unfortunately, the restricted CCSD(T) depicted above is inadequate to describe open-shell molecules such as the ones under study. Thus, one must turn to the unrestricted version of this method UCCSD(T). The first formulations of it [16, 27, 28] use an

<sup>2</sup>CCSD(T) is different from CCSD[T] where the contribution of the single excitations are not taken into account and from CCSD-T where triples corrections are computed as defined by M. J. O. Deegan *et al.*[26]

Unrestricted-HF (UHF) reference wave function. However this idea has the disadvantages of being expensive and leading to spin contamination (artificial mixing of multiple electronic spin states). This is why different studies decided to start with a restricted HF reference [29, 30] but the spin contamination of the wave-function was still present. In 1993, Knowles *et al.* [20, 21] proposed a RHF-UCCSD formulation.

Today, UCCSD(T) is considered as the "gold standard" for single reference cases, but may fail for multi-reference ones. The  $T_1$  [31] and  $D_1$  diagnostics [32, 33] can be used to qualitatively spot a multi-reference character. Defining  $T_1$  with the one-electron excitation amplitudes  $t_1$ :

$$T_1 = \frac{\|t_1\|}{\sqrt{N}} \quad (2.36)$$

And the  $D_1$  for open-shell [34]:

$$D_1 = \max(\|f_i^a\|_2, \|f_x^a\|_2, \|f_i^x\|_2) \quad (2.37)$$

where the 2-norm of a matrix,  $\|R\|_2$ , is the maximum Euclidean norm of the vectors formed by the multiplication of  $R$  with a unit vector [35], and the  $f$  amplitudes being linked to the  $t$  amplitudes by:

$$f_i^a = \frac{t_{ia}^{a\alpha} + t_{i\beta}^{a\beta}}{2} \quad (2.38)$$

$$f_x^a = \frac{t_{x\alpha}^{a\alpha}}{\sqrt{2}} \quad (2.39)$$

$$f_i^x = \frac{t_{i\beta}^{x\beta}}{\sqrt{2}} \quad (2.40)$$

If for lighter elements a  $T_1$  diagnostic higher than 0.02 is usually a sign of multi-reference character the value is raised at 0.05 [36, 37] for systems with transition metals and other heavy elements.

## 2.3 Density Functional Theory

At the birth of quantum chemistry in the 1960's, the limited computational power raised difficulties to perform accurate calculations using large basis sets (see Section 2.5.1) or including many atoms with HF method. In this context, the great adventure of Density Functional Theory (DFT) started in 1964 with Hohenberg and Kohn [38]



when they demonstrated that the exact energy of the ground state of any electron gas in an external potential is a functional of the density  $F[\rho]$ .

$$E[\rho] \equiv \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho] \quad (2.41)$$

where  $v$  would be the Coulomb attraction between the nuclei and the electrons.  $\rho$ , the total electron density of  $N$  electrons is defined as:

$$\rho(\mathbf{r}) = N \int \dots \int |\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d\sigma d\mathbf{x}_2 \dots d\mathbf{x}_N \quad (2.42)$$

$\sigma$  being the arbitrary spin of the electron one,  $\mathbf{x}_i$  being the map of the spin-spatial coordinated of the other  $N-1$  electrons.

$F[\rho]$  is a universal functional of the total electron density  $\rho$  that corresponds to the sum of the two electron energy functional  $W[\rho]$  and the kinetic energy terms  $T[\rho]$ . Considering  $F[\rho]$ , it can be rewritten as:

$$F[\rho] = T[\rho] + W[\rho] \quad (2.43)$$

Thus the "only" down side is the determination of the universal functional  $F[\rho]$ , since the energy is simply obtained by the variational principle. Hohenberg and Kohn stated themselves the problem of obtaining this universal functional in the conclusion of their paper: *"We have developed a theory of electronic ground state which is exact in two cases : The case of a nearly constant density [...] and the case of a slowly varying density. Actual electronic systems do not belong to either of them."*

The answer to this problem arrived one year later in 1965, with Kohn and Sham [39] by proposing that the exchange-correlation term, at the heart of the problem of Hohenberg and Kohn (and more generally in quantum chemistry), can be approximate by using the true chemical potential  $\mu(\rho)$  of the homogeneous interacting electron gas.

$$\frac{\delta E}{\delta \rho} = \mu \quad (2.44)$$

First, the density is rewritten as a Slater determinant of spin orbitals  $\phi_i$  for a non interacting reference system.

$$\rho(\mathbf{r}) = \sum_i^N \phi_i^*(\mathbf{r})\phi_i(\mathbf{r}) \quad (2.45)$$

Then, the variational principle is applied to equation 2.41 in order to obtain  $N$  coupled one-particle equations for the non-interacting electrons, the so-called the Kohn-Sham equations:

$$\left\{ -\frac{1}{2m} \nabla^2 + \phi(\mathbf{r}_i) + v_{xc}(\rho(\mathbf{r}_i)) \right\} |\phi_i\rangle = \epsilon_i |\phi_i\rangle \quad (2.46)$$

with:

$$\phi(\mathbf{r}) = v_{ext}(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.47)$$

and

$$v_{xc}(\rho(\mathbf{r})) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\mathbf{r})} \quad (2.48)$$

Here, the issue is the formulation of  $E_{xc}$ . In practice, the exact functional is replaced by an approximated one with a certain number of exact conditions being enforced [10] as listed below:

- For a hydrogen-like system the functional should give the exact exchange energy and a correlation energy equals to zero.
- For solid-state physics, it is important to recover the electron gas solution when the density becomes constant. However, it is less true for molecular densities since as the electron gas model does not properly describe a molecular system.
- Multiplying by a constant factor the molecular coordinates ( $\rho_\lambda(x,y,z) = \lambda^3 \rho(\lambda x, \lambda y, \lambda z)$ ) should result in a linear scaling of the exchange energy.  $E_x[\rho_\lambda] = \lambda E_x[\rho]$ .
- On the contrary, there is no full scaling concerning the correlation energy.
- The exact functional should fulfill the Lieb-Oxford inequality saying that  $E_x[\rho] \geq E_{xc}[\rho] \geq 2.273 E_x^{LDA}[\rho]$  (see Section 2.3.1).
- As  $r$  tends to infinity the exchange potential should have an asymptotic behaviour in  $-r^{-1}$  while the correlation potential shows a  $-\frac{1}{2}\alpha r^{-4}$  behaviour ( $\alpha$  being the polarisability of the  $N_{elec} - 1$  system).

A good starting point to find the universal or approximate functional is to separate the exchange term from the correlation one in equation ??, such as  $E_{xc}[\rho] = E_x[\rho] + E_c[\rho]$ , with :

$$E_x[\rho] = \int \rho(\mathbf{r}) \epsilon_x([\rho], \mathbf{r}) d\mathbf{r} \quad (2.49)$$

$$E_c[\rho] = \int \rho(\mathbf{r}) \epsilon_c([\rho], \mathbf{r}) d\mathbf{r} \quad (2.50)$$

The exchange energy, by definition, involves only electrons with identical spins while the correlation due to electrons with the same spin is different, and thus separable, from the correlation from electrons with opposite spins:

$$E_x[\rho] = E_x^\alpha[\rho_\alpha] + E_x^\beta[\rho_\beta] \quad (2.51)$$

$$E_c[\rho] = E_c^{\alpha\alpha}[\rho_\alpha] + E_c^{\beta\beta}[\rho_\beta] + E_c^{\alpha\beta}[\rho_\alpha, \rho_\beta] \quad (2.52)$$

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

Now that the basis of DFT are exposed, the next part will focus of the expressions of  $E_x[\rho]$  and  $E_c[\rho]$  and the approximations leading to their formulations.

### 2.3.1 Local Density Approximation

In the Local Density Approximation (LDA)[39–41], the exchange energy is given by the Dirac formula:

$$E_x^{LDA}[\rho] = -C_x \int \rho(\mathbf{r})^{\frac{4}{3}} d^3\mathbf{r} \quad (2.53)$$

In the case of an open-shell system where  $\alpha$  and  $\beta$  densities are different, LSDA (Local Spin Density Approximation) is used, the exchange energy reads :

$$E_x^{LSDA}[\rho] = -C_x \int (\rho_\alpha(\mathbf{r})^{\frac{4}{3}} + \rho_\beta(\mathbf{r})^{\frac{4}{3}}) d^3\mathbf{r} \quad (2.54)$$

Concerning the correlation part, it is fitted on high precision calculations performed with Quantum Monte Carlo method to a uniform electron gas. The analytic interpolation formula used for this fit defines the functional, for example Vosko, Wilk and Nusair' one [41] (VWN) or the popular PW92 constructed by Perdew and Wang in 1992 [40].

### 2.3.2 Generalised Gradient Approximation

The goal of the Generalised Gradient Approximation's (GGA) [42] is to improve the exchange and correlation energies by including the electron density and its derivative, at given point (removing the *local* or homogeneous character of LDA) in the functional. For example, in this thesis, we have used the Perdew-Burke-Ernzerhof (PBE) [43] GGA functional defined by its exchange functional:

$$\epsilon_x^{PBE} = \epsilon_x^{LDA} F(x) \quad (2.55)$$

where  $x$  is a gradient of the density:

$$x = \frac{|\nabla\rho|}{\rho^{\frac{4}{3}}} \quad (2.56)$$

and

$$F(x) = 1 + a - \frac{a}{1 + bx^2} \quad (2.57)$$

$a$  and  $b$  being parameters. The correlation part is expressed as:

$$\epsilon_c^{PBE} = \epsilon_c^{LDA} H(x) \quad (2.58)$$

$$H(x) = cf_3^3 \ln \left[ 1 + dt^2 \left( \frac{1 + At^2}{1 + At^2 + A^2t^4} \right) \right] \quad (2.59)$$

$$A = d \left[ \exp \left( - \frac{\epsilon_c^{PBE}}{cf_3^3} \right) - 1 \right]^{-1} \quad (2.60)$$

$$f_3(\zeta) = \frac{1}{2} \left[ (1 + \zeta)^{\frac{2}{3}} + (1 - \zeta)^{\frac{2}{3}} \right] \quad (2.61)$$

$$t = \left[ 2(3\pi^3)^{\frac{1}{3}} f_3 \right]^{-1} x \quad (2.62)$$

The parameters  $a$ ,  $b$  and  $c$  are determined in a non-empirical way.  $\zeta$  is the relative spin polarisation ( $= (n_{\uparrow} - n_{\downarrow}) / n$  with  $n = 3/4 \pi r_s^3$ ,  $r_s$  being the Wigner-Seitz radius that is the radius of a sphere whose volume is equal to the mean volume per atom in a solid).

### 2.3.3 Hybrid-Generalised Gradient Approximation

Hybrid-GGA functionals combine a LDA part, a GGA part and an exact HF exchange weighted in order to fit experimental data. For example in this work, the well-used B3LYP [44] and PBE0 [45, 46] functionals have been used. The B3LYP functional is:

$$E_{xc}^{B3LYP} = (1 - a)E_x^{LSDA} + aE_x^{exact} + b\delta E_x^{B88} + (1 - c)E_c^{LSDA} + cE_c^{LYP} \quad (2.63)$$

The LYP and B88 part of the correlation and exchange energies are obtained with the GGA approximation.  $E_x^{exact}$  is obtained when the KS orbitals used are identical to HF one.  $E_x^{LSDA}$  is described in the equation 2.54. The default values for  $a$ ,  $b$  and  $c$  are 0.2, 0.7 and 0.8 respectively, however most of the quantum chemistry codes allow the user to modify these values. The defaults values are kept in the present work.

PBE0 consists in the addition of 25% of  $E_x^{exact}$  to the PBE functional presented in the previous paragraph.

### 2.3.4 Strengths and Weaknesses of DFT

As one understood, DFT is a great tool for quantum chemists. It is fast and black box once the functional is (smartly) chosen. Its computational cost scales as  $N^3$  ( $N$  being the number of orbitals). On the other side, the impossibility to systematically improve results and the problem of describing spin states are severe drawbacks [47, 48]. In a vision restricted to the treatment of actinides, the main deficiency of DFT is its single determinant description, while the large number of unpaired  $f$ ,  $s$  and  $d$  actinides electrons may results in a strongly multi-determinantal wave-function.

We can also point out that the exchange-correlation functional does not account for long-range ( $\frac{C_6}{R_6}$ ) correlation corresponding to the London part of the dispersion energy notably present when Van der Waals interaction are important.

Dispersion can be patched to KS energies as proposed by Grimme *et al.* [49–51] with the D3 empirical correction:

$$E_{disp} = E^{(2)} + E^{(3)} \quad (2.64)$$

With the two-body  $E^{(2)}$  term defined as:

$$E^{(2)} = \sum_{AB} \sum_{n=6,8,10} s_n \frac{C_n^{AB}}{r_{AB}^n} f_{d,n}(r_{AB}) \quad (2.65)$$

with

$$f_{d,n}(r_{AB}) = \frac{1}{1 + 6 \left( \frac{r_{AB}}{s_{r,n} R_0^{AB}} \right)^{-\alpha_n}} \quad (2.66)$$

$C_n^{AB}$  are tabulated for atom pairs,  $s_n$  and  $s_{r,n}$  are a scaling factor adjusted for each functional and  $R_0^{AB}$  is the cutoff radii

The three-body  $E^{(3)}$  term is:

$$E^{(3)} = \sum_{ABC} f_{d,(3)}(\bar{r}_{ABC}) E^{ABC} \quad (2.67)$$

$\bar{r}_{ABC}$  being the geometrically averaged radii of atoms A, B and C and  $E^{ABC}$  the triple dispersion term:

$$E^{ABC} = \frac{C_9^{ABC}(3\cos\theta_a\cos\theta_b\cos\theta_c + 1)}{(r_{AB}r_{BC}r_{CA})^3} \quad (2.68)$$

where  $C_9^{ABC}$  is a constant and  $\theta_a$ ,  $\theta_b$  and  $\theta_c$  are the internal angles of the triangle formed by  $r_{AB}$ ,  $r_{BC}$  and  $r_{CA}$

This dispersion correction can be efficient but still relies on empirical corrections. A second solution is a new type of functionals, the Double Hybrids described in Chapter 5.

## 2.4 Treatment of relativistic effects

All the methods presented so far were based on the non-relativistic Schrödinger equation. For relatively light atoms ( $Z < 36$ ), this approximation is fully legitimate but increasing the atomic number of the atom implies for the electrons closer to the nucleus to have a velocity approaching the speed of light [52], making relativistic effects no longer negligible and affecting their electronic structure.

Relativistic effects can be separated in two types: those independent of the electron spin (or scalar) and those dependent of the electron spin (or spin-orbit). The first stems from the fact that, because of the stronger nuclear attraction (as  $Z$  increases), the inner electrons are accelerated and get closer to the nucleus. The consequence is, the contraction and the stabilisation of the  $s$  and  $p$  orbitals. Furthermore, as the inner  $s$  and  $p$  electrons are drawn towards the core, they increasingly more effective in screening outer shells and as consequence, the  $d$  and  $f$  electrons are destabilised. The second category, the spin-orbit one, can be seen, in a classic representation, as the interaction of the electron magnetic moment and the magnetic induction created by the kinetic orbital motion and results in the splitting of orbitals with angular momenta greater than 0.

### 2.4.1 Dirac equation

According to relativistic theory, since the speed of light and the Physics laws are the same in all inertial frames, the researched equation must be invariant under Lorentz transformation [53]<sup>3</sup>. We see, for instance, the time-dependent Schrödinger equation:

$$\frac{-\hbar}{2m} \left[ \frac{\partial^2 \psi(\mathbf{r}, t)}{\partial x^2} + \frac{\partial^2 \psi(\mathbf{r}, t)}{\partial y^2} + \frac{\partial^2 \psi(\mathbf{r}, t)}{\partial z^2} \right] = -i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (2.69)$$

<sup>3</sup>Invariant under Lorentz transformation means that the value of a quantity is the same in all Galilean referentials

does not fulfil this requirement, since the spatial coordinates  $x$ ,  $y$  and  $z$  appear as quadratic derivatives while the time appears as its first derivative.

Paul. A. M. Dirac [54] suggested instead an Hamiltonian with linear derivatives of both time and space, introducing the algebraic quantities  $\alpha$  and  $\beta$ . The Dirac equation, in an external electromagnetic potential describes the relativistic motion of an electron as:

$$\left( \beta m_0 c^2 + e\phi + \boldsymbol{\alpha} \cdot \boldsymbol{\pi} - ih \frac{\partial}{\partial t} \right) \psi = 0 \quad (2.70)$$

with

$$\boldsymbol{\pi} = \mathbf{p} + e\mathbf{A} \quad (2.71)$$

recalling :

$$\mathbf{p} \rightarrow \mathbf{p} - q\mathbf{A}; E \rightarrow -q\phi \quad (2.72)$$

$\phi$  being the scalar potential and  $\mathbf{A}$  the vector potential describing the magnetic field and  $q = -e$  for an electron and  $q = +e$  for a positon.  $\alpha$  retains the information about the spin of the particle. Both  $\alpha$  and  $\beta$  are  $4 \times 4$  matrices defined as:

$$\alpha_x = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \alpha_y = \begin{pmatrix} 0 & 0 & 0 & -i \\ 0 & 0 & i & 0 \\ 0 & -i & 0 & 0 \\ i & 0 & 0 & 0 \end{pmatrix}, \alpha_z = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \quad (2.73)$$

$$\beta = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \quad (2.74)$$

This can be rewritten with the Pauli matrices, the zero  $2 \times 2$  matrix  $0_2$  and the  $2 \times 2$  Identity matrix  $1_2$ :

$$\alpha_x = \begin{pmatrix} 0_2 & \sigma_x \\ \sigma_x & 0_2 \end{pmatrix}, \alpha_y = \begin{pmatrix} 0_2 & \sigma_y \\ \sigma_y & 0_2 \end{pmatrix}, \alpha_z = \begin{pmatrix} 0_2 & \sigma_z \\ \sigma_z & 0_2 \end{pmatrix} \quad (2.75)$$

$$\beta = \begin{pmatrix} 1_2 & 0_2 \\ 0_2 & -1_2 \end{pmatrix} \quad (2.76)$$

The Pauli matrices being:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (2.77)$$

Since  $\alpha$  and  $\beta$  appears in the equation 2.70 as  $4 \times 4$  matrices the wave function must be a four-component vector:

$$\psi(\mathbf{r}, t) = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{pmatrix} \quad (2.78)$$

Among the four components, two (one for the spin  $\alpha$  and one for the  $\beta$ ) are the large (L) ones and the other two are the small (S) components (also one for the spin  $\alpha$  and one for the  $\beta$ ) we can rewrite  $\psi(\mathbf{r}, t)$  as:

$$\psi(\mathbf{r}, t) = \begin{pmatrix} \psi^L(\mathbf{r}, t) \\ \psi^S(\mathbf{r}, t) \end{pmatrix} = \begin{pmatrix} \psi_\alpha^L(\mathbf{r}, t) \\ \psi_\beta^L(\mathbf{r}, t) \\ \psi_\alpha^S(\mathbf{r}, t) \\ \psi_\beta^S(\mathbf{r}, t) \end{pmatrix} \quad (2.79)$$

The solution of the time-independent Dirac equation for a free electron can then be found by solving the matrix equation:

$$\begin{pmatrix} mc^2 - E & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & -mc^2 - E \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = 0 \quad (2.80)$$

leading to the four two-fold degenerate solutions, corresponding to the large and small components:

$$E^+ = +\sqrt{c^2 p^2 + m^2 c^4} \quad (2.81)$$

and

$$E^- = -\sqrt{c^2 p^2 + m^2 c^4} \quad (2.82)$$

indicating that an electron could occupy a positive or negative state. Since the physical meaning of the former states would be a problem, Dirac supposed all the negative states to be occupied [55], That so the electrons would not be able to occupy them



due to the Pauli principle. In the presence of a potential such as the nucleus ( $V = e\phi = \frac{-Z}{r}$  see equation 2.71), two continuum of states appear, with one corresponding to electronic (positive) states and one for the negative solutions, and bound states in between the continuum.

In this formalism only the one electron equation can be exactly resolved, therefore, some approximations must be made to describe many-electrons systems.

## 2.4.2 Dirac-Coulomb-Breit Hamiltonian

While multiple electrons are present their motions are dependent from each other. Thus we introduce the many-electron Dirac-Coulomb-Breit Hamiltonian  $\hat{H}^{DCB}$  as the sum of the Dirac one-electronic Hamiltonian and the two-electronic Breit correction term  $g_{ij}^B$ :

$$\hat{H}^{DCB} = \sum_{i=1}^N \hat{h}_i + \sum_{i<j} g_{ij}^B \quad (2.83)$$

where

$$g_{ij}^B = -\frac{1}{2r_{ij}} \left( \alpha_i \cdot \alpha_j + \frac{(\alpha_i \cdot r_{ij})(\alpha_j \cdot r_{ij})}{r_{ij}^2} \right) \quad (2.84)$$

the first term in parenthesis being the Gaunt interaction [56] and the second the retarded effect important for long distance interactions [57, 58].

## 2.4.3 Dirac Equation approximations

Since working with the four-component framework can be expensive even for relatively small systems, simplifying the Dirac equation by keeping only two components, the large ones, could save a lot of computational effort. To do so, the large and small components must be separated. It can be done with the elimination of the small components or by decoupling the small and large components with a unitary transformation.

### Small Components elimination

In a similar way than in equation 2.80, the time independent Dirac equation for one free electron can be written to take into account an external potential  $V$  (shifting by

$-mc^2$  to set the electronic solutions to zero):

$$\begin{pmatrix} V - E & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - 2mc^2 - E \end{pmatrix} \begin{pmatrix} \psi^L \\ \psi^S \end{pmatrix} = 0 \quad (2.85)$$

which is equivalent to resolve the two equations system:

$$\begin{aligned} c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi^S + V\psi^L &= E\psi^L \\ c(\boldsymbol{\sigma} \cdot \mathbf{p})\psi^L + (V - 2mc^2)\psi^S &= E\psi^S \end{aligned} \quad (2.86)$$

Thus it is possible to express  $\psi^S$  as a function of  $\psi^L$ :

$$\psi^S = K(E) \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc} \psi^L \quad (2.87)$$

with  $K(E)$  a local multiplicative operator that depends on the electron energy:

$$K(E) = \left( 1 - \frac{V - E}{2mc^2} \right)^{-1} \quad (2.88)$$

By inserting equation 2.87 in the first equation 2.86 we obtained the 2-component equation:

$$\left( \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) K(E) (\boldsymbol{\sigma} \cdot \mathbf{p}) + V \right) \psi^L = E\psi^L \quad (2.89)$$

This equation allows to retrieve the Schrödinger equation in the non-relativistic limit ( $c \rightarrow \infty$  and  $K \rightarrow 1$ ).

### Pauli Hamiltonian

The  $K(E)$  term can be expanded as a geometric series as:

$$K(E) = \sum_{k=0}^{\infty} \left( \frac{V - E}{2mc^2} \right)^k \quad (2.90)$$

The Pauli approximation is obtained by retaining the two first terms of the series:

$$K(E) \approx K^{Pauli}(E) = 1 + \frac{V - E}{2mc^2} \quad (2.91)$$

This expansion is only valid if

$$|V - E| \ll 2mc^2$$

but is not the case in the region close to the nucleus. As  $r \rightarrow 0$  and  $V = \frac{-Z}{r} \rightarrow \infty$ , making the condition  $|V - E| \ll 2mc^2$  not true. Away from the nucleus,  $K(E)$  can be expanded to the first order leading to the Pauli Hamiltonian  $\hat{H}^{Pauli}$  [59, 60]:

$$\hat{H}^{Pauli} = \hat{T} + V - \frac{1}{8m^2c^2}\mathbf{p}^4 + \frac{\hbar^2}{8m^3c^2}(\nabla^2V) + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma} \cdot (\nabla V) \times \mathbf{p} \quad (2.92)$$

$\hat{T}$  being the kinetic energy operator,  $V$  remains the potential created by the nucleus ( $-\frac{Ze^2}{r}$ ) the third term being the mass-speed correction term coming from the relativistic variation of the mass with the speed. The fourth term is a correction due to the fast oscillation of the electron around its mean position. It is also called the Darwin term. Finally the last term is the spin-orbit coupling.

### Zeroth Order Relativistic Approximation Hamiltonian

To obtain an approximate Hamiltonian valid in all regions of space one can expand  $K(E)$  differently as:

$$K(E) = \left[1 + \frac{E}{2mc^2 - V}\right]^{-1} = 1 - \frac{E}{2mc^2 - V} + \left[\frac{E}{2mc^2 - V}\right]^2 + \dots \quad (2.93)$$

Thus, by keeping the zeroth order of expansion 2.93, we obtain the Zeroth Order Relativistic Approximation (ZORA) Hamiltonian:

$$\hat{H}^{ZORA} = V + (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (2.94)$$

Of course, this formulation retains the spin-orbit coupling in  $\boldsymbol{\sigma} \cdot \mathbf{p}$ , it is easy to disregard this part to obtain the Scalar Relativistic (SR) ZORA Hamiltonian. In 1998, Christoph van Wüllen [61] showed that the scalar relativistic effects could be fully included in a kinetic operator  $\hat{T}_{SR}^{ZORA}$ :

$$\hat{T}_{SR}^{ZORA} = \mathbf{p} \frac{c^2}{2mc^2 - V} \mathbf{p} \quad (2.95)$$

This new operator is really useful when the SOC is small enough to be disregarded and allows to decrease the computational cost.

### Decoupling small and large components with unitary transform: the Douglas-Kroll-Hess Hamiltonian

The Douglas-Kroll-Hess (DKH) [62, 63] Hamiltonian does not rely on the elimination of the small components as before but is derived from a unitary transformation  $U$ , acting on the Dirac-Coulomb Breit Hamiltonian  $\hat{H}^{DCB}$ , in order to obtain a diagonal Hamiltonian:

$$U^\dagger \hat{H}^{DCB} U = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix} \quad (2.96)$$

with  $U^\dagger U = 1$ .

The first transformation in the DKH approximation is actually the Foldy Wouthuysen transformation [64] in a free particle case.

$$\hat{U}^{(0)} = \hat{A}_i (a + \beta \alpha \mathbf{P}_i) \quad (2.97)$$

with

$$\hat{A}_i = \sqrt{\frac{\hat{E}_i + m_e c^2}{2\hat{E}_i}}; \mathbf{P}_i = \frac{c \mathbf{p}_i}{\hat{E}_i + m_e c^2} \quad (2.98)$$

with  $\hat{E}_i$  the kinetic energy operator for the positive energy states, defined as:

$$\hat{E}_i = \sqrt{m_e^2 c^4 + p_i^2 c^2} \quad (2.99)$$

After this first transformation the resulting Hamiltonian matrix,  $\hat{H}^{DKH1}$  is not diagonal but the coupling is already reduced. The potential  $\hat{V}$  needs to be now added and the decomposition to be pushed one step further.

$$\hat{U}^{(1)} = \sqrt{1 + \hat{W}_1^2} + \hat{W}_1 \quad (2.100)$$

with

$$\hat{W}_1(i) = \hat{W}_1 \phi(\mathbf{p}_i) = \int d^3 p_j \hat{W}(\mathbf{p}_i, \mathbf{p}_j) \phi(\mathbf{p}_j) \quad (2.101)$$

where:

$$\hat{W}(\mathbf{p}_i, \mathbf{p}_j) = \int d^3 p_j \hat{A}_i (\boldsymbol{\sigma} \mathbf{P}_i - \boldsymbol{\sigma} \mathbf{P}_j) \hat{A}_j \frac{\hat{V}(\mathbf{p}_i, \mathbf{p}_j)}{\hat{E}_i + \hat{E}_j} \phi(\mathbf{p}_j) \quad (2.102)$$

$\hat{V}(\mathbf{p}_i, \mathbf{p}_j)$  being the the Fourier transform of the potential energy and  $\phi(p_i)$  the (bi-spinor) wave function associated to an electron having the momentum  $\mathbf{p}_i$ . The decoupled Hamiltonian for two particles is thus:

$$\hat{H}^{Decoupled} = \beta \hat{E}_i + \hat{A}_i (\hat{V} + \boldsymbol{\sigma} \mathbf{P}_i \hat{V} \boldsymbol{\sigma} \mathbf{P}_i) \hat{A}_i - \beta (\hat{W}_1 \hat{E}_i \hat{W}_1 + \frac{1}{2} [\hat{W}_1^2, \hat{E}_i]_+) \quad (2.103)$$

Using the Dirac relation  $((\boldsymbol{\sigma} \cdot \mathbf{u})(\boldsymbol{\sigma} \cdot \mathbf{v}) = \mathbf{u} \cdot \mathbf{v} + i \boldsymbol{\alpha}(\mathbf{u} \times \mathbf{v}))$ , it is possible to separate the terms spin-independent to the spin-dependent leading to the  $\hat{H}^{SF}$  and  $\hat{H}^{SO}$ , respectively.

$$\hat{H}^{SF} = \sum_i \hat{E}_i + \sum_i \hat{V}_{eff}^{SF}(i) + \sum_{i < j} \frac{1}{r_{ij}} \quad (2.104)$$

with

$$\begin{aligned} \hat{V}_{eff}^{SF}(i) &= -\hat{A}_i [V(i) + \mathbf{P}_i V(i) \mathbf{P}_i] \hat{A}_i - \hat{W}_1(i) \hat{E}_i \hat{W}_1(i) - \frac{1}{2} [\hat{W}_1^2(i), \hat{E}_i] \\ V(i) &= \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} \end{aligned} \quad (2.105)$$

and  $\hat{H}^{SO}$ :

$$\begin{aligned} \hat{H}^{SO} &= \alpha \hbar c \left\{ \sum_i \sum_a Z_a \frac{\hat{A}_i}{\hat{E}_i + m_e c^2} \boldsymbol{\sigma}_i \left( \frac{\mathbf{r}_{ia}}{r_{ia}^3} \times \mathbf{p}_i \right) \frac{\hat{A}_i}{\hat{E}_i + m_e c^2} \right. \\ &\quad \left. - \sum_{i \neq j} \frac{\hat{A}_i \hat{A}_j}{\hat{E}_i + m_e c^2} \cdot \left( \boldsymbol{\sigma}_i \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \frac{\hat{A}_i \hat{A}_j}{\hat{E}_i + m_e c^2} - 2 \boldsymbol{\sigma}_i \left( \frac{\mathbf{r}_{ij}}{r_{ij}^3} \times \mathbf{p}_i \right) \frac{\hat{A}_i \hat{A}_j}{\hat{E}_i + m_e c^2} \right\} \end{aligned} \quad (2.106)$$

This SO Hamiltonian is the sum of one-electron and two-electrons terms. The matrix elements of the SO operator are still expensive to calculate. A solution is to approximate this Hamiltonian. The Atomic Mean Field Approximation (AMFI) is used to reduce the number of integrals to calculate using a "simple" idea since the SO interaction is short range as it behaves (as  $\frac{1}{r^3}$ ), it is relevant to disregard all multi-center two-electron SO integrals [65]. For a balanced treatment of SO effects, it is also appropriate to only include one-center one-electron SO integrals.

To simplify the SO Hamiltonian in a context of CI-SO coupling, Hess *et al.* [65] showed that the doubly excited determinants SO contributions can be negligible if the matrix elements of the SO operator between two Slater determinant that differ from only one single-excitation (from the spin orbital  $i$  to the spin orbital  $j$ ) are modified

in a way that defines the effective mean field one-electronic operator as:

$$\hat{H}_{ij}^{SO} = \langle \phi_i(1) | \hat{h}^{SO}(1) | \phi_j(2) \rangle + \frac{1}{2} \sum_k n_k \left\{ \langle \phi_i(1) | \tilde{H}_{kk}^{SO}(1) | \phi_j(1) \rangle - \langle \phi_i(1) | \tilde{H}_{kj}^{SO}(1) | \phi_k(1) \rangle - \langle \phi_k(1) | \tilde{H}_{ik}^{SO}(1) | \phi_j(1) \rangle \right\} \quad (2.107)$$

with

$$\langle \phi_i(1) | \tilde{H}_{kk}^{SO}(1) | \phi_j(1) \rangle = \langle \phi_i(1) | [\phi_k(2) | \tilde{H}_{1,2}^{SO} | \phi_k(2)] | \phi_j(1) \rangle \quad (2.108)$$

$$\langle \phi_i(1) | \tilde{H}_{kj}^{SO}(1) | \phi_k(1) \rangle = \langle \phi_i(1) | [\phi_k(2) | \tilde{H}_{1,2}^{SO} | \phi_j(2)] | \phi_k(1) \rangle \quad (2.109)$$

$$\langle \phi_k(1) | \tilde{H}_{ik}^{SO}(1) | \phi_j(1) \rangle = \langle \phi_k(1) | [\phi_i(2) | \tilde{H}_{1,2}^{SO} | \phi_k(2)] | \phi_j(1) \rangle \quad (2.110)$$

and :

$$\hat{h}^{SO}(1) = \alpha \hbar c \left\{ \sum_a Z_\alpha \frac{\hat{A}_1}{\hat{E}_1 + m_e c^2} \boldsymbol{\sigma}_1 \left( \frac{\mathbf{r}_{1a}}{r_{1a}^3} \times \mathbf{p}_1 \right) \frac{\hat{A}_1}{\hat{E}_1 + m_e c^2} \right\} \quad (2.111)$$

$$\tilde{H}_{1,2}^{SO} = \alpha \hbar c \left\{ \frac{\hat{A}_1 \hat{A}_2}{\hat{E}_1 + m_e c^2} \cdot \left( \boldsymbol{\sigma}_1 \frac{\mathbf{r}_{12}}{r_{12}^3} \times \mathbf{p}_1 \right) \frac{\hat{A}_1 \hat{A}_2}{\hat{E}_1 + m_e c^2} - 2 \boldsymbol{\sigma}_1 \left( \frac{\mathbf{r}_{12}}{r_{12}^3} \times \mathbf{p}_1 \right) \frac{\hat{A}_1 \hat{A}_2}{\hat{E}_1 + m_e c^2} \right\} \quad (2.112)$$

$n_k$  is the occupation of spin-orbital  $k$ ,  $\phi_i$  an occupied and  $\phi_j$  a virtual orbital. Since equation 2.107 describes the valence electrons in a field created by the electrons in the orbitals  $k \neq i$ ,  $n_k$  and  $\phi_k$  must have a physical meaning. For this reason, the AMFI module must be used with atomic natural orbitals such as the relativistic contracted ANO-RCC basis sets (see Section 2.5.1).

#### 2.4.4 Relativistic Effective Core Potential

In chemistry, many molecule's properties involve the valence electrons and eventually the sub-valence shells. It is then possible to speed up the calculation by replacing the core electrons by an effective core potential (ECP) [66]. Since the number of electrons is smaller and the number of functional basis can be reduced, the calculation becomes less expensive. The second advantage of ECP is its convenience because it can be used with DFT and wave function methods. The Hamiltonian is reduced to the sum of the interaction between the valence electrons and the interaction of the former with the nucleus/core electrons and called the valence Hamiltonian  $\hat{H}^v$ :

$$\hat{H}^v = \sum_i^{n_{valence}} -\frac{1}{2} \nabla_i^2 + \sum_{i < j}^{n_{valence}} \frac{1}{r_{ij}} + \sum_i^{n_{valence}} \sum_I^N V_{cv}^I(i) + \sum_{I < J}^N \frac{Q_I Q_J}{R_{IJ}} + V_{CPP} \quad (2.113)$$

The first term is the kinetic energy of the valence electrons. The second is the interaction between the valence electrons, the third one is the interaction between the electron/nuclei and valence electrons. The fourth term is the repulsion between effective cores. The last term is the core polarisation potential (CPP).  $V_{cv}$  in equation 2.113 is parametrised to include not only to the scalar relativistic effects but also the spin-orbit relativistic effects so it is adjusted to reproduce data with great accuracy.

$$V_{cv}^I(i) = \sum_i^{n_{valence}} \frac{Q_I}{r_{iI}} + \sum_i^{n_{valence}} V_{PP}^I(i) \quad (2.114)$$

The name of the ECP is given under the form ECPnXY where usually XY represents the level of the fully relativistic method used to generate the target all-electron data to which the ECP parameters are adjusted: MWB for multi-configurational Wood-Boring or MDF for multi-configuration Dirac-Fock [67].

## 2.5 Basis Sets, Basis Sets Superposition Error and Complete Basis Set Extrapolation

### 2.5.1 Basis Sets

Back to equation 2.10, the wave-function is described by a Slater determinant composed of orthonormal spin-orbitals. In a molecule, each spin-orbital represents a molecular orbital (MO)  $\phi_i$  which can be represented by a Linear Combination of Atomic Orbitals (LCAO) [68],  $\chi_k$ .

$$\phi_i = \sum_j^{N_{AO}} c_{ij} \psi_j = \sum_j^{N_{AO}} c_{ij} \sum_k^{Nb} d_{jk} \chi_k \quad (2.115)$$

$d_{jk}$  being the expansion coefficients,  $\chi_k$  the atomic basis functions, and Nb the number of the basis function used. A minimum basis set contains roughly<sup>4</sup> as much basis function as there are atomic orbitals.

The only restriction for mathematical functions to be used as basis functions is to decay to zero as the distance between the nuclei and the electron increases. In practice, two families of orbitals are used: the Slater Type Orbitals (STO) [69] and the Gaussian Type Orbitals (GTO) [70] both products of a radial part  $\mathcal{R}_l(r)$  and a spherical harmonic function  $Y_{lm_l}(\theta, \phi)$ .

<sup>4</sup>sometimes extra orbitals are added for polarization

- Slater Type Orbitals

Slater-type orbitals, the radial part only depends on  $n$  as

$$\mathcal{R}_n = N_{Slater} r^{n-1} e^{-\zeta r} \quad (2.116)$$

$n$  being the principal quantum number,  $N_{Slater}$  the normalisation constant,  $r$  is the distance between the electron and the nucleus and  $\zeta$  a constant related to the effective charge of the nucleus  $Z^*$  such that the energy level of this orbital equals to

$$E_n = \frac{1}{2} \left( \frac{Z^*}{n} \right)^2 \quad (2.117)$$

STO basis are successful for atoms as they describe the cusp at the nucleus. However, their limitation is that two-electrons integrals involving 3 or 4 centres cannot be computed analytically.

- Gaussian Type Orbitals

To overcome the integration issue, GTO (Gaussian Type Orbitals) were introduced defined as:

$$\mathcal{R}_n = N_6(\alpha) r^{n-1} e^{-\alpha r^2} \quad (2.118)$$

for their radial part. If the GTOs allow the calculations to be performed faster, the  $r^2$  dependency alter the description of the electron behaviour near the nucleus [10]. Therefore a larger basis will be needed to reach the same accuracy as with an STO.

Linear combinations (contractions) of primitive GTOs functions are able to approximate the nodal structures of atomic orbitals (AO). The quality of a basis set is linked to the number of Gaussian primitives and to the optimisation of the contraction coefficients.

In the current work, we aim at computing reaction energies with an accuracy of a few  $\text{kJ}\cdot\text{mol}^{-1}$ . Thus the choice of the atomic basis set is crucial. In all the PhD projects, basis sets of at least triple- $\zeta$  quality were used to determine the optimal geometries, using correlation consistent Dunning's basis sets [71, 72], aug-cc-pVTZ/aug-cc-pVQZ, and the proper small-core RECP basis sets for the heavy elements. For the largest molecular complexes (See Chapter 3), efficient computational speed up was achieved with the resolution of the identity algorithm, using Ahlrichs def2-TZVP basis sets and their auxiliary counterparts [73, 74]. Note that for heavy elements, the def2-basis sets are bound to small-core RECPs.



To reach chemical accuracy (or higher) for thermodynamics properties of plutonium gas-phase molecules, the electronic energies were extrapolated to the complete basis set limit, from calculations with the extended all-electron atomic natural orbital relativistic correlation consistent (ANO-RCC) Roos's basis sets [75–77], which offer from triple to quadruple- $\zeta$  quality expansions in the Douglas-Kroll-Hess relativistic framework [78].

We will comment on the choice of the basis sets in the appropriate introductory sections of each research project.

### 2.5.2 Basis Sets Superposition Error

The Basis Sets Superposition Error (BSSE) introduced by Boys and Bernardi [79] occurs when 2 atoms (A and B) are close to each other. The basis set of the atom A will be superposed with the basis set of the atom B describing twice the same stabilising energy. Thus, the total energy is lower than what it should be and must be corrected.

$$E_{corrected} = E_{uncorrected} + E_{BSSE} \quad (2.119)$$

In order to compute the corrected total energy, the energy of atom A has to be calculated in the presence of the basis of the atom B and the energy of atom B in the presence of the basis of the atom A.

$$E_{BSSE} = E_A^A - E_A^{AB} + E_B^B - E_B^{AB} \quad (2.120)$$

where the superscripts refers to the basis set used and the subscripts the atom.

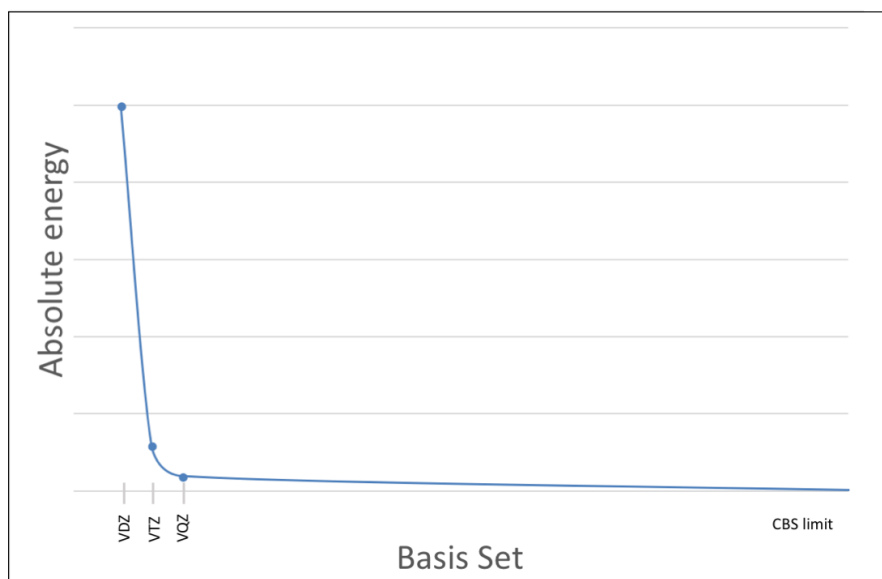
### 2.5.3 Complete Basis Set Extrapolation

A way to avoid BSSE, among others, is to extrapolate the energy to the Complete Basis Set (CBS) limit *i.e.* to approach the results with infinite basis sets (see Figure 2.2).

In this work we compared two ways of extrapolating energies, one by extrapolating the total energy, the second by extrapolating separately the SCF energy and the correlated energy before summing the two.

## 2.5. Basis Sets, Basis Sets Superposition Error and Complete Basis Set Extrapolation

FIGURE 2.2: Theoretical convergence to the complete basis set limit with increasing the number of basis functions



The total energy CBS value can be derived from a two-points extrapolation formula [80]:

$$E_{XY}^{CBS} = \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3} \quad (2.121)$$

where  $X$  and  $Y$  are the size of the basis sets (typically  $n=3$  and  $n=4$  for triple and quadruple- $\zeta$  basis sets).

Peterson *et. al.* [81] proposed specific formulas for the uncorrelated energy  $E_{CBS}^{SCF}$  and the correlated energy  $E_{CBS}^{Corr}$  extrapolations:

$$E_n^{SCF} = E_{CBS}^{SCF} + A(n+1)e^{-6.57\sqrt{n}} \quad (2.122)$$

$$E_n^{corr} = E_{CBS}^{corr} + \frac{B}{(n + \frac{1}{2})^4} \quad (2.123)$$

In these formulas  $n$  is the size of the basis set (typically  $n=3$  and  $n=4$  for triple and quadruple- $\zeta$  basis sets),  $E^{SCF}$  is either the SCF or CASSCF energy and  $E^{corr}$  the correlation part of the total energy.

## 2.6 Conclusion

As mentioned before, only a few and basic methods of Quantum Chemistry were depicted here. Nonetheless, it already triggers some general questions at the heart of the modelling of Actinides.

How to properly describe the relativistic effects ?

How to retrieve electronic correlation ?

If the first question is almost answered in the present section, the former question will be addressed more particularly in the Chapter 4. Indeed, a good way to describe the static correlation is to use methods including multiple Slater determinants in the wave function. These methods are called "multi-reference" quantum chemical methods.

## Chapter 3

# Coordination of Alkyl cations $[(XA_2)X(CH_2SiMe_3)]$ ( $X = Th, U$ ) or $[(XN_2)Zr(CH_3)]$ with an arene for Ethylene polymerisation: Exploration of the bonding

### 3.1 Introduction

The amount of polyethylene produced every year implies a constant need for improving the industrial production process. Since the pioneering process by Karl Ziegler and Giulio Natta in the early 1950's on the polymerisation of simple olefins, there had been intense interest in the application of early transition metal catalysts for the selective polymerisation of inexpensive olefins. Following to Ziegler-Natta catalysts [82], metallocene catalysts were discovered in the late 1980's and resulted in numerous industrial processes for improving the properties of polyolefinic materials along with performance parameters. In particular, beside the requirement of higher activity, research have focused on the control of particle size, particle size distribution, and the morphology of the resultant polyolefin (number of carbon in the chain). In the metallocene family, group 4 transition metal metallocene complexes have the largest activity, such as  $[Cp_2ZrMe][B(C_6F_4TBS)_4]$  synthesised by Marks and co-workers [83–91]  $1.1 \times 10^7$  g of polyethylene.(mol of  $M=Zr$ )<sup>-1</sup>.h<sup>-1</sup>.atm<sup>-1</sup>[92]). The brother complex with Th was also synthesised but is an order of magnitude less active than the Zr-complex ( $9.2 \times 10^5$  g of polyethylene.(mol of Th)<sup>-1</sup>.h<sup>-1</sup>.atm<sup>-1</sup>), suggesting that the nature of the metallic centre may play a key role in the catalytic

activity. In the 1990s, new catalysts with well-defined metal complexes and other ligand motifs were summarised as the "post metallocenes" family [93].

During my first-year PhD stay at Mc Master University in Hamilton (Ontario, Canada), discussions were initiated with David Emslie's research group, currently working on the synthesis of cationic metal alkyl complexes, that are open post-metallocene catalysts of electropositive metals. These are typically generated by reaction of a neutral dialkyl complex with strong electrophiles such as  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ ,  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $(\text{Al}(\text{CH}_3)_x\text{O}_y)_n$  (Methylaluminoxane-MAO). The subsequent polymerisation is achieved by repeated ethylene coordination and 1,2-insertion steps [1]. These activation and polymerization reactions are commonly conducted in arene or alkane solvents; the former is standard in academic laboratories [2], while the latter is favoured in industry [3, 94]. However, in sterically open post-metallocene catalysts of electropositive metals, arene solvents have significant potential to coordinate, negatively impacting ethylene polymerisation activity. At the same time arene coordination is known to increase the thermal stability of metal alkyl cations prior to exposure to ethylene, which is of key importance for industrial polymerisation processes often conducted at elevated temperatures (140 °C). Therefore, Emslie's group has explored, in a systematic fashion, the suitability of tetravalent actinides, namely Thorium and Uranium, to create thermally robust and highly reactive cationic monoalkyl derivatives, as an alternative to the Zirconium based ones.

The chapter begins with a review of all the Zr, Th, and U complexes that were synthesised and crystallised when possible for structural characterisation. We will also present the evaluated ethylene polymerisation activities at room and elevated (70-80 °C) temperatures. The experimental work scanned several arene solvents, from benzene, toluene, to halogenated derivatives of benzene (bromo-benzene, fluoro-benzene and di fluorobenzene), with different electron donor capabilities, noting for example that Hayes *et al.* showed a good activity for a scandium complex in Bromobenzene [95, 96]. In an attempt to link the catalytic properties with the complexes structures and coordination, the second part will present the quantum chemical calculations that allow an in-depth discussion of the influence of the cation and the impact of arene solvent coordination. We finally investigate the strength of the interaction between cationic metal alkyl complex with ethylene to shed some light on the competition between ethylene and arene coordination in the initial steps of the catalytic reaction.

## 3.2 Systems presentation and theoretical studies

### 3.2.1 Catalysts synthesis strategy, structures and catalytic power

Using a neutral dialkyl **1-X** (X = Th, U or Zr) the arene-coordinated alkyl cations could be derived, where the arene (benzene, toluene, bromo-benzene, fluorobenzene or the (o)-difluoro-benzene) is introduced by the solvent. The catalytic power and the robustness of the compounds were tested by exposing them to ethylene during 30 min at temperatures between 20 and 70 °C (80 °C for **n-Zr**). It is important to note that early transition metal and f-element olefin polymerisation catalysts are frequently generated *in situ* without isolation and characterisation, this lack of information is the main source of uncertainties in the mechanism.

TABLE 3.1: Name of the different ligands, counter ion and arene of the compounds discussed in this Chapter

	Formula	Name
Ligands	XA <sub>2</sub>	4,5-bis(2,6-diisopropylanido)-2,7-di-tert-butyl-9,9-dimethylxanthene
Ligands	XN <sub>2</sub>	4,5-bis(2,4,6-triisopropylanido)-2,7-di-tert-butyl-9,9-dimethylxanthene
	CH <sub>2</sub> SiMe <sub>3</sub>	(trimethylsilyl)methyl
Counter ion	B(C <sub>6</sub> F <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	diskal tetrakis(pentafluorophenyl)borate
Arene	C <sub>6</sub> H <sub>6</sub>	Benzene
	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	Toluene
	C <sub>6</sub> H <sub>5</sub> Br	Bromobenzene
	C <sub>6</sub> H <sub>5</sub> F	Fluorobenzene
	C <sub>6</sub> H <sub>5</sub> F <sub>2</sub>	Difluorobenzene
	C <sub>2</sub> H <sub>2</sub>	Ethylene

The different metallic centres are chosen first because the literature reports their efficiency (see Section 3.1) and because of their electronic structure in the tetravalent oxidation state. Zr(IV) is a 4d<sup>0</sup>-element with the smallest ionic radius, while Th(IV) is a 5f<sup>0</sup>-element and U(IV) a 5f<sup>2</sup>-element with larger ionic radii (see Table 3.3). In the actinides, while the 5f-orbitals are expected to participate into the bonding, the 6d-orbitals in U(IV) complexes may also play a role in the bonding, allowing back donation electron transfer [97].

The choice of the arene is made in order to tune the donating capacity. This donating power is directly connected to the strength of the cation arene bond. If too strong it could hinder or even shutter ethylene coordination and impact the catalytic activity (see Section 3.2.2).

We start the a survey on Emslie's work with the cation derivatives of the neutral dialkyl **1-Th**, **2-Th**, **3-Th** and **5-Th** cations [99–102]. All of them could be synthesised but only **2-Th** could be characterised with X-ray diffraction (see Figure 3.1). Unfortunately only **5-Th** exhibits a catalytic power but it is not thermally robust (see Table

TABLE 3.2: Numbers and Formula of the different compounds of the present Chapter

Number	Formula	X-ray structure
1-U	$[(XA_2)U(CH_2SiMe_3)_2]$	yes
2-U	$[(XA_2)U(CH_2SiMe_3)(C_6H_6)]^+[B(C_6F_5)_4]^-$	yes
3-U	$[(XA_2)U(CH_2SiMe_3)(C_6H_5CH_3)]^+[B(C_6F_5)_4]^-$	yes
4-U	$[(XA_2)U(CH_2SiMe_3)(C_6H_5Br)]^+[B(C_6F_5)_4]^-$	no
5-U	$[(XA_2)U(CH_2SiMe_3)(C_6H_5F)]^+[B(C_6F_5)_4]^-$	yes
6-U	$[(XA_2)U(CH_2SiMe_3)(C_6H_4F_2)]^+[B(C_6F_5)_4]^-$	no
E-U	$[(XA_2)U(CH_2SiMe_3)(C_2H_2)]^+[B(C_6F_5)_4]^-$	not synthesised
1-Th	$[(XA_2)Th(CH_2SiMe_3)_2]$	no
2-Th	$[(XA_2)Th(CH_2SiMe_3)(C_6H_6)]^+[B(C_6F_5)_4]^-$	yes
3-Th	$[(XA_2)Th(CH_2SiMe_3)(C_6H_5CH_3)]^+[B(C_6F_5)_4]^-$	no
4-Th	$[(XA_2)Th(CH_2SiMe_3)(C_6H_5Br)]^+[B(C_6F_5)_4]^-$	not synthesised
5-Th	$[(XA_2)Th(CH_2SiMe_3)(C_6H_5F)]^+[B(C_6F_5)_4]^-$	no
6-Th	$[(XA_2)Th(CH_2SiMe_3)(C_6H_4F_2)]^+[B(C_6F_5)_4]^-$	not synthesised
2'-Th	$[(XN_2)Th(CH_3)(C_6H_6)]^+[B(C_6F_5)_4]^-$	not synthesised
E-Th	$[(XA_2)Th(CH_2SiMe_3)(C_2H_2)]^+[B(C_6F_5)_4]^-$	not synthesised
2-Zr	$[(XA_2)Zr(CH_2SiMe_3)((C_6H_5CH_3))]^+[B(C_6F_5)_4]^-$	not synthesised
2'-Zr	$[(XN_2)Zr(CH_3)(C_6H_6)]^+[B(C_6F_5)_4]^-$	no
3'-Zr	$[(XN_2)Zr(CH_3)(C_6H_5CH_3)]^+[B(C_6F_5)_4]^-$	yes
4'-Zr	$[(XN_2)Zr(CH_3)(C_6H_5Br)]^+[B(C_6F_5)_4]^-$	no
5'-Zr	$[(XN_2)Zr(CH_3)(C_6H_5F)]^+[B(C_6F_5)_4]^-$	not synthesised
6'-Zr	$[(XN_2)Zr(CH_3)(C_6H_4F_2)]^+[B(C_6F_5)_4]^-$	not synthesised
E'-Zr	$[(XN_2)Zr(CH_3)(C_2H_2)]^+[B(C_6F_5)_4]^-$	not synthesised

TABLE 3.3: Ionic Radii of metallic center in Å from [98]

Element	Ionic Radius
Zr	0.72
Th	0.94
U	0.89

3.5). 4-Th could not be synthesised and no attempt was made for the generation of 6-Th.

The benzene 2-U and toluene 3-U derivatives of 1-U, are more soluble than their thorium equivalents [103–107]. Thus it could be crystallised to obtain a deep brown solids (see Figures 3.2 and 3.3 for structure). The distances are, as expected from the ionic radii, shorter in the uranium complexes than in the thorium ones (see Table 3.4). 4-U (bromobenzene) was readily obtained but not structurally characterised

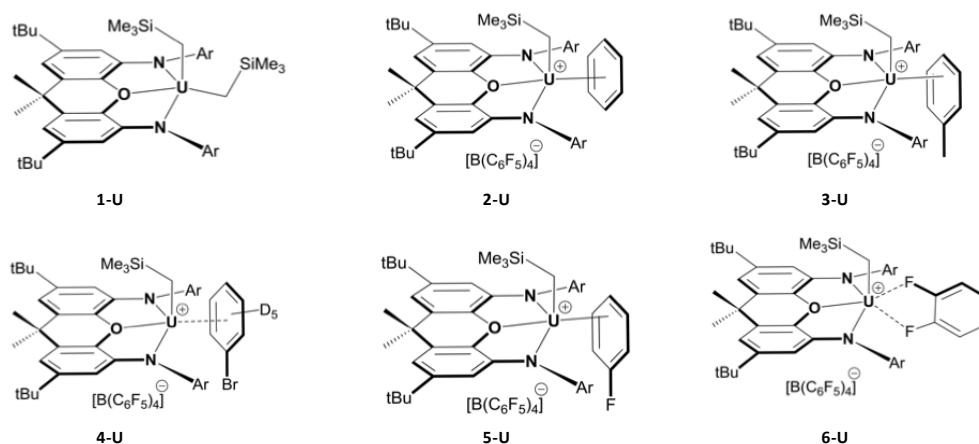


FIGURE 3.1: Structures of the catalysts containing uranium, thorium ones are strictly equivalent.

and catalytically silent.

TABLE 3.4: Important bond lengths in Å and angles in degree for the neutral **1-U** and the cationic **2-U**, **2-Th**, **3-U**, **3'-Zr** and **5-U** given by X-ray diffraction [108].

Compounds	<b>1-U</b>	<b>2-U</b>	<b>2-Th</b>
An-O	2.484(5), 2.504(4)	2.441(2)	2.496(5)
An-N	2.261(5), 2.262(5), 2.272(5), 2.280(5)	2.224(2), 2.236(6)	2.278(3), 2.288(3)
An-C <sub>arene</sub>	–	3.099(3) - 3.248(3)	3.18 - 3.31
N <sub>1</sub> ... N <sub>2</sub>	4.00, 4.02	3.94	4.04
Arene Bend			
Angle <sup>1</sup>	17.5, 18.8	18.9	8.7
O-An-C <sub>apical</sub>	94.8(2), 95.0(2)	87.26(8)	91.3(1)
An-C-Si	128.2(3), 130.4(3), 130.5(4), 130.8(3)	133.7(2)	131.0(2)
Compounds	<b>3-U</b>	<b>3'-Zr</b>	<b>5-U</b>
An-O	2.417(9)	2.220	2.431(3)
An-N	2.21(1), 2.22(1)	2.138; 2.122	2.215(3), 2.218(3)
An-C <sub>arene</sub>	3.05(2) - 3.78(2)	2.697 - 2.840	3.129(5) - 3.598(6)
N <sub>1</sub> ... N <sub>2</sub>	3.98	3.91	3.98
Arene Bend			
Angle <sup>1</sup>	5.9		7.2
O-An-C <sub>apical</sub>	88.8(4)		89.6(1)
An-C-Si	136.8(7)	–	134.8(2)

<sup>1</sup> Angle between the carbons of the arene and the planar ligand.



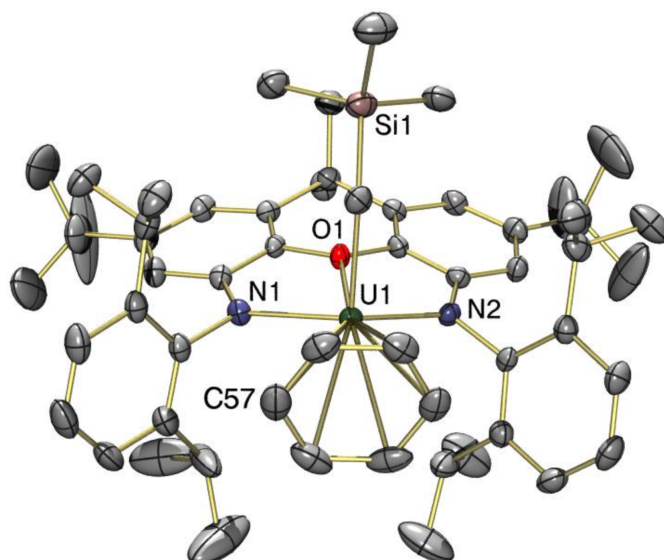


FIGURE 3.2: X-ray crystal structure of  $\eta^6$ -2-U [108]. Hydrogen atoms are not represented

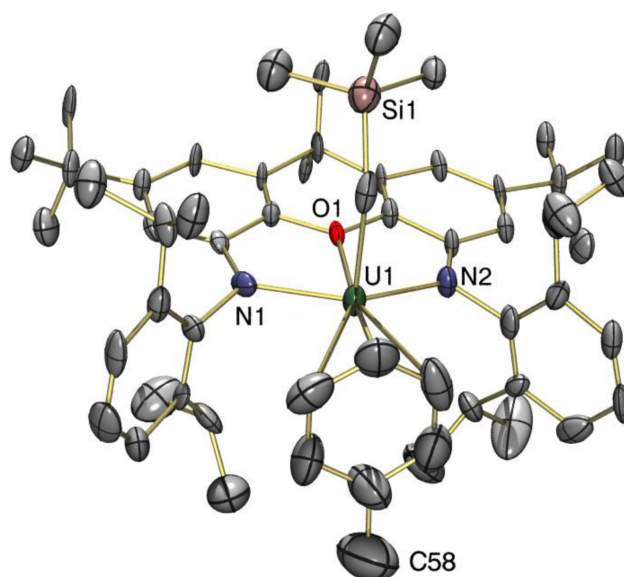


FIGURE 3.3: X-ray crystal structure of  $\eta^6$ -3-U [108]. Hydrogen atoms are not represented

Bromobenzene was then exchanged (conceptually) with fluorobenzene to have an expected less donating ligand character, leading to **5-U** which could be X-ray analysed (see Figure 3.4). This makes it the first  $5f$ -element complex bearing a  $\pi$ -coordinated

fluoroarene ligand crystallographically characterised. Table 3.4 shows a resemblance between **5-U** and **3-U** with the same distance  $N_{1-2}$  (3.98 Å) and the smallest arene bend angle (7.2 ° and 5.9°, respectively).

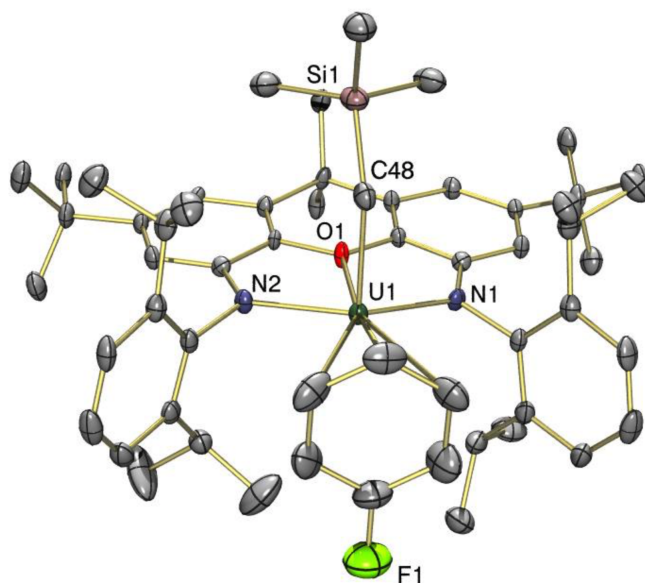


FIGURE 3.4: X-ray crystal structure of  $\eta^6$ -**5-U** [108]. Hydrogen atoms are not represented

In order to further decrease the coordination between arene and the uranium metallic center, the cation with *o*-difluorobenzene was synthesised but could not be crystallised.

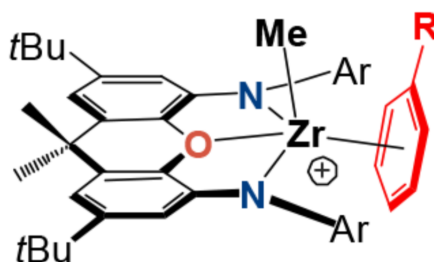
The activity of **5-U** is slightly larger than **6-U**,  $1.12 \times 10^4$  g of polyethylene.(mol of U) $^{-1}$ .h $^{-1}$ .atm $^{-1}$  at 20 °C (see Table 3.5). However, at higher temperature (70 °C) no polymerisation is observed, indicating that **6-U** has a reduced thermal stability. An attempt was made to use the *m*-difluorobenzene, unfortunately no polyethylene was formed after 30 minutes at 20 °C.

At the same time, close equivalents were synthesised with a zirconium center [109].

**2'-Zr** polymerises so slowly that its activity is negligible. **3'-Zr** presents excellent performance with an activity of  $2.73 \times 10^5$  g.mol $^{-1}$ .h $^{-1}$ .atm $^{-1}$  observed after 30 minutes at 20 °C and  $1.11 \times 10^5$  g.mol $^{-1}$ .h $^{-1}$ .atm $^{-1}$  observed after 30 minutes at 80 °C. The decrease of the activity as the temperature increases can probably be explained by the decomposition of the catalyst. **4'-Zr** could be obtained (see Figure 3.6) and presents an activity close to that of **3'-Zr**. Its structure could not be resolved since

TABLE 3.5: Activities of complexes at and 1 atm in g of polyethylene. (mol of X=Th, U or Zr)<sup>-1</sup>.h<sup>-1</sup>.atm<sup>-1</sup> and after 30 min of ethylene exposure.

Complex	Activity (20°C)	Activity (70°C) <sup>1</sup>
2-U	0	0
3-U	0	0
4-U	0	0
5-U	12 800	39 200
6-U	11 200	0
2-Th	0	0
3-Th	0	0
5-Th	16 800	57 600
2'-Zr	NA	NA
3'-Zr	273 000	113 000
4'-Zr	52 200	NA

FIGURE 3.5: Structures of the compounds containing zirconium, with R = H, CH<sub>3</sub>, F, Br .

the synthesis leads to a mixture of two isomers (see Figure 3.6). There is no report of synthesis concerning 5'-Zr or 6'-Zr yet.

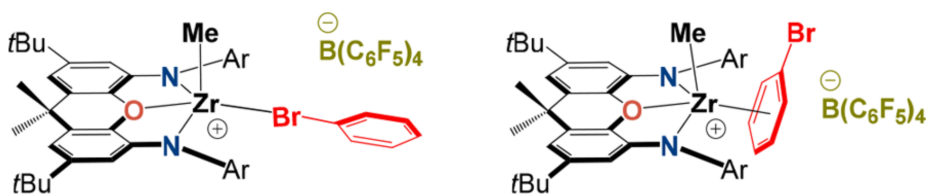


FIGURE 3.6: Possible structures of 4'-Zr [109]

### 3.2.2 Finding the catalytic mechanism

The rationalisation of the catalytic mechanism is not easy since several hypotheses can be put forward:

- First, is it a concerted mechanism like in Figure 3.7 where both arene and ethylene are bonded at the same time to the metallic center or not ?
- If not, the relative bonding strengths of ethylene versus arene with the metal will be important. If the arene-metal bond is too strong, the ethylene will not be able to insert itself and the catalysis will not occur.

The success of the zirconium complexes over the actinides ones raises the question on the nature of the arene bonds to the metals. Having the smallest ionic radius Zr could be expected to form stronger bonds than the Th and U, contradicting the observed efficiency.

Gardner *et al.* [110] reported a larger catalytic power for Th complexes ( $[\text{Th}\{\text{N}(\text{CH}_2\text{CH}_2\text{NSiPri}_3)_2(\text{CH}_2\text{CH}_2\text{NSiPri}_2\text{C}[\text{H}]\text{MeCH}_2)\}]$ ) than for the U ones (as for **5-U** and **5-Th**), and proposed as an explanation that electrostatic interactions are dominant in Th-complexes making the Th-ligand bond reacting more easily than the U-ligand one. Conversely, Domeshek *et al.* [111], in their complexes bis(N,N'-bis(trimethylsilyl)-2-pyridylaminate) $\text{An}(\mu\text{-Cl})_2\text{Li}(\text{TMEDA})$  ( $\text{An} = \text{Th}, \text{U}$ ) found that U-complexes are more efficient than the Th ones. They proposed three explanations. The first is that the  $5f^2$  electrons of uranium can participate to a back-donation leading to an improved coordination to the olefin facilitating the activation of the double bond. The second is that the thorium complexes form stronger bonds with the arene making the insertion of ethylene harder. Another explanation is that the  $5f$  orbitals in the U complex could stabilise the 4-member transition state (Figure 3.7), thus facilitating the catalysis [112].

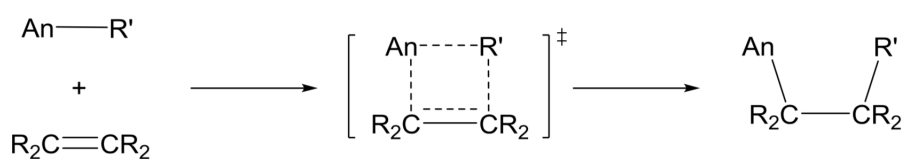


FIGURE 3.7: Four-center transition state in neutral organoactinide-mediated transformation where R' is the arene [108]

The last explanation appears as the simplest, as the larger size of Th(IV) might make it sterically more accessible than the U(IV).

Of course, the true explanation can be a mixture of these hypothesis calling for a theoretical study of the systems to rationalise their catalytic activities and the mechanism of polymerisation by answering the following questions:

- Why do Zr complexes present such short bonds between the arene and the metal?
- What is the dominant nature of the bonding (electrostatic, covalent?...)?
- What is the participation of d and f orbitals into the bonding?
- What is the strength of the ethylene-metal versus the arene-metal bond?

### 3.2.3 Theoretical Studies of the Th, U and Zr cationic complexes

The theoretical studies of the complexes cited in the previous section are very limited. One theoretical study explored the catalysis reaction path [110]. It includes a full geometry optimisation followed by an anharmonic frequency calculation with the B3PW91 [113, 114] functional. Scalar relativistic effects were included by the Stuttgart-Dresden RECP [115, 116] and the corresponding basis sets. These articles emphasised the important role of the 5f-orbitals of thorium [110] and uranium [110, 117].

This study confirm that the explanations proposed by experimentalists such as electrostatic interaction, back-donation and strength of the bonds must be tested and assessed by an in-depth exploration of the bond between the various metallic centre and the arene solvents. In this context, we have used the ETS-NOCV bonding analysis [118, 119] that has been proven useful to elucidate the nature of the bonding interaction in multiple transition metal complexes [97, 120–129].

We start by optimising the structures of the complexes and compare the computed geometries to X-ray data, when available. Ultimately our results should address the previous and the following questions:

- How well do quantum chemistry structures agree with X-ray data?
- Is it possible to predict the geometries of the uncrystallised complexes?
- What are the driving forces of the cation interactions? How do they relate to the catalytic activity?

## 3.3 Optimisation of the Arene-Coordinated Uranium, Thorium or Zirconium Alkyl Cations

The complexes were optimised at the DFT level with the TURBOMOLE package [130]. Def-TZVP with RECP [131] was used for U, Th and Zr, and def2-TZVP basis

set [73] for all the other atoms. The resolution of identity for the Coulomb integrals was used to reduce the computational cost. We first considered the pure GGA PBE functional but it was not satisfying. Indeed in the  $\eta^6$ -2-U and  $\eta^6$ -2-Th benzene complexes, the benzene ended up being tilted in the optimised structure deviating from its expected orientation observed in the crystal. The hybrid PBE0 [45] functional previously reported good geometrical agreement with the experimental data for Actinides containing molecules [132]. In our case PBE0 brought the theoretical structure in excellent agreement with the experimental one. All the geometries provided by Emslie's team are available in Appendix A. The inclusion of the solvent effect with the COSMO continuum solvent model marginally affected the geometries while significantly increasing the computational time. This led us to consider only gas-phase optimised geometries.

### 3.3.1 Optimisation of Benzene-Coordinated Alkyl Cations

For  $\eta^6$ -2-Th and  $\eta^6$ -2-U, X-ray structures were available and were used as starting points (see Table 3.2). For the 2'-Zr no X-ray structure was available. Thus the X-ray structure of  $\eta^6$ -3'-Zr was used by substituting the methyl group of toluene by a hydrogen atom. As a complement of information concerning the influence of the (trimethylsilyl)methyl group, the structure  $\eta^6$ -2-Zr, being the strict equivalent of  $\eta^6$ -2-Th and the structure  $\eta^6$ -2'-Th being the strict equivalent of  $\eta^6$ -2'-Zr, were optimised. The starting points of those optimisations were the optimised  $\eta^6$ -2-Th and  $\eta^6$ -2'-Zr geometries where the Th atom was substituted by a Zr atom and vice versa respectively.

### 3.3.2 Optimisation of Toluene-Coordinated Alkyl Cations

For  $\eta^6$ -3-U and  $\eta^6$ -3'-Zr, X-ray structures were available and were used as starting points. Since the X-ray data of  $\eta^6$ -3-U and  $\eta^6$ -3'-Zr present the arene facing the metallic center (as in the benzene complexes), we only tested the orientation of the methyl group of the arene for the toluene structure  $\eta^6$ -3-Th. By convention, as in [96], we will name as "exo" structure the structure where the methyl group is on the same side as the CH<sub>2</sub>SiMe<sub>3</sub> group and as "endo" structure, the structure where the methyl group sits on the opposite side of CH<sub>2</sub>SiMe<sub>3</sub> as illustrated by Figure 3.8.

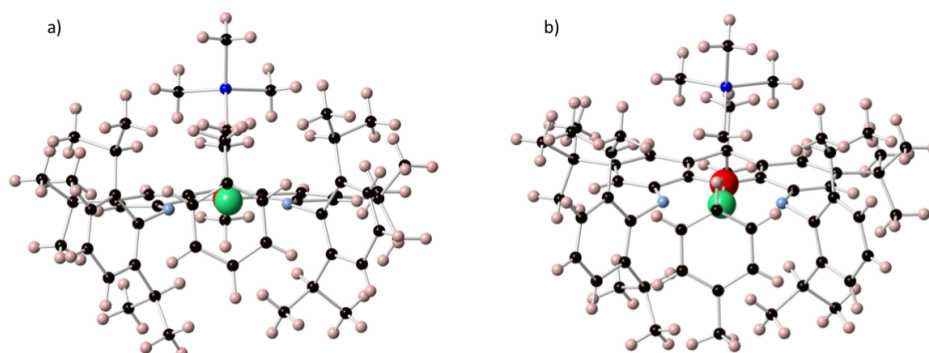


FIGURE 3.8: Starting geometries for the optimisation of the toluene complex  $\eta^6$ -3-Th with a) the "exo" starting point b) the "endo" starting point.

### 3.3.3 Optimisation of Halogeno-Coordinated Alkyl Cations

The X-ray structure of fluorobenzene,  $\eta^6$ -5-U, is also presenting a "endo" structure. Thus we also expect a "endo" structure for  $\eta^6$ -5-Th. We also explored the orientation of the arene in the fluorobenzene complexes  $\eta^1$ -5-Th and  $\eta^1$ -5'-Zr having the fluorobenzene of the arene ring facing the metallic centre, with the "horizontal" and the "vertical" orientations as shown in Figure 3.9.

The bromo-benzene 4-U and fluorobenzene 5-U were optimised with the  $\eta^6$ -5-U X-ray structure as starting point substituting fluorine by bromine.

The  $\eta^6$ -3-Th,  $\eta^6$ -3-U and  $\eta^6$ -5-U have a similar orientation of the methyl group of the toluene or the fluor of the fluorobenzene; all are in the "endo" orientation. Thus the bromo-benzene  $\eta^6$ -4-Th and  $\eta^6$ -4-U were optimised in the "endo" convention.

For the 4'-Zr, Motolko *et al.* [109] reported the "exo" and the "horizontal" structures as possible structures and probably a mixing of the two. Thus we tested these two orientations presented in Figure 3.10.

### 3.3.4 Optimisation of Difluoro-Coordinated Alkyl Cations

For difluoro-benzene complexes, only the 6-Th was optimised so far. There are no X-ray data for any of the metallic center thus, five orientations were tested. Three

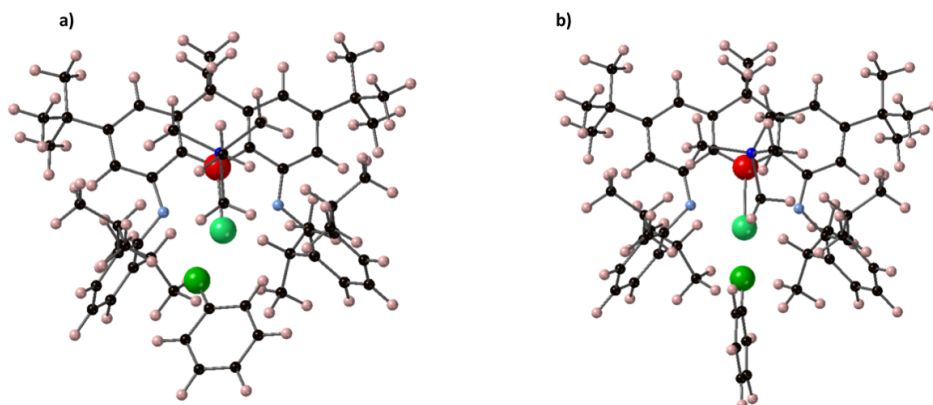


FIGURE 3.9: Starting geometries for the optimisation of  $\eta^1$ -5-Th with a) the "horizontal" starting point and b) the "vertical" starting point.

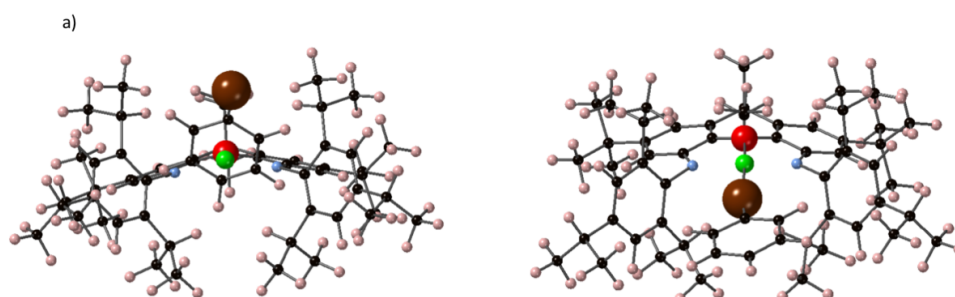


FIGURE 3.10: Starting geometries for the optimisation of the bromobenzene complex 4'-Zr with a) the "exo" starting point and b) the "horizontal" starting point.

correspond to the arene facing Th with different initial positions of the two fluor atoms. Again, we kept the "exo" and "endo" notations, adding the label "side" to the third possibility as it can be seen in Figure 3.11. The last two starting points are the "horizontal" and the "vertical" presented earlier.



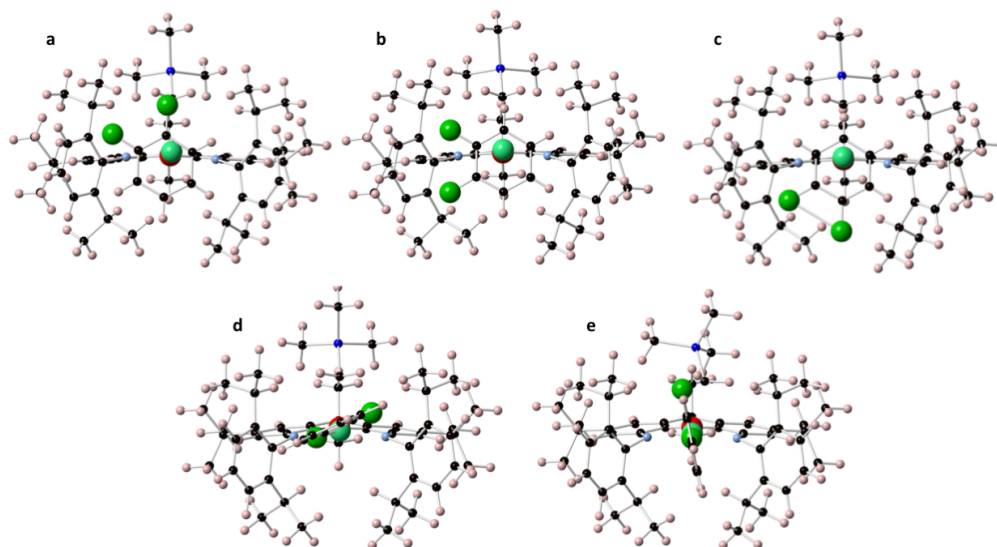


FIGURE 3.11: Starting geometries for the optimisation of 6-Th: (a)  $\eta^6$ -6-Th-exo, (b)  $\eta^6$ -6-Th-side, (c)  $\eta^6$ -6-Th-endo, (d)  $\eta^1$ -6-Th-horizontal and (e)  $\eta^1$ -6-Th-vertical.

### 3.3.5 Optimisation of Ethylene-Coordinated Alkyl Cations

The E'-Zr, E-Th and E-U are optimised with two starting points, one with CH<sub>2</sub> pointing to the metal one with the two carbons of the ethylene facing the metal/actinide centre. The starting structures are the optimised structures of the benzene 2'-Zr, 2-Th and 2-U.

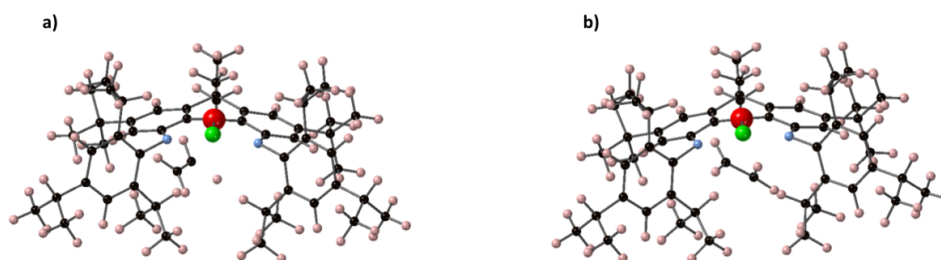


FIGURE 3.12: Starting geometries for the optimisation of E'-Zr: (a)  $\eta^1$ -E'-Zr and (b)  $\eta^2$ -E'-Zr.

## 3.4 Bonding studies

### 3.4.1 Dissociation curves - Benzene-Coordinated Alkyl Cations

For the benzene complexes, to quantify the strength and the nature of the benzene cation bonds, interaction curves were computed scanning the cation benzene distance from 2.7 Å to 4.0 Å for Th and U and from 2.2 Å to 3.4 Å in steps of 0.1 Å plus additional points at 4.5, 5, 6 and 10 Å.

Since the curves were smooth and presented only a single minimum (see Figure 3.17), the estimation of the binding energy was done at the structures accounting for the BSSE correction as described in the following paragraph.

### 3.4.2 Estimation of the binding energies at the equilibrium including BSSE and dispersion

For the BSSE calculation, the complex is divided into two fragments the first one (A) being composed of the catalyst and the second fragment (B) corresponding to the arene. If all the setup from the previous calculation was kept (DFT-TURBOMOLE-PBE0), tests on basis sets, using larger ones, such as def2-QZVP, def2-TZVPP and aug-cc-pVTZ for 2'-Zr were performed. The interaction energies changed by a few kJ/mol with a largest basis sets proving that def2-TZVP is sufficiently accurate.

Because of the  $\pi$ -coordination of the arene to the metallic center, dispersion effects might be important. They can be captured by the MP2 method at considerable computational cost, or with a DFT-based approach with an empirical dispersion correction, namely the D3 correction [50].

### 3.4.3 Decomposition of the bond energy: the ETS-NOCV method

The ETS-NOCV method [118, 119], implemented in the ADF package, decomposes the interaction between two fragments within a system chosen by the user, to offer a quantitative picture of the chemical bond.

#### ETS - Extended Transition State decomposition analysis

The total energy between the interacting fragments is divided in 4 components [133]:

$$\Delta E_{tot} = \Delta E_{dist} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \quad (3.1)$$

- $\Delta E_{dist}$ : the distortion term corresponding to the energy between the free fragments and their geometry within the complex.
- $\Delta E_{elstat}$ : the electrostatic stabilising interaction between the 2 fragments when they are brought to their position in the final complex.
- $\Delta E_{Pauli}$ : the destabilising repulsive interaction between the occupied orbitals of the 2 fragments.
- $\Delta E_{orb}$ : the stabilising interaction between the occupied orbitals of one fragment and the unoccupied orbitals of the other one and the mixing of the unoccupied and occupied orbitals of a same fragment (intrafragment polarisation) once the two fragments have been united.

The change in the electronic density  $\Delta\rho$  responsible for  $\Delta E_{orb}$  can be written as:

$$\Delta\rho(1) = \sum_{\lambda} \sum_{\nu} \Delta P_{\lambda\nu} \lambda(1) \nu(1) \quad (3.2)$$

With "(1)" corresponding to the molecular orbital,  $\lambda$  are the occupied orbitals and  $\nu$  the unoccupied orbitals of the 2 fragments and  $\Delta P_{\lambda\nu}$  the deformation density function of  $\lambda$  and  $\nu$ . Then  $\Delta E_{orb}$  can be written as:

$$\Delta E_{orb} = \sum_{\lambda} \sum_{\nu} \Delta P_{\lambda\nu} F_{\lambda\nu}^{TS} \quad (3.3)$$

where  $F_{\lambda\nu}^{TS}$  is the Kohn-Sham Fock matrix element that can be defined in terms of potential (transition state -TS) that is midway between the combined fragments and the final molecule (this is why it is called transition state).

### NOCV - Natural orbitals for chemical valence

Derived from Nalewajski-Mrozek valence theory [134, 135], the deformation density is defined as :

$$\Delta\rho(r) = \rho^{system} - \sum_i \rho_i^{frag}(r) \quad (3.4)$$

The deformation density  $\Delta\rho$  can be expanded as a sum of pairs of  $(\Psi_{-k}, \Psi_k)$  the natural orbitals for chemical valence (NOCV) that provide an orbital representation of the deformation density:

$$\Delta\rho(r) = \sum_{k=1}^{M/2} \nu_k [-\Psi_{-k}^2(r) + \Psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta\rho_k(r) \quad (3.5)$$

In equation 3.5,  $\Psi_{-k}$  and  $\Psi_k$  NOCV are the eigenvectors of the  $\Delta P$  matrix corresponding to eigenvalues  $\pm \nu_k$ , where  $\Delta P = P_{AB} - (P_A + P_B)$ , and  $P_{AB}$ ,  $P_A$  and  $P_B$  are the molecular, and the fragment charge and bond order matrices [134, 135].

As a result the orbital interaction can be expressed in terms of the NOCV orbitals as:

$$\Delta E_{orb} = \sum_{k=1}^{M/2} \Delta E_{orb}(k) = \sum_{k=1}^{M/2} \nu_k [-F_{-k,-k}^{TS}(r) + F_{k,k}^{TS}(r)] \quad (3.6)$$

where  $F_{-k,-k}^{TS}$  and  $F_{k,k}^{TS}$  are the diagonal Kohn-Sham matrix elements defined over NOCVs with respect to the TS density. In this expression, only few complementary NOCV pairs (often 2 to 4) contribute significantly to  $\Delta E_{orb}$ . Each pair represents one charge-transfer contribution  $\Delta\rho_k$ , with its energy contribution  $\Delta E_{orb}(k)$ . To discuss trends across complexes the same fragment types must be used *i.e.* the fragments A and B must describe the same parts of the molecule.

ETS-NOCV calculations were performed for all the benzene complexes with the PBE0 functional, QZ4P basis sets and included scalar relativistic effects with the ZORA Hamiltonian. As for the BSSE calculation, the first fragment includes the cationic complex and the second one the arene. One has to note that ETS-NOCV analysis cannot be performed with spin-orbit coupling. Nevertheless, for benzene complexes a simple-point calculation with Spin-Orbit ZORA Hamiltonian was ran showing that spin-orbit coupling has no effect on the interaction energy.



## 3.5 Results and discussions

### 3.5.1 Geometries of the arene-coordinated uranium, thorium or zirconium alkyl cation with the arene solvent

#### Geometries of benzene-coordinated alkyl cations

TABLE 3.6: Important bond lengths in Å and angles in degree for  $\eta^6\text{-2-U}$  (X-ray and optimised structures),  $\eta^6\text{-2-Th}$  (X-ray and optimised structures),  $\eta^6\text{-2'-Th}$  (optimised structure),  $\eta^6\text{-2'-Zr}$  (optimised structure) and  $\eta^6\text{-2-Zr}$  (optimised structure).

Compounds	$\eta^6\text{-2-U}$ X-ray	$\eta^6\text{-2-U}$ opt	$\eta^6\text{-2'-U}$ opt
M-O	2.441(2)	2.428	2.473
M-N	2.224(2), 2.236(6)	2.222, 2.231	2.221, 2.220
M- $C_{arene}$	3.099(3) - 3.248(3)	3.028 - 3.795	3.127 - 3.248
M-Arene Centroid	2.932	3.136	3.177
$N_1 \dots N_2$	3.94	3.99	3.896
Arene Bend Angle <sup>1</sup>	18.9	23.5	1.1
O-M- $C_{apical}$	87.26(8)	91.90	81.25
M-C-Si	133.7(2)	135.7	–
Compounds	$\eta^6\text{-2-Th}$ X-ray	$\eta^6\text{-2-Th}$ opt	$\eta^6\text{-2'-Th}$
M-O	2.496(5)	2.487	2.500
M-N	2.278(3), 2.288(3)	2.278, 2.282	2.273, 2.274
M- $C_{arene}$	3.18 - 3.31	3.19 - 3.41	3.171-3.302
M-Arene Centroid	2.950	2.999	2.925
$N_1 \dots N_2$	4.04	4.02	3.963
Arene Bend Angle <sup>1</sup>	8.7	10.8	0.8
O-M- $C_{apical}$	91.3(1)	91.4	82.8
M-C-Si	131.0(2)	132.4	–
Compounds	$\eta^6\text{-2'-Zr}$ opt	$\eta^6\text{-2-Zr}$ opt	
M-O	2.248	2.263	
M-N	2.144, 2.149	2.103, 2.099	
M- $C_{arene}$	2.781 - 2.881	4.43 - 2.699	
M-Arene Centroid	2.470	3.403	
$N_1 \dots N_2$	3.87	3.829	
Arene Bend Angle <sup>1</sup>	2.4	30.1	
O-M- $C_{apical}$	82.2	96.2	
M-C-Si	–	132.3	

<sup>1</sup> Angle between the carbons of the arene and the planar ligand.

Table 3.6 gathers all the results for the benzene complexes. The distances between the metal centres and both the oxygen and nitrogen atoms of the  $\text{XA}_2$  (4,5-bis(2,4,6-triisopropylanilido)-2,7-di-tert-butyl-9,9-dimethylxanthene) group almost perfectly vary with respect to the ionic radii variations; for instance the Th-O distance in  $\eta^6\text{-2-Th}$  comes out 0.22 Å longer the Zr-O one in  $\eta^6\text{-2-Zr}$ , and 0.06 Å longer than the U-O one in  $\eta^6\text{-2-U}$ . Contrariwise the metal-arene distances do not follow the ionic radii trends since the Th- $C_{\text{arene}}$  distance are about 0.47 Å and 0.17 Å longer than the Zr- $C_{\text{arene}}$  and U- $C_{\text{arene}}$  ones respectively, suggesting that the various cations interact differently with the benzene ring. The computed structure of  $\eta^6\text{-2'-Zr}$  is also reported though it could not be crystallised by Emslie *et al.* The difference between  $\eta^6\text{-2'-Zr}$  and  $\eta^6\text{-2-Zr}$  is that a methyl group is attached to Zr in the former while the latter carries a bulkier  $\text{CH}_2\text{SiMe}_3$  group. This is confirmed by the fact that  $\eta^6\text{-2'-Th}$  present similar O-M- $C_{\text{apical}}$  angle and arene bend angle than  $\eta^6\text{-2-Zr}$ . As consequences,  $\eta^6\text{-2'-Th}$  also present a short distance M-Arene Centroid than  $\eta^6\text{-2-Th}$ . Albeit Zr-O and Zr-N distances are nearly the same in both  $\eta^6\text{-2-Zr}$  and  $\eta^6\text{-2'-Zr}$  complexes, the Zr- $C_{\text{arene}}$  distance is shorter in the former than in the latter.

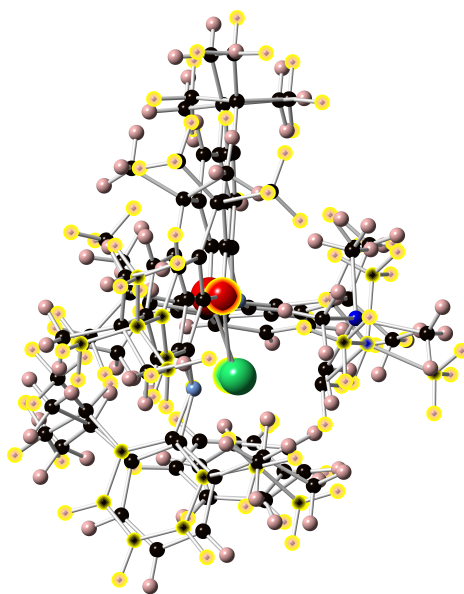


FIGURE 3.13: Superposition of the X-ray and the optimised (yellow atoms) structures of  $\eta^6\text{-2-Th}$

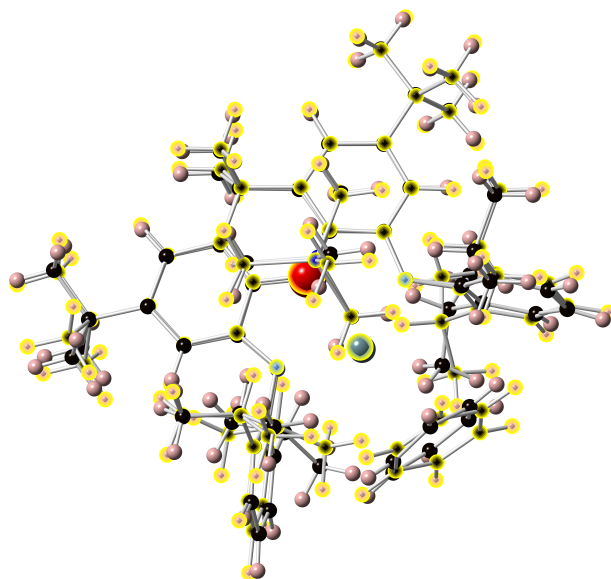


FIGURE 3.14: Superposition of the X-ray and the optimised (yellow atoms) structures of  $\eta^6$ -2-U

### Geometries of toluene-coordinated alkyl cations

TABLE 3.7: Important bond lengths in Å and angles in degree for  $\eta^6$ -3-U (X-ray structures),  $\eta^6$ -2-Th (optimised structure) and  $\eta^6$ -3'-Zr (X-ray and optimised structures).

Compounds	$\eta^6$ -3-U-endo X-ray	$\eta^6$ -3-Th-endo opt	$\eta^6$ -3'-Zr-exo opt	$\eta^6$ -3'-Zr-exo X-ray
M-O	2.480	2.417(9)	2.247	2.220
M-N	2.21(1), 2.22(1)	2.277, 2.273	2.161, 2.148	2.138, 2.142
M-C <sub>arene</sub>	3.05(2) - 3.78(2)	3.084 - 4.005	2.747 - 2.908	2.697 - 2.840
M-Arene Centroid	3.138	3.271	2.449	2.383
N <sub>1</sub> ... N <sub>2</sub>	3.98	4.04	3.91	3.91
Arene Bend Angle <sup>1</sup>	11.8	13.4	12.7	
O-M-C <sub>apical</sub>	5.9	92.20	87.7	81.0
M-C-Si	136.8(7)	133.8	-	-

<sup>1</sup> Angle between the carbons of the arene and the planar ligand.

The structures of  $\eta^6$ -3-U-endo and  $\eta^6$ -3-Th-exo are not be obtained yet. For those available the computed geometries agree well with the available crystallographic data (see Table 3.7). The main observation is that the M-C<sub>arene</sub> distances in toluene complexes are slightly shorter than in the benzene ones.



### Geometries of halogeno-coordinated alkyl cations

The structures of bromobenzene  $\eta^6$ -4-U and the fluorobenzene  $\eta^6$ -5-U and  $\eta^1$ -5-Th-**horizontal** are not reported yet.

The fluorobenzene  $\eta^6$ -5'-Zr-**exo** is slightly more stable than  $\eta^1$ -5-Th-**vertical** with a difference in energy of 0.35 kJ.mol<sup>-1</sup>. This difference is so small that both structures will be kept for the rest of the study. The  $\eta^1$ -5'-Zr-**vertical** relaxed to an "horizontal" orientation but forming an important tilt angle with the molecular plane. The most stable is the optimised 5'-Zr-**vertical**, with an energy 4.2 kJ.mol<sup>-1</sup> lower than that obtained with the  $\eta^1$ -5'-Zr-**horizontal**. The last isomer,  $\eta^6$ -5'-Zr-**exo** is the least stable lying 15.7 kJ.mol<sup>-1</sup> above  $\eta^1$ -5'-Zr-**vertical**. Nevertheless, as the structures are close in energy both the  $\eta^1$ -5'-Zr-**horizontal** (from the optimised  $\eta^1$ -5'-Zr-**vertical** starting point) and  $\eta^1$ -5'-Zr-**exo** are kept for the next steps of the study. The currently optimised structures cannot be compared to crystal data, though, they reveal very

similar bond distances to the toluene ones.

TABLE 3.8: Important bond lengths in Å and angles in degree for  $\eta^6$ -5-U (optimised and X-ray structures),  $\eta^6$ -5-Th (optimised structure),  $\eta^6$ -5'-Zr (optimised structure) and  $\eta^1$ -5'-Zr **-horizontal** (optimised structure) and the relative energy  $\Delta E$  in  $\text{kJ}\cdot\text{mol}^{-1}$  with respect to the most stable isomer.

Compounds	$\eta^6$ -5-U X-ray	$\eta^6$ -5-Th-endo opt	$\eta^1$ -5-Th-vertical
M-O	2.431	2.477	2.476
M-N	2.215, 2.218	2.267, 2.275	2.267, 2.270
M-C <sub>arene</sub>	3.128 - 3.598	3.140 - 3.822	–
M-Arene Centroid	3.077	3.204	–
N <sub>1</sub> ... N <sub>2</sub>	3.98	4.033	4.040
Arene Bend			
Angle <sup>1</sup>	1.6	8.4	78.9
O-M-C <sub>apical</sub>	89.6	92.3	94.9
M-C-Si	134.8	133.2	132.5
$\Delta E$		0.0	0.3
Compounds	$\eta^6$ -5'-Zr-exo opt	$\eta^1$ -5'-Zr -horizontal opt	
M-O	2.277	2.257	
M-N	2.088, 2.082	2.068, 2.070	
M-C <sub>arene</sub>	2.687 - 4.417	–	
M-Arene Centroid	3.401	–	
N <sub>1</sub> ... N <sub>2</sub>	3.790	3.813	
Arene Bend			
Angle <sup>1</sup>	10.7	11.1	
O-M-C <sub>apical</sub>	91.3	101.5	
M-C-Si	–	–	
$\Delta E$	15.7	0.0	

<sup>1</sup> Angle between the carbons of the arene and the planar ligand.

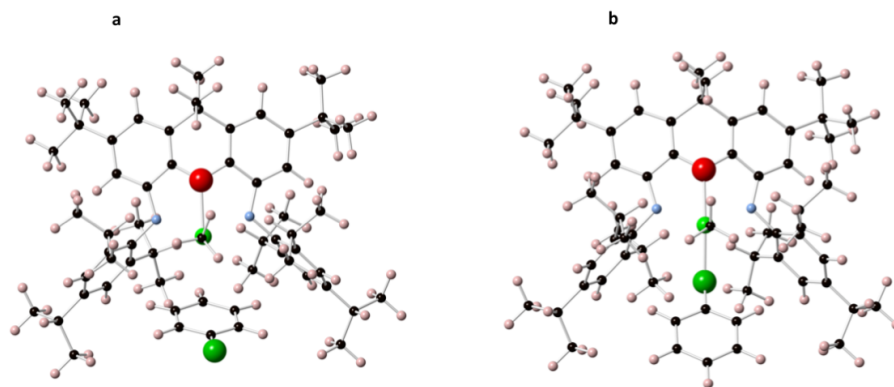


FIGURE 3.15: Optimised geometries for a)  $\eta^6$ -5'-Zr-exo, b)  $\eta^1$ -5'-Zr-horizontal

TABLE 3.9: Important bond lengths in Å and angles in degree for  $\eta^6$ -4-Th (optimised structure) and 4'-Zr (optimised structures) and the relative energy  $\Delta E$  in  $\text{kJ}\cdot\text{mol}^{-1}$  with respect to the most stable isomers.

Compounds	$\eta^6$ -4-Th-endo opt	$\eta^6$ -4'-Zr-exo opt	$\eta^1$ -4'-Zr-horizontal opt
M-O	2.472	2.276	2.260
M-N	2.263, 2.263	2.082, 2.088	2.069, 2.077
M-C <sub>arene</sub>	3.058 - 4.335	2.697 - 4.406	–
M-Arene Centroid	3.481	3.390	–
N <sub>1</sub> ... N <sub>2</sub>	4.03	3.789	3.789
Arene Bend			
Angle <sup>1</sup>	4.9	11.4	13.5
O-M-C <sub>apical</sub>	92.9	91.1	90.8
M-C-Si	133.3	–	–
$\Delta E$		0.0	9.7

<sup>1</sup> The angle between the carbons of the arene and the planar ligand.

In the case of bromobenzene isomers,  $\eta^6$ -4'-Zr-exo is more stable than  $\eta^1$ -4'-Zr-horizontal by  $9.7 \text{ kJ}\cdot\text{mol}^{-1}$  but since David Emslie suspected the presence of these two isomers from NMR analysis [109], both will be kept for the next steps of the bonding study.

### Geometries of difluorobenzene-coordinated alkyl cations

$\eta^1$ -6-Th-vertical and  $\eta^1$ -6-Th-horizontal are converging to the same  $\eta^1$ -6-Th-vertical structure, thus only this one will be kept for the results. The most stable isomer is the  $\eta^1$ -6-Th-vertical and the other three are less than 15 kJ.mol<sup>-1</sup> higher in energy, forcing us to consider all of them. Nonetheless the final structure of  $\eta^1$ -6-Th-horizontal

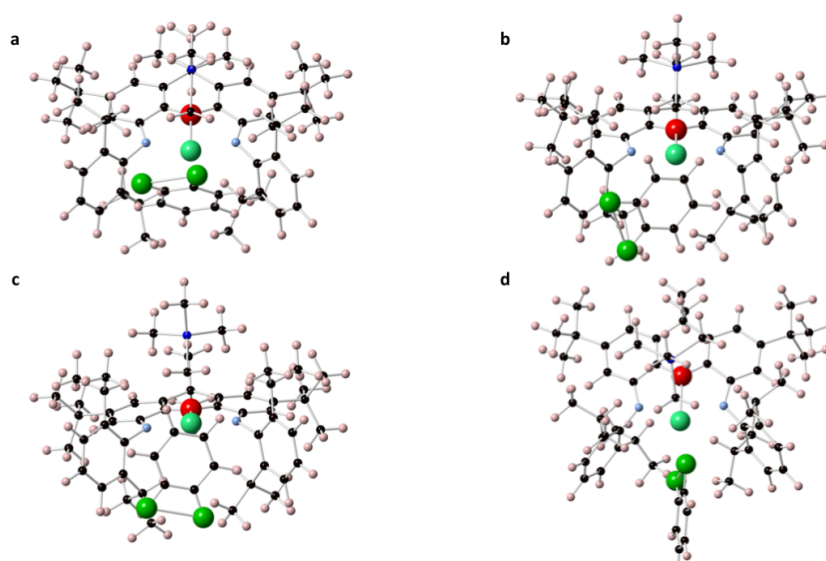


FIGURE 3.16: Optimised geometries for a)  $\eta^6$ -6-Th-exo, b)  $\eta^6$ -6-Th-side, c)  $\eta^6$ -6-Th-endo and, d)  $\eta^1$ -6-Th-vertical

TABLE 3.10: Important bond lengths in Å and angles in degree for  $\eta^6$ -6-Th-exo,  $\eta^6$ -6-Th-side,  $\eta^6$ -6-Th-endo,  $\eta^1$ -6-Th-horizontal and  $\eta^1$ -6-Th-vertical optimised structures and the relative energies  $\Delta E$  in kJ.mol<sup>-1</sup> with respect to the most stable isomer.

Compounds	$\eta^1$ -6-Th-vertical opt	$\eta^6$ -6-Th-exo opt	$\eta^6$ -6-Th-side opt	$\eta^6$ -6-Th-endo opt
M-O	2.46	2.492	2.477	2.475
M-N	2.252, 2.254	2.279, 2.280	2.259, 2.258	2.262, 2.258
M-C <sub>arene</sub>	–	3.060 - 4.298	3.107 - 4.373	3.030 - 4.326
M-Arene Centroid	–	3.461	3.531	3.464
N <sub>1</sub> ... N <sub>2</sub>	4.000	4.036	4.004	4.014
Arene Bend Angle <sup>1</sup>	–	28.6	24.9	13.0
O-M-C <sub>apical</sub>	93.6	93.5	93.3	93.5
M-C-Si	132.3	133.8	132.4	132.3
$\Delta E$	0.0	12.4	15.5	9.6

<sup>1</sup> The angle between the carbons of the arene and the planar ligand.

The arene bend angles in the  $\eta^6$ -6-Th-exo and  $\eta^6$ -6-Th-side isomers are larger than in the  $\eta^6$ -6-Th-endo one because of the steric repulsion of the two fluorine atoms.

### Optimisation of Ethylene-Coordinated Alkyl Cations

The  $E'-Zr$  optimised structures with both starting points are giving the same result with the two carbons of the ethylene facing the zirconium atom. For this reason, for U and Th complexes, the optimisation where the  $CH_2$  is pointing to the actinide is disregarded. The important information on the complexes can be found in Table 3.11

TABLE 3.11: Important bond lengths in Å and angles in degree for  $\eta^2-E'-Zr$  and  $\eta^2-E-Th$  optimised structures.

Compounds	$E'-Zr$	$E-Th$
M-O	2.268	2.467
M-N	2.070, 2.076	2.251, 2.254
M- $C_{ethylene}$	2.796, 2.842	3.113, 3.094
$N_1 \dots N_2$	3.790	4.005
Ethylene Bend		
Angle <sup>1</sup>	37.4	12.9
O-M- $C_{apical}$	92.1	95.6
M-C-Si	–	131.4

<sup>1</sup> The angle between the carbons of the ethylene and the planar ligand.

All the distance M- $C_{ethylene}$  are shorter than in the other complexes thus a stronger bond could be expected. Unfortunately, as I write this lines, no result about  $\eta^2-E-U$  is available.

### 3.5.2 Bonding studies

#### Dissociation curves - Benzene-Coordinated Alkyl Cations

Figure 3.17 presents the results for the dissociation of benzene from the alkyl Zr, Th and U cations. The curves display only one minimum corresponding to the distance benzene - metallic center found in the geometry optimisations. The bonding energies derived from the curves are  $-145.5 \text{ kJ.mol}^{-1}$ ,  $-90.4 \text{ kJ.mol}^{-1}$  and  $-80.3 \text{ kJ.mol}^{-1}$  for  $\eta^6-2'-Zr$ ,  $\eta^6-2-Th$  and  $\eta^6-2-U$ , respectively.

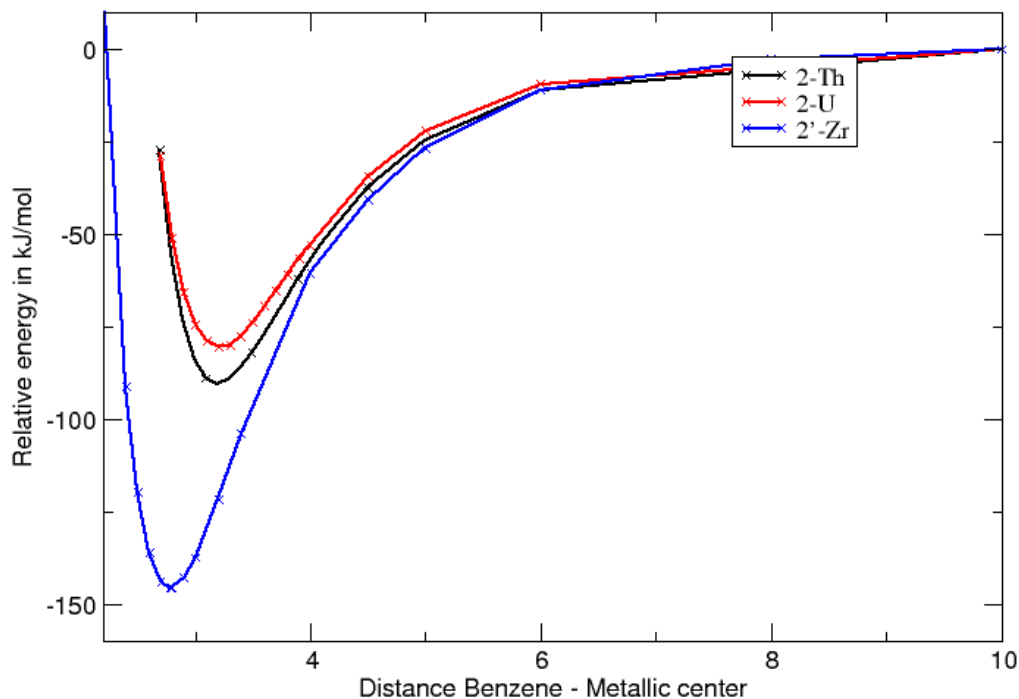


FIGURE 3.17: Dissociation curves for  $\eta^6$ -**2-Th** (black),  $\eta^6$ -**2-U** (red) and  $\eta^6$ -**2'-Zr** (blue) for a benzene - metallic center distance between 2.2 Å and 10 Å

TABLE 3.12: BSSE corrections (in  $\text{kJ}\cdot\text{mol}^{-1}$ ) to the benzene interaction energies in  $\eta^6$ -**2'-Zr** computed at different levels of calculation with different basis sets.

	$\Delta E$	$\Delta E(\text{BSSE})$	$\Delta E_{\text{corrected}}$
PBE0-def2-TZVP	-147.4	-4.6	-142.8
(PBE0 + D3)-def2-TZVP	-204.4	-4.6	-199.9
MP2-def2-TZVP	-281.9	-42.2	-239.7
MP2-def2-TZVPP	-289.4	-36.9	-252.6
MP2-aug-cc-pVTZ	-305.2	-45.0	-260.2

### BSSE corrections and decompositions of the bond energies: an ETS-NOCV study

To evaluate the accuracy of the QM methods on the bonding energies, we have performed PBE0, PBE0 + D3 and MP2 calculations for the  $\eta^6$ -**2'-Zr** complex (see Table 3.12). MP2 energies are somewhat sensitive to the size of the basis set; increasing

the basis quality from def2-TZVP to def2-TZVPP and aug-cc-PVTZ increases the binding energy by 13 and 20  $\text{kJ}\cdot\text{mol}^{-1}$  ( $< 10\%$  of the total interaction energy), respectively, while expanding significantly the computational time. Thus, the def2-TZVP basis sets are kept for all other complexes.

TABLE 3.13: Bonding energies in  $\text{kJ}\cdot\text{mol}^{-1}$  for the benzene molecules  $\eta^6\text{-2'-Zr}$ ,  $\eta^6\text{-2-Zr}$ ,  $\eta^6\text{-2-Th}$  and  $\eta^6\text{-2-U}$  at PBE0, PBE0 + D3 and MP2 levels.

	$\Delta E$			$\Delta E(\text{BSSE})$			$\Delta E_{\text{corrected}}$		
	PBE0	PBE0 + D3	MP2	PBE0	PBE0 + D3	MP2	PBE0	PBE0 + D3	MP2
$\eta^6\text{-2'-Zr}$	-147.4	-204.4	-305.2	-4.6	-4.6	-45.0	-142.8	-199.9	-260.2
$\eta^6\text{-2-Zr}$	-92.8	-147.1	-190.5	-3.2	-3.2	-29.1	-89.6	-143.8	-161.5
$\eta^6\text{-2-Th}$	-92.5	-141.7	-189.7	-3.5	-3.5	-25.7	-89.0	-138.1	-164.1
$\eta^6\text{-2-U}$	-77.8	-128.0		-3.5	0.2		-74.2	-128.2	

From Table 3.13, we note that for both Zr and Th complexes, the MP2 energies are larger than the PBE0 ones. Assuming that PBE0 with D3 correction captures most of the dispersion effects, it is interesting to note that the PBE0 trends across the metal centres match the MP2 ones. However, the MP2 values come out lower than the PBE0 + D3 ones, which is in line with the fact that MP2 is known to overestimate

dispersion contributions [136, 137].

TABLE 3.14: Bonding energy decomposition in  $\text{kJ}\cdot\text{mol}^{-1}$  for the zirconium cations with the ETS-NOCV method .

	$\eta^2\text{-E'-Zr}$	$\eta^6\text{-2'-Zr}$	$\eta^6\text{-2-Zr}$	$\eta^6\text{-3'-Zr-exo}$
$\Delta E_{Dist}$	29.7	95.4	38.1	112.0
$\Delta E_{Pauli}$	130.8	296.4	137.6	311.7
$\Delta E_{elstat}^1$	-119.3 (54%)	-200.5 (45%)	-105.6 (45%)	-217.6 (45%)
$\Delta E_{orb}^1$	-99.6 (46%)	-242.2 (55%)	-126.3 (55%)	-263.2 (55%)
$\Delta E_{orb}^{\sigma}{}^2$	-62.8 (63%)	-45.2 (19%)	–	-46.0 (19%)
$\Delta E^{\pi}1_{orb}{}^2$	-12.5 (13%)	-60.2 (25%)	-71.1 (56%)	-66.1 (25%)
$\Delta E^{\pi}2_{orb}{}^2$	–	-63.2 (26%)	-13.0 (10%)	-66.9 (25%)
$\Delta E_{orb}^{other}{}^2$	-24.7 (24%)	-77.0 (30%)	-41.0 (32%)	-84.1 (31%)
$\Delta E_{int}^{PBE0}$	-88.1	-146.3	-94.3	-169.2
$\Delta E_{Disp}{}^3$	-33.1	-52.5	-51.0	-61.9
$\Delta E_{int}^{PBE0+D3}$	<b>-91.5</b>	<b>-103.4</b>	<b>-107.2</b> not finish	<b>-119.1</b>
	$\eta^6\text{-4'-Zr-exo}^*$	$\eta^1\text{-4'-Zr-horizontal}$	$\eta^6\text{-5'-Zr-exo}$	$\eta^1\text{-5'-Zr-horizontal}$
$\Delta E_{Dist}$	36.3	29.1	30.7	22.3
$\Delta E_{Pauli}$	133.3	115.3	136.7	100.3
$\Delta E_{elstat}^1$	-95.1 (43%)	-97.5 (48%)	-103.0 (45%)	-108.7 (54%)
$\Delta E_{orb}^1$	-125.6 (57%)	-105.9 (52%)	-125.3 (55%)	-91.7 (44%)
$\Delta E_{orb}^{\sigma}{}^2$	-73.6 (59%)	-65.5 (62%)	-74.5 (59%)	-44.5 (49%)
$\Delta E^{\pi}1_{orb}{}^2$	-10.5 (8%)	-10.8 (10%)	-9.6 (8%)	-14.2 (15%)
$\Delta E^{\pi}2_{orb}{}^2$	-8.4 (7%)	–	-8.4 (7%)	-9.6 (10%)
$\Delta E_{orb}^{other}{}^2$	-33.4 (26%)	-30.2 (28%)	-33.1 (24%)	-23.8 (26%)
$\Delta E_{int}^{PBE0}$	-87.3	-88.1	-91.5	-100.0
$\Delta E_{Disp}{}^3$	-55.5	-47.3	-52.5	-36.8
$\Delta E_{int}^{PBE0+D3}$	<b>-106.5</b>	<b>-106.3</b>	<b>-113.0</b>	<b>-114.5</b>

\* Most stable isomers.

<sup>1</sup> Values in parenthesis give the percentage contribution to the total attractive interaction ( $\Delta E_{elstat} + \Delta E_{orb}$ ).

<sup>2</sup> Values in parenthesis give the percentage contribution to the total orbital energy for the  $\sigma$ - and  $\pi$ -donor NOCV-pair contributions.

<sup>3</sup>  $\Delta E_{Disp}$  is the difference between  $\Delta E_{int}^{PBE0}$  and  $\Delta E_{int}^{PBE0+D3}$  with the BSSE correction.

Tables 3.14 and 3.15 summarise the energy decomposition analysis performed at the PBE0 level and the dispersion contributions that range from 40 to 70  $\text{kJ}\cdot\text{mol}^{-1}$ , representing at least 27% of the bonding energy. Thus, dispersion does not change the trends observed but is not negligible. Comparing the benzene  $\eta^6\text{-2'-Zr}$  and the



toluene  $\eta^6\text{-3'-Zr-exo}$  in Table 3.14, we see that the  $\eta^6\text{-3'-Zr-exo}$ , which is catalytically more active than  $\eta^6\text{-2'-Zr}$ , exhibits a stronger bond between Zr and the toluene solvent, which is counter intuitive with the hypothetical mechanism.  $\eta^6\text{-2-Zr}$  does not present an important  $\sigma$  interaction while  $\eta^6\text{-2'-Zr}$  does. It can come from the fact that  $\eta^6\text{-2-Zr}$  presents a large arene bond angle ( $30.1^\circ$ ) which prevents  $\sigma$  overlaps.

Fluorobenzene  $5'\text{-Zr}$  forms the weakest arene bond to zirconium. In case of the  $\eta^6\text{-5'-Zr-exo}$  isomer, it can be explained by the fact that the center of the fluorobenzene ring is shifted upwards as a result of hydrogen bonding between fluorine and a hydrogen atom of the  $\text{CH}_2\text{SiMe}_3$  group.

The weakest bond is observed between the ethylene and the zirconium. Such a weak bond discredits the hypothesis of a competition between the arene from solvent and the ethylene. Nonetheless, the ethylene complex is presenting a bond different from the one between the arene and the zirconium. Indeed, it presents a  $\sigma$  donation from the ethylene carbons to the 4d and 5s orbitals of the zirconium and a  $\pi$ -retrodonation from the 2p orbitals of the carbons around Zr to the 2p orbitals of the ethylene carbons (see Figure ??). Further explorations of possible transition states involving both

ethylene and the arene are foreseen.

TABLE 3.15: Bonding energy decomposition in  $\text{kJ}\cdot\text{mol}^{-1}$  for the thorium cations with the ETS-NOCV method.

	$\eta^2\text{-E-Th}$	$\eta^6\text{-2-Th}$	$\eta^6\text{-2'-Th}$	$\eta^6\text{-3-Th-endo}$
$\Delta E_{Dist}$	1.4	15.5	29.8	17.3
$\Delta E_{Pauli}$	90.4	143.9	153.5	119.7
$\Delta E_{elstat}^1$	-87.6 (56%)	-115.6 (49%)	-120.8 (48%)	-102.0 (49%)
$\Delta E_{orb}^1$	-69.3 (44%)	-120.9 (51%)	-130.3 (52%)	-104.9 (51%)
$\Delta E_{orb}^{\sigma 2}$	-43.1 (62%)	-22.6 (19%)	-24.5 (19%)	-10.5 (10%)
$\Delta E^{\pi 1}_{orb 2}$	-8.7 (12%)	-33.0 (27%)	-35.6 (27%)	-39.7 (38%)
$\Delta E^{\pi 2}_{orb 2}$	–	-26.4 (22%)	-28.5 (22%)	-20.9 (20%)
$\Delta E_{orb}^{other 2}$	-17.8 (26%)	-39.7 (33%)	-42.6 (32%)	-34.2 (32%)
$\Delta E_{int}^{PBE0}$	-66.5	-92.6	-97.6	-87.1
$\Delta E_{Disp}^3$	-25.2	-45.6	-50.5	-52.1
$\Delta E_{int}^{PBE0+D3}$	<b>-90.2</b>	<b>-122.7</b>	<b>-118.3</b>	<b>-121.9</b>
	$\eta^6\text{-4-Th-endo}$	$\eta^6\text{-5-Th-endo}$	$\eta^1\text{-5-Th-verical}$	
$\Delta E_{Dist}$	8.1	-0.6	-6.1	
$\Delta E_{Pauli}$	94.4	113.1	63.4	
$\Delta E_{elstat}^1$	-72.7 (45%)	-91.4 (48%)	-72.4 (55%)	
$\Delta E_{orb}^1$	-87.8 (55%)	-97.8 (52%)	-59.3 (45%)	
$\Delta E_{orb}^{\sigma 2}$	–	-11.7 (12%)	–	
$\Delta E^{\pi 1}_{orb 2}$	–	-33.5 (34%)	–	
$\Delta E^{\pi 2}_{orb 2}$	–	-21.3 (22%)	–	
$\Delta E_{orb}^{other 2}$	-87.8 (100%)	-32.1 (32%)	-59.3 (100%)	
$\Delta E_{int}^{PBE0}$	-66.1	-76.1	-68.3	
$\Delta E_{Disp}^3$	-50.8	-48.7	-21.3	
$\Delta E_{int}^{PBE0+D3}$	<b>-108.8</b>	<b>-125.4</b>	<b>-95.7</b>	
	$\eta^1\text{-6-Th-vertical}^*$	$\eta^6\text{-6-Th-exo}$	$\eta^6\text{-6-Th-side}$	$\eta^6\text{-6-Th-endo}$
$\Delta E_{Dist}$	6.5	6.8	6.8	31.8
$\Delta E_{Pauli}$	70.2	97.3	89.6	93.2
$\Delta E_{elstat}^1$	-80.2 (56%)	-71.4 (45%)	-68.6 (45%)	-69.8 (44%)
$\Delta E_{orb}^1$	-62.0 (44%)	-87.0 (55%)	-82.2 (55%)	-89.0 (56%)
$\Delta E_{orb}^{\sigma 2}$	–	-15.5 (18%)	-38.0 (46%)	-41.4 (47%)
$\Delta E^{\pi 1}_{orb 2}$	–	-39.7 (46%)	-16.2 (20%)	-13.8 (16%)
$\Delta E^{\pi 2}_{orb 2}$	–	–	–	–
$\Delta E_{orb}^{other 2}$	-62.0 (100%)	-32.3 (37%)	-28.6 (34%)	-34.4 (37%)
$\Delta E_{int}^{PBE0}$	-72.0	-61.1	-61.2	-65.6
$\Delta E_{Disp}^3$	-22.7	-45.9	-44.2	-44.4
$\Delta E_{int}^{PBE0+D3}$	<b>-88.2</b>	<b>-100.2</b>	<b>-98.6</b>	<b>-78.2</b>

\* Most stable isomers.

<sup>1</sup> Values in parenthesis give the percentage contribution to the total attractive interaction ( $\Delta E_{elstat} + \Delta E_{orb}$ ).

<sup>2</sup> Values in parenthesis give the percentage contribution to the total orbital energy

We can see that the bonding interaction decreases along the arene series of the Th-complexes (see Table 3.15); as the bonding strength decreases, so does the 7s and 5f characters of the acceptor orbital while the 6d character increase in the main deformation densities contributions (See figure 3.18, ?? and the Appendix C).

Regarding the 6-Th isomers,  $\eta^6$ -6-Th-vertical is the most stable one and presents the strongest arene-metal interaction. In  $\eta^1$ -6-Th-vertical and  $\eta^6$ -6-Th-endo the orbital interaction is composed of multiple small interactions. In  $\eta^1$ -6-Th-vertical, the arene ring orientation does not favour any bonding symmetry, while  $\eta^6$ -6-Th-endo, the arene ring is shifted perpendicularly to the molecular plane. Just as in Zr complexes,  $\eta^2$ -E-Th presents the weakest bond and the  $\pi$  retrodonation from the 2p orbitals of the carbons close to the Th center and the 4d orbitals of the thorium to the 2p orbitals of the ethylene carbons. The same exploration of transition state must then be done to shed light on the mechanism.

Finally the useful complexes to compare the metals are the  $\eta^6$ -2-Th,  $\eta^6$ -2-Zr,  $\eta^6$ -2'-Th and  $\eta^6$ -2'-Zr ones (see Tables 3.14 and 3.15 and Figures 3.18, ??, 3.19 and ??). The interaction strength is roughly the same comparing metals but the Zr benzene bond is somewhat more covalent than the Th-benzene one (larger  $\Delta E_{orb}$  percentage). Again the absence of  $\sigma$  interaction in 2-Zr is explained by the large arene bend angle. Being smaller in the thorium equivalent, the  $\sigma$  donation contributions into the 6d and 5f orbitals of Th amounts to 20% while  $\pi$ -type interactions sums up to 49% of the covalent contribution.

### 3.6 Conclusion and Perspectives

Although a lot of information have been already collected, the catalytic mechanism could not be revealed. So far we have shown that our QM calculations are able to reproduce X-ray data and certainly predict the geometries of uncrystallised complexes. We have seen that the Zr-cations have a bonding interaction slightly more covalent than the Th-ones, in which the arene interaction is electrostatically driven. The stronger bonds in thorium systems mainly involve 7s and 5f orbitals while the weakest involve mainly 6d orbitals. The study of hypothetical transition states will be done to explore the possible reaction paths.

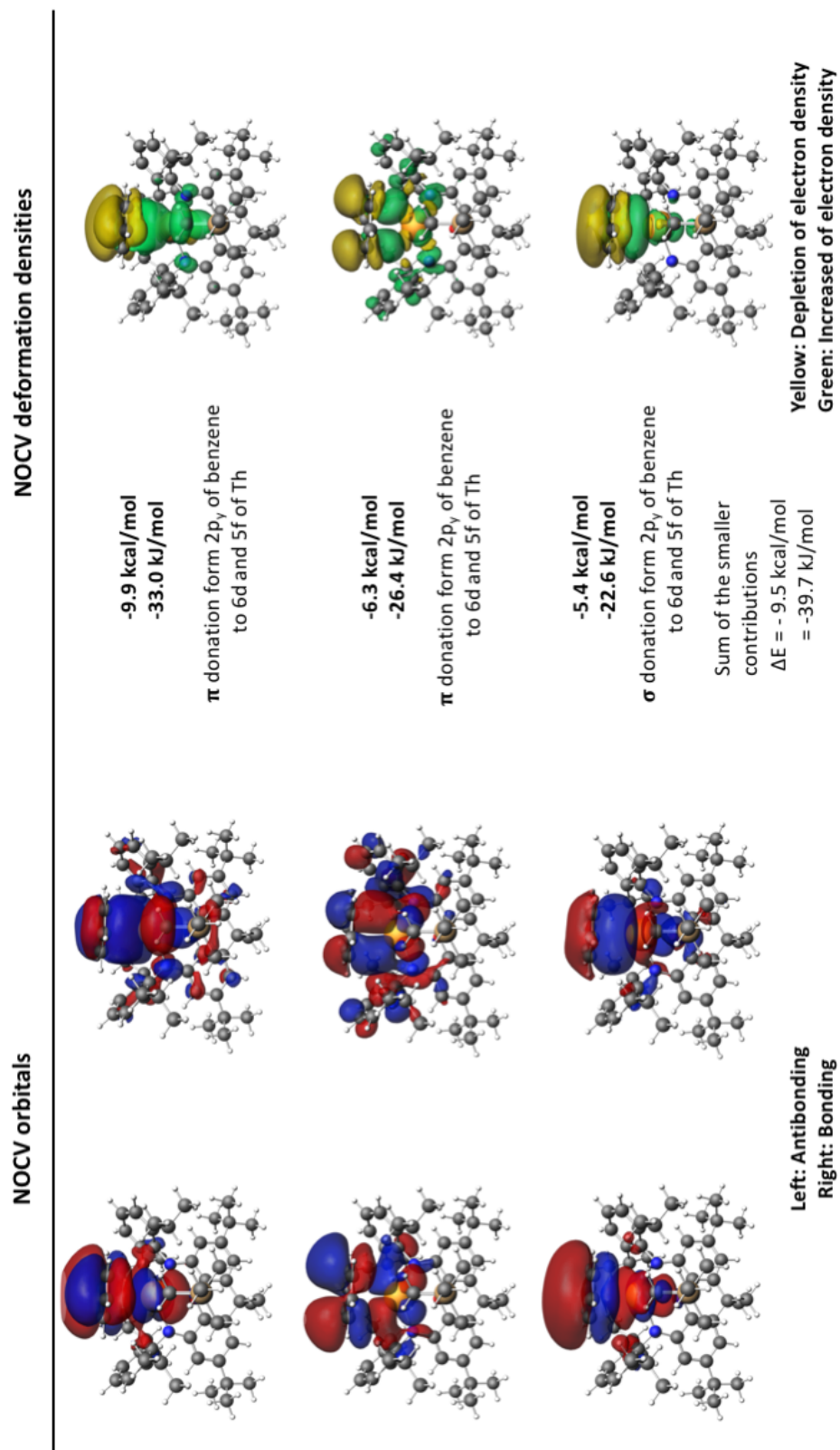


FIGURE 3.18: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions. Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -2-Th.

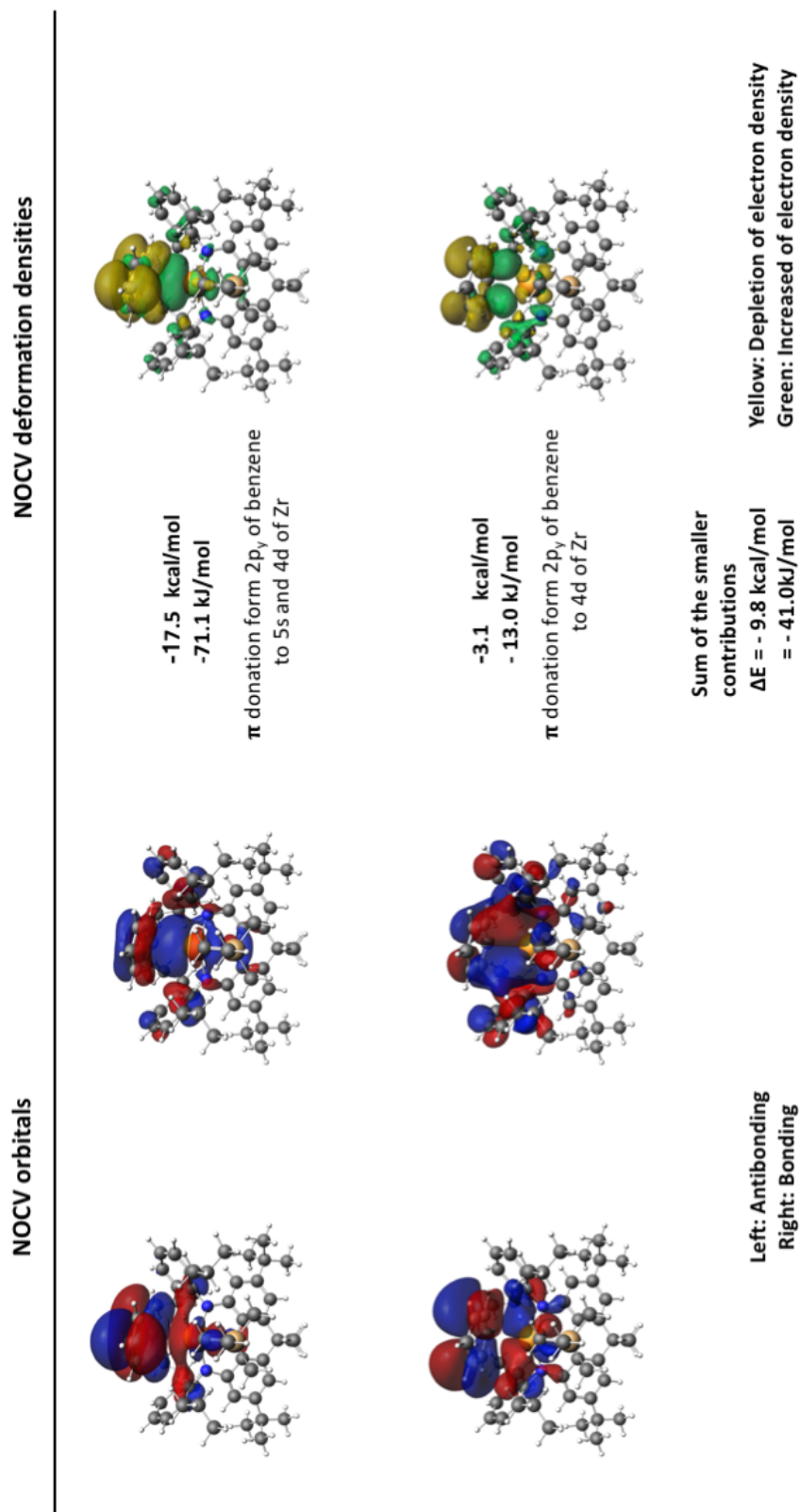


FIGURE 3.19: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6\text{-Zr}$ .

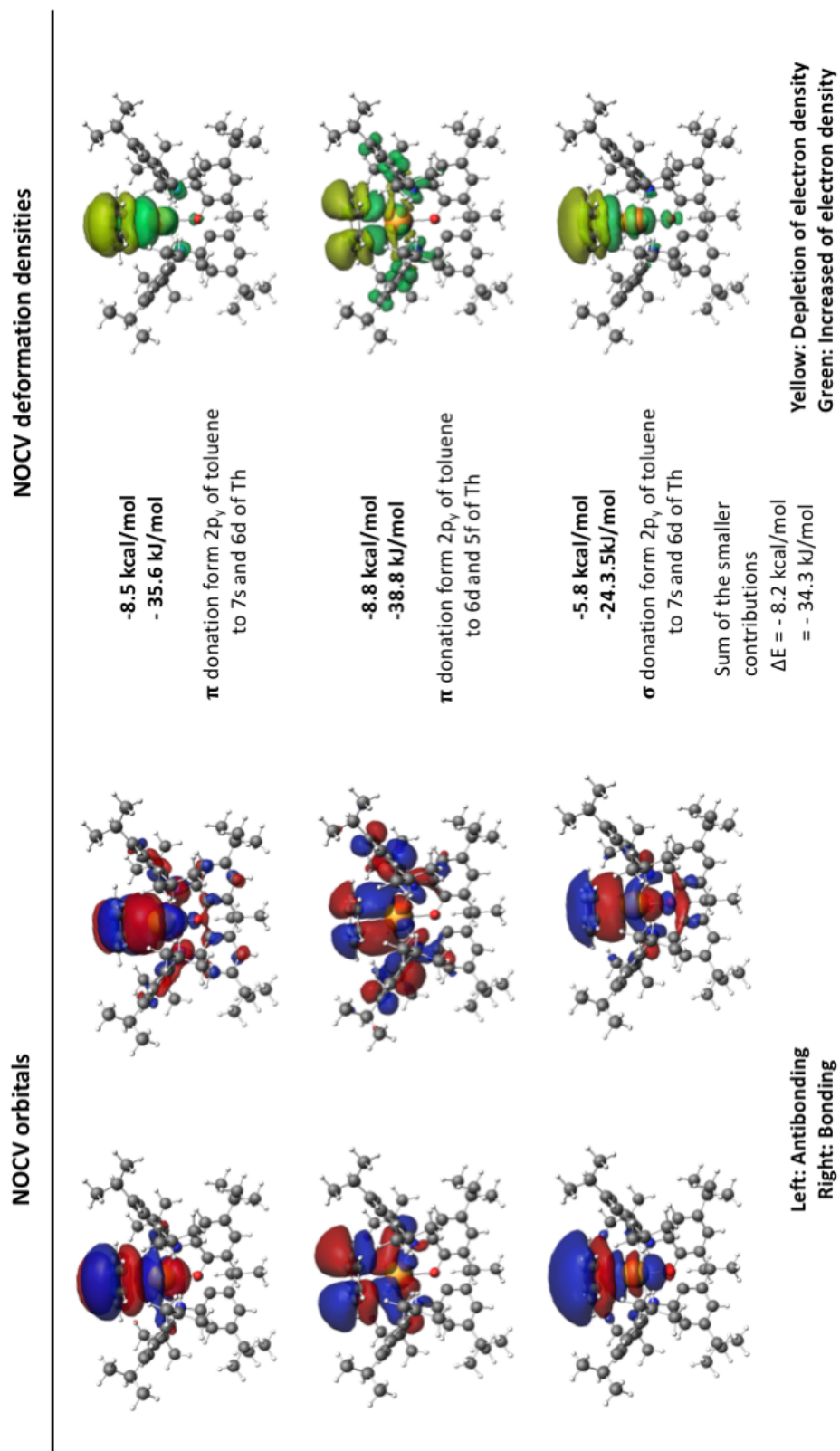


FIGURE 3.20: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6\text{2'-Th}$ .



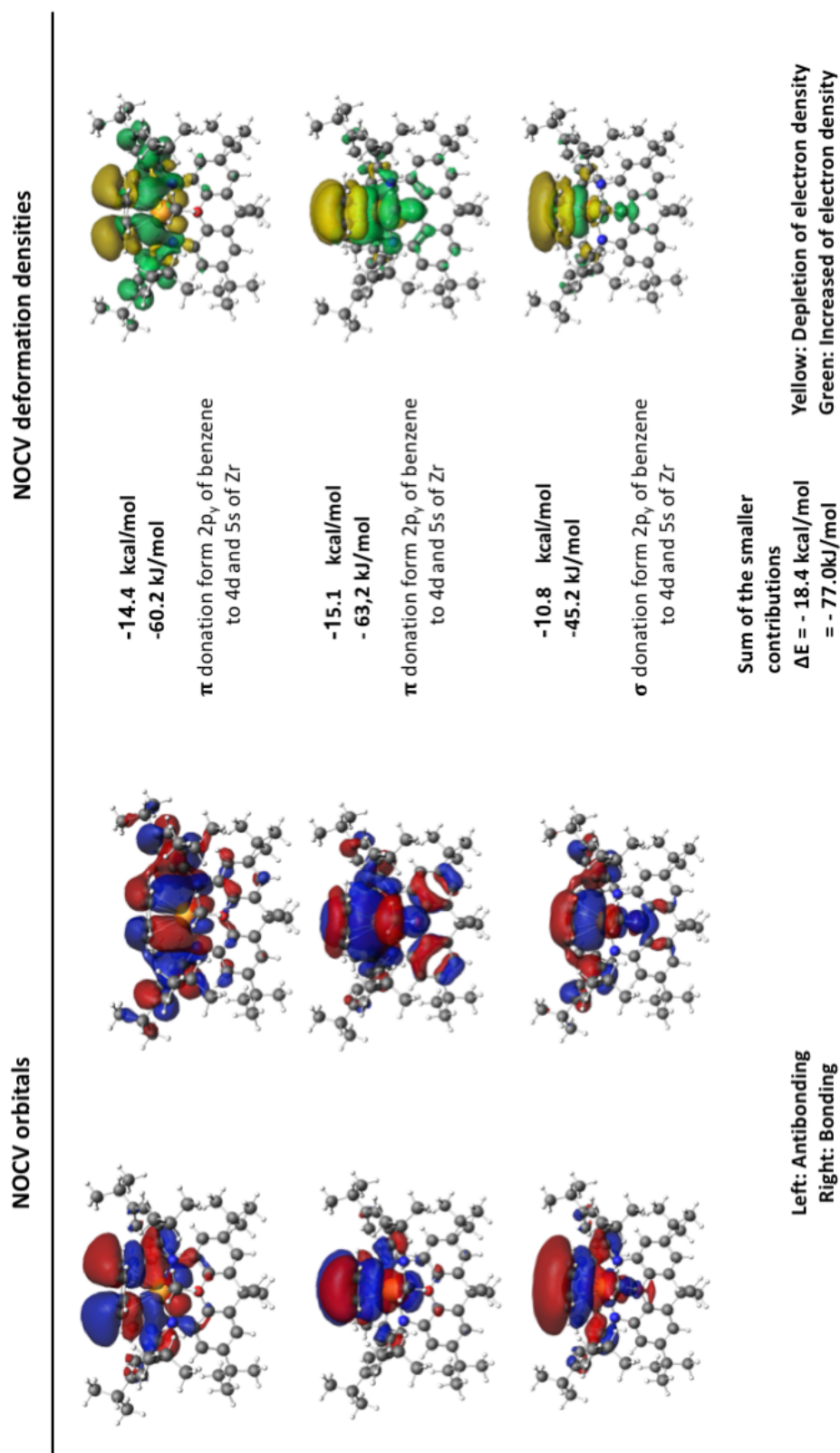


FIGURE 3.21: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6\text{Zr}$ .

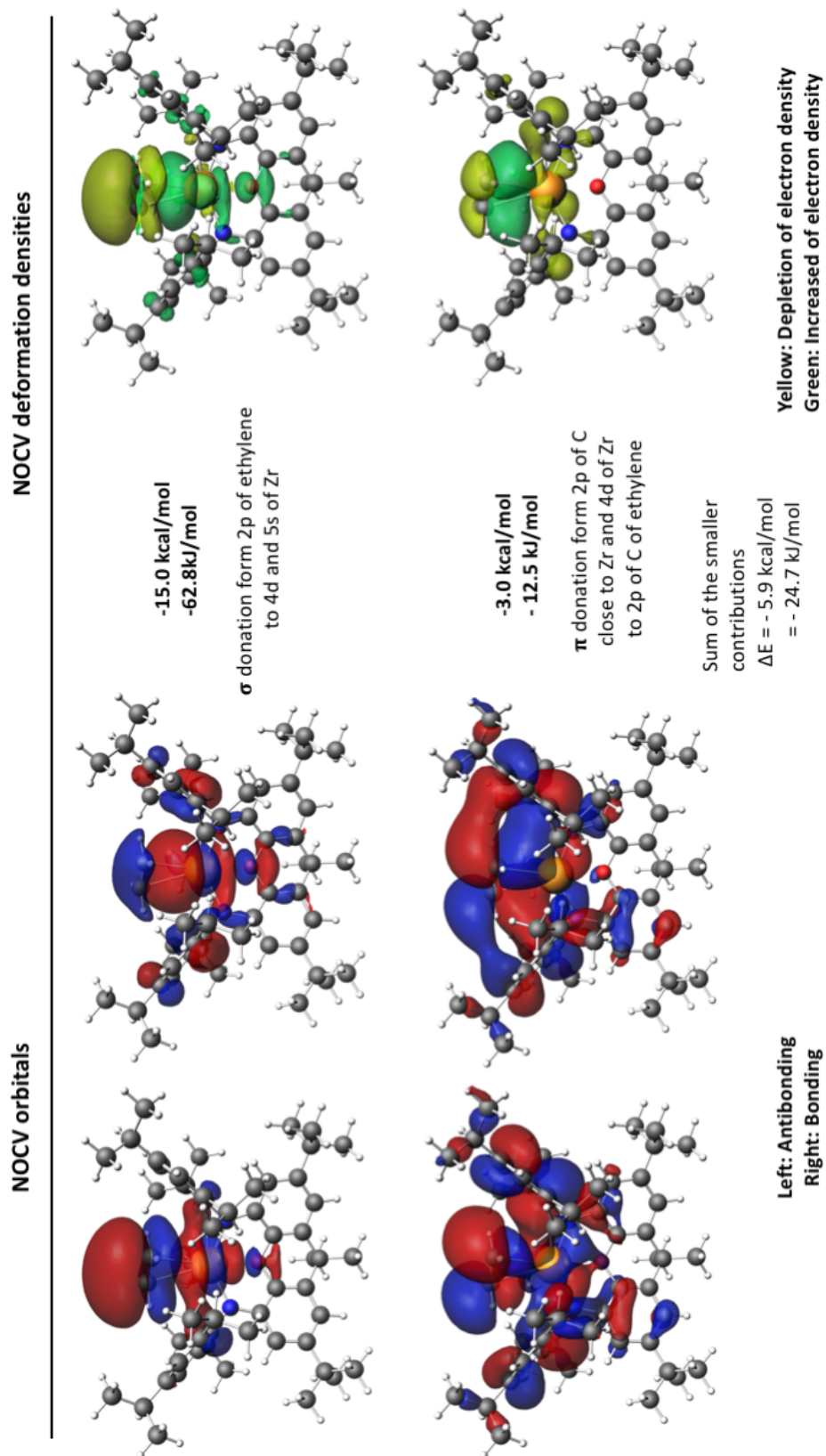


FIGURE 3.22: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^2\text{-E-Zr}$ .





## Chapter 4

# Thermodynamic properties and electronic structures of Plutonium Oxides

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As mentioned previously a nuclear accident would release numerous compounds. To confine this compounds would first imply to know the amount of the species released. This is what the IRSN (French Institute for Radioprotection and Nuclear Safety) aims to do. They decided to focused on Plutonium and its oxide because of its toxicity and volatility mentioned in the Introduction. In order to make a good prediction, the enthalpies of formation, the heat capacity and the entropy of each molecule involved must be known with the highest possible accuracy. In this Chapter, the enthalpies of formation of  $\text{PuO}_2$ ,  $\text{PuO}_3$  and  $\text{PuO}_2(\text{OH})_2$  will be discussed. Before a discussion of the computational protocol used and of the results obtained for these species, the existing experimental and theoretical results are reviewed below.

## 4.1 Review of available data for Plutonium Oxides

### 4.1.1 Experimental data

From a number of experimental investigations on  $\text{PuO}_2$  [138–144], the most rescent which addresses the determination of  $\Delta_f H^\ominus$  is that of Gotcu-Freis *et al.* [138]. They carried out the measurements of the vapour pressure with a Knudsen cell coupled with a quadrupole mass spectrometer. This apparatus is designed for the study of radioactive materials at high temperature and built in a glove box shielded by 5 cm thick lead bricks. This simple description of the experimental setup is enough to emphasize the difficulty of manipulating plutonium. Gotcu-Freis *et al.* extracted the values  $\Delta_f H^\ominus = -(428.7 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H^\ominus = -(440 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}$ , using the 2<sup>nd</sup> and 3<sup>rd</sup> law of thermodynamics, respectively. Previously the values reported in the thermodynamic databases were slightly higher  $\Delta_f H^\ominus = -(412 \pm 20.0) \text{ kJ}\cdot\text{mol}^{-1}$  [139] and  $\Delta_f H^\ominus = -(410 \pm 20.0) \text{ kJ}\cdot\text{mol}^{-1}$  [140]. Konings in his 2014's review [141] selected  $\Delta_f H^\ominus = -(428.7 \pm 20.0) \text{ kJ}\cdot\text{mol}^{-1}$  as the preferred value.

Unfortunately, the thermodynamic properties of  $\text{PuO}_3$  and  $\text{PuO}_2(\text{OH})_2$  are not as much documented (see Table 4.1). The first molecule was observed in a small amount by Ronchi *et al.* [145] after sublimation of free surfaces of  $\text{PuO}_2$  in presence of oxygen but no thermodynamic data was reported. Krikorian *et al.* [146] favoured the transpiration method starting from a  $\text{PuO}_2$  solid sample and flows of  $\text{O}_2$  or  $\text{H}_2\text{O}$  to generate  $\text{PuO}_3$  and  $\text{PuO}_2(\text{OH})_2$  molecules respectively. They reported the values of standard enthalpy of formation of  $-(562.8 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{PuO}_3$  and  $-(1\ 018.2 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$  for  $\text{PuO}_2(\text{OH})_2$ . This study is the unique source of experimental data

for  $\text{PuO}_2(\text{OH})_2$ . Konings *et al.* [141] reported the value of  $\Delta_f H^\ominus = -(567.6 \pm 15.0)$   $\text{kJ}\cdot\text{mol}^{-1}$  for  $\text{PuO}_3$ . One can note that the measurement of  $\Delta_f H^\ominus$  is never direct as they are derived from measured reaction quantities (such as the partial vapour pressure) for a given chemical reaction. Thus the validity of the results on  $\text{PuO}_2(\text{OH})_2$  and  $\text{PuO}_3$  needs to be confirmed.

Accounting for the fact that the manipulation of plutonium is neither easy nor safe, a reasonable alternative is to determine the enthalpies of formation with accurate relativistic correlated quantum chemical methods.

However, simulations of such systems remain challenging and to prove the capabilities of *ab initio* methods one has to answer to the following questions:

- Is it possible to reproduce the  $\Delta_f H^\ominus$  value for  $\text{PuO}_2$  ?
- Can we confirm the values of  $\Delta_f H^\ominus$  for  $\text{PuO}_3$  and  $\text{PuO}_2(\text{OH})_2$  ?

#### 4.1.2 Computational protocol for prediction of thermochemistry data

On the quantum chemical side, these molecules have been studied from a structural point of view but, predictions of enthalpies of formation are lacking, justifying our study.

Since our goal is to calculate the enthalpies of formation  $\Delta_f H^\ominus$  of different species, we need to define the target quantities. The enthalpy  $H$  is defined as:

$$H = U + pV \quad (4.1)$$

$U$  being the internal energy of the system,  $p$  its pressure and  $V$  its volume. The enthalpy of formation of a molecule is then the change in enthalpy to form one mole of the molecule. Hess law states that the enthalpy of a given reaction is the sum of standard enthalpies of formation of products minus the sum of the reactants.

$$\Delta_r H^\ominus = \sum_i v_i \Delta_f H^\ominus \quad (4.2)$$

with  $v_i$  the stoichiometric number.

In practice  $\Delta_r H^\ominus$  is calculated as:

$$\Delta_r H^\ominus = \sum_i (E_i + \text{ZPE}_i + H_{\text{corr},i}) \quad (4.3)$$

summing up the electronic energy  $E_i$ , the Zero Point Energy (ZPE) and the thermal correction to enthalpy  $H_{corr,i}$ .

The enthalpy of formation of the molecule of interest can thus be extracted by the computation of the  $\Delta_f H^\circ$  for a chosen reaction as in the equation 4.4 and the subtraction of the known  $\Delta_f H^\circ$  of the other reactants and products (see Table 4.2). For example for the reaction :  $A + Pu \rightarrow PuX + C$  we can obtain  $\Delta_f H^\circ$  as:

$$\Delta_f H^\circ(PuX) = \Delta_f H^\circ - \Delta_f H^\circ(A) - \Delta_f H^\circ(Pu) + \Delta_f H^\circ(C) \quad (4.4)$$

where  $\Delta_f H^\circ(Pu)$ ,  $\Delta_f H^\circ(A)$  and  $\Delta_f H^\circ(C)$  are tabulated. Since the enthalpy of formation is path independent, the results from the reactions  $R_1$  to  $R_5$  should be close to each other. The average of the results will be our final  $\Delta_f H^\circ$  and the mean deviation the reported error.

Since it is established that DFT is able, even for open-shell systems, to yield good geometries and vibrational frequencies that contribute to the Zero Point Energy (ZPE) and the thermal correction to the enthalpy ( $H_{corr}$ ), this will be the method of choice to estimate these thermodynamic contributions. However, the accurate estimation of the electronic energy of each molecules remains the most sensitive part, in particular for Pu and its derivatives since one can expect large contributions of the electron correlation as well as the relativistic effects. This will thus concentrate most of our attention in the following paragraphs.

Among the prior theoretical investigations on Pu oxides [147–152], the only one that focussed on the trioxide and oxyhydroxide molecules is that of Boguslawski *et al.* [147] employing the spin-free DMRG method which underlines the complexity of the electronic structure of  $PuO_2(OH)_2$ ,  $PuO_2$  and  $PuO_3$ . This method, allowing to include all the valence orbitals in the active space for the DMRG wave-function, can indicate which orbitals are important for the description of the correlation *via* an entanglement figure (see section 4.2.3). The entanglement diagrams show that the 5f-orbitals plutonium orbitals and the p-orbitals of bonded oxygens are important for the description of the non-dynamical correlation and that the wave-function has a strong multi-reference character.

This study, however, only provides a partial picture of the problem as it lacks the treatment of SOC in order to establish the true nature of the ground state.

While there are no subsequent theoretical investigations for  $PuO_2(OH)_2$  reported in the literature, for  $PuO_3$ , a study, based on CASSCF/CASPT2 + RASSI simulations by Kovacs *et al.* [148] represents a priori a good starting point for a deeper understanding of its electronic structure. Despite a different active space from what

Boguslawski *et al.* predicted, they reached an agreement on the nature ground state (spin-free  $^3B_2$  in the symmetry  $C_{2v}$ ).

Concerning  $PuO_2$ , its electronic structure was studied by Liao *et al.* [149], Moskaleva *et al.* [152] and Archibong *et al.* [150] using single reference approaches, U-DFT for the two first and U-CCSD(T) for the last one, and only including the scalar relativistic effects. The only theoretical study of  $PuO_2$  including the SOC was carried out by La Macchia *et al.* [151]. While all spin-free studies (i.e all aforementioned papers including the one using DMRG) proposed that the lowest  $^5\Sigma_g$  state as the molecule's ground state, La Macchia *et al.* found that the SOC effect is so important that the ground state is no longer mainly composed of the  $^5\Sigma_g$ , as there is a strong contribution of the  $^5\Phi_u$ , and that the geometry of the molecule is strongly modified compared to the spin-free one, with SOC being responsible for a decrease of the Pu-O bond length of 0.048 Å.

TABLE 4.1:  $\Delta_f H^\circ$  (kJ/mol) of the different compounds given in the literature.

Molecule	References	$\Delta_f H^\circ$
$PuO_2$	Gotcu-Freis <i>et al.</i> [138]	$-(428.7 \pm 7)$
	Gotcu-Freis <i>et al.</i> [138]	$-(440 \pm 7)$
	Glushko <i>et al.</i> [139]	$-(412 \pm 20)$
	Cordfunke <i>et al.</i> [140]	$-(4120 \pm 20)$
	Konings <i>et al.</i> [141]	$-(428.7 \pm 20)$
$PuO_3$	Krikorian <i>et al.</i> [146]	$-(562.8 \pm 5)$
	Konings <i>et al.</i> [141]	$-(567.6 \pm 15)$
$PuO_2(OH)_2$	Krikorian <i>et al.</i> [146]	$-(1\ 018.2 \pm 3.3)$

The results discussed above raise a few questions that will condition our capability of computing the desired thermodynamics:

- What is the geometry and nature of ground state of  $PuO_2$  ?
- What is the ground state electronic structure of  $PuO_3$  and  $PuO_2(OH)_2$  ?
- Have static and dynamical correlation effects been treated properly before?

An appealing choice would be to use four-component-based multireference methods, such as 4c-FSCC [153–155] or EOM-CC [156] to answer these questions. Unfortunately, the relativistic FSCC implementation at our disposal at this time, cannot be used to investigate  $PuO_3$  and  $PuO_2(OH)_2$ ; it requires that the reference wave function to be a single determinant. For these systems, such a reference is a very poor choice. For  $PuO_2$ , on the other hand, once SOC is included self-consistently in the calculation as it is done in four-component approach, the ground state can be represented by a single determinant and the CCSD(T) method (and EOM-CC) applied.

Another option would be to extend the work of Boguslawski *et al.* and include a better description of the electronic correlation, in particular the dynamic contribution, and also include the effect of the spin-orbit coupling. Recent developments make it now possible to use DMRG-SCF and DMRG-NEVPT2 to include, respectively static and dynamic correlation, with an active space up to 50 electrons in 50 orbitals. Though, SOC is still only included via State Interaction (see Section 4.2.2). Preliminary calculations, however, were not successful and require further investigation that will be pursued beyond this thesis.

For these reasons, the only generally applicable method to treat such highly correlated systems in a relativistic framework is the CASPT2 method, combined with a posteriori treatment of SOC.

In this chapter, we provide a detailed description of the CASSCF approach that relies on the selection of important orbitals (active space) for the treatment of the static correlation. The choice of the active space is at the heart of this work and will be discussed in details for the three molecules.

## 4.2 Multireference Approaches

All the quantum chemical methods listed so far in Chapter 2 refer to single determinant wave function, thus not applicable for the foreseen multi-reference gas-phase plutonium molecules. Indeed, partial population of the valence 7s, 5f and 6d orbitals can induce significant multi-reference contributions to the wave functions and connected to the presence of quasi-degenerated electronic states, reflected by strong static correlation. We will now describe the various multi-reference methods that can account for static and dynamical correlation.

### 4.2.1 The ideal multi reference method: Full Configuration Interaction

The most complete way to capture electronic correlation, for the ground state or excited states, is to use the Full Configuration Interaction (FCI) method, for which the wave function is written as a linear combination of all the possible determinants created by single up to N-excitations from the HF determinant, N being the number of electrons:

$$|\psi_{FCI}\rangle = c_0 |\Phi_{HF}\rangle + \sum_{a,r} c_a^r |\Phi_a^r\rangle + \sum_{\substack{a<b \\ r<s}} c_{ab}^{rs} |\Phi_{ab}^{rs}\rangle + \sum_{\substack{a<b<c \\ r<s<t}} c_{abc}^{rst} |\Phi_{abc}^{rst}\rangle + \dots \quad (4.5)$$

One recognises  $\Phi_{HF}$  the HF solution the excited determinants from the HF one.  $\Phi_a^r$  is a singly excited (S-type) determinant generated by the promotion of one electron from the spin orbital  $a$  to the spin orbital  $r$ ; the  $\psi_{ab}^{rs}$  is a doubly excited (D-type) determinant created by the promotion of two electrons from the spin orbitals  $a$  and  $b$  to the spin orbitals  $r$  and  $s$  etc...

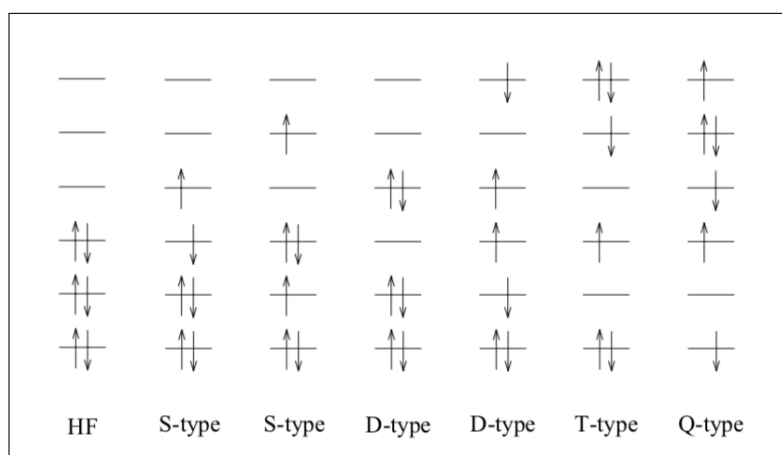


FIGURE 4.1: Various Excited Slater determinants generated from a HF reference [10]

The expansion coefficients are determined from a variational procedure in order to minimise the energy. In order to find the expansion coefficients all the possible excited determinants must be generated but also all the combinations of them : the Configurational State Functions (CSFs). It is the number of CSFs that will limit the use of this method. Indeed it was shown [10] that just for singlet the number of generated CSFs is:

$$\frac{M!(M+1)!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}+1\right)!\left(M-\frac{N}{2}\right)!\left(M-\frac{N}{2}+1\right)!} \quad (4.6)$$

$M$  being the number of basis functions and  $N$  the number of electrons. If one takes the plutonium atom as example, the number of electron is 94 and the chosen basis set is the contracted ANO-RCC-TZP corresponding to 87 basis functions, the number of CSFs is  $4.461\,4245 \times 10^{48}$  only for singlet configurations (!!). For this reason, one is forced to cut the number of excitations to obtain a *truncated*-CI expansion or reduce the number of determinants by selecting the orbitals that can participate into the excited determinants.



## 4.2.2 Multiple-steps correlated methods

### Inclusion of static correlation: Complete Active Space Self Consistent Field

The main idea of the Complete Active Space Self Consistent Field (CASSCF) method is to proceed to a FCI calculation but only with a set of selected orbitals forming the so-called active space. The molecular orbitals are thus divided in three groups: the inactive orbitals, lowest in energy and doubly occupied, the active space containing at most 18 electrons in 18 active orbitals. The occupations of the active orbitals can vary between zero and two electrons. The third and last type of orbitals are the unoccupied orbitals also called virtual orbitals (see Figure 4.2) which will remain unoccupied.

CASSCF is far from "black box" being a method since the selection of the active space is in general not trivial especially due to the constraint of the number of electrons and the active orbitals. The choice of active space, and making sure it accurately represents the physics of the system, represent the main challenges of this type of calculation. That said, one can follow the rules proposed by Roos *et al.* [157] to build an active space suitable for the ground state or excited states of a given system:

- the orbitals participating to the target state.
- the valence orbitals (*i.e.* first row for light atoms; 7s, 5f and 6d for an actinide atom).
- orbitals with an occupation between 0.05 and 1.95 electron from the MP2 first-order density matrix.
- if bonding orbitals are taken, the corresponding anti-bonding should be included as well.

Certainly, the number of electrons and orbitals corresponding to the point above can quickly be greater than 18. So, the choice of the orbitals to exclude is left to the appreciation of the user, nonetheless, this choice must be argued.

One solution to extend the size of the active space is to use the Restricted Active Space Self Consistent Field (RASSCF) method, Figure 4.2. The RAS1 is composed of doubly occupied orbitals, the RAS2 is the full CI active space and RAS3 includes unoccupied orbitals. A FCI will be done in the RAS2 space and excitations from RAS1 orbitals to RAS3 ones are added with a user-defined constrain on the maximum numbers of holes and particles in RAS1 and RAS3, respectively.

In order to compute the Spin-Orbit Coupling (SOC) in the system not only the ground state is needed but also some of the excited states (this need will be explain in the

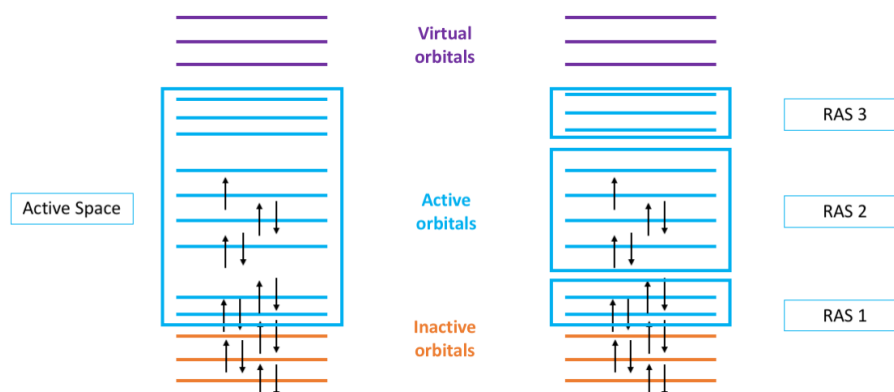


FIGURE 4.2: Representation of the CASSCF and RASSCF approaches. On the left hand side, the CASSCF method within the active space (9;9) on the right hand side, the RASSCF method with the active spaces: RAS1(4;2), RAS2(5;4), RAS3(0,3).

section 4.2.2) that can be coupled by the SO operator. If only one state is computed at a time, we refer to a State Specific (SS) calculation, for a ground or excited state. The SS approach has the main disadvantages to be computationally expensive since a specific set of orbitals is optimised for each state. Instead, it is faster to use the SA procedure for which a set of common orbitals to several state sharing the same multiplicity and symmetry is optimised.

Note that SA-CASSCF energies will be higher than the SS ones but as we often only consider energy differences, the errors on the individual energies will compensate.

This multi-reference method CASSCF or RASSCF thoroughly includes the static electronic correlation but only a limited part of the dynamical correlation, since only double excitations are included within the active space. A rather economical way of including dynamical correlation, due to the excitations from active space to the virtual orbitals, is to use second-order perturbation theory.

### Multi-Reference Perturbation Theory at the 2<sup>nd</sup> order

The Complete Active Space Perturbation Theory at the 2<sup>nd</sup> order or CASPT2 is, as indicated by his name a perturbative method. It allows to account for the dynamical correlation to the wave function, starting from a CASSCF calculation by adapting the MP2 approach introduced in Section 2.2.2. The contributing single and double excitations are represented in Figure 4.3. They are classified according to the number of holes and particles. It is useful to by-pass the diagonalisation problem of the

operator  $\hat{H}'$ . Instead of the diagonalisation of the full  $\hat{H}'$  will be done by block *i.e.* for each excitation type at a time.

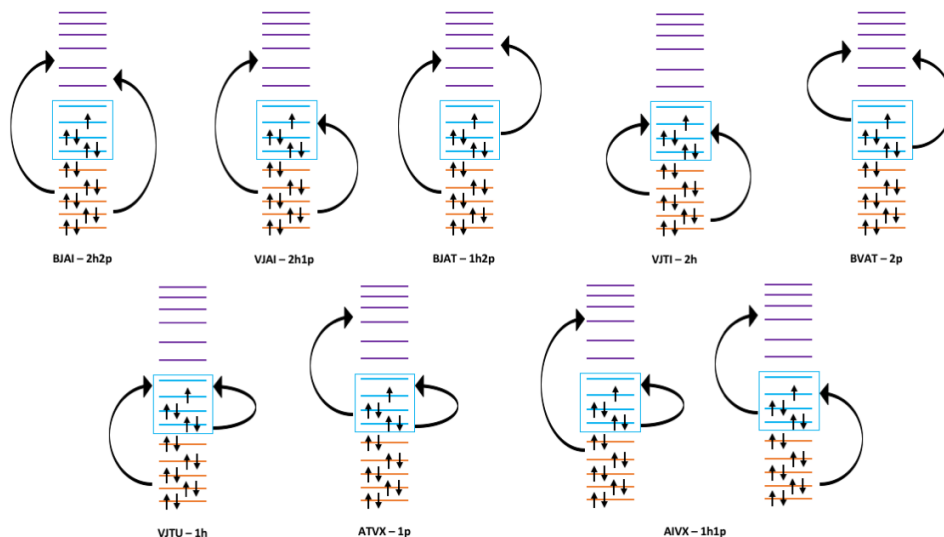


FIGURE 4.3: Representation of the possible di-excitation in CASPT2 method. NAME of the excitation in CASPT2 method - number of *holes* (electron(s) outside the active space promoted to the active or virtual orbitals) number of *particle* (electron occupying a virtual orbital - outside the active space - after the perturbation).

Originally, the Hamiltonian used was the Zeroth-Order Hamiltonian with the standard Fock matrix formulation [158]:

$$\hat{H}_0 = \hat{P}_0 \hat{F} \hat{P}_0 + \hat{P}_k \hat{F} \hat{P}_k + \hat{P}_{SD} \hat{F} \hat{P}_{SD} + \hat{P}_{TQ\dots} \hat{F} \hat{P}_{TQ\dots} \quad (4.7)$$

where  $\hat{P}_0$  is the projector on the one-dimensional space  $V_0$ , spanned by the CAS reference wave function  $\phi_0$  under consideration,  $\hat{P}_k$  is the projector on the space  $V_k$ , spanned by the orthogonal complement to  $\phi_0$  in the restricted FCI subspace used to generate the CAS wave function.  $\hat{P}_{SD}$  is the projector on the space  $V_{SD}$ , spanned by all the single and double replacement states generated from  $V_0$ , finally  $\hat{P}_{TQ\dots}$  is the projector on the space  $V_{TQ}$ , spanned by all higher excitation not included in  $V_k$  and  $V_{SD}$ .

This formulation raises the intruder state problem [159]. When excited determinants are close in energy to the reference ones, their contribution will diverge due to a denominator approaching zero. Those intruder states can be spotted by a low ( $< 0.60$ )

value of the weight of the CAS/RAS wave function in the final wave function. To eliminate this problem a level shift of the active orbitals was introduced. Based on the Ionisation Potential (IP) and Electronic affinity (EA) [160], the IPEA shift was determined thanks to a benchmark on atomic data. During our study IPEA value was kept at its default value: 0.25 a.u.. Since it is known that the higher states are much more sensitive to the value of the level shift [159] it was decided to use the available "imaginary shift". It actually uses real quantities to treat the potential energy function differently from the IPEA level shift in order to reduce the sensitivity of the energies to the size of the imaginary shift. It was fixed at 0.05 a.u., the smallest value reported by Forsberg *et al.* [159] to reach accurate results.

Finally, another possibility to fix the problem of intruder states is to use the Hamiltonian by Angeli *et al.* [161] which is based on the generalised zeroth order Hamiltonian by Dylla [162]. It behaves as a true many-body Hamiltonian inside the CAS subspace, including all two-electrons interactions, while the CASPT2 method uses the monoelectronic Fock Hamiltonian. N-Electron Valence state Perturbation Theory at the 2<sup>nd</sup> order (NEVPT2) method is intrinsically intruder state free; however, current implementations limit its use to active spaces of 14 electrons in 14 orbitals, thus inapplicable to our systems.

#### ***A posteriori* treatment of spin orbit coupling : the RASSI method**

The Restricted Active Space State Interaction (RASSI) methods is able to compute the coupling elements for any one-electron operator between CASSCF/RASSCF wave-function that can be non-orthogonal. In our case, the one-electron operator is SOC, computed with the atomic mean field spin-orbit operator described by equation 2.106 in Section 2.4.3, that couples states of different spins and spatial symmetries. In order to also include the dynamical correlation, the method was adapted by Malmqvist *et al.* [163] to use the CASPT2 wave-functions as basis. So the diagonal RASSI matrix [65] is dressed with the CASPT2 energies while the spin orbit matrix elements ( $V_{SO}$ ) appear as off-diagonal elements. The so-constructed matrix is diagonalised to obtain the SO-eigenstates.

The lowest eigenvalue is the energy of ground state at spin-orbit CASPT2 (SO-CASPT2) level. Every SO-state is expressed as a linear combinaison of the Spin-Free (SF) states that constituted the basis. The SOC contribution to the molecule total energy is thus energy difference between the lowest SO state and the lowest SF state.

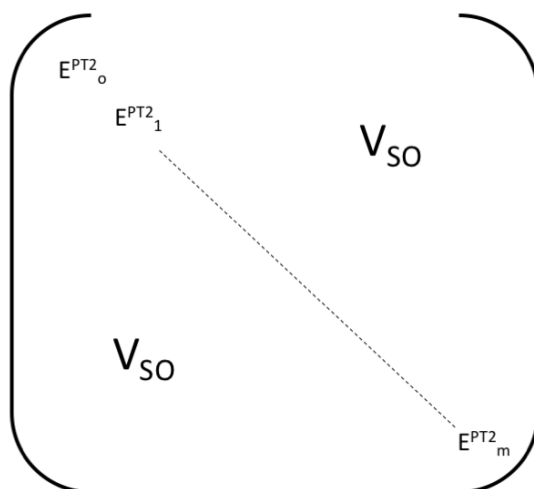


FIGURE 4.4: Matrix representation with, in diagonal, the CASPT2 energies and outside the diagonal, the spin orbit element.

### 4.2.3 Opening the active spaces to include electronic correlation: the Density Matrix Renormalisation Group

TABLE 4.2:  $\Delta_f H^\ominus$  of the different compounds given in kJ/mol

Species	$\Delta_f H^\ominus$	$\Delta\Delta_f H^\ominus$
O ( $^3P$ )	249.23 [164]	0.00
H ( $^1S$ )	218.00 [165]	0.01
Pu ( $^5F$ )	349.00 [166]	3.0
H <sub>2</sub> (1S)	0.00[165]	0
H <sub>2</sub> O	-241.81[164]	0.03
H <sub>2</sub> O <sub>2</sub>	-135.88 [167]	
O <sub>2</sub>	0.00[165]	0.00
OH	37.36 [164]	0.13

## 4.3 Technical Considerations and Computational details

### 4.3.1 Geometries, enthalpic corrections and basis sets

The first information a computational chemist needs is the geometry of the system under study. In our case, all the geometries (except PuO<sub>2</sub> see section 4.3.1) were optimised with DFT (see section 2.3) and the B3LYP functional [168, 169] using the GAUSSIAN09 [170] package. The plutonium atom was described by a relativistic effective core potential (RECP) ECP60MWB [171] with the corresponding basis set of

TABLE 4.3: Reactions used to calculate  $\Delta_r H^\circ$ 

	PuO <sub>2</sub>	PuO <sub>3</sub>	PuO <sub>2</sub> (OH) <sub>2</sub>
R <sub>1</sub>	Pu + O <sub>2</sub> → PuO <sub>2</sub>	Pu + $\frac{3}{2}$ O <sub>2</sub> → PuO <sub>3</sub>	Pu + O <sub>2</sub> + 2 H <sub>2</sub> → PuO <sub>2</sub> (OH) <sub>2</sub>
R <sub>2</sub>	Pu + 2 O → PuO <sub>2</sub>	Pu + 3 O → PuO <sub>3</sub>	Pu + 4 O + 2 H → PuO <sub>2</sub> (OH) <sub>2</sub>
R <sub>3</sub>	Pu + H <sub>2</sub> O <sub>2</sub> → PuO <sub>2</sub> + H <sub>2</sub>	Pu + $\frac{3}{2}$ H <sub>2</sub> O <sub>2</sub> → PuO <sub>3</sub> + $\frac{3}{2}$ H <sub>2</sub> O	Pu + 3 H <sub>2</sub> O <sub>2</sub> → PuO <sub>2</sub> (OH) <sub>2</sub> + 2 H <sub>2</sub> O
R <sub>4</sub>	Pu + OH → PuO <sub>2</sub> + 2 H	Pu + 3 OH → PuO <sub>3</sub> + 3 H	Pu + 4 OH → PuO <sub>2</sub> (OH) <sub>2</sub> + 2 H
R <sub>5</sub>	Pu + 2 H <sub>2</sub> O → PuO <sub>2</sub> + 2 H <sub>2</sub>	Pu + 3 H <sub>2</sub> O → PuO <sub>3</sub> + 3 H <sub>2</sub>	Pu + 4 H <sub>2</sub> O → PuO <sub>2</sub> (OH) <sub>2</sub> + 2 H <sub>2</sub>

quadruple  $\zeta$  [71] quality, while for the lighter atoms by augmented triple  $\zeta$  (aug-cc-pVTZ) basis sets were used. This basis set quality is known to reproduce properly the geometries and the enthalpic corrections. All the geometries are available in Annex A. The calculation of harmonic frequencies is necessary to compute the zero point energy (ZPE) and the thermal corrections to the enthalpy of equation 4.3 and the entropy. Anharmonic frequencies were also computed but no significant difference in the value of the entropies  $S$  were seen in comparison to the harmonic ones, thus only contributions obtained at the harmonic level were kept.

Once the geometries of the different molecules were obtained and to reach accurate electronic energies for the determination of  $\Delta_r H^\circ$ , two methods were used. The first is the UCCSD(T) method which represents the gold standard for single-reference wave function. The second is the multi-reference wave-function method that involves CASSCF plus CASPT2 calculations to check whether the wave function has a multi-reference character or not. In both cases, the scalar relativistic effects are included via the DKH2 Hamiltonian and the SOC was calculating with the RASSI procedure and added to the UCCSD(T) and CASPT2 spin free energies. All atoms are described with the ANO-RCC basis sets [172, 173] with qualities sequentially increased from triple- $\zeta$  ( $n=3$ ) to quadruple- $\zeta$  ( $n=4$ ) to extrapolate the energies to the CBS limit with the total energy extrapolation (CBS-TE) and the extrapolation separating the uncorrelated and correlated energies (CBS-CE). The two extrapolation methods yield to small differences of a few  $\text{kJ}\cdot\text{mol}^{-1}$  for the reaction energies.

### Geometry of PuO<sub>2</sub>

Because of disagreement in literature [147, 149, 152, 174] concerning the distance Pu-O and the nature of the ground state, a more accurate exploration of the potential energy surface was needed. It was first done with the State Specific-Spin-Free-CASPT2 method for the lowest quintet  $A_g$  and  $A_u$  states in  $D_{2u}$  symmetry. Scanning distances from 1.724 Å to 1.884 Å in steps of 0.02 Å.

In addition to the CASPT2 calculations, Andre Gomes performed calculations based on the molecular mean-field [175] approximation to the Dirac-Coulomb ( ${}^2\text{DC}^M$ )

Hamiltonian, at MP2, CCSD and CCSD(T) [176, 177] levels of theory with the DIRAC electronic structure code [178] using  $D_{\infty h}$  symmetry. The Dyall basis sets [179, 180] of triple- and quadruple-zeta qualities were employed for the plutonium atom, and Dunning's aug-cc-pVXZ ( $X=T, Q$ ) sets [181] for the oxygen atoms. In all calculations, the  $(SS|SS)$ -type two-electron integrals were approximated by a point-charge model [182]. Electrons in molecular spinors with energies comprised between -3 and 100 au were included in the correlated treatment, which amounted to correlating 28 electrons for  $\text{PuO}_2$ .

The SCF calculations were closed-shell ones, with 52 and 58 electrons in  $g$  and  $u$  irreducible representations, respectively. The equilibrium structure and spectroscopic constants for each electronic structure method were determined via a polynomial fit of the potential energy surface constructed from single-point calculations for Pu-O internuclear distances between 1.750 Å and 1.880, in steps of 0.005. Energies and potential energy curves at the complete basis set limit were obtained with the two-point extrapolation (see equation 2.121).

### 4.3.2 Results of the single-reference gold standard method: UCCSD(T)

The UCCSD(T) [183] calculations were performed with the Molpro Quantum Chemistry software [156]. The frozen orbitals were the 1s orbital of O and 1s to 5d (included) orbitals of Pu. No core-valence correlation was considered here due to the excessive computational cost and that we expect them not to exceed few  $\text{kJ mol}^{-1}$  for actinide molecules [184].

In order to look at the influence of the inclusion of the spin-orbit *a priori*,  $^2\text{DC}^M$ -CCSD(T) calculation were performed (by Andre Gomes). It could be done on Pu,  $\text{PuO}_2$ ,  $\text{H}_2$ , OH,  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  allowing us to obtain the energies for reactions  $R_3$ ,  $R_4$  and  $R_5$  for  $\text{PuO}_2$ . The setup from the PES exploration of  $\text{PuO}_2$  was kept (see Section 4.3.1).

In addition, thanks to the recent implementation made by Andre Gomes used recent implementation in DIRAC code [185] of variant of EOM-CCSD, we were able to compute the ionization potential for atomic Pu and  $\text{PuO}_2$  (EOM-IP-CCSD) and the excitation energies (EOM-EE-CCSD) for  $\text{PuO}_2$ .

In the case of EOM-IP-CCSD for Pu, we requested the number of states as follows: five  $\Omega = 1/2_g$ , two  $\Omega = 3/2_g$ , one  $\Omega = 5/2_g$ , three  $\Omega = 1/2_u$ , two  $\Omega = 3/2_u$  and one  $\Omega = 5/2_u$ , whereas for  $\text{PuO}_2$  we requested two  $\Omega = 1/2_g$ , one  $\Omega = 3/2_g$ , three  $\Omega = 1/2_u$ , two  $\Omega = 3/2_u$  and one  $\Omega = 5/2_u$  states. In the case of EOM-EE-CCSD

we requested the number of states as follows: six  $\Omega = 0_g$ , four  $\Omega = 1_g$ , three  $\Omega = 2_g$ , two  $\Omega = 3_g$ , one  $\Omega = 4_g$ , one  $\Omega = 5_g$ , ten  $\Omega = 0_u$ , nine  $\Omega = 1_u$ , seven  $\Omega = 2_u$ , five  $\Omega = 3_u$ , three  $\Omega = 4_u$ , and one  $\Omega = 5_u$ .

### 4.3.3 Multi-reference calculations: Actives Spaces, Number of States and Shifts

#### Actives spaces

All the multi-reference wave-function calculations were performed with the MOL-CAS software [186]. As previously mentioned the choice of active space is crucial since a poor choice of active space can lead not only to poor accuracy but to false results. The easiest choice of active space is the one for the atomic plutonium. One would be tempted to wisely but simply consider the 5f-orbitals. The Paris-Sud database [167] reports the nonet  $^9\text{H}$ , involving the 6d and 7s orbitals, as the closest in energy to the septuplet ground state. Thus the former orbitals were also included to lead to an active space of 8 electrons in 13 orbitals (8,13). First calculations yield for the appearance of a spurious orbital in the CAS, making us reconsider our previous active space. Finally, we proposed the following organisation: the 7s orbital in the RAS1 with 1 hole allowed, the 5f orbitals in the RAS2 and the 6d orbitals in the RAS3 with one particule permitted. Concerning the molecules with no plutonium atom, the active space is simply composed of the oxygen valence orbitals. For those molecules, spin-orbit coupling was not imputed as it is expected to be negligible.

Concerning the plutonium oxides and oxyhydroxides, the choice of the active space was guided by the DMRG study of Boguslawski *et al.* [147], to which our research team contributed. This study followed the rules laid out in the Section 4.2.2 to define the 'full valence' space. The analysis of the entanglement diagrams lead to the definition of "optimal active spaces" listed in Table 4.4.

TABLE 4.4: Full active space and optimal active space presented in the article of Boguslawski *et al.* [147]

Molecules	Full Valence	Optimal Active Space
$\text{PuO}_2$	(28,25)	(18,17)
$\text{PuO}_3$	(34,26)	(14,14)
$\text{PuO}_2(\text{OH})_2$	(42,35)	(20,22)

Note that neither orbital optimisation nor SOC were included in [147]. The suggested optimal active space for  $\text{PuO}_2(\text{OH})_2$  is too large for the CASSCF method.



Instead, we restricted ourselves to a minimal active space of 2 electrons in 4 orbitals (see Figure 4.5). Concerning  $\text{PuO}_3$  and  $\text{PuO}_2$  attempts to use the optimal active spaces was made but turned out unsuccessful as these are suited for the ground state only but do not apply for the excited states. Thus the active spaces had to be modified.

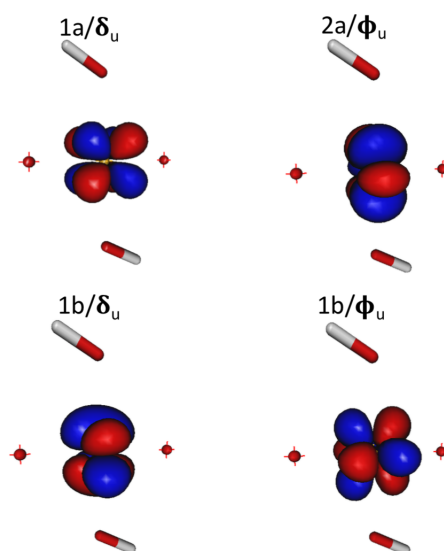


FIGURE 4.5: Molecular orbitals of  $\text{PuO}_2(\text{OH})_2$  at the CASSCF level. Isosurface = 0.05 a.u.

- **$\text{PuO}_2$  active space**

For  $\text{PuO}_2$ , the optimal active space matches the MO diagram of the uranyl molecule proposed by Denning *et al.* [187]. This paper emphasised the mixing of the 5f, 6d and the 2p-orbitals of the oxygens, thus a chemically relevant model should include (14, 18) which is already approaching the limit of the CASSCF code. Moreover we would like to add the 7s orbitals that have been proven important for the description of plutonium and for  $\text{PuO}_2$  [147], bringing the active space to 16 electrons in 19 orbitals, which is undoable.

After a close look at the DFT-B3LYP results for  $\text{PuO}_2$ , it appears that the lowest orbitals of the (16;19) active space are the degenerate  $\pi_g$  orbitals formed by the combination of Pu's 6d and oxygen 2p-orbitals. These orbitals did not appear as strongly entangled to the other valence orbitals in the entanglement diagram on the Figure 3 in [147] and can thus be eliminated from the active space cutting it down to a CAS(12, 17) (see Table 4.5 for details). This is slightly larger than the one used in the study of La Macchia *et al.* but the results can still be comparable.

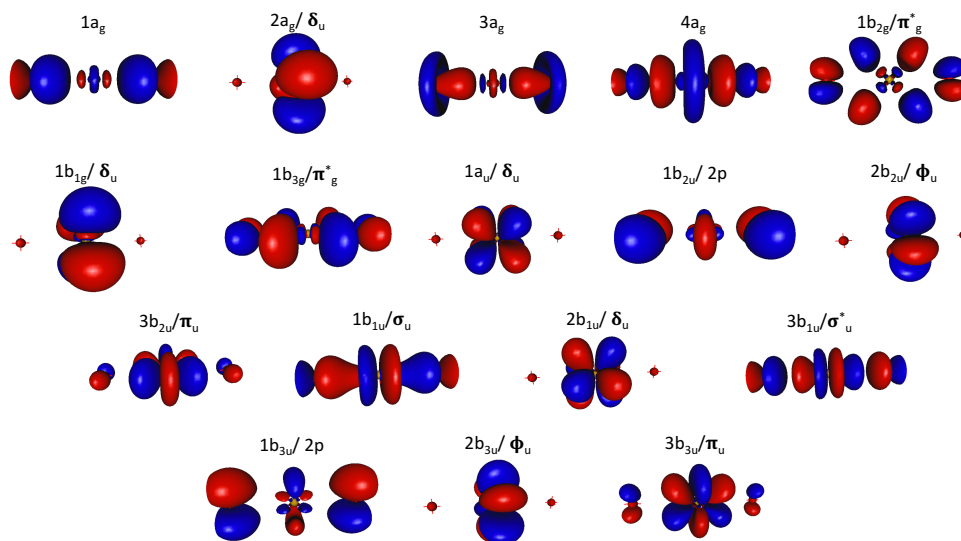


FIGURE 4.6: Molecular orbitals of  $\text{PuO}_2$  at the CASSCF level; Isosurface = 0.05 a.u.

TABLE 4.5: Active spaces for the various plutonium oxides and oxyhydroxides.

Molecule	Active Space (electron, orbitals)	Orbitals
$\text{PuO}_2$	(12,17)	$\pi_u(2), \pi_g(2), \sigma_g, \sigma_u, \pi_u^*(2), \pi_g^*(2), \sigma_g^*, \sigma_u^*, f_\delta(2), f_\phi(2)$
$\text{PuO}_3$	(14,13)	$1a_1, 2a_1/\pi_u, 2a_1, 4a_1/p_x^0, 5a_1/\phi_u, 6a_1/\pi_u, 1b_1/\phi_u, 2b_1/\pi_u, 1b_2/p_z^0, 2b_2/\sigma_u, 3b_2/\delta_u, 4b_2/\sigma_u^*, 1a_2/\delta_u$
$\text{PuO}_2(\text{OH})_2$	(4,4)	$1a/\delta, 2a/\phi, 1b/\delta, 2b/\phi$
Pu	(8,13)	7s, 5f, 6d
O	(6,4)	2s, 2p <sub>x</sub> , 2p <sub>y</sub> , 2p <sub>z</sub>
$\text{O}_2$	(12, 8)	$\sigma_{2s}, \sigma_{2s}^*, \sigma_{2p}(3), \sigma_{2p}^*(3)$
OH	(7,5)	$\sigma, \sigma_{nb}, 2p_x^O, 2p_y^O, \sigma^*$
$\text{H}_2\text{O}_2$	(14, 10)	$1 \sigma^{O-O}, 1 \sigma^{*O-O}, \sigma^{O-H}(2), 2 \sigma^{O-O}, \pi^{O-O}, 2p^O, 1 \sigma^{*O-O}, \sigma^{O-H}(2)$
$\text{H}_2\text{O}$	(8,6)	$2a_1, 1b_2, 3a_1, 1b_1, 4a_1, 1b_2$
$\text{H}_2$	(2, 2)	$\sigma, \sigma^*$
H	(1,1)	1s

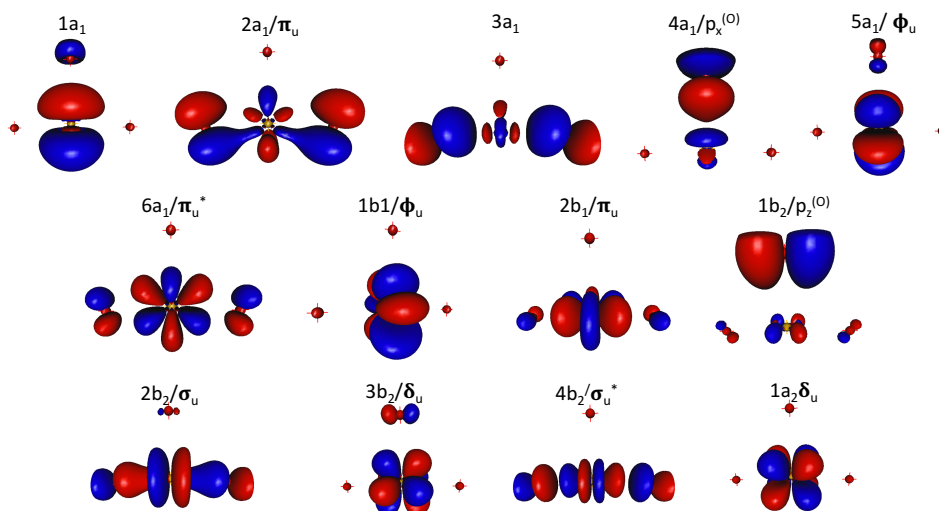
#### • $\text{PuO}_3$ active space

Concerning  $\text{PuO}_3$ , from a chemical view point, assuming Pu to be in oxidation state (VI), we can depict it as a plutonyl  $\text{PuO}_2^{2+}$  in interaction with a  $\text{O}^{2-}$  anion. Thus from the  $\text{PuO}_2$  active space we selected all the orbitals that could mix with the 2p-orbitals of the apical oxygen, leading to an active space of 12 electrons in 10 orbitals (2p<sub>x</sub> and 2p<sub>z</sub> of the oxygen plus the  $2b_{2u}/\phi_u, 2b_{3u}/\phi_u, 1b_{1u}/\sigma_u, 2b_{1u}/\delta_u, 3b_{1u}/\sigma_u^*, 1a_u/\delta_u,$

TABLE 4.6: Totale energy of the ground state of Pu, PuO<sub>3</sub> and PuO<sub>2</sub>(OH)<sub>2</sub> for different value of the imaginary shift.

Molecule	0.01	0.05	0.01	No Imaginary shift
Pu	-29539.80490586	-29539.80507744	-29539.80592767	-29539.80604535
PuO <sub>3</sub>	-29765.45793749	-29765.45814830	-29765.45837134	-29765.45737950
PuO <sub>2</sub> (OH) <sub>2</sub>	-29841.93260283	-29841.93266384	-29841.93267515	-29841.93267545

$3b_{3u}/\pi_u$  and  $3b_{3u}/\pi_u$  of PuO<sub>2</sub>). It is enough for the description of the ground state but not for the excited states. Thus, 2 electrons and 3 orbitals (corresponding to the  $1a_g$ ,  $1b_{2u}/2p$  and the visible of Figure 4.6 and the  $1a_g$  of Figure 4.7) were added to obtain the active space mentioned in the Table 4.5 or in Figure 4.7.

FIGURE 4.7: Active CASSCF orbitals of PuO<sub>3</sub> at the CASSCF level; Isosurface = 0.05 a.u.

- **CASPT2 - Numbers of state computed**

The number of states that are computed at CASSCF levels was dependent on the number of states that could be described properly (with a significant ( $> 0.6$ ) reference weight) at the CASPT2 level. To keep high reference weights, beside the default IPEA value (0.25 a.u.), an imaginary shift had to be added. Indeed the Molcas manual recommends its use to improve the description of CASPT2 excited states results when transition metals or actinides are involved to avoid intruder state problems. Since the computation of PuO<sub>2</sub> is quite expensive, tests on the value of the imaginary shift was done on Pu, PuO<sub>3</sub> and PuO<sub>2</sub>(OH)<sub>2</sub> only with smaller active spaces, (6,7), (12,10) and (2,4) for Pu, PuO<sub>3</sub> and PuO<sub>2</sub>(OH)<sub>2</sub>, respectively.

As shown in [159] the total energy is barely modified and the minimal value of the shift with noticeable effect on the description of the excited states is 0.05 a.u.. This

is the value kept in all the CASPT2 calculations since the 0.01 does not increase the number of states properly described and the value 0.1 impact the total energies and the excitation energies.

TABLE 4.7: Number of electronic states at CASSCF level of calculations

Multiplicity	Pu ( $C_i$ )	PuO <sub>2</sub> ( $D_{2h}$ )								PuO <sub>3</sub> ( $C_{2v}$ )				PuO <sub>2</sub> (OH) <sub>2</sub> ( $C_2$ )	
		A <sub>g</sub>	B <sub>2g</sub>	B <sub>1g</sub>	B <sub>3g</sub>	A <sub>u</sub>	B <sub>2u</sub>	B <sub>1u</sub>	B <sub>3u</sub>	A <sub>1</sub>	B <sub>1</sub>	B <sub>2</sub>	A <sub>2</sub>	A	B
Singlet	0	5	5	5	5	5	5	5	5	20	20	20	20	7	4
Triplet	50	5	10	10	10	7	10	7	10	20	20	20	20	2	4
Quintuplet	120	5	5	5	5	5	5	5	5	20	20	20	20	0	0
Septuplet	110	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nonet	35	0	0	0	0	0	0	0	0	0	0	0	0	0	0

TABLE 4.8: Number of electronic states at CASPT2 level of calculations

Multiplicity	Pu ( $C_i$ )	PuO <sub>2</sub> ( $D_{2h}$ )								PuO <sub>3</sub> ( $C_{2v}$ )				PuO <sub>2</sub> (OH) <sub>2</sub> ( $C_2$ )	
		A <sub>g</sub>	B <sub>2g</sub>	B <sub>1g</sub>	B <sub>3g</sub>	A <sub>u</sub>	B <sub>2u</sub>	B <sub>1u</sub>	B <sub>3u</sub>	A <sub>1</sub>	B <sub>1</sub>	B <sub>2</sub>	A <sub>2</sub>	A	B
Singlet	0	2	0	2	0	3	3	3	3	10	9	7	7	7	4
Triplet	27	2	3	3	3	6	7	6	7	16	15	13	14	2	4
Quintuplet	113	4	3	2	3	4	4	4	4	8	7	6	7	0	0
Septuplet	103	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Nonet	35	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Concerning the number of states included in the CASPT2, all of the 16 states were incorporated for PuO<sub>2</sub>(OH)<sub>2</sub>. Nonetheless, it was not possible for the atom of Pu or for the di and tri oxides (see Table 4.9). Thus we set a limit at 3 eV from the ground state for PuO<sub>3</sub> and only 2 eV for Pu and PuO<sub>2</sub>. Even if these limits can seem arbitrary, they ensure a good description of all states introduced in the SO-RASSI calculations and which couple to the spin-free ground states.

TABLE 4.9: Number of states available for computation and states taken for computation for the plutonium atom and the various plutonium oxides and oxyhydroxides.

	Pu	PuO <sub>2</sub>	PuO <sub>2</sub> (OH) <sub>2</sub>	PuO <sub>3</sub>
Number of available states	20 825	136 634 576	16	2 740 106
Number of states included in RASSI	278	81	16	119

TABLE 4.10: Fine structure transition energies ( $\text{cm}^{-1}$ ) of atomic Pu computed at the SO-CASPT2 with the ANO-RCC-TZVP basis set, and analysis of the various  $J$ -states in terms of the dominating  $LS$  terms.

Exp.[188–190]	This work	$J$ -value	Weight of $LS$ states
0	0	0	54% ${}^7F$ , 38% ${}^5D$ , 7% ${}^3P$
2204	1806	1	64% ${}^7F$ , 32% ${}^5D$
4300	4208	2	82% ${}^7F$ , 17% ${}^5D$
6145	6353	3	88% ${}^7F$ , 10% ${}^5D$
7775	8091	4	93% ${}^7F$
9179	9552	5	90% ${}^7F$
10 238	11 010	6	85% ${}^7F$ , 10% ${}^5G$
9773	12 499	0	44% ${}^7F$ , 21% ${}^5D$ , 8% ${}^3P$
13 528	13 612	1	66% ${}^9H$ , 9% ${}^7F$ , 7% ${}^7G$

## 4.4 Results and Discussions

### 4.4.1 Electronic Structures Analysis

#### Atomic Pu

To compute the enthalpies of formation of the plutonium molecules, an accurate description of the plutonium atom, i.e. its electronic structure, is mandatory. Thus, in Table 4.10 (the higher excited states can be found in the Appendix B), the SO-CASPT2 calculations are reported and compared to available data from the literature [188–190]. The *ab initio* energy levels are able to accurately reproduce the experimental assignments with errors between 91 and  $397 \text{ cm}^{-1}$  for the first five excited states under  $9500 \text{ cm}^{-1}$ . Deviations between our results and the available data appear after the sixth state. The experimental assignment predicts the sixth state at  $9773 \text{ cm}^{-1}$  with a  $J = 0$  while such state is found at  $12488 \text{ cm}^{-1}$  in the current study though uncertainties remain for the attribution of this electronic state. The computed seventh state with  $J = 6$  is about  $800 \text{ cm}^{-1}$  higher energy than the experimental value. Looking closely at the nature of the Pu low-lying states, one can first notice the remarkable mixing between the  ${}^7F$ ,  ${}^5D$  and  ${}^3P$  spin-orbit free states and that the contribution of the  ${}^5D$  state decreases as the energy increases. Finally, the most important result is the overall good reproduction of the SO splitting of  ${}^7F$  spin-free state, making us confident for the exploration of the other plutonium molecules.

### PuO<sub>3</sub> and PuO<sub>2</sub>(OH)<sub>2</sub>

For PuO<sub>3</sub>, at the spin-orbit level, we report the description of the ground state and the six lowest excited states in Table ??, (the higher excited states can be found in the Appendix B). It is noteworthy that the 1a<sub>g</sub>, 2a<sub>g</sub>/δ<sub>u</sub> and 3a<sub>g</sub> orbitals are doubly occupied in all the calculated spin-free states. The PuO<sub>3</sub> orbitals are composed of a mixture of orbitals belonging to the plutonyl subunit and the distant oxygen. Thus, for the sake of clarity, we labelled these orbitals with the labels associated to those of the PuO<sub>2</sub><sup>2+</sup> ion (with linear energy D<sub>2h</sub> notations), and those of the distant oxygen atom are denoted by p<sub>x,y,z</sub><sup>(O)</sup>. The SO ground state is composed of 47% <sup>3</sup>B<sub>2</sub>, 24% <sup>3</sup>A<sub>2</sub> and 14% <sup>3</sup>B<sub>1</sub> spin-free states. The composition is similar to the one previously reported by Kovács [191] (52% <sup>3</sup>B<sub>2</sub> and 24% <sup>3</sup>A<sub>2</sub>). More striking is the difference between our computed vertical excitation energies with that of Kovács’s SO-CASPT2 spectrum [191]. While we predict the first excited state to be at 1235 cm<sup>-1</sup>, he places it at 471 cm<sup>-1</sup>. The overall determined spectrum from our calculations is much denser and lower by about 4000 cm<sup>-1</sup> than his. Such discrepancy may find its origin in the description of the spin-free states. We agree with Kovács that the spin-free ground state has <sup>3</sup>B<sub>2</sub> symmetry, though with a different orbital character. Indeed, the <sup>3</sup>B<sub>2</sub> exhibits a strong multi-determinantal character with 57% corresponding to the configuration in which the 4a<sub>1</sub>/p<sub>z</sub><sup>(O)</sup> and 2b<sub>2</sub>/σ<sub>u</sub> orbitals are doubly occupied (See Table ?? and Figure 4.7) and the singly occupied orbitals 5b<sub>1</sub>/Φ<sub>u</sub>, 1b<sub>2</sub>/p<sub>z</sub><sup>(O)</sup>, 3b<sub>2</sub>/δ<sub>u</sub> and 1a<sub>2</sub>/δ<sub>u</sub> and 22% from the electronic configuration in which of the 4a<sub>1</sub>/p<sub>z</sub><sup>(O)</sup>, 1b<sub>2</sub>/p<sub>z</sub><sup>(O)</sup> and 2b<sub>2</sub>/σ<sub>u</sub> orbitals are doubly occupied and the 5b<sub>1</sub>/Φ and 1a<sub>2</sub>/δ<sub>u</sub> singly occupied. Kovács, however, finds the ground state to be mainly composed of plutonyl orbitals (79%). Such a difference can be explained by the fact that the considered active spaces are different (a CAS(10,16) in his case and CAS(14,13) in our work). Looking closely at the entanglement diagram of PuO<sub>3</sub> derived from DMRG calculations [147] (Figure 6a, Full-Valence CAS) there is a strong correlation within the non-bonding plutonyl-like orbitals (5f<sub>δ</sub>, 5f<sub>φ</sub>) and also between the b<sub>2</sub>/p<sup>(O)</sup> and the 5f<sub>δ<sub>u</sub></sub> orbitals, in agreement with our analysis of the <sup>3</sup>B<sub>2</sub> ground-state wave function.

Concerning PuO<sub>2</sub>(OH)<sub>2</sub>, the low energy part of the vertical spectrum including SO coupling reported in the Table ?? shows two close-lying states separated by about 323 cm<sup>-1</sup>, followed by a state at 2222 cm<sup>-1</sup>. The analysis of the two lowest states shows that they correspond to a fifty-fifty combination of <sup>3</sup>A(1) and <sup>3</sup>B(1) spin-free states, with a small contribution (6% in each case) of the <sup>3</sup>B(2). The next three states also have strong SO-mixings between triplet states but also singlet excited states of <sup>1</sup>A(1) and <sup>1</sup>B(1) symmetries, placed at the spin-free level at about 5764 and 7444 cm<sup>-1</sup>, respectively.

TABLE 4.11: Lowest electronic levels in  $\text{cm}^{-1}$  of  $\text{PuO}_3$ , computed at the SF-CASPT2 and SO-CASPT2 levels with the ANO-RCC-TZVP basis set, and analysis of the various states.

No.	Term Symbol	$\Delta E$	Character : % [orbital(number of electron)]
SF	${}^3B_2(1)$	0	36% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$
			21% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(1)]$
	${}^3A_2(1)$	3161	22% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$
			43% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$
			23% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(O)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(1)]$
			17% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$
${}^3B_1(1)$	4663	38% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
		12% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
${}^1A_1(1)$	7239	12% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 1b_1/\Phi_u(1), 2b_1/\pi_u(2), 1b_2/p^{(O)}(2)]$	
		32% $[4a_1/p^{(O)}(2), 1b_2/p^{(O)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(2)]$	
${}^3A_2(2)$	7287	28% $[4a_1/p^{(O)}(2), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(2)]$	
		11% $[4a_1/p^{(O)}(1), 5a_1/\Phi_u(\bar{1}), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(2)]$	
${}^3B_1(2)$	8038	20% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(2)]$	
		18% $[4a_1/p^{(O)}(1), 5a_1/\Phi_u(\bar{1}), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
SO	X	0	17% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$
			31% $[4a_1/p^{(O)}(1), 5a_1/\Phi_u(\bar{1}), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$
			11% $[4a_1/p^{(O)}(2), 5a_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$
			10% $[4a_1/p^{(O)}(2), 1b_2/p^{(O)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$
a	1235	0	10% $[4a_1/p^{(O)}(2), 1b_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(O)}(\bar{1}), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$
			47% ${}^3B_2(1) + 24\% {}^3A_2(1) + 14\% {}^3B_1(1)$
			59% ${}^3B_2(1) + 25\% {}^3A_2(1)$
			73% ${}^3B_2(1)$
b	1783	0	51% ${}^3A_2(1)$
			24% ${}^3B_1(1) + 18\% {}^1A_1(1) + 17\% {}^3A_2(2) + 10\% {}^3B_1(2)$
c	3777	0	
d	5660	0	

TABLE 4.12: Lowest electronic levels in  $\text{cm}^{-1}$  of  $\text{PuO}_2(\text{OH})_2$ , computed at the SF-CASPT2 and SO-CASPT2 levels with the ANO-RCC-TZVP basis set, and analysis of the various states.

	State	$\Delta E$	Character : % [orbital(number of electron)]
SF	${}^3B(1)$	0	49% [2a/ $\Phi_u(1)$ , 1b/ $\delta_u(1)$ ]
			48% [1a/ $\delta_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^3A(1)$	889	41% [1a/ $\delta_u(1)$ , 2a/ $\Phi_u(1)$ ]
			59% [1b/ $\delta_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^3B(2)$	2136	75% [1a/ $\delta_u(1)$ , 1b/ $\delta_u(1)$ ]
			20% [2a/ $\Phi_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^3A(2)$	4698	59% [1a/ $\delta_u(1)$ , 2a/ $\Phi_u(1)$ ]
			41% [1b/ $\delta_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^3B(3)$	5351	52% 2a/ $\Phi_u(1)$ , 1b/ $\delta_u(1)$
			46% [1a/ $\delta_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^1A(1)$	5764	[58% 1b/ $\delta_u(1)$ , 2b/ $\Phi_u(\bar{1})$ ]
			30% [1a/ $\delta_u(1)$ , 2a/ $\Phi_u(\bar{1})$ ]
		5% [2a/ $\Phi_u(2)$ ]	
	${}^1B(1)$	7444	50% [1a/ $\delta_u(1)$ , 1b/ $\delta_u(\bar{1})$ ]
			28% [2a/ $\Phi_u(1)$ , 2b/ $\Phi_u(\bar{1})$ ]
			16% [1a/ $\delta_u(1)$ , 2b/ $\Phi_u(1)$ ]
	${}^1A(2)$	9626	39% [1a/ $\delta_u(1)$ , 2a/ $\Phi_u(\bar{1})$ ]
			29% [2a/ $\Phi_u(2)$ ]
			13% [1b/ $\delta_u(1)$ , 2b/ $\Phi_u(\bar{1})$ ]
			10% [1a/ $\delta_u(2)$ ]
			7% [2a/ $\Phi_u(2)$ ]
SO	X	0	46% ${}^3A(1)$ , 41% ${}^3B(1)$ , 6% ${}^3B(2)$
	a	323	45% ${}^3B(1)$ , 45% ${}^3A(1)$ , 6% ${}^3B(2)$
	b	2222	35% ${}^3B(2)$ , 25% ${}^3B(1)$ , 14% ${}^1A(1)$ , 13% ${}^3A(2)$ , 10% ${}^3B(3)$
	c	3757	40% ${}^3A(2)$ , 25% ${}^3B(2)$ , 19% ${}^1B(1)$ , 7% ${}^3B(1)$ , 6% ${}^3A(1)$
	d	4158	36% ${}^3B(3)$ , 34% ${}^3B(2)$ , 14% ${}^1A(2)$ , 11% ${}^3B(1)$ ,



**PuO<sub>2</sub> molecule**

- PuO<sub>2</sub> Geometry

As explained in the section 4.1 La Macchia *et al.* showed that the spin-orbit coupling was of great importance not only to describe the electronic structure but also the geometry of PuO<sub>2</sub>. In their study, the spin-free results gave a  $^5\Sigma_g^+$  as ground state with a Pu-O distance of 1.792 Å. At the spin-orbit level, the ground state was found to be a  $1_u$  composed by 96% of the  $^5\Phi_u$  with a bond length of 1.744 Å. At the latter, our SO-CASPT2 calculation predicted a  $0_g$  ground state.

The  $^5\Sigma_g^+$  is the lowest at SF level as found in La Macchia's study by the similarities stop here. The equilibrium distance is here longer with 1.804 Å (versus 1.792 Å of La Macchia *et al.*). At this distance, the energy gap to the  $^5\phi_u$  state is estimated to 7992 cm<sup>-1</sup>, while it was equal to 1800 cm<sup>-1</sup> in La Macchia's study. In spite of this disagreement, the "reduction" of the bond distance while the spin orbit is included might be true and must be tested.

TABLE 4.13: Comparison of CBS extrapolated  $^2DC^M$ -EOM-CCSD and SO-CASPT2 PuO<sub>2</sub> vertical transition energies in cm<sup>-1</sup> computed at the 1.744 and 1.808 Å Pu–O distances.

$\Omega$	d(Pu-O)=1.744 Å			d(Pu-O)=1.808 Å	
	$^2DC^M$ -EOM-CCSD This work	SO-CASPT2 This work	SO-CASPT2 Ref. [192]	$^2DC^M$ -EOM-CCSD This work	SO-CASPT2 This work
$0_g$	0	0	1794	0	0
$1_g$	2435	1438	2315	2325	2462
$2_g$	6012	4235	4131	5378	5904
$1_u$	5721	1778	0	8548	5851
$2_u$	5926	1805	535	8782	6265
$3_u$	6622			9882	
$4_u$	12751			15471	

At the  $^2DC^M$  level, the PuO<sub>2</sub> ground-state is found to be well-described a closed-shell ( $\Omega = 0_g$ ) determinant, corresponding to occupied  $f_{3/2}$  and  $f_{5/2}$  spinors. This allowed us to employ accurate single-reference approaches such as CCSD(T) to determine the optimal Pu–O bond length, which is equals to 1.808 Å after extrapolation, with a corresponding harmonic vibrational frequency of 793 cm<sup>-1</sup>. We note that the CBS- $^2DC^M$ -CCSD(T) Pu–O bond length is longer than the one predicted by La Macchia *et al.* [192] at the SO-CASPT2 level.

TABLE 4.14: CBS extrapolated Ionization Potentials of PuO<sub>2</sub> in eV computed at the <sup>2</sup>DC<sup>M</sup>-EOM-CCSD level (d(Pu-O)= 1.808 Å) and comparison with experiments.

<sup>2</sup> DC <sup>M</sup> -EOM-CCSD		Exp			
State	IP	[[193]]	[[194]]	[[195]]	[[196]]
		9.4	10.1	7.03	6.6
3/2 <sub>u</sub>	7.65				
5/2 <sub>u</sub>	7.90				
1/2 <sub>u</sub>	9.81				
3/2 <sub>u</sub>	10.81				

Furthermore, our <sup>2</sup>DC<sup>M</sup>-EOM-EE-CCSD calculations (see Table 4.13) confirm that, at the CBS-<sup>2</sup>DC<sup>M</sup>-CCSD(T) equilibrium structure, the  $\Omega = 0_g$  state is indeed the ground-state: it is sufficiently well-separated from the lowest-lying states of both  $g$  ( $\Omega = 1_g$ , by over 2000 wavenumbers) and  $u$  ( $\Omega = 1_u$ , by over 5000 wavenumbers), and considering a shorter bond length—namely 1.744 Å, as was proposed by La Macchia et al. [192] for the ground state from SO-CASPT2—does not alter this picture. Thus, our results differ qualitatively from La Macchia et al., since they suggest the PuO<sub>2</sub> ground-state is of  $\Omega = 1_u$  symmetry, and corresponding mainly to the occupation of the two 5f <sub>$\delta$</sub> , one 5f <sub>$\phi$</sub>  and the 7s orbitals (See Figure 4.6).

From Table 4.13, we observe significant variations for the  $u$  states (of nearly 3000 wavenumbers) when the internuclear distance is varied from 1.808 Å to 1.744 Å, while the  $g$  states remain more or less at the same energies. With this, at the longer distance, the  $\Omega = 2_g$  state becomes lower than the  $\Omega = 1_u$  one.

- PuO<sub>2</sub> Electronic Structure

The SO-CASPT2 transition energies computed at the <sup>2</sup>DC<sup>M</sup> optimal bond length are reported in Table 4.15 (the higher excited states can be found in the Appendix B). The spin-orbit  $0_g$  ground state is composed by the spin-free ground state <sup>5</sup>Σ<sub>g</sub><sup>+</sup>(1) up to 48% and by the <sup>3</sup>Σ<sub>g</sub>(1) up to 22%, which lies 10.308 cm above it. La Macchia *et al.* also found large SO effects this with a SO-value of 8548 cm<sup>-1</sup>. Note that the vertical transition energies computed at the SO-CASPT2 level are in very good agreement with the <sup>2</sup>DC<sup>M</sup> ones for the  $g$ -states, but the  $u$ -states come out about 2300 cm<sup>-1</sup> lower in energy at the SO-CASPT2 than at the <sup>2</sup>DC<sup>M</sup>-EOM-CCSD level. However, we note that the electronic state spacing within either the  $g$  or  $u$  symmetries agrees with the SO-CASPT2 calculations. This thus points out to the importance of the choice of the active space to accurately predict the relative energies of  $g$  states involving mostly non-bonding 5f Pu atomic-centered orbitals, versus the  $u$  states involving the more diffuse plutonium 7s orbital.

TABLE 4.15: Lowest electronic levels in  $\text{cm}^{-1}$  of  $\text{PuO}_2$ , computed at the SF-CASPT2 and SO-CASPT2 levels ( $d(\text{Pu-O}) = 1.808 \text{ \AA}$ ) with the ANO-RCC-TZVP basis set, and analysis of the various states.

	State	$\Delta E$	Character : % [orbital(number of electron)]
SF	$^5\Sigma_g^+$	0	84% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	$^5\Sigma_g^-$	4798	45% [ $1a_u/\delta_u(1)$ , $3b_{2u}/\pi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ] 45% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(3)$ , $3b_{3u}/\pi_u(1)$ ]
	$^5\Phi_{u(1)} (^5B_{3u}(1))$	5421	85% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	$^5\Phi_{u(2)} (^5B_{2u}(1))$	5421	85% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	$^5\Delta_{u(1)} (^5A_u(1))$	7452	79% [ $3a_g(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	$^5\Delta_{u(2)} (^5B_{1u}(1))$	7462	80% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	$^3\Sigma_g^-$	10 308	24% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(2)$ , $2b_{1u}/\delta_u(1)$ ] 24% [ $1a_u/\delta_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(2)$ ] 19% [ $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(2)$ , $2b_{3u}/\Phi_u(1)$ ] 16% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]
	SO	$0_g^-$	0
$1_g$		2462	67% $^5\Sigma_g^+$ , 15% $^3\Sigma_g^-$
$1_u$		5851	27% $^5\Phi_{u(1)}$ , 27% $^5\Phi_{u(2)}$ , 13% $^5\Delta_{u(1)}$ , 13% $^5\Delta_{u(2)}$
$2_g$		5904	85% $^5\Sigma_g^+$
$2_u$		6265	21% $^5\Phi_{u(1)}$ , 21% $^5\Phi_{u(2)}$ , 24% $^5\Delta_{u(1)}$
$3_u$		7195	38.85% $^5\Phi_{u(1)}$ , 24.97% $^5\Phi_{u(2)}$

Finally, for the computed ionization energies for  $\text{PuO}_2$  (IPs, see Table 4.14), our calculations could be grouped into three regions with respect to their energies: one below 8 eV, one between 8 and 10 eV and the last at energies higher than 10 eV. We see that, if one considers only the lowest EOM-IP-CCSD state ( $\Omega = 3/2_u$ ), we observe a good agreement with the results of Rauh et al. [193] (and to a lesser extent, with the results of Capone et al. [194]) but poor agreement with a second measurement of Capone et al. [196] and of Santos et al. [195]. However, if we compare the first  $\Omega = 1/2_u$  state to this second measurement of Capone, and the second  $\Omega = 3/2_u$  state with that of Santos et al. [195], we see an overall good agreement between the calculated and experimental values. This leads us to suggest that experiments may have measured  $\text{PuO}_2^+$  in different electronically excited states, something that would explain the rather different experimental values.

- Spin-free calculations

Beside calculations including spin-orbit coupling, it is informative to discuss the nature of  $\text{PuO}_2$  ground-state at the scalar relativistic level (spin free). In our study, CASPT2 and UCCSD(T) calculations give the  $^5\Sigma_g^-$  state ( $(5f_\delta)^2(5f_\phi)^2$  occupations) lower in energy than the  $^5\Phi_u$  state ( $(5f_\delta)^2(5f_\phi)^1(7s)^1$ ) by  $7994 \text{ cm}^{-1}$  at the distance Pu-O of  $1.804 \text{ \AA}$ , as found in the previous studies [174, 192]. With the ANO-RCC

AVTZ basis set, the equilibrium Pu–O distance is 1.818 Å and 1.808 Å at UCCSD(T) and CASPT2 levels, respectively, distances that are close to the fully-relativistic ones. These values are also in line with the SF-CASPT2 (CAS(12,14)) of La Macchia (d(Pu–O))= 1.792 Å), but significantly shorter by about 0.4/0.5 Å than the estimations Archibong and Ray [174]. These large discrepancies are probably related to the choice of a large-core RECP (78 electrons), which was proven to yield too long bond distances for actinide molecules [197], while the small-core ECP gives exactly the same distances that the all-electron Douglas-Kroll relativistic approach.

The ground state  ${}^5\Sigma_g^+(1)$  is dominated up to 84% by the configuration that corresponds to the occupation of the two  $5f_\delta$  and two  $5f_{\text{CE}}$  orbitals carrying one electron each. It corresponds to the description of the ground state of Boguslawski *et al* [147]. and also to the  ${}^5\Sigma_g^+(1)$  reported by La Macchia *et al.* [192]. The former study places the first excited state at  $1800\text{ cm}^{-1}$  corresponding to  ${}^5\Phi_u$  state, while in our SO-CASPT2 it appears at higher energy, of  $5421\text{ cm}^{-1}$ . We note that in our SF-CASPT2 calculation, the spin-free spectrum is less dense than La Macchia’s results [192]. Such differences can be explained by the choice of different active space, the fact that we computed a larger number of spin-free states, and most likely the change in the interatomic Pu–O distance. SO-coupling is not expected to change the energy of the  $\Lambda = 0$   ${}^5\Sigma_g^+$  state, while it lifts the degeneracy of the  ${}^5\Phi_u$  state. Given the small energy gap of  $1800\text{ cm}^{-1}$  between the  ${}^5\Sigma_g^+$  and  ${}^5\Phi_u$  state, the  $1_u$  state becomes the ground state in their study, while in our work, it remains a state of  $g$  symmetry.

TABLE 4.17: Standard enthalpies of formation  $\Delta_f H^\ominus$  of  $\text{PuO}_2$ ,  $\text{PuO}_2(\text{OH})_2$ ,  $\text{PuO}_3$  in  $\text{kJ mol}^{-1}$  in the gas phase calculated at various level of theory and extrapolated to the CBS-CE limit, and from the average of five reactions listed in Table 4.3, except for  ${}^2\text{DC}^M\text{-CCSD(T)}$ . The standard deviations  $\Delta\Delta_f H^\ominus$  includes the uncertainty on the average value as well as the experimental error bars.

$\Delta_f H^\ominus$	$\text{PuO}_2$	$\text{PuO}_2(\text{OH})_2$	$\text{PuO}_3$
UCCSD + $\Delta E_{\text{SO}}$	$-348.4 \pm 28.2$		
UCCSD(T) + $\Delta E_{\text{SO}}$	$-404.3 \pm 22.6$	$-518.8 \pm 32.9$	$+599.1 \pm 28.3$
CASPT2 + $\Delta E_{\text{SO}}$	$-364.4 \pm 17.8$	$-1008.7 \pm 34.3$	$-539.8 \pm 24.1$
Reference	$-410 \pm 20$ [198] ; $-412 \pm 20$ [139] ; $-440 \pm 7$ [138] ; $-428.7 \pm 7$ [138] ; $-428.7 \pm 20$ [141] ;	$-1018.2 \pm 3.3$ [199]	$-562.8 \pm 5$ [199] ; $-567.6 \pm 15$ [141]

#### 4.4.2 Thermodynamic properties

TABLE 4.16: Standard enthalpies of formation  $\Delta_f H^\ominus$  of  $\text{PuO}_2$ ,  $\text{PuO}_2(\text{OH})_2$ ,  $\text{PuO}_3$  in  $\text{kJ mol}^{-1}$  in the gas phase calculated at various level of theory and extrapolated to the CBS-TE limit, and from the average of five reactions listed in Table 4.3, except for  ${}^2\text{DC}^M\text{-CCSD(T)}$ . The standard deviations  $\Delta\Delta_f H^\ominus$  includes the uncertainty on the average value as well as the experimental error bars.

$\Delta_f H^\ominus$	$\text{PuO}_2$	$\text{PuO}_2(\text{OH})_2$	$\text{PuO}_3$
$\Delta E_{\text{SO}}^1$	34.4	46.9	59.0
B3LYP <sup>1</sup> + $\Delta E_{\text{SO}}$	$-304.1 \pm 16.4$	$-787.0 \pm 30.1$	$-397.3 \pm 21.6$
${}^2\text{DC}^M\text{-CCSD(T)}$	-432		
UCCSD + $\Delta E_{\text{SO}}$	$-347.6 \pm 21.1$		
UCCSD(T) + $\Delta E_{\text{SO}}$	$-406.6 \pm 9.3$	$-260.9 \pm 26.9$	$+438.0 \pm 8.5$
CASPT2 + $\Delta E_{\text{SO}}$	$-367.3 \pm 17.1$	$-1009.3 \pm 44.5$	$-545.0 \pm 23.3$
Reference	$-410 \pm 20$ [198] ; $-412 \pm 20$ [139] ; $-440 \pm 7$ [138] ; $-428.7 \pm 7$ [138] ; $-428.7 \pm 20$ [141] ;	$-1018.2 \pm 3.3$ [199]	$-562.8 \pm 5$ [199] ; $-567.6 \pm 15$ [141]

<sup>1</sup>  $\Delta E_{\text{SO}}$  is estimation of the SO contribution.

All the values of enthalpy of formation can be found in the Table 4.16. From our discussion of the electronic structures of the different Pu molecules detailed in section 4.4.1, one will not be surprised to see that the single-reference methods, here DFT and CCSD(T), fail at describing  $\text{PuO}_2(\text{OH})_2$  and  $\text{PuO}_3$  thermodynamic properties,

while they should be in principle usable for  $\text{PuO}_2$  molecule. Thus, for this methods, we will focus only on the  $\text{PuO}_2$  molecule. One can observe that the enthalpy obtained with the B3LYP functional and the  $+\Delta E_{SO}$  correction gives a value about 25% off the experimental one ( $100 \text{ kJ mol}^{-1}$ ). A change in the density functional will not ensure a better agreement with experience as observed previously for actinide systems [200] or for transition metal molecules [201]. The  $\Delta_f H^\ominus(298.15 \text{ K})$  computed with  ${}^2\text{DC}^M$  approach ( ${}^2\text{DC}^M$ ) is in almost perfect agreement with the available results [138, 141]. Note that the absence of error value is because the calculation was done only for the reaction  $R_4$ , as the other reactions involved species with a multi-determinantal character.  $\text{UCCSD}+\Delta E_{SO}$  result ( $-385.0\pm 21.1 \text{ kJ mol}^{-1}$ ) is lower than  ${}^2\text{DC}^M\text{-CCSD(T)}$  one, while the  $\text{UCCSD(T)}+\Delta E_{SO}$  agrees with the best theoretical estimations and the experimental data, thus highlighting the importance of the perturbative triple contributions. For the reaction 4,  $\text{UCCSD(T)} + \Delta E_{SO}$  and  $\text{CASPT2} + \Delta E_{SO}$  give  $-416.22 \text{ kJ mol}^{-1}$  and  $-387.7 \text{ kJ mol}^{-1}$ , respectively. The  $\text{SO-CASPT2}$  value deviates by about  $40 \text{ kJ mol}^{-1}$  from both  ${}^2\text{DC}^M\text{-CCSD(T)}$  and experiments, probably because of the incompleteness of the active space. Nevertheless, the  $\text{SO-CASPT2}$  results for  $\text{PuO}_2(\text{OH})_2$  and  $\text{PuO}_3$  show great agreement with the experiment values by Krikorian et al. [199].

## 4.5 Conclusion and Perspectives

Concerning  $\text{PuO}_2$ , where the static correlation is not important and the wave function can be described by single-reference methods that include the dynamic correlation such as  $\text{UCCSD(T)}$  the  $\Delta_f H^\ominus$  could be reproduced. The distance Pu-O found for the linear  $\text{PuO}_2$  is  $1.808 \text{ \AA}$  and the ground state a  $0_g$  mainly composed by the spin-free state  ${}^5A_g$ .

About  $\text{PuO}_2(\text{OH})_2$ ,  $\text{SO-CASPT2}$  method is enough to reproduce the only experimental data available but the enthalpy of formation given by this method for  $\text{PuO}_3$  is smaller than expected. Since the detection of  $\text{PuO}_3$  is complicated one could argue on the validity of the two measurements but we would rather point out the fact that our active space size might not be large enough and could lead to a mistreatment of the static correlation. In order to improve the description, larger active spaces can be handled with the DMRG method recently implemented in Molcas. Exploratory DMRG calculations will be performed in coming weeks.

Our thermodynamics data are about to be implemented by our IRSN colleagues (F. Virot) in the accident simulation code to quantify the amounts of each volatile Pu species released.



## Chapter 5

# How well are the f-elements described by a Double-Hybrid Functional ?

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Our interest here is to see how double hybrids work for the geometries and thermochemistry of species containing actinides and lanthanides. This project was triggered by two reasons: the first is that we have seen that the B3LYP is not accurate to compute the thermochemistry of  $\text{PuO}_2$ , thus raising the question of whether other functionals and double hybrids in particular could be more accurate for such f-element complexes. The second, because we are involved in the implementation and benchmarking of double-hybrids four-component-based methods in Dirac in a collaboration with Benjamin Helmich-Paris (Mulheim) and Lucas Visscher (Amsterdam); therefore, we want to investigate if there are significant changes between spin-free (Molpro) and SOC (Dirac) calculations. This chapter presents the first step of the study. It consists in a systematic comparison of structural and thermodynamic properties computed at the spin-free level with the state of the art CCSD(T) method as reference. This is, to the best of our knowledge, the first application of double-hybrid B2-BLYP to actinide chemistry. However, we can refer to recent assessments of double hybrid, in particular B2-PLYP for transition metal thermochemistry [202, 203], leading to average uncertainties of up to  $8 \text{ kcal.mol}^{-1}$ , which is about  $4 \text{ kcal.mol}^{-1}$  better than B3LYP. After a brief description of the current development of double-hybrids and the B2-PLYP functional and a review of the available thermodynamic data, we will reach the aim of this chapter and present the first results regarding the f element properties.

## 5.1 Motivations for double-hybrid functionals

One of the biggest weakness of DFT is not accounting for the dispersion effects as we have seen in the Section 2.3.4. A widely used solution is the Grimme dispersion correction [49–51] which we have used in the Chapter 3. We have seen that even if it lead to good qualitative results, this correction could not be used as quantitative method for such a large system. When the system has a reasonable size, MP2 is a good but expensive solution to include dispersion effects.

The idea of double-hybrids (B2-PLYP) [204] is to add non-locality responsible for dispersive (van der Waals) interactions to hybrid functionals by considering virtuals orbitals and having a well-balanced performance for properties (energetics, etc). It relies on a combination of KS-DFT (Kohn Sham Density Functional Theory) and Perturbation Theory (PT) where the exchange-correlation energy is expressed as:

$$E_{xc} = (1 - a_x)E_x^{GGA} + a_x E_x^{HF} + bE_c^{GGA} + cE_c^{PT2} \quad (5.1)$$

where

$$E_c^{PT2} = \frac{1}{4} \sum_{ia} \sum_{jb} \frac{[(ia|jb) - (ib|ja)]^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (5.2)$$

with  $\epsilon_i$  being the KS eigenvalue of the orbital  $i$ , the bracket terms corresponding to the two electrons integrals over the KS orbitals. The parameters  $a_x$ ,  $b$  and  $c$  were parametrised to reproduce thermodynamic properties of light elements namely the G2/97 set of heat of formation. During this parametrisation, the relation  $b + c = 1$  was found and confirmed [205] and  $c \leq a_x$ , leading to only two parameters with a value of 0.53 and 0.27 for  $a_x$  and  $c$ , respectively. The GGA functional used is the BLYP one. Multiple rigorous analysis were done concerning the parametrisation [205–207] and showing that the value of  $a_x$  and  $c$  are very close to a theoretical optimum.

Even if it is not used in this thesis we can note that it is also possible to perform TDDFT with double hybrid [208, 209] or to add long-range dispersion [210].

During the past 10 years the development of many other double-hybrid functionals was done [207, 211–233] and listed and compared in a review of Grimme *et al* [234]. This work exposes the functional DSD-BLYP-D3 [221] and PWPB95-D3 [203] as the most accurate and robust ones though we have not evaluated them in this thesis.

Most specific performances are also tested such as: spin-state energetics [235], ionisation energies and aqueous redox potentials of organic molecules [236], non-linear optical properties [237] and thermochemistry of 3d transition metals [202]. This last study is particularly interesting since it states that the Mean Average Deviation (MAD) of B2-PLYP is  $32.6 \text{ kJ.mol}^{-1}$  for the determination of enthalpies of formation. Since the DIRAC implementation concerns only the B2-PLYP functional, it will be compared to HF, CCSD(T), B3LYP hybrid functional, PBE GGA functional and the limiting cases of B2-PLYP, MP2 and BLYP functional.

## 5.2 Literature review of the available enthalpies of formation $\Delta_r H^\ominus$ .

The enthalpies of formation theoretical and experimental of the reactions listed in the Table 5.1 are only reported for reaction including  $\text{UF}_6$ . The enthalpies are extracted from the work of Peterson *et al.* and [184] Privalov *et al.* The former study includes four-component CCSD(T) calculations with a pseudopotential (PP) [179] or all electron basis sets [238]. The latter one includes SCF, MP2, B3LYP and CCSD(T) single point energy using geometries obtained at the HF level with a scalar relativistic pseudopotential or experimental data.

All the reactions were chosen for the fact that they involve close shell species and because the information about the structures are readily accessible.

TABLE 5.1: Reactions used to calculate  $\Delta_r H^\ominus$  and their previously reported values.

Reactions	$\Delta_r H^\ominus$ in $\text{kJ}\cdot\text{mol}^{-1}$
R <sub>1</sub> : $\text{H}_2 + \text{F}_2 \rightarrow 2 \text{HF}$	
R <sub>2</sub> : $\text{La}^{3+} + \text{H}_2\text{O} \rightarrow \text{LaH}_2\text{O}^{3+}$	
R <sub>3</sub> : $\text{CeF}_4 + \text{CeO}_2 \rightarrow 2 \text{CeOF}_2$	
R <sub>4</sub> : $\text{ThF}_4 + \text{ThO}_2 \rightarrow 2 \text{ThOF}_2$	
R <sub>5</sub> : $\text{UO}_2^{2+} + \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{H}_2\text{O})^{2+}$	
R <sub>6</sub> : $\text{Ac}^{3+} + \text{H}_2\text{O} \rightarrow \text{AcH}_2\text{O}^{3+}$	
R <sub>7</sub> : $\text{UF}_6 + \text{SO}_3 \rightarrow \text{UO}_3 + \text{SF}_6$	4C-CCSD(T): 525.5 <sup>1</sup> , 527.2 <sup>2</sup> [184] Exp: 528.9 [184]
R <sub>8</sub> : $\text{UF}_6 + 3 \text{H}_2\text{O} \rightarrow \text{UO}_3 + 6 \text{HF}$	4C-CCSD(T): 481.6 <sup>1</sup> , 479.9 <sup>2</sup> [184] SCF: 539 ; MP2: 487, 534 <sup>‡</sup> ; CCSD(T): 558, 464 <sup>*</sup> [239] B3LYP: 627, 500 <sup>*</sup> ; Exp: 435 [239]
R <sub>9</sub> : $\text{UF}_6 + \text{H}_2\text{O} \rightarrow \text{UOF}_4 + 2 \text{HF}$	
R <sub>10</sub> : $\text{UF}_6 + 2 \text{H}_2\text{O} \rightarrow \text{UO}_2\text{F}_2 + 4 \text{HF}$	4C-CCSD(T): 204.2 <sup>1</sup> , 202.1 <sup>2</sup> [184] SCF: 170; MP2: 232, 263 <sup>‡</sup> ; CCSD(T): 232, 263 <sup>*</sup> [239] B3LYP: 332, 246 <sup>*</sup> ; Exp: 187 [239]
R <sub>11</sub> : $\text{UO}_2^{2+} + 4 \text{H}_2\text{O} \rightarrow \text{UO}_2(\text{H}_2\text{O})_4^{2+}$	
R <sub>12</sub> : $\text{PaO}_2^+ + \text{H}_2\text{O} \rightarrow \text{PaO}_2(\text{H}_2\text{O})^+$	

<sup>1</sup> Values FC-CCSD(T)/CBS with pseudo potential.

<sup>2</sup> Values FC-CCSD(T)/CBS with the all electron basis sets.

\* Corrected values

We aim to reproduce results as close as possible to the experimental ones or to the corresponding method in use.

Concerning the geometries of the molecules, when possible it will be compared to experimental data, otherwise the quantum chemical method used to determined them will be specified.

### 5.3 Computational details

As in the previous Chapters, the geometry of the molecules under interest is a key information for the description of thermodynamic properties. Therefore the different molecules were first optimised for each of the quantum chemistry methods at the spin-free level with the Molpro2015.1 package [156], followed by an harmonic frequency calculation. The reaction enthalpies are computed as in Chapter 4 in equation 4.3:

$$\Delta_r H^\ominus = \sum_i (E_i + \text{ZPE}_i + H_{\text{corr},i}) \quad (5.3)$$

The light elements (first and second rows) are described with aug-cc-pVQZ basis sets [cite], for actinides the scalar relativistic effects were included with the relativistic pseudopotential with 60 e<sup>-</sup> in core, namely ECP60MDF [cite] with the corresponding quadruple- $\zeta$  quality basis sets [cite]. For lanthanides, the small-core relativistic pseudo potential with 28 e<sup>-</sup> in core, namely ECP28WB, [171, 240] and the corresponding quadruple- $\zeta$  basis sets were used. Peterson *et al.* [184] reports that quadruple- $\zeta$  basis sets used are close enough from the CBS for us to overcome the need of CBS extrapolations. Since all the molecules involved in the reactions under study (see Table 5.1) are closed-shell, no spin state problem should appear and spin-orbit coupling is expected to be negligible [184].

In most of the reactions the bonding picture changes a lot from the reactants to the products resulting in large differences of dynamical correlation across the reactions making it then relevant for benchmarking correlation methods. A particular attention will be paid to the R<sub>1</sub> since its enthalpy of reaction is computationally challenging because as mentioned in the reference [239], Privalov *et al.* could not reproduce it.

## 5.4 Results and Discussions

The optimisations of  $\text{UO}_2(\text{H}_2\text{O})_4^{2+}$  are still in progress, thus, the results of the reaction R<sub>11</sub> will not be reported. Table 5.2 presents the reported geometries of molecules with an f-element with the corresponding reference data.

## 5.4.1 Geometries and total energies

TABLE 5.2: Geometries of the various molecules under study, the distance are given in Å and angles in degree symmetry is given in parenthesis.

Molecule		CCSD(T)	MP2	B2PLYP	B3LYP	BLYP	PBE	HF	Literature
ThF <sub>4</sub> (Td)	r(Th-F)	2.112	2.113	2.116	2.117	2.132	2.113	2.116	Exp: 2.124 [241]
	angle(F-Th-F)	109.5	109.5	109.5	109.5	109.4	109.4	109.5	107.2
ThOF <sub>2</sub> (Cs)	r(Th-O)	1.890	1.896	1.895	1.888	1.906	1.890	1.870	Exp: 1.886 [242]
	r(Th-F)	2.138	2.136	2.139	2.141	2.152	2.130	2.154	Exp: 2.157
	angle(F-Th-F)	106.9	120.6	106.0	106.1	104.8	103.8	110.6	107
	angle(F-Th-O)	106.9	120.6	106.0	106.1	104.8	103.8	110.6	
ThO <sub>2</sub> (C <sub>2v</sub> )	r(Th-O)	1.907	1.912	1.913	1.905	1.923	1.906	1.891	CCSD(T): 1.905 [243]
	angle(O-Th-O)	117.0	114.4	117.8	119.9	119.0	119.2	120.4	117
UF <sub>6</sub> (O <sub>h</sub> )	r(U-F)	2.000	1.999	2.016	2.014	2.041	2.022	1.984	Exp: 1.999 [244]
UO <sub>3</sub> (C <sub>2v</sub> )	r(U-O <sub>apical</sub> )	1.8	1.865 <sup>1</sup>	1.871 <sup>1</sup>	1.81162	1.880	1.863	1.747	4C-CCSD(T): 1.801[184]
	r(U-O)	1.9	1.865 <sup>1</sup>	1.871 <sup>1</sup>	1.852977	1.854	1.829	1.828	1.852
	angle(O <sub>apical</sub> -U-O)	99.4	119.9 <sup>1</sup>	120 <sup>1</sup>	101.4286	106.5	103.1	97.7	99.5
UO <sub>2</sub> F <sub>2</sub> (C <sub>2v</sub> )	r(U-O)	1.769	1.788	1.798	1.788	1.816	1.816	1.713	4C-CCSD(T): 1.768 [184]
	r(U-F)	2.076	2.073	2.077	2.073	2.093	2.093	2.092	2.075
	angle(O-U-O)	169.1	169.5	166.4	169.5	163.9	163.9	170.2	169.2
	angle(F-U-F)	114.0	112.8	111.7	112.8	118.6	118.6	118.9	114.1
UO <sub>2</sub> H <sub>2</sub> O <sup>2+</sup> (Cs)	r(U-O)	1.713	1.732	1.734	1.716	1.748	1.733	1.660	CCSD(T): 1.789 [243]
	r(U-OH <sub>2</sub> )	2.324	2.317	2.325	2.330	2.343	2.314	2.373	2.453
	angle(O-U-O)	89.8	88.8	89.5	90.1	90.1	89.4	90.7	90.0
LaF <sub>3</sub> (C <sub>3v</sub> )	r(La-F)	2.120	2.120	2.123	2.123	2.134	2.112	2.138	Exp: 2.12 [245]
	angle(F-La-F)	116.2	115.9	115.8	115.8	115.1	114.3	119.5	
CeO <sub>2</sub> (C <sub>2v</sub> )	r(Ce-O)	1.821	1.822	1.819	1.835	1.850	1.829	1.790	HF: 1.82 [246]
	angle(O-Ce-O)	121.8	115.4	128.4	139.1	132.6	132.9	116.6	132
CeF <sub>4</sub> (Td)	r(Ce-F)	2.028	2.026	2.036	2.042	2.070	2.049	2.031	CISD: 2.04 [247]
CeOF <sub>2</sub> (C <sub>s</sub> )	r(Ce-O)	1.786	1.787	1.804	1.791	1.832	1.811	1.748	B3LYP: 1.794 [248]
	r(Ce-F)	2.082	2.078	2.087	2.090	2.109	2.086	2.098	2.091
	angle(F-Ce-F)	110.5	110.7	109.0	109.6	109.2	108.3	114.9	110.5
AcF <sub>3</sub> (C <sub>3v</sub> )	r(Ac-F)	2.195	2.195	2.197	2.197	2.209	2.186	2.210	MP2: 2.272 [249]
	angle(F-Ac-F)	113.4	113.3	113.0	112.7	111.6	110.9	116.7	
PaO <sub>2</sub> <sup>+</sup> (D <sub>∞h</sub> )	r(Pa-O)	1.773	1.794	1.784	1.775	1.799	1.784	1.738	CCSD(T): 1.776 [243]
PaO <sub>2</sub> H <sub>2</sub> O <sup>+</sup> (D <sub>∞h</sub> )	r(Pa-O)	1.789	1.799	1.801	1.791	1.816	1.800	1.754	CCSD(T): 1.788 [243]
	r(Pa-OH <sub>2</sub> )	2.449	2.441	2.455	2.465	2.475	2.442	2.511	2.447
	angle(O-Pa-OH <sub>2</sub> )	88.7	88.7	89.1	89.6	88.5	88.8	90.6	98.5

<sup>1</sup> The symmetry is D<sub>3h</sub>

Looking at Table 5.2 the B2-PLYP presents good performances at reproducing the literature data. This is highlighted in Figures 5.1 and 5.2 presenting the bond length and angular deviation with respect to CCSD(T). Unfortunately, B2-PLYP and MP2 predict the wrong symmetry for UO<sub>3</sub> giving it as a D<sub>3h</sub> symmetry for the molecule instead the expected C<sub>2v</sub>.

Concerning the distances, it is the functional B3LYP that is the closest to CCSD(T) with a MAD of 0.006 Å followed by MP2 with 0.012 Å. B2-PLYP functional arrives third with an average error of 0.014 Å. However, while UO<sub>3</sub> is taken out of the set, the MAD of MP2 and B2-PLYP are reduced to 0.007 Å and 0.008 Å, respectively.

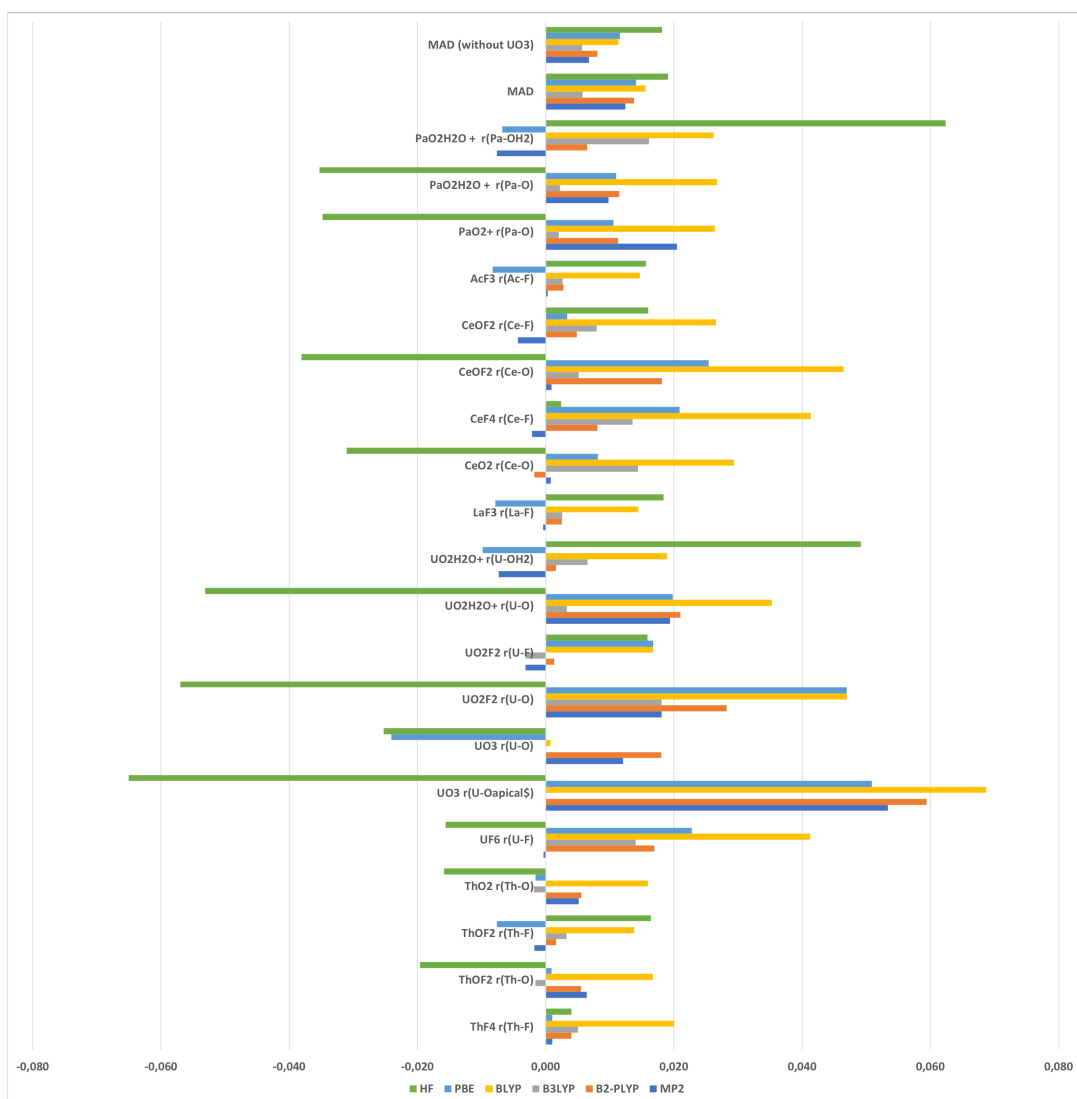


FIGURE 5.1: Error in the bond length in Å with respect to CCSD(T) values and MAD over all complexes

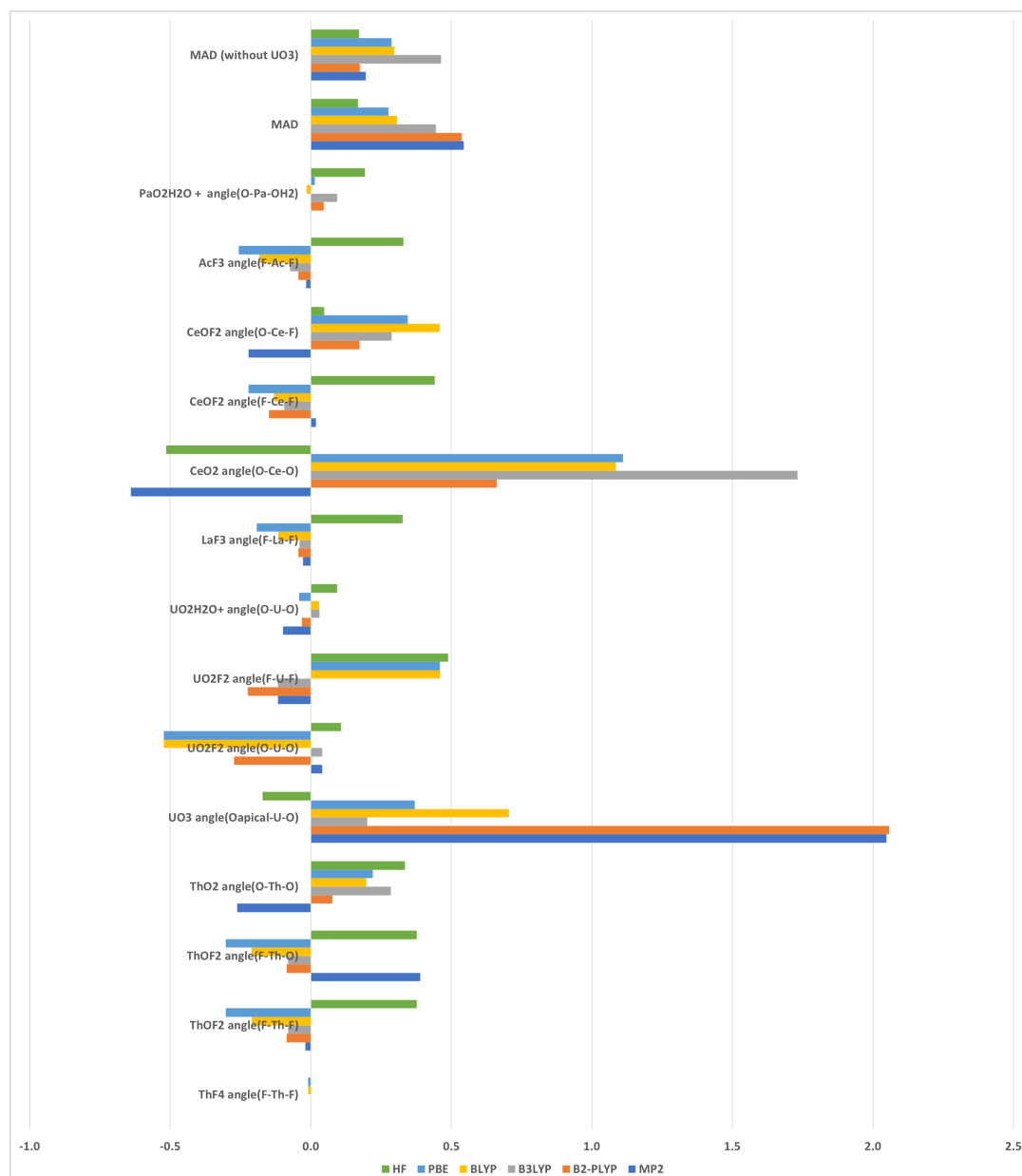


FIGURE 5.2: Differences in the angles (in degrees) with respect to CCSD(T) and the MAD over all complexes

For the intramolecular angles, MP2 and B2-PLYP perform the worst with a MAD of 5.4 due to the bad description of  $\text{UO}_3$ . While this molecule is taken off the set the MAD of B2-PLYP is the best with 1.7 degrees and MP2 the second best value with MADs of 2.0 degrees. Explanations about the failure of MP2 and B2-PLYP to describe  $\text{UO}_3$  are still under investigation.

This small B2-PLYP MAD makes use confident about its capability in giving very accurate geometries while MP2 is performing well.

In Table 5.3, we reported the difference in total energies. One can note that the behaviour of each method/functional depends on the actinide/lanthanide present. Nonetheless, in every cases containing an heavy atom, the B2-PLYP is the closest to CCSD(T) after MP2. MP2 underestimates the total energies while all other methods overestimate it. So far, the smallest MAD is obtained with B2-PLYP attesting its good performance.

#### 5.4.2 Enthalpies of Reactions

As mentioned previously, only scarce experimental values of reaction enthalpies are available for f elements. The only ones to benchmark with are those studying reactions R7, R8, R10 and R12. Thus, we will start the discussion by scrutinize the results obtained for these four reactions. For the reactions  $R_8$  and  $R_{10}$  we could see that computed reaction enthalpies were far from the experimental values (see Table 5.3). This was already noticed in [184] by Peterson *et al.*, thus we decided to correct the results in the same way they did. Peterson *et al.* attributed the error to the description of HF, and because of that they took the difference between the experimental value and theirs for reaction  $R_{10}$ . This difference was then divided by 4 (the number of HF molecules in reaction  $R_{10}$ ) to obtain the correction factor for each HF molecule. This correction was then apply to each reaction involving HF.

Table 5.3 presents the enthalpies of reaction of the chosen reactions. The results obtained on reactions  $R_8$  and  $R_{10}$  validate our correction since in reaction  $R_8$  we are closer to the experimental enthalpy of reaction. Figure 5.3 exposes the differences in between the enthalpies of reactions with respect to CCSD(T) values. So far the smallest MAD is HF's with  $27.8 \text{ kJ.mol}^{-1}$ . The second lowest MAD is the one is given by the B2-PLYP functional (with  $28.4 \text{ kJ.mol}^{-1}$ ). All the other MADs are above  $35 \text{ kJ.mol}^{-1}$ .



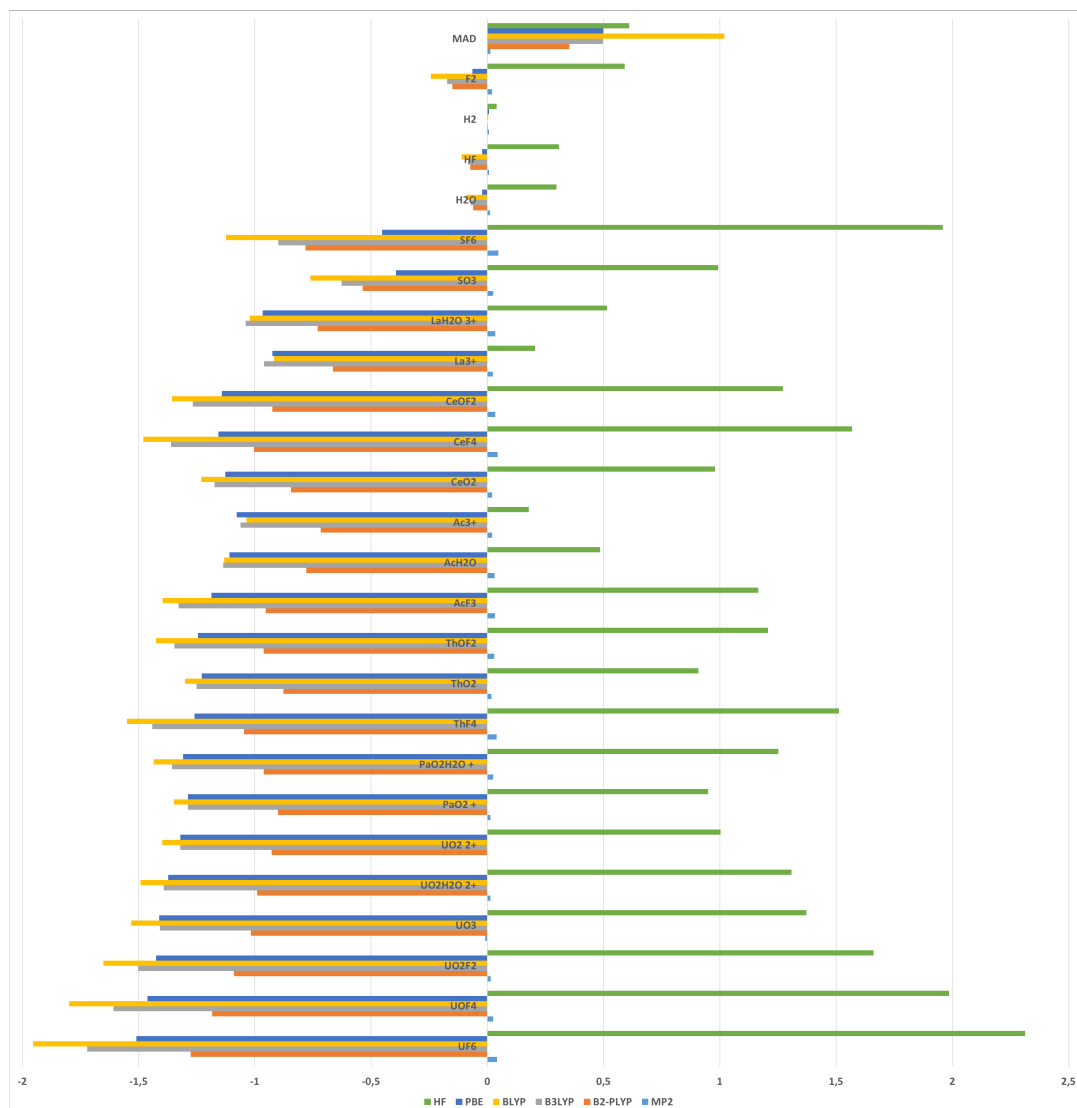


FIGURE 5.3: Difference in energy between the total energy given by the CCSD(T) and the considered method and functionals in a.u.

TABLE 5.3:  $\Delta_r H^\ominus$  in  $\text{kJ}\cdot\text{mol}^{-1}$  for the reaction under study.

	CCSD(T)	MP2	B2-PLYP	B3LYP	BLYP	PBE	HF	Exp
R <sub>1</sub>	-547.3	-612.6	-578.1	-563.5	-533.0	-544.5	-617.7	
R <sub>2</sub>	-381.0	-383.4	-391.7	-401.0	-413.7	-428.5	-345.8	
R <sub>3</sub>	-146.0	-136.1	-147.6	-148.0	-162.2	-143.8	-164.5	
R <sub>4</sub>	13.3	16.4	13.6	11.0	11.2	11.4	2.8	
R <sub>5</sub>	-275.9	-276.8	-276.8	-278.3	-280.5	-356.1	-250.2	
R <sub>6</sub>	-338.2	-340.4	-344.6	-347.1	-348.9	-360.9	-310.4	
R <sub>7</sub>	539.2	457.1	570.2	643.6	686.7	635.2	604.6	539.3
R <sub>8</sub>	468.7	356.0	472.2	545.0	553.2	553.2	527.9	
R <sub>8,corrected</sub>	456.9	424.9	401.6	420.2	553.2	377.9	550.8	435
R <sub>9</sub>	43.7	56.4	110.3	140.3	158.6	160.4	75.5	
R <sub>9,corrected</sub>	39.8	79.4	86.8	98.7	99.1	102.0	83.2	
R <sub>10</sub>	194.9	141.1	234.1	270.2	306.1	303.8	171.7	
R <sub>10,corrected</sub>	187.0	187.0	187.0	187.0	187.0	187.0	187.0	187
R <sub>12</sub>	-152.4	-155.6	-151.3	-146.8	-117.6	-149.7	-132.8	

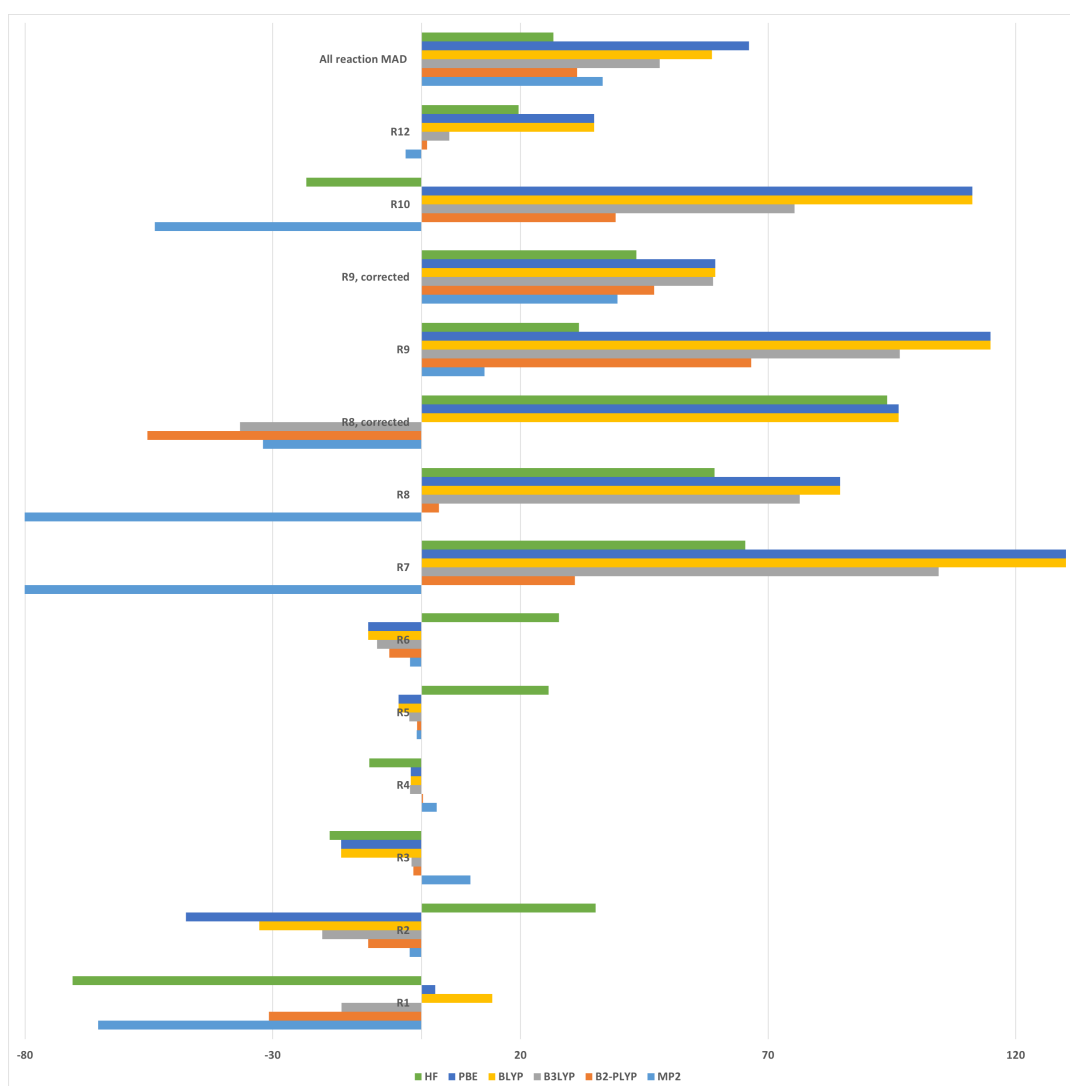


FIGURE 5.4: Differences in the enthalpies of reaction with respect to CCSD(T) values in  $\text{kJ.mol}^{-1}$

## 5.5 Conclusion and Perspectives

Even if we can observe in B2-PLYP some imperfection of MP2, such as the inaccuracies in the description of the geometry of  $\text{UO}_3$ , it still yields to good results in the description of the geometry. The thermodynamic properties of f-element are even better describe with B2-PLYP than MP2, which is what was desired. The MAD reported for B2-PLYP ( $28.4 \text{ kJ.mol}^{-1}$ ) is smaller than the one found in the study of Wilson *et al.* on transition metals ( $32.6 \text{ kJ.mol}^{-1}$ ). All of this, demonstrate that this double hybrid is suitable to answer this kind of problems. The follow-up of the current work will be to use the double-hybrid implementation in DIRAC program to assess the importance of SOC to our results.

## Chapter 6

# Conclusions and perspectives

With respect to the quantum chemical methods used in this thesis to study actinides several conclusions need to be drawn. First, for closed-shell systems or for systems with a dominant single reference character, DFT with hybrid methods, such as semi-empirical dispersion corrections or double hybrid functional, performs well. For large systems it is cheap and efficient. With B2-PLYP, enough correlation can be included to describe properly closed-shell systems. Nonetheless, DFT is still failing for multireference systems. For this type of systems, we chose the CAS method. This method is neither black-box nor cheap. The choice of active space can be tedious and we have seen that in cases, where very accurate results are wanted, this method may fail because of the limited size of active space and probably a lack of accurate dynamic electron correlation treatment.

To the question raised in the introduction about the efficiency of the available tools to describe the structure, the bonding and the thermodynamics of actinide systems, we can not give a simple answer.

First, concerning the geometries, the three studies showed that the structures of actinides and f-elements systems can have their geometries reproduced or unravelled. We have seen that the X-ray structures were well reproduced for the catalysts in Chapter 3 as well as structural experimental values in Chapter 5 with the double-hybrid (B2-BLYP) functional, proving its capability, in most cases, at being as accurate as other quantum chemistry methods but also being predictive. It is worth noticing the failure of the DFT at converging to the expected triplet state for the uranium complexes in Chapter 3. In Chapter 5, only  $\text{UO}_3$  structure turned out to be problematic both at MP2 and B2-PLYP levels; and the explanations of this failure are expected soon. Finally, for  $\text{PuO}_2$ , in Chapter 4 we reported a bond length and a ground state different from what was reported before at spin-orbit level [151].

Chapters 3 and 4 were focusing on the bonding. In the case of closed-shell systems, the exploration of the bonding via the determination of the electronic structure is

rather easy and the ETS-NOCV is a powerful tool to analyse and explore the metal arene chemical bonds and determine the main forces driving them. In particular we have seen that the zirconium-arene bond was mainly covalent while the thorium-arene one was mostly driven by electrostatic forces. In cases of open-shell systems, like in Chapter 4, the electronic wave functions are more difficult to describe. The CAS methods present the main disadvantages to include a limited number of orbitals in the active space thus requiring a thorough analysis of results. For example, in  $\text{PuO}_3$ , the full valence active space is (34; 26) but we could only compute a active space of (14,14) which might not be large enough.

The third properties we wanted to reproduce were thermodynamics. This part is particularly satisfactory in Chapter 5 where the double hybrid B2-PLYP already exhibits great performances at the spin-free level, compared to either experimental or state-of-the-art CCSD(T) data. In Chapter 4, multireference methods were needed to predict the enthalpies of formation of plutonium oxyhydroxide  $\text{PuO}_2(\text{OH})_2$  and trioxide  $\text{PuO}_3$ . The enthalpy of formation of  $\text{PuO}_2(\text{OH})_2$  was within very good agreement with experimental data but its uniqueness imposes to confirm this value with another method. For  $\text{PuO}_2$ , the single reference method UCCSD(T) perform very well. Regarding  $\text{PuO}_3$  and  $\text{PuO}_2$ , the results with SO-CASPT2 method are good but not excellent, demonstrating the limit of actual relativistic multireference method accuracy.

As perspectives, the study of the alkyl cation catalysts calls for a further investigation of the possible transition states to have a better comprehension of the catalytic mechanism. Concerning the thermodynamic properties of plutonium oxides and oxyhydroxyde, in the next weeks, we will use the DMRG methods to be able to handle all valence orbitals in the active space to confirm our conclusions on  $\text{PuO}_3$  and  $\text{PuO}_2(\text{OH})_2$ . With DMRG we can expect to also be able to predict other thermodynamic values such as the one of uranyl complexes or  $\text{RuO}_2$  (also important for nuclear safety) for which it is not easy to properly describe because of a ground and first excited states close to each other in energy [201].

To shed light on the possible formation of  $\text{PuO}_3$  we wait for the results of IRSN on accident simulation. At the moment, the double hybrid B2-PLYP is tested on  $\text{PuO}_2$  hoping to obtain results as good as the one computed with UCCSD(T) method. In addition we plan to benchmark the implementation of the double hybrid in the DIRAC package to have results in the fully relativistic context.

Finally, the broad range of uses and theoretical challenges to describe actinides makes them a wonderful subject for the development of both experimental and computational chemistry.

## Appendix A

# Geometries

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## A.1 Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)] (X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: Exploration of the bonding

### A.1.1 X-Ray structures of Alkyl cations containing Thorium

#### X-Ray structure of $\eta^6$ -2-Th

Th	13.572531	10.195293	14.464022	C	15.992251	5.394201	12.387399
Si	13.448412	7.436393	17.277993	H	16.053977	4.497544	12.079063
O	13.505595	7.925594	13.428804	C	13.429707	5.120134	12.400889
N	11.533051	9.429158	13.797651	C	12.203748	6.048476	12.562765
C	10.901366	5.592226	12.256356	C	12.283644	7.315836	13.063811
H	10.792612	4.709827	11.921041	C	14.695748	7.239794	13.098499
N	15.572197	9.327770	13.767395	C	14.706170	5.945503	12.620578
C	9.770801	6.390663	12.427868	C	13.455092	4.557743	10.957491
C	9.943419	7.681786	12.928914	H	14.231605	3.970005	10.849573
H	9.184008	8.241008	13.042613	H	13.515482	5.299149	10.319620
C	11.204383	8.166551	13.264229	H	12.633689	4.050799	10.791760
C	15.830055	8.022389	13.295063	C	13.364508	3.990600	13.406835
C	17.066703	7.444156	13.025269	H	14.146097	3.409198	13.296990
H	17.857644	7.959021	13.135114	H	12.548182	3.469398	13.260375
C	17.163700	6.111844	12.593599	H	13.357828	4.361303	14.314499

C	8.348976	5.918571	12.065573	C	16.846522	11.122668	12.674537
C	7.779819	6.834239	10.992178	C	17.778016	12.168240	12.782454
H	8.336952	6.780376	10.188578	H	17.943151	12.724294	12.030885
H	7.767795	7.756243	11.323640	C	18.463142	12.405870	13.969548
H	6.867297	6.553835	10.776343	H	19.054745	13.147276	14.036996
C	7.451151	6.026297	13.322042	C	18.287585	11.566244	15.052578
H	6.543973	5.726883	13.102353	H	18.774175	11.726248	15.852325
H	7.423094	6.957806	13.624597	C	17.389492	10.468394	14.985130
H	7.815893	5.462322	14.035069	C	16.145630	10.888207	11.350619
C	8.306757	4.470612	11.572236	H	15.295100	10.403441	11.558746
H	8.871372	4.380313	10.776343	C	15.757374	12.150814	10.599050
H	7.383012	4.228230	11.348692	H	15.225626	12.729047	11.184888
H	8.638899	3.874953	12.275627	H	15.228298	11.910016	9.808939
C	18.537694	5.516184	12.265992	H	16.567020	12.626074	10.317693
C	18.968436	6.042139	10.890042	C	16.978523	9.955113	10.454518
H	19.001303	7.021174	10.909313	H	17.216340	9.148755	10.955564
H	18.322590	5.749062	10.211703	H	17.793514	10.417699	10.171234
H	19.856375	5.690446	10.668426	H	16.452120	9.706393	9.666334
C	19.586226	5.912234	13.316261	C	17.314406	9.490942	16.152952
H	19.631919	6.889686	13.381782	H	16.553660	8.865183	15.975659
H	20.462942	5.562126	13.052248	C	18.583654	8.652900	16.289776
H	19.332644	5.538363	14.185383	H	18.771503	8.199819	15.441852
C	18.498147	3.962084	12.196616	H	18.458867	7.984368	16.995095
H	17.836267	3.681681	11.531766	H	19.335316	9.235886	16.522955
H	18.253115	3.600887	13.073446	C	17.031965	10.205416	17.496141
H	19.380741	3.623065	11.938385	H	16.991884	9.543221	18.216876
C	10.472762	10.428789	13.873193	H	16.176893	10.679092	17.442182
C	10.172685	11.186036	12.726568	H	17.748088	10.848602	17.681143
C	9.254284	12.234777	12.826778	C	13.547547	9.235886	16.700249
H	9.026354	12.740136	12.055938	H	14.365210	9.589163	17.131919
C	8.673102	12.538943	14.058195	H	12.791343	9.684215	17.155044
H	8.101807	13.294606	14.133351	C	14.955744	6.496804	16.715665
C	8.919737	11.759517	15.162423	H	14.894285	5.568463	17.020147
H	8.481245	11.960710	15.981440	H	15.760046	6.911865	17.095304
C	9.815959	10.660082	15.104610	H	15.009186	6.518983	15.738626
C	10.781122	10.877117	11.366036	C	11.928254	6.550667	16.636654
H	11.297639	10.024818	11.460464	H	11.925582	5.627078	16.964261
C	9.726444	10.645824	10.302277	H	11.938943	6.549083	15.655760
H	10.164668	10.450967	9.446644	H	11.123952	7.011669	16.952699
H	9.173319	11.449013	10.211703	C	13.372792	7.379204	19.153447
H	9.162631	9.886992	10.562435	H	13.320419	6.446110	19.450220
C	11.757240	11.941700	10.901605	H	12.580247	7.865553	19.463710
H	12.117974	11.696149	10.024774	H	14.178163	7.795848	19.525377
H	12.492068	12.016157	11.547183	C	14.776713	12.922319	15.844616
H	11.292295	12.803504	10.834156	H	15.589031	12.871625	16.334100
C	9.943419	9.745998	16.303266	C	14.819467	13.261338	14.414708
H	10.739170	9.161429	16.151025	H	15.634457	13.438769	13.963767
C	8.720398	8.835083	16.416965	C	13.654431	13.302527	13.796109
H	8.582785	8.366160	15.569041	H	13.670464	13.348469	12.847976
H	7.928121	9.373711	16.627019	C	12.434617	13.285101	14.391583
H	8.866028	8.179225	17.131919	H	11.639668	13.468868	13.904027
C	10.164668	10.484236	17.638746	C	12.398544	12.980935	15.784876
H	10.950266	11.065637	17.563589	H	11.562177	12.987272	16.237745
H	10.311634	9.828377	18.353700	C	13.560908	12.672016	16.503684
H	9.376399	11.024448	17.848800	H	13.528842	12.315571	17.384369
C	16.641839	10.305221	13.803817				

## A.1.2 X-Ray structures of Alkyl cations containing Uranium

### X-Ray structure of $\eta^6$ -2-U

U	26.777247	13.503446	-5.391782	C	30.257583	16.196670	-4.027539
C	25.497402	16.315921	-4.020626	H	31.048407	15.690409	-4.171598
C	27.893793	16.400190	-4.055059	C	29.183435	18.242011	-3.352548
C	25.430473	17.597350	-3.505585	H	29.244576	19.142671	-3.056607
C	26.632399	18.515068	-3.328096	C	23.158568	15.962366	-3.969999
C	27.914952	17.674466	-3.553844	H	22.400133	15.407714	-4.110156
O	26.717354	15.703364	-4.374315	C	29.007950	15.612476	-4.269500
Si	26.631072	16.262875	-8.133831	N	28.754519	14.348168	-4.765203
C	24.096018	18.044889	-3.237884	C	30.354856	17.521319	-3.574698
H	23.961710	18.921763	-2.897945	C	24.403820	15.486983	-4.276868

A.1. Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 119  
Exploration of the bonding

C	26.755000	14.493941	-7.517706	H	21.753414	15.271735	-6.610376
H	27.582991	14.155731	-7.942175	H	21.165420	14.217298	-7.660837
H	26.014113	14.031340	-7.983711	H	22.059889	15.442003	-8.171844
C	22.984861	17.224017	-3.464068	C	31.745780	15.016128	-7.290026
C	26.656266	19.034331	-1.896880	H	31.958778	15.448323	-6.436657
H	25.852805	19.570197	-1.730358	H	31.602658	15.700958	-7.976267
H	27.452665	19.589755	-1.764128	H	32.489374	14.436399	-7.557159
H	26.678646	18.277243	-1.275016	C	22.448796	11.451407	-3.829330
C	21.507655	19.145925	-2.621513	H	22.198153	10.955051	-3.059089
H	20.581249	19.405101	-2.434346	C	23.048285	13.020830	-6.113177
H	21.882572	19.742619	-3.302546	C	31.476420	12.117041	-6.057834
H	22.038066	19.213498	-1.800228	H	31.962150	11.966677	-6.860292
C	32.136413	17.576864	-1.871746	C	23.189072	13.937936	-7.294136
H	32.160015	16.597673	-1.903774	H	23.957727	14.552269	-7.115890
H	31.477376	17.866163	-1.206623	C	20.956590	16.798913	-2.077153
H	33.021484	17.917039	-1.624046	H	20.050732	17.095963	-1.850022
C	29.814411	13.343790	-4.831172	H	21.518646	16.821537	-1.274675
C	26.579170	19.651369	-4.322192	H	20.922369	15.883851	-2.426315
H	25.768992	20.181213	-4.169628	C	25.101379	17.176726	-7.485641
H	26.565710	19.288665	-5.232495	H	25.116140	17.184210	-6.505788
H	27.368347	20.221366	-4.209327	H	24.291945	16.720178	-7.796677
C	32.773442	17.694354	-4.294861	H	25.105468	18.098108	-7.819462
H	32.799566	16.715508	-4.334237	N	24.756569	14.219735	-4.803727
H	33.655035	18.034497	-4.035020	C	23.685898	13.247855	-4.894962
H	32.532489	18.050408	-5.175523	C	26.550285	16.284225	-9.996505
C	20.679690	17.628652	-4.399922	H	27.327675	15.813040	-10.362619
H	19.773461	17.946297	-4.204289	H	26.551612	17.211739	-10.312920
H	20.641089	16.697617	-4.703401	H	25.729063	15.839122	-10.292976
H	21.076323	18.185034	-5.102414	C	30.108673	13.705849	-1.494609
C	31.739727	18.132602	-3.271332	H	30.289149	14.530998	-1.991562
C	21.540230	17.718094	-3.127766	H	30.956523	13.277097	-1.254409
C	21.880182	11.161747	-5.093721	H	29.607625	13.918315	-0.679593
H	21.309073	10.407725	-5.181944	C	28.969588	11.466217	-1.616584
C	30.161611	13.499830	-8.495930	H	28.468832	10.863644	-2.205283
H	30.124018	14.174566	-9.205638	H	28.430628	11.671200	-0.824164
H	29.294009	13.049366	-8.427158	H	29.804747	11.033975	-1.340758
H	30.855745	12.841255	-8.707738	C	28.129862	17.204837	-7.576894
C	30.028630	12.532901	-3.691824	H	28.938128	16.746716	-7.888707
C	30.498085	14.192065	-7.136667	H	28.139472	17.254471	-6.598197
H	29.750695	14.825877	-6.937473	H	28.103473	18.110796	-7.949675
C	30.568704	13.211348	-5.982792	C	22.932561	13.064852	-1.345834
C	23.382822	12.479164	-3.740216	H	23.345893	13.263844	-0.479850
C	29.288062	12.758400	-2.363339	H	22.342390	12.287750	-1.255243
H	28.420965	13.210892	-2.571568	H	22.410354	13.838636	-1.644066
C	22.127932	11.928080	-6.176361	C	24.938240	11.680020	-1.885629
H	21.683459	11.738521	-6.994313	H	25.315200	11.931837	-1.016786
C	23.479803	13.182263	-8.621181	H	25.663250	11.561272	-2.534237
H	24.294972	12.647655	-8.520836	H	24.440404	10.840785	-1.794868
H	23.601289	13.830272	-9.346231	C	25.637524	10.440018	-5.444645
H	22.726360	12.592456	-8.833046	H	24.825993	10.249767	-4.988849
C	31.705241	19.675266	-3.193034	C	28.009889	10.501915	-5.432921
H	31.461049	20.041413	-4.068639	H	28.839978	10.383985	-4.986235
H	32.589621	20.009073	-2.934462	C	25.574737	10.778353	-6.701535
H	31.043203	19.953795	-2.526301	H	24.732888	10.854368	-7.135190
C	31.661489	11.272571	-4.984758	C	27.995367	10.828474	-6.763773
H	32.262332	10.539710	-5.051257	H	28.812288	10.915857	-7.240763
C	24.012019	12.762677	-2.362468	C	26.776345	11.033079	-7.419501
H	24.560907	13.592982	-2.458987	H	26.751681	11.334091	-8.320222
C	30.954213	11.502818	-3.788722	C	26.829335	10.342762	-4.735580
H	31.113026	10.944549	-3.036663	H	26.831194	10.172242	-3.801014
C	21.928421	14.794371	-7.448177				

X-Ray structure of  $\eta^6$ -3-U-endo

U	26.475973	25.967895	3.207091	C	22.987114	23.307995	4.618426
Si	26.597014	23.130531	0.474077	H	22.200615	23.824542	4.480790
O	26.538359	23.792852	4.259045	C	24.205522	23.867324	4.368006
N	24.504125	25.166614	3.840404	C	28.855200	24.003590	4.354625
N	28.481946	25.255346	3.786880	C	30.092271	23.499720	4.627984
C	24.048222	21.259237	5.310425	H	30.857441	24.030527	4.436824
H	23.984236	20.362409	5.620104	C	30.273566	22.232120	5.176613
C	22.872472	22.003952	5.071475	C	29.135141	21.430363	5.409828



H	29.252449	20.549381	5.746270	H	22.952455	24.936861	6.700158
C	26.607678	20.975611	5.337187	C	24.280173	28.048819	7.028953
C	25.333282	21.839164	5.094414	H	24.701417	27.795299	7.877704
C	25.338614	23.081412	4.593575	H	24.909372	28.585965	6.501352
C	27.751435	23.102010	4.606956	H	23.472344	28.573289	7.208644
C	27.802091	21.904128	5.149850	C	29.564383	26.263088	3.689388
C	26.676997	19.864877	4.362271	C	29.828327	27.045831	4.811497
H	25.906494	19.270689	4.488437	C	30.777458	28.126459	4.668127
H	26.663666	20.227727	3.452350	H	31.009409	28.684204	5.402182
H	27.506154	19.357837	4.499906	C	31.366667	28.322938	3.337654
C	26.610344	20.497092	6.790003	H	31.963873	29.047054	3.192372
H	26.565020	21.271913	7.388334	C	31.070729	27.498998	2.324506
H	25.834509	19.918750	6.944843	H	31.475977	27.663785	1.481490
H	27.434169	19.996390	6.969694	C	30.220243	26.435798	2.429644
C	21.502097	21.374905	5.390712	C	30.084272	25.456577	1.278860
C	21.038195	21.912050	6.730744	H	29.313769	24.848129	1.468109
H	20.166380	21.523848	6.954401	C	31.353336	24.612039	1.169899
H	21.688724	21.672791	7.422743	H	31.265355	23.979823	0.426287
H	20.955546	22.888102	6.681042	H	32.123839	25.198304	1.009325
C	20.462318	21.761523	4.278161	H	31.489307	24.116090	2.003357
H	20.763587	21.414517	3.414118	C	29.806998	26.201292	-0.032497
H	19.587837	21.374905	4.499906	H	29.721683	25.553232	-0.764640
H	20.385001	22.737575	4.228459	H	28.975175	26.711501	0.049702
C	21.563417	19.798328	5.425121	H	30.548174	26.812909	-0.223657
H	21.864686	19.465583	4.553431	C	29.191129	26.747944	6.164910
H	22.189950	19.509949	6.120943	H	28.724561	25.863794	6.103739
H	20.670273	19.441815	5.618192	C	30.278898	26.641783	7.264080
C	31.689265	21.763108	5.572314	H	30.929426	25.954110	7.015572
C	31.739921	20.352902	6.065507	H	30.734801	27.505336	7.355837
H	31.364000	19.755546	5.384977	H	29.860320	26.402524	8.116654
H	32.670389	20.100967	6.241374	C	28.156682	27.803221	6.505175
H	31.217365	20.275262	6.891318	H	27.754101	27.598821	7.376864
C	32.270474	22.716977	6.616048	H	28.585924	28.682619	6.541495
H	32.227817	23.635987	6.277694	H	27.455498	27.807975	5.818910
H	31.750585	22.650427	7.443770	C	26.517031	24.898833	1.110640
H	33.203609	22.476133	6.793826	H	25.714535	25.260099	0.661414
C	32.585074	21.896206	4.301100	H	27.284867	25.331402	0.655679
H	32.555747	22.819969	3.976128	C	28.159348	22.157648	1.118286
H	33.510211	21.660115	4.528580	H	28.156682	22.148141	2.098937
H	32.254478	21.292511	3.603366	H	28.132687	21.237054	0.781844
C	23.429687	26.152173	3.796438	H	28.972509	22.598139	0.797137
C	23.240394	27.003049	4.897519	C	26.655668	23.116271	-1.372529
C	22.304593	28.069418	4.782823	H	26.695659	22.189338	-1.691766
H	22.149959	28.655683	5.513054	H	25.853172	23.548839	-1.729998
C	21.606074	28.245297	3.557488	H	27.450166	23.601128	-1.678385
H	21.006202	28.974167	3.452350	C	25.066672	22.141803	1.022706
C	21.792701	27.378576	2.544340	H	25.013350	22.137050	1.999534
H	21.296807	27.508505	1.745291	H	24.258844	22.558526	0.653767
C	22.664516	26.313792	2.601688	H	25.135991	21.221208	0.693911
C	22.768494	25.302881	1.470020	C	26.319739	28.335614	1.288418
H	23.515002	24.669081	1.678385	H	26.314407	27.849172	0.472165
C	21.440776	24.478941	1.317092	C	27.476827	28.606563	1.856164
H	21.536756	23.837218	0.581126	H	28.284655	28.354628	1.422230
H	21.256815	23.995668	2.148638	C	27.535481	29.267300	3.096792
H	20.699600	25.087388	1.122109	H	28.367304	29.392475	3.542195
C	23.080428	26.017490	0.086022	C	26.378393	29.722051	3.664537
H	23.141748	25.344078	-0.623182	C	25.167984	29.420996	3.052825
H	22.363247	26.649706	-0.124254	H	24.354824	29.685608	3.465731
H	23.930914	26.500763	0.152928	C	25.133325	28.725400	1.825578
C	23.901587	26.768543	6.237551	H	24.309500	28.538429	1.389733
H	24.760071	26.293193	6.046391	C	26.429049	30.560252	4.859287
C	23.056433	25.803583	7.147472	H	25.517243	30.796342	5.128823
H	23.515002	25.675238	8.003869	H	26.866290	30.067472	5.585695
H	22.171288	26.194954	7.306135	H	26.935608	31.376269	4.666216

### X-Ray structure of $\eta^6$ -5-U-endo

O	-0.156498	15.730261	3.745891	C	-2.629433	13.191173	2.747389
U	-0.224668	17.934927	4.767428	H	-2.694950	12.297283	2.430165
Si	-0.080636	15.164970	7.520860	C	-3.796538	13.913524	2.975866
N	-2.182485	17.109810	4.142043	C	-3.704761	15.241769	3.425267
N	1.792832	17.216825	4.188683	H	-4.496004	15.750090	3.561221

A.1. Geometries from the Chapter Coordination of Alkyl cations [(X<sub>A2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 121  
Exploration of the bonding

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C	-2.457020	15.816188	3.670739	H	-3.177707	16.618800	6.321828
C	2.133414	15.964120	3.655633	C	-5.216161	16.453556	6.669264
C	3.403436	15.499864	3.338408	H	-5.960190	17.064171	6.852423
H	4.159136	16.060119	3.474362	H	-5.124649	15.819335	7.409454
C	3.574522	14.206241	2.819142	H	-5.392553	15.964120	5.838438
C	2.462856	13.408350	2.615212	C	-3.595212	17.951766	7.838084
H	2.586197	12.533345	2.265888	H	-2.793093	18.502579	7.730455
C	-0.069761	12.936225	2.720954	H	-3.437653	17.278201	8.531068
C	-1.349862	13.745133	2.973978	H	-4.347464	18.521464	8.100550
C	-1.328112	15.030886	3.440373	C	2.832615	18.217730	4.301411
C	1.064718	15.108000	3.415826	C	3.138450	18.984146	3.155249
C	1.153046	13.844279	2.907890	C	4.053566	20.035411	3.302532
C	-0.003183	11.777945	3.716056	H	4.283804	20.567339	2.549124
H	-0.029178	12.132039	4.629964	C	4.630221	20.310817	4.539329
H	0.830236	11.279066	3.581991	H	5.204225	21.061496	4.633741
H	-0.769228	11.181494	3.576327	C	4.379029	19.509779	5.621290
C	-0.089655	12.396429	1.282115	H	4.816958	19.689186	6.444563
H	-0.877981	11.829879	1.155603	C	3.484337	18.422318	5.538208
H	0.721483	11.869223	1.119726	C	3.340571	17.484363	6.705140
H	-0.122015	13.147108	0.651443	H	2.567630	16.876895	6.518204
C	-5.172129	13.310778	2.654865	C	4.597861	16.615653	6.867529
C	-6.205282	13.724674	3.716056	H	4.747993	16.102610	6.046144
H	-5.920402	13.395760	4.595976	H	4.474784	16.000316	7.619048
H	-7.076897	13.340679	3.489468	H	5.371333	17.191645	7.039359
H	-6.275839	14.701973	3.740603	C	3.055692	18.224025	8.028796
C	-5.615364	13.841131	1.280227	H	3.822267	18.793723	8.255385
H	-5.625974	14.821578	1.295333	H	2.912456	17.569345	8.744439
H	-6.514565	13.509070	1.076297	H	2.254634	18.777985	7.926832
H	-4.989371	13.531103	0.592907	C	2.522272	18.696150	1.793828
C	-5.141095	11.766929	2.598218	H	2.116703	17.783375	1.833481
H	-4.554360	11.478933	1.867469	C	1.416440	19.670301	1.472827
H	-6.047723	11.426999	2.441494	H	0.681695	19.553844	2.111052
H	-4.801043	11.414409	3.446038	H	1.087529	19.505058	0.564584
C	5.005021	13.753001	2.481147	H	1.758614	20.586224	1.535139
C	5.575576	14.687809	1.425621	C	3.570278	18.680413	0.713755
H	6.517217	14.464336	1.263233	H	3.867360	19.596335	0.532484
H	5.509263	15.614748	1.739069	H	3.190970	18.290122	-0.101965
H	5.068947	14.588663	0.592907	H	4.334201	18.140616	1.008320
C	5.888572	13.850574	3.736827	C	-0.198142	16.931976	6.892076
H	5.572924	13.213205	4.409040	H	0.546417	17.391511	7.356583
H	5.838175	14.760201	4.099369	H	-1.023869	17.275054	7.320706
H	6.816951	13.644413	3.498909	C	1.435008	14.266044	6.886411
C	5.056480	12.308299	1.954328	H	1.432355	14.270765	5.906415
H	4.790433	11.691389	2.668083	H	1.424398	13.339105	7.209300
H	5.968148	12.098990	1.665428	H	2.241371	14.714563	7.213077
H	4.442954	12.213874	1.195256	C	0.005040	15.189835	9.397770
C	-3.244550	18.098125	4.197558	H	0.769228	15.732779	9.682895
C	-4.012452	18.241336	5.364490	H	0.114058	14.273913	9.731989
C	-4.911388	19.330371	5.428690	H	-0.822278	15.573830	9.756536
H	-5.421730	19.470435	6.216086	C	-1.594159	14.203094	6.995929
C	-5.055684	20.186491	4.369387	H	-2.389912	14.602826	7.401901
H	-5.639236	20.932449	4.446805	H	-1.506626	13.273008	7.290495
C	-4.361257	19.983478	3.177908	H	-1.673734	14.231421	6.019709
H	-4.514572	20.554749	2.435830	C	-0.328911	20.403669	6.686258
C	-3.434470	18.930639	3.072166	H	-0.342174	20.025969	7.558625
C	-2.726250	18.678839	1.748510	C	-1.509278	20.693239	6.042368
H	-1.867367	18.205140	1.948664	H	-2.339514	20.527995	6.476663
C	-3.572931	17.753474	0.872367	C	-1.499199	21.225166	4.756477
H	-3.684336	16.889485	1.319880	H	-2.310336	21.404574	4.295746
H	-3.127309	17.619705	0.011329	C	-0.297081	21.483261	4.174899
H	-4.453564	18.159501	0.723196	C	0.901853	21.182675	4.771582
C	-2.385402	19.952003	0.987550	H	1.721479	21.325886	4.316517
H	-3.212190	20.381636	0.683543	C	0.885938	20.664911	6.055586
H	-1.827579	19.728530	0.213371	H	1.705564	20.487078	6.506875
H	-1.896545	20.564191	1.576680	F	-0.272413	22.093876	2.962649
C	-3.917227	17.260890	6.521981				

### A.1.3 X-Ray structures of Alkyl cations containing Zirconium

#### X-Ray structure of $\eta^6$ -3'-Zr-exo

Zr	7.285954	8.774163	15.782526	C	5.793157	12.598983	18.628951
O	8.282123	10.391022	14.632517	H	6.121621	12.880460	17.749951
N	6.037782	10.513949	15.737937	H	5.053736	13.180551	18.904895
N	8.621293	7.924604	14.345425	H	6.518045	12.660645	19.285003
C	7.683726	13.944571	13.954353	C	4.786192	10.718832	19.930090
H	8.083844	14.707173	13.554143	H	4.468725	9.792612	19.882577
C	6.413363	14.079126	14.540962	H	5.512989	10.781503	20.582487
C	5.844292	12.955691	15.147673	H	4.048384	11.303261	20.202379
H	4.984944	13.030522	15.547883	C	0.476312	11.367248	17.050041
C	6.501660	11.731730	15.178739	H	0.375806	11.343025	18.044169
C	9.525022	8.743962	13.625413	C	0.167541	12.787874	16.595007
C	10.531792	8.332530	12.766515	H	0.818146	13.405717	16.987907
H	10.671907	7.404743	12.623974	H	0.220425	12.837202	15.617325
C	11.343474	9.257527	12.106808	H	-0.735038	13.033770	16.885571
C	11.096220	10.627797	12.284070	C	-0.505722	10.357198	16.467086
H	11.640386	11.257814	11.827209	H	-0.273983	9.458964	16.781406
C	9.764440	12.571519	13.303783	H	-1.414166	10.580861	16.757650
C	8.378486	12.736923	13.939733	H	-0.458407	10.382440	15.489404
C	7.752986	11.682390	14.572028	C	8.724414	6.550147	13.901357
C	9.358702	10.107644	13.766126	C	7.912949	6.118556	12.826820
C	10.070439	11.091258	13.115556	C	8.096091	4.819031	12.346203
C	9.834116	13.312058	11.969750	H	7.544826	4.513116	11.635328
H	9.634537	14.260729	12.110463	C	9.052372	3.957291	12.870679
H	10.734898	13.220060	11.591469	C	9.808169	4.402191	13.950698
H	9.179132	12.929556	11.348419	H	10.450845	3.813735	14.330806
C	10.797486	13.166765	14.268673	C	9.663728	5.672445	14.497103
H	10.611125	14.119810	14.400249	C	6.864113	7.023863	12.198180
H	10.744894	12.702701	15.131226	H	6.530177	7.631103	12.918193
H	11.695268	13.057588	13.892220	C	7.428729	7.903651	11.098060
C	12.440608	8.749381	11.182122	H	6.714230	8.464996	10.728916
C	13.324447	7.701830	11.956958	H	8.134606	8.476678	11.465376
H	13.740545	8.134607	12.731793	H	7.801984	7.342060	10.387184
H	12.761565	6.958546	12.260313	C	5.647374	6.247618	11.660912
H	14.023335	7.358586	11.361211	H	5.283776	5.679046	12.371787
C	11.825687	8.061895	10.014386	H	4.960606	6.881427	11.364866
H	11.207569	7.370662	10.330534	H	5.924244	5.689371	10.904351
H	11.335317	8.715614	9.471636	C	10.476433	6.072451	15.719662
H	12.529310	7.648445	9.471636	H	9.989020	6.820522	16.171041
C	13.413114	9.838731	10.772775	C	11.869091	6.582939	15.366966
H	13.789554	10.258385	11.575022	H	12.345549	6.825247	16.187488
H	14.135691	9.446844	10.239162	H	12.364905	5.883029	14.895486
H	12.943058	10.511657	10.240989	H	11.790337	7.372226	14.789494
C	5.689633	15.432942	14.502585	C	10.597018	4.916060	16.741203
C	6.524951	16.475573	15.222598	H	11.127022	5.215100	17.510556
H	7.412773	16.524700	14.809596	H	9.703872	4.651283	17.042731
H	6.085299	17.350191	15.154982	H	11.038640	4.151161	16.317236
H	6.615473	16.228322	16.165558	C	9.260431	2.545222	12.327929
C	4.317907	15.369288	15.149500	H	10.246890	2.386918	12.364477
H	3.771037	14.697344	14.690812	C	8.642170	1.500104	13.241650
H	4.413528	15.121533	16.094288	H	8.911817	1.676107	14.168163
H	3.883354	16.243402	15.083712	H	7.666109	1.541500	13.172207
C	5.517302	15.862992	13.031494	H	8.951510	0.610315	12.974843
H	4.977773	15.196934	12.558186	C	8.883953	2.312729	10.968311
H	5.065259	16.732238	12.996773	H	9.290919	2.995402	10.394494
H	6.396836	15.935524	12.607527	H	9.193640	1.425966	10.690540
C	4.635503	10.649064	16.114390	H	7.908521	2.357655	10.886076
C	4.260817	10.961367	17.426494	C	8.775268	9.430622	17.320502
C	2.913795	11.137363	17.715230	H	8.307558	9.853784	18.069754
H	2.652761	11.333561	18.608849	H	9.275254	8.652146	17.643959
C	1.934866	11.036785	16.730238	H	9.398000	10.073301	16.918465
C	2.325160	10.725841	15.440063	C	6.607178	7.309345	18.119095
H	1.660592	10.635369	14.767565	C	7.250882	6.408794	17.260196
C	3.667875	10.537688	15.094677	H	8.069384	6.017177	17.537968
C	4.020244	10.264885	13.632723	C	6.744188	6.074138	16.035810
H	5.013773	10.190733	13.552315	H	7.186440	5.422365	15.504024
C	3.534732	11.429597	12.735448	C	5.590706	6.675344	15.562502
H	3.766245	11.240789	11.801625	H	5.258827	6.458109	14.698122
H	2.561892	11.521268	12.819511	C	4.931415	7.581915	16.339165
H	3.967172	12.261118	13.018702	H	4.138094	7.994394	16.019363
C	3.391500	8.966358	13.128348	C	5.427308	7.904468	17.607411
H	3.640094	8.826729	12.190870	H	4.960818	8.539566	18.139196
H	3.716534	8.215453	13.667444	C	7.083585	7.573345	19.498814
H	2.416275	9.025349	13.203274	H	6.495514	8.231630	19.926435
C	5.298783	11.151457	18.550371	H	7.071395	6.740065	20.014153
H	6.087771	10.578845	18.329250	H	7.998037	7.924672	19.467747

### A.1.4 Optimised geometries of Alkyl cations containing Thorium

#### Optimised geometry of $\eta^6$ -2-Th and the name of the fragment f in the ETS-NOCV in which each atom belongs

Th	13.5411509	10.1377154	14.5509358	f=U	C	10.2305495	10.3306062	10.2068517	f=U
Si	13.4112173	7.5322504	17.4978204	f=U	H	10.8007652	10.0548590	9.3166019	f=U
O	13.4985180	7.8349960	13.6124273	f=U	H	9.5010599	11.0900207	9.9142923	f=U
N	11.5227749	9.3960006	13.7995967	f=U	H	9.6858193	9.4486246	10.5451961	f=U
C	10.9455192	5.5470351	12.3276461	f=U	C	11.9584772	12.0530811	10.7679995	f=U
H	10.8362841	4.5394039	11.9548734	f=U	H	12.5061723	11.7733943	9.8652660	f=U
N	15.5376637	9.3173458	13.8106982	f=U	H	12.6859752	12.4209590	11.4964693	f=U
C	9.8258568	6.3633255	12.4096511	f=U	H	11.3042754	12.8873466	10.5044660	f=U
C	9.9815248	7.6658022	12.8964944	f=U	C	9.6856998	9.7777687	16.0817399	f=U
H	9.1316192	8.3345344	12.9572021	f=U	H	10.5426491	9.1050062	16.0069246	f=U
C	11.2234660	8.1309948	13.3013923	f=U	C	8.4251433	8.9127275	16.1276204	f=U
C	15.7913673	8.0286696	13.3459828	f=U	H	8.3418233	8.2784856	15.2451328	f=U
C	17.0187729	7.5006963	12.9720467	f=U	H	7.5263993	9.5319572	16.1895833	f=U
H	17.8956188	8.1335073	13.0341862	f=U	H	8.4433803	8.2625803	17.0056007	f=U
C	17.1226427	6.1945221	12.4820930	f=U	C	9.8119876	10.5679219	17.3819215	f=U
C	15.9685601	5.4300640	12.3804617	f=U	H	10.7036482	11.1984294	17.3977057	f=U
H	16.0374282	4.4192964	12.0068144	f=U	H	9.8739262	9.8845784	18.2319737	f=U
C	13.4451964	5.0751477	12.6312720	f=U	H	8.9464597	11.2129345	17.5505540	f=U
C	12.2213251	5.9770285	12.7095653	f=U	C	16.6044161	10.2635307	13.8450668	f=U
C	12.3047788	7.2583693	13.1939544	f=U	C	16.7787840	11.1528864	12.7545679	f=U
C	14.6742893	7.2043935	13.2214293	f=U	C	17.7877195	12.1065971	12.8322780	f=U
C	14.7078764	5.9193695	12.7389865	f=U	H	17.9362931	12.7967494	12.0117006	f=U
C	13.4425255	4.2973168	11.3110614	f=U	C	18.6182955	12.1910936	13.9374748	f=U
H	14.3003684	3.6274961	11.2517737	f=U	H	19.4005878	12.9405693	13.9717481	f=U
H	13.4715311	4.9718018	10.4535549	f=U	C	18.4522472	11.3108758	14.9886070	f=U
H	12.5523668	3.6736791	11.2287250	f=U	H	19.1161199	11.3728628	15.8433492	f=U
C	13.4074615	4.0789474	13.8032364	f=U	C	17.4577070	10.3361746	14.9682044	f=U
H	14.2796188	3.4222287	13.7710610	f=U	C	15.9297148	11.0708127	11.4977558	f=U
H	12.5082246	3.4614699	13.7473022	f=U	H	14.9128837	10.7741860	11.7951912	f=U
H	13.4059143	4.5973764	14.7637199	f=U	C	15.8265003	12.3878320	10.7349313	f=U
C	8.4395024	5.8845547	11.9793421	f=U	H	15.5639355	13.2360915	11.3706355	f=U
C	7.9176908	6.7810542	10.8503947	f=U	H	15.0700117	12.3039652	9.9530766	f=U
H	8.5838292	6.7503773	9.9846807	f=U	H	16.7676868	12.6329311	10.2376493	f=U
H	7.8214859	7.8214193	11.1686322	f=U	C	16.4421692	9.9914081	10.5407292	f=U
H	6.9292862	6.4430363	10.5290679	f=U	H	16.4464425	9.0022685	10.9946364	f=U
C	7.4777847	5.9633618	13.1704677	f=U	H	17.4630052	10.2261678	10.2276067	f=U
H	6.4876781	5.6046543	12.8780991	f=U	H	15.8179199	9.9548450	9.6445553	f=U
H	7.3622998	6.9872296	13.5318342	f=U	C	17.3648884	9.3733850	16.1341247	f=U
H	7.8299581	5.3480955	14.0018572	f=U	H	16.4718301	8.7616463	15.9910548	f=U
C	8.4539888	4.4440075	11.4745932	f=U	C	18.5702046	8.4333869	16.1724097	f=U
H	9.0968831	4.3240268	10.5991082	f=U	H	18.6555576	7.8490821	15.2572107	f=U
H	7.4433857	4.1532997	11.1803993	f=U	H	18.4762324	7.7339345	17.0065442	f=U
H	8.7837445	3.7442284	12.2464610	f=U	H	19.4997500	8.9918326	16.3103739	f=U
C	18.4863186	5.6656603	12.0377325	f=U	C	17.2415441	10.0901175	17.4769903	f=U
H	18.9881421	6.5088337	10.8587986	f=U	H	17.1033516	9.3630039	18.2805042	f=U
H	19.0965641	7.5610272	11.1309185	f=U	H	16.3937546	10.7770891	17.5005999	f=U
H	18.2996336	6.4479457	10.0124772	f=U	H	18.1402206	10.6649430	17.7121421	f=U
H	19.9653575	6.1483343	10.5274803	f=U	C	13.4931435	9.2830186	16.8053328	f=U
C	19.4892647	5.7671788	13.1915918	f=U	H	14.3816515	9.7454179	17.2697837	f=U
H	19.6540149	6.8018053	13.4986825	f=U	H	12.6316977	9.8147787	17.2471611	f=U
H	20.4560660	5.3615223	12.8833908	f=U	C	14.9126528	6.5317840	16.9803795	f=U
H	19.1473189	5.2033597	14.0628291	f=U	H	14.8187365	5.5078077	17.3538912	f=U
C	18.4249925	4.2074922	11.5900877	f=U	H	15.8303965	6.9446519	17.4074739	f=U
H	17.7678338	4.0709094	10.7278683	f=U	H	15.0428410	6.4776692	15.8967079	f=U
H	18.0861434	3.5483540	12.3932988	f=U	C	11.8474905	6.6589310	16.9367496	f=U
H	19.4228595	3.8776437	11.2937161	f=U	H	11.8420964	5.6339427	17.3191504	f=U
C	10.5226752	10.4095246	13.7394240	f=U	H	11.7489874	6.6064370	15.8496706	f=U
C	10.3924842	11.1763814	12.5587559	f=U	H	10.9543500	7.1515076	17.3302000	f=U
C	9.4745988	12.2211291	12.5401612	f=U	C	13.3884479	7.6116642	19.3749136	f=U
H	9.3631736	12.8172040	11.6410803	f=U	H	13.3422745	6.6090710	19.8097699	f=U
C	8.6829065	12.5007577	13.6402780	f=U	H	12.5222756	8.1700561	19.7406040	f=U
H	7.9697568	13.3162732	13.6040570	f=U	H	14.2860040	8.0995391	19.7649674	f=U
C	8.7817089	11.7146781	14.7742515	f=U	C	14.9635327	13.0048072	15.1370528	f=B
H	8.1297067	11.9162214	15.6167982	f=U	H	16.0276938	13.0028906	14.9293386	f=B
C	9.6845539	10.6577207	14.8487296	f=U	C	14.0518998	13.2555576	14.1108529	f=B
C	11.1667063	10.8589817	11.2945455	f=U	H	14.4129924	13.4643714	13.1114026	f=B
H	11.8752658	10.0584404	11.5264475	f=U	C	12.6851956	13.2744506	14.3762951	f=B

H	11.9749179	13.4871561	13.5868063	f=B	H	12.7760406	12.5675868	17.6921270	f=B
C	12.2238385	13.0253003	15.6668106	f=B	C	14.4981855	12.7588473	16.4235351	f=B
H	11.1596929	13.0395968	15.8654698	f=B	H	15.2011788	12.5782390	17.2268758	f=B
C	13.1300729	12.7600194	16.6864401	f=B					

### Optimised geometry of $\eta^6$ -2'-Th and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	6.448660	8.349540	15.663848	f=B	C	8.059835	16.032898	16.559612	f=U
C	7.300386	9.148847	14.911264	f=B	C	2.373532	14.098188	13.786825	f=U
C	6.925039	10.448375	14.570928	f=B	H	10.152131	10.330023	23.888875	f=U
C	5.699877	10.954523	14.987350	f=B	H	8.450525	7.308436	21.378778	f=U
C	4.845149	10.153568	15.744930	f=B	H	6.221636	15.391464	19.216544	f=U
C	5.217007	8.854583	16.079916	f=B	H	8.801289	15.121396	22.622734	f=U
H	8.256217	8.763558	14.578559	f=B	H	10.459639	12.330648	24.238107	f=U
Th	7.164431	10.644975	17.851354	f=U	H	10.002900	13.958665	23.806240	f=U
C	9.379337	10.971753	16.902655	f=U	H	8.744294	12.767600	24.174469	f=U
O	8.269407	11.505852	19.921606	f=U	H	11.824988	12.142624	22.141416	f=U
C	8.688510	10.620761	20.908436	f=U	H	11.103007	12.465198	20.558827	f=U
C	9.324873	11.041861	22.054830	f=U	H	11.358488	13.796020	21.696255	f=U
C	9.682854	12.512835	22.223304	f=U	H	8.428081	17.782964	19.900585	f=U
C	8.678455	13.348153	21.439599	f=U	H	6.782925	17.546487	19.293858	f=U
C	8.078501	12.823486	20.321152	f=U	H	7.112413	18.826152	20.456160	f=U
C	8.365939	9.300966	20.626994	f=U	H	4.984813	16.574685	20.818948	f=U
C	8.713481	8.339491	21.572384	f=U	H	5.357082	16.227597	22.511691	f=U
C	9.353649	8.701681	22.755722	f=U	H	5.286129	17.901841	21.943617	f=U
C	9.650656	10.046886	22.973504	f=U	H	8.933574	17.373606	22.393645	f=U
C	8.355137	14.672802	21.748207	f=U	H	7.546741	18.388853	22.782707	f=U
C	7.480591	15.423653	20.971475	f=U	H	7.650387	16.766923	23.457643	f=U
C	6.917940	14.836237	19.833472	f=U	H	11.640703	8.634550	24.297409	f=U
C	7.203610	13.520925	19.493551	f=U	H	11.550679	6.930088	24.745862	f=U
C	9.736427	7.670919	23.817652	f=U	H	11.756464	7.390254	23.049753	f=U
C	9.081644	8.043433	25.153185	f=U	H	8.200520	6.195917	23.330624	f=U
N	7.699676	9.092247	19.423501	f=U	H	9.755592	5.905573	22.528094	f=U
C	7.296067	7.779314	19.050671	f=U	H	9.569888	5.568591	24.244652	f=U
C	8.212604	6.884735	18.461359	f=U	H	7.992544	8.059968	25.064985	f=U
C	7.754086	5.636466	18.050225	f=U	H	9.348778	7.310570	25.918811	f=U
C	6.433287	5.239485	18.194469	f=U	H	9.404244	9.024079	25.507326	f=U
C	5.549754	6.133385	18.792223	f=U	H	8.457690	4.940785	17.603033	f=U
C	5.948273	7.386616	19.238601	f=U	H	4.518457	5.831085	18.931744	f=U
N	6.689588	12.792345	18.424627	f=U	H	5.219483	9.316942	19.783169	f=U
C	5.804834	13.415369	17.499156	f=U	H	4.397689	8.719048	22.029836	f=U
C	4.411124	13.178389	17.596127	f=U	H	4.869599	7.036302	21.762049	f=U
C	3.571541	13.739065	16.642895	f=U	H	6.105086	8.298043	21.846915	f=U
C	4.046292	14.544896	15.611789	f=U	H	2.880197	8.812384	20.072817	f=U
C	5.411699	14.775050	15.549290	f=U	H	3.345861	8.153629	18.502933	f=U
C	6.308386	14.229095	16.463696	f=U	H	3.132745	7.088407	19.893355	f=U
C	7.088977	16.853075	21.347217	f=U	H	9.832313	8.249140	18.605377	f=U
C	7.854314	17.363808	22.565489	f=U	H	10.302822	6.411946	20.214725	f=U
C	9.714309	12.913093	23.695877	f=U	H	10.466955	5.272560	18.873125	f=U
C	11.079816	12.742952	21.614541	f=U	H	11.611734	6.604369	19.047000	f=U
C	9.681194	7.215740	18.284940	f=U	H	9.526918	7.732119	16.168719	f=U
C	10.126998	7.102465	16.828350	f=U	H	11.169676	7.411654	16.726623	f=U
C	5.978854	3.873659	17.737045	f=U	H	10.053588	6.074735	16.464599	f=U
C	4.915656	3.964707	16.644952	f=U	H	6.854906	3.374881	17.308324	f=U
C	4.961000	8.267096	19.984546	f=U	H	6.253572	2.933285	19.681652	f=U
C	3.505638	8.065806	19.579893	f=U	H	4.597109	3.460537	19.367043	f=U
C	3.819112	12.378437	18.744211	f=U	H	5.227143	2.020410	18.567851	f=U
C	2.457881	11.761962	18.444061	f=U	H	5.272237	4.536188	15.784462	f=U
C	3.108121	15.160683	14.601050	f=U	H	4.641388	2.967195	16.294703	f=U
C	2.122265	16.121320	15.262480	f=U	H	4.005624	4.444141	17.016024	f=U
C	7.782213	14.549984	16.314864	f=U	H	2.505624	13.557923	16.711566	f=U
C	8.319906	14.149930	14.942119	f=U	H	5.794312	15.410401	14.756373	f=U
C	7.371238	17.801557	20.177554	f=U	H	4.509890	11.552785	18.975309	f=U
C	5.590301	16.887479	21.672558	f=U	H	3.298689	12.635573	20.832968	f=U
C	11.260601	7.659871	23.985513	f=U	H	4.681936	13.614883	20.330078	f=U
C	9.285294	6.260050	23.448736	f=U	H	3.048178	14.075460	19.840086	f=U
C	5.098534	8.071927	21.496682	f=U	H	2.443194	11.181806	17.518788	f=U
C	10.562128	6.323028	19.159695	f=U	H	2.166043	11.098397	19.259802	f=U
C	5.488537	3.024870	18.908129	f=U	H	1.681735	12.526691	18.367518	f=U
C	3.715116	13.226717	20.013531	f=U	H	8.328201	13.979937	17.070267	f=U

A.1. Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 125  
Exploration of the bonding

H	9.130050	16.234179	16.471880	f=U	H	1.498399	16.605965	14.508211	f=U
H	7.543497	16.656840	15.825489	f=U	H	1.457184	15.594541	15.951904	f=U
H	7.742040	16.343841	17.554241	f=U	H	9.871404	10.025805	16.646618	f=U
H	9.397846	14.319703	14.894657	f=U	H	9.413709	11.606802	16.011060	f=U
H	8.138224	13.095654	14.726289	f=U	H	10.003158	11.456396	17.663952	f=U
H	7.860456	14.737197	14.143512	f=U	H	7.590831	11.058690	13.973750	f=B
H	3.726010	15.742515	13.908517	f=U	H	5.407176	11.967868	14.736753	f=B
H	3.071820	13.431188	13.275369	f=U	H	3.884992	10.544719	16.056569	f=B
H	1.726274	13.487868	14.422540	f=U	H	4.550204	8.224420	16.654750	f=B
H	1.741605	14.566840	13.029173	f=U	H	6.736682	7.341461	15.938480	f=B
H	2.640904	16.899829	15.825484	f=U					

Optimised geometry of  $\eta^6$ -3-Th-endo and the name of the fragment f in the ETS-  
NOCV in which each atom belongs

Th	26.469113	25.919467	3.054570	f=Th	C	23.437643	26.045708	3.736822	f=Th
Si	26.498129	23.187135	0.209239	f=Th	C	23.193232	26.811633	4.899734	f=Th
O	26.545771	23.688876	4.136458	f=Th	C	22.251709	27.832567	4.840704	f=Th
N	24.479648	25.075114	3.757777	f=Th	H	22.052590	28.425707	5.726678	f=Th
N	28.517924	25.221841	3.760973	f=Th	C	21.550486	28.094794	3.676630	f=Th
C	24.105598	21.278497	5.415433	f=Th	H	20.820296	28.895638	3.649621	f=Th
H	24.052209	20.284913	5.836461	f=Th	C	21.758117	27.308521	2.557807	f=Th
C	22.935505	22.003301	5.237570	f=Th	H	21.170142	27.492155	1.666019	f=Th
C	23.021269	23.288249	4.689001	f=Th	C	22.679653	26.264577	2.564402	f=Th
H	22.129472	23.886926	4.549660	f=Th	C	22.752016	25.336264	1.369209	f=Th
C	24.244585	23.822236	4.316302	f=Th	H	23.644763	24.718343	1.483349	f=Th
C	28.834930	23.976126	4.298954	f=Th	C	21.543678	24.396568	1.366107	f=Th
C	30.095976	23.511931	4.639610	f=Th	H	21.603724	23.704147	0.522898	f=Th
H	30.946854	24.165120	4.489640	f=Th	H	21.492525	23.805016	2.280166	f=Th
C	30.271912	22.231574	5.176165	f=Th	H	20.611991	24.960193	1.271014	f=Th
C	29.152555	21.435039	5.371738	f=Th	C	22.833622	26.056432	0.026414	f=Th
H	29.274497	20.444078	5.784788	f=Th	H	22.931493	25.326972	-0.780787	f=Th
C	26.640519	20.976713	5.274151	f=Th	H	21.934328	26.641345	-0.179127	f=Th
C	25.365650	21.783038	5.072275	f=Th	H	23.689098	26.732023	-0.040362	f=Th
C	25.380943	23.041064	4.525425	f=Th	C	23.882047	26.522059	6.217689	f=Th
C	27.754998	23.120629	4.514888	f=Th	H	24.563594	25.682679	6.062735	f=Th
C	27.858350	21.862623	5.053187	f=Th	C	22.873655	26.093737	7.283140	f=Th
C	26.668153	19.821188	4.259757	f=Th	H	23.391056	25.834750	8.209990	f=Th
H	25.803826	19.169318	4.401271	f=Th	H	22.169142	26.897423	7.509556	f=Th
H	26.648363	20.196642	3.234743	f=Th	H	22.301963	25.222208	6.962220	f=Th
H	27.572801	19.223325	4.386791	f=Th	C	24.703823	27.707821	6.711773	f=Th
C	26.670432	20.405166	6.697648	f=Th	H	25.221499	27.453694	7.639612	f=Th
H	26.651614	21.203516	7.441974	f=Th	H	25.456603	28.016314	5.981290	f=Th
H	25.815150	19.752300	6.873370	f=Th	H	24.071507	28.575248	6.916668	f=Th
H	27.568157	19.807784	6.858219	f=Th	C	29.534589	26.220856	3.708390	f=Th
C	21.565837	21.440444	5.616069	f=Th	C	29.742928	27.052520	4.833574	f=Th
C	20.892009	22.367916	6.633781	f=Th	C	30.701983	28.055733	4.751219	f=Th
H	19.915904	21.967019	6.917791	f=Th	H	30.877429	28.696796	5.607479	f=Th
H	21.495885	22.461869	7.539534	f=Th	C	31.453602	28.241287	3.604421	f=Th
H	20.728952	23.368796	6.228016	f=Th	H	32.200623	29.025774	3.564420	f=Th
C	20.690088	21.347737	4.361113	f=Th	C	31.264721	27.406359	2.519459	f=Th
H	21.148432	20.701537	3.608780	f=Th	H	31.876719	27.539654	1.634518	f=Th
H	19.711579	20.932108	4.615291	f=Th	C	30.319452	26.384784	2.546155	f=Th
H	20.524517	22.327814	3.909266	f=Th	C	30.216109	25.460988	1.351702	f=Th
C	21.661712	20.047701	6.233881	f=Th	H	29.349086	24.815817	1.506254	f=Th
H	22.092698	19.321863	5.540052	f=Th	C	31.446241	24.558303	1.250698	f=Th
H	22.256036	20.047567	7.150917	f=Th	H	31.355726	23.889038	0.391749	f=Th
H	20.660483	19.696860	6.492125	f=Th	H	32.356540	25.148614	1.117881	f=Th
C	31.679939	21.758846	5.537326	f=Th	H	31.566469	23.942200	2.141915	f=Th
C	31.690734	20.333640	6.084065	f=Th	C	30.025468	26.218907	0.039455	f=Th
H	31.307353	19.614486	5.356066	f=Th	H	29.851268	25.518546	-0.780545	f=Th
H	32.716728	20.044169	6.320659	f=Th	H	29.177639	26.906995	0.078308	f=Th
H	31.106100	20.243909	7.002891	f=Th	H	30.910057	26.805036	-0.220261	f=Th
C	32.268408	22.686666	6.606896	f=Th	C	29.008315	26.849444	6.143433	f=Th
C	32.339373	23.718410	6.255516	f=Th	H	28.164802	26.176540	5.954794	f=Th
H	31.657825	22.678132	7.513038	f=Th	C	29.909590	26.164717	7.172527	f=Th
H	33.276153	22.359312	6.874867	f=Th	H	30.266565	25.198930	6.815215	f=Th
C	32.571260	21.798332	4.290836	f=Th	H	30.778685	26.788618	7.397685	f=Th
H	32.672828	22.810963	3.895951	f=Th	H	29.364612	26.001022	8.105411	f=Th
H	33.574293	21.439714	4.535737	f=Th	C	28.457855	28.149350	6.722713	f=Th
H	32.168149	21.163421	3.498296	f=Th	H	27.861080	27.941690	7.613142	f=Th

H	29.258894	28.827417	7.024926 f=Th	H	25.048904	21.204938	0.430768 f=Th
H	27.826359	28.679312	6.006731 f=Th	C	26.827615	28.441463	1.316750 f=A
C	26.484300	24.957442	0.858341 f=Th	H	27.085837	27.949098	0.386075 f=A
H	25.609820	25.448510	0.394133 f=Th	C	27.820063	28.983913	2.131822 f=A
H	27.365781	25.442901	0.403947 f=Th	H	28.865567	28.874316	1.869306 f=A
C	28.047737	22.290222	0.770925 f=Th	C	27.470234	29.689727	3.274113 f=A
H	28.154622	22.260180	1.858087 f=Th	H	28.253011	30.128912	3.882477 f=A
H	28.022145	21.257050	0.412318 f=Th	C	26.133457	29.867310	3.638993 f=A
H	28.950212	22.749567	0.359284 f=Th	C	25.150973	29.272326	2.846033 f=A
C	26.484766	23.216983	-1.668929 f=Th	H	24.105505	29.373111	3.116053 f=A
H	26.497324	22.202336	-2.077350 f=Th	C	25.490418	28.582979	1.686483 f=A
H	25.591738	23.716558	-2.054552 f=Th	H	24.702520	28.189350	1.055050 f=A
H	27.356506	23.743600	-2.067007 f=Th	C	25.764723	30.726492	4.805827 f=A
C	24.987683	22.236778	0.789041 f=Th	H	24.755135	30.515800	5.157193 f=A
H	24.893503	22.203574	1.877209 f=Th	H	26.459298	30.603577	5.638495 f=A
H	24.064604	22.661076	0.385989 f=Th	H	25.799387	31.780010	4.512007 f=A

### Optimised geometry of $\eta^6$ -4-Th-endo and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	-0.405504	20.474935	6.472660 f=B	C	-5.051963	11.934404	1.913275 f=Th
H	-0.451964	19.897584	7.391840 f=B	H	-4.461375	11.881833	0.995315 f=Th
C	-1.580961	20.887258	5.843236 f=B	H	-6.056915	11.579727	1.675306 f=Th
H	-2.548584	20.589392	6.230125 f=B	H	-4.624376	11.241402	2.642110 f=Th
C	-1.525375	21.714859	4.730646 f=B	C	4.991460	13.666076	2.472793 f=Th
H	-2.437800	22.049040	4.254497 f=B	C	5.605641	14.606920	1.429624 f=Th
C	-0.289387	22.128361	4.248432 f=B	H	6.611113	14.269476	1.165878 f=Th
C	0.890761	21.705107	4.846807 f=B	H	5.689967	15.629811	1.802986 f=Th
H	1.848502	22.028407	4.460721 f=B	H	5.005237	14.626711	0.516798 f=Th
C	0.828943	20.882566	5.963866 f=B	C	5.863277	13.672319	3.733919 f=Th
H	1.751910	20.590332	6.451028 f=B	H	5.445883	13.018721	4.503511 f=Th
Br	-0.214734	23.294165	2.778681 f=B	H	5.958830	14.674531	4.156801 f=Th
O	-0.137029	15.618435	3.854669 f=Th	H	6.869528	13.318038	3.496458 f=Th
Th	-0.207254	17.846730	4.922957 f=Th	C	4.995106	12.251723	1.898777 f=Th
Si	-0.118522	15.157580	7.798293 f=Th	H	4.601785	11.521239	2.610039 f=Th
N	-2.193952	17.020068	4.221336 f=Th	H	6.020457	11.958932	1.663655 f=Th
N	1.830457	17.131702	4.248284 f=Th	H	4.415627	12.184283	0.974691 f=Th
C	-2.590922	13.195811	2.629948 f=Th	C	-3.237475	17.989542	4.256989 f=Th
H	-2.649661	12.196827	2.222161 f=Th	C	-4.030672	18.149565	5.415555 f=Th
C	-3.759238	13.920825	2.819720 f=Th	C	-5.001467	19.147346	5.425738 f=Th
C	-3.667255	15.213281	3.349689 f=Th	H	-5.621181	19.275276	6.305987 f=Th
H	-4.558044	15.812622	3.494180 f=Th	C	-5.207280	19.962933	4.328997 f=Th
C	-2.438551	15.756988	3.687913 f=Th	H	-5.976300	20.726544	4.355224 f=Th
C	2.153015	15.892179	3.702890 f=Th	C	-4.442450	19.787016	3.189331 f=Th
C	3.412718	15.428971	3.359864 f=Th	H	-4.626331	20.416672	2.326806 f=Th
H	4.264951	16.080615	3.510567 f=Th	C	-3.455403	18.810081	3.123461 f=Th
C	3.584121	14.146308	2.825456 f=Th	C	-2.699432	18.621235	1.823636 f=Th
C	2.462686	13.351421	2.632720 f=Th	H	-1.814047	18.009960	2.034213 f=Th
H	2.583210	12.359043	2.22378 f=Th	C	-3.546606	17.848541	0.810246 f=Th
C	-0.052978	12.900052	2.731413 f=Th	H	-3.840670	16.870516	1.190998 f=Th
C	-1.326425	13.706023	2.946988 f=Th	H	-2.986463	17.698609	-0.115853 f=Th
C	-1.306004	14.970620	3.477839 f=Th	H	-4.453714	18.407897	0.566263 f=Th
C	1.070082	15.041016	3.483720 f=Th	C	-2.233279	19.937665	1.209300 f=Th
C	1.168536	13.781983	2.949052 f=Th	H	-3.075021	20.541094	0.863108 f=Th
C	-0.017853	11.736482	3.735730 f=Th	H	-1.603845	19.742514	0.338989 f=Th
H	-0.029700	12.103119	4.763913 f=Th	H	-1.658794	20.545727	1.911388 f=Th
H	0.885644	11.139244	3.596541 f=Th	C	-3.908763	17.243891	6.622137 f=Th
H	-0.882813	11.084915	3.595519 f=Th	H	-3.024594	16.619234	6.479860 f=Th
C	-0.034995	12.340189	1.302920 f=Th	C	-5.115906	16.310986	6.727828 f=Th
H	-0.892939	11.689904	1.129312 f=Th	H	-6.041430	16.878823	6.853081 f=Th
H	0.861273	11.743464	1.130502 f=Th	H	-5.010901	15.650904	7.592229 f=Th
H	-0.059071	13.144276	0.565289 f=Th	H	-5.217683	15.685165	5.840912 f=Th
C	-5.133420	13.357466	2.459291 f=Th	C	-3.743717	18.023576	7.925264 f=Th
C	-6.023893	13.339843	3.706953 f=Th	H	-2.909258	18.729106	7.886016 f=Th
H	-5.581815	12.728508	4.497247 f=Th	H	-3.560794	17.337950	8.755902 f=Th
H	-7.003768	12.922166	3.462486 f=Th	H	-4.642262	18.594119	8.171093 f=Th
H	-6.185632	14.343492	4.105414 f=Th	C	2.801737	18.172617	4.277836 f=Th
C	-5.780717	14.244655	1.389207 f=Th	C	2.987104	18.971199	3.124594 f=Th
H	-5.918110	15.270121	1.739052 f=Th	C	3.880039	20.034852	3.186067 f=Th
H	-6.765218	13.852638	1.121674 f=Th	H	4.035063	20.650536	2.307169 f=Th
H	-5.170988	14.274494	0.482843 f=Th	C	4.586737	20.313735	4.342532 f=Th

A.1. Geometries from the Chapter Coordination of Alkyl cations  $[(XA_2)X(CH_2Y)]$   
 ( $X = Th, U$  or  $Zr$ ;  $Y = SiMe_3, H$ ) with an arene for Ethylene polymerisation: 127  
 Exploration of the bonding

H	5.281749	21.145330	4.368413 f=Th	C	3.290381	18.176866	0.766672 f=Th
C	4.424848	19.510406	5.456396 f=Th	H	4.036423	18.942970	0.540609 f=Th
H	5.008658	19.715130	6.346571 f=Th	H	2.773134	17.930509	-0.163594 f=Th
C	3.550639	18.426862	5.449285 f=Th	H	3.813374	17.283323	1.109274 f=Th
C	3.499367	17.521187	6.661331 f=Th	C	-0.186655	16.922252	7.134223 f=Th
H	2.662577	16.833095	6.525282 f=Th	H	0.666802	17.451565	7.594321 f=Th
C	4.772863	16.678442	6.753621 f=Th	H	-1.089616	17.373716	7.581814 f=Th
H	4.912909	16.065453	5.862802 f=Th	C	1.445115	14.287914	7.233342 f=Th
H	4.723898	16.009073	7.615874 f=Th	H	1.548189	14.256041	6.145824 f=Th
H	5.654796	17.312999	6.873193 f=Th	H	1.438215	13.255484	7.595246 f=Th
C	3.289628	18.282035	7.968393 f=Th	H	2.341017	14.763455	7.640635 f=Th
H	4.139740	18.926328	8.203837 f=Th	C	-0.122014	15.200019	9.675767 f=Th
H	3.179184	17.580687	8.798633 f=Th	H	0.740214	15.748334	10.065100 f=Th
H	2.396106	18.911775	7.947592 f=Th	H	-0.084483	14.188510	10.090308 f=Th
C	2.292167	18.676893	1.811438 f=Th	H	-1.023474	15.682360	10.063522 f=Th
H	1.574111	17.869313	1.983082 f=Th	C	-1.613888	14.177721	7.228798 f=Th
C	1.528826	19.884834	1.276874 f=Th	H	-2.542246	14.587068	7.635410 f=Th
H	0.798356	20.263812	1.996235 f=Th	H	-1.533799	13.147503	7.588106 f=Th
H	0.994162	19.621003	0.361992 f=Th	H	-1.712607	14.141432	6.140946 f=Th
H	2.200758	20.710783	1.033392 f=Th				

Optimised geometry of  $\eta^6$ -5-Th-endo and the name of the fragment f in the ETS-  
 NOCV in which each atom belongs

O	-0.113290	15.647010	3.880077 f=Th	H	4.960728	14.632329	0.470099 f=Th
Th	-0.166280	17.900891	4.905746 f=Th	C	5.885668	13.677860	3.668690 f=Th
Si	-0.087969	15.235443	7.805776 f=Th	H	5.484188	13.024211	4.446653 f=Th
N	-2.165704	17.090403	4.182502 f=Th	H	5.989379	14.680056	4.089744 f=Th
N	1.866667	17.148530	4.243142 f=Th	H	6.886933	13.323698	3.410802 f=Th
C	-2.582531	13.236490	2.659033 f=Th	C	4.978106	12.256545	1.852919 f=Th
H	-2.647753	12.231946	2.266731 f=Th	H	4.600553	11.526823	2.573438 f=Th
C	-3.744286	13.977853	2.822147 f=Th	H	5.997753	11.962887	1.595146 f=Th
C	-3.642578	15.277400	3.331435 f=Th	H	4.377755	12.188769	0.942284 f=Th
H	-4.527883	15.890055	3.450659 f=Th	C	-3.232968	18.037255	4.205087 f=Th
C	-2.411730	15.815317	3.675216 f=Th	C	-4.047439	18.169601	5.351552 f=Th
C	2.177651	15.904927	3.703822 f=Th	C	-5.047945	19.137940	5.350668 f=Th
C	3.429527	15.439816	3.335895 f=Th	H	-5.683965	19.244069	6.222313 f=Th
H	4.284286	16.093500	3.460955 f=Th	C	-5.262442	19.950175	4.253546 f=Th
C	3.589099	14.153768	2.806751 f=Th	H	-6.053750	20.690938	4.270148 f=Th
C	2.463456	13.358168	2.644887 f=Th	C	-4.477767	19.797994	3.123648 f=Th
H	2.575219	12.362194	2.241297 f=Th	H	-4.670010	20.423302	2.259974 f=Th
C	-0.051179	12.912731	2.797166 f=Th	C	-3.461474	18.850414	3.068484 f=Th
C	-1.316937	13.737753	2.983853 f=Th	C	-2.686820	18.683362	1.775485 f=Th
C	-1.287019	15.010633	3.495873 f=Th	H	-1.760730	18.142998	2.005339 f=Th
C	1.087975	15.057754	3.505926 f=Th	C	-3.470813	17.825691	0.779073 f=Th
C	1.175797	13.793946	2.980461 f=Th	H	-3.694297	16.837867	1.180846 f=Th
C	-0.022519	11.789710	3.847225 f=Th	H	-2.897702	17.696742	-0.142317 f=Th
H	-0.029347	12.196750	4.860118 f=Th	H	-4.415323	18.311951	0.520501 f=Th
H	0.876608	11.181124	3.729836 f=Th	C	-2.312948	20.009436	1.119460 f=Th
H	-0.893001	11.140054	3.734421 f=Th	H	-3.194104	20.538000	0.749816 f=Th
C	-0.040024	12.295266	1.392980 f=Th	H	-1.669647	19.828636	0.256191 f=Th
H	-0.902325	11.644219	1.247149 f=Th	H	-1.782123	20.680727	1.796939 f=Th
H	0.850499	11.684131	1.243645 f=Th	C	-3.918135	17.263826	6.558240 f=Th
H	-0.059345	13.068393	0.622849 f=Th	H	-3.021209	16.656145	6.422648 f=Th
C	-5.119217	13.426088	2.446149 f=Th	C	-5.108788	16.309217	6.655917 f=Th
C	-6.039502	13.454456	3.671479 f=Th	H	-6.045253	16.859893	6.776672 f=Th
H	-5.623928	12.862134	4.490162 f=Th	H	-4.996685	15.650719	7.520671 f=Th
H	-7.017604	13.039826	3.415047 f=Th	H	-5.194104	15.681975	5.768721 f=Th
H	-6.200833	14.471030	4.035639 f=Th	C	-3.777868	18.042059	7.864942 f=Th
C	-5.727284	14.295041	1.338655 f=Th	H	-2.946677	18.750839	7.837847 f=Th
H	-5.854070	15.331563	1.658642 f=Th	H	-3.603172	17.355608	8.696696 f=Th
H	-6.712233	13.912474	1.059194 f=Th	H	-4.683927	18.606127	8.098320 f=Th
H	-5.097090	14.290747	0.445920 f=Th	C	2.840200	18.187015	4.265407 f=Th
C	-5.047940	11.988066	1.939097 f=Th	C	3.047763	18.953298	3.095430 f=Th
H	-4.440792	11.902783	1.034528 f=Th	C	3.896610	20.052422	3.158550 f=Th
H	-6.053188	11.641543	1.690572 f=Th	H	4.059220	20.652462	2.270186 f=Th
H	-4.644479	11.308689	2.694082 f=Th	C	4.546634	20.388381	4.333813 f=Th
C	4.988060	13.671321	2.425766 f=Th	H	5.202499	21.250933	4.365176 f=Th
C	5.581391	14.610664	1.369169 f=Th	C	4.386708	19.598153	5.458293 f=Th
H	6.580098	14.271050	1.083497 f=Th	H	4.940889	19.840506	6.357663 f=Th
H	5.675937	15.633130	1.741149 f=Th	C	3.556916	18.479574	5.448482 f=Th



C	3.541588	17.557385	6.650437	f=Th	H	1.590072	14.320769	6.170590	f=Th
H	2.690467	16.882410	6.539847	f=Th	H	1.464248	13.327870	7.623986	f=Th
C	4.807905	16.696664	6.659002	f=Th	H	2.371390	14.832884	7.669985	f=Th
H	4.896362	16.103399	5.748857	f=Th	C	-0.097001	15.293656	9.683222	f=Th
H	4.792615	16.007682	7.506909	f=Th	H	0.763556	15.846266	10.070285	f=Th
H	5.701321	17.320076	6.749304	f=Th	H	-0.059517	14.285856	10.106740	f=Th
C	3.412374	18.278769	7.988585	f=Th	H	-1.000217	15.778226	10.064110	f=Th
H	4.275761	18.914900	8.195622	f=Th	C	-1.582102	14.249737	7.242728	f=Th
H	3.352749	17.549112	8.799206	f=Th	H	-2.510253	14.662636	7.646296	f=Th
H	2.518608	18.904182	8.048089	f=Th	H	-1.502411	13.222293	7.609940	f=Th
C	2.400678	18.593323	1.773874	f=Th	H	-1.681352	14.205223	6.155251	f=Th
H	1.888765	17.637203	1.900539	f=Th	C	-0.653737	20.458107	6.769763	f=F
C	1.363050	19.627863	1.350755	f=Th	H	-0.802646	20.044086	7.759425	f=F
H	0.560101	19.731821	2.088269	f=Th	C	-1.744219	20.879930	6.011475	f=F
H	0.901674	19.343836	0.402473	f=Th	H	-2.752289	20.766436	6.389852	f=F
H	1.808500	20.617403	1.223588	f=Th	C	-1.551659	21.460755	4.766006	f=F
C	3.442791	18.400287	0.673786	f=Th	H	-2.387660	21.804933	4.170855	f=F
H	3.967942	19.330621	0.445382	f=Th	C	-0.257589	21.607648	4.291723	f=F
H	2.959241	18.061882	-0.245333	f=Th	C	0.846552	21.174993	5.010291	f=F
H	4.185743	17.653395	0.957927	f=Th	H	1.845147	21.305425	4.609919	f=F
C	-0.160675	16.994646	7.128982	f=Th	C	0.637143	20.613982	6.267054	f=F
H	0.680462	17.537292	7.596724	f=Th	H	1.496325	20.321749	6.858551	f=F
H	-1.072379	17.438398	7.565636	f=Th	F	-0.068418	22.190126	3.114084	f=F
C	1.477541	14.358441	7.256920	f=Th					

### Optimised geometry of $\eta^1$ -5-Th-vertical and the name of the fragment f in the ETS-NOCV in which each atom belongs

F	3.119340	-0.636733	0.186344	f=F	C	11.521915	-2.305854	3.182466	f=Th
C	2.014853	-0.687149	1.035935	f=F	C	11.251282	-3.813960	3.113269	f=Th
C	1.700597	0.445550	1.745456	f=F	C	9.457161	2.164247	-5.645014	f=Th
C	0.593352	0.379012	2.581655	f=F	C	8.740421	3.508102	-5.823638	f=Th
C	-0.145619	-0.791110	2.675385	f=F	C	6.373052	0.122556	4.013963	f=Th
C	0.212898	-1.907548	1.933512	f=F	C	7.475555	0.022295	5.068638	f=Th
C	1.315831	-1.867080	1.090968	f=F	C	6.161005	-3.775823	0.668605	f=Th
H	-1.008557	-0.832425	3.328262	f=F	C	7.457071	-4.571961	0.836244	f=Th
H	0.310538	1.251594	3.157492	f=F	C	6.039514	-1.958288	-3.692289	f=Th
H	2.291261	1.348372	1.649296	f=F	C	5.447996	-3.309395	-3.300225	f=Th
H	1.616679	-2.720310	0.496932	f=F	C	4.234459	2.718295	-2.590626	f=Th
H	-0.367118	-2.819419	2.004548	f=F	C	4.590786	3.765419	-3.646902	f=Th
C	4.109276	1.348825	-3.220747	f=Th	C	5.380478	2.084610	0.936174	f=Th
C	5.101309	0.353378	-3.075817	f=Th	Si	6.586760	3.519221	1.137846	f=Th
C	4.981896	-0.877438	-3.766851	f=Th	C	5.733265	4.944052	2.014684	f=Th
C	3.868138	-1.085298	-4.570686	f=Th	C	8.068775	2.997617	2.165803	f=Th
C	2.884339	-0.121193	-4.700504	f=Th	C	7.185553	4.128737	-0.532651	f=Th
C	3.009147	1.080217	-4.030536	f=Th	C	13.006470	-2.074558	2.913146	f=Th
N	6.200583	0.550602	-2.193367	f=Th	C	11.209640	-1.801578	4.595647	f=Th
C	7.470551	0.855122	-2.671320	f=Th	C	10.952872	2.391555	-5.846906	f=Th
C	8.509243	0.643006	-1.763948	f=Th	C	8.972531	1.185563	-6.721003	f=Th
C	9.836814	0.844015	-2.042634	f=Th	C	5.227287	0.979348	4.552066	f=Th
C	10.123126	1.343938	-3.319057	f=Th	C	5.067161	-4.677179	0.106418	f=Th
C	9.135744	1.602238	-4.260843	f=Th	C	6.802168	-2.077842	-5.011726	f=Th
C	7.802587	1.338081	-3.925835	f=Th	C	2.973444	3.136102	-1.837771	f=Th
O	8.054338	0.176101	-0.536288	f=Th	H	12.224542	-0.790430	0.997994	f=Th
C	8.991264	-0.369642	0.333479	f=Th	H	8.797646	-2.244560	3.114924	f=Th
C	10.344190	-0.245064	0.146417	f=Th	H	7.009004	1.505719	-4.644286	f=Th
C	10.923629	0.553459	-1.015309	f=Th	H	11.155768	1.536107	-3.572384	f=Th
C	11.152432	-0.871807	1.102749	f=Th	H	10.691904	2.475491	-0.003748	f=Th
C	10.628904	-1.591390	2.168493	f=Th	H	11.903692	2.474509	-1.292638	f=Th
C	9.237881	-1.679481	2.302074	f=Th	H	12.260406	1.700796	0.259655	f=Th
C	8.397146	-1.065383	1.387935	f=Th	H	12.861150	-0.435421	-0.963686	f=Th
Th	5.638157	-0.067164	-0.105750	f=Th	H	12.497338	0.325262	-2.499861	f=Th
N	7.006346	-1.067641	1.375915	f=Th	H	11.700636	-1.192661	-2.063707	f=Th
C	6.241745	-1.808171	2.321446	f=Th	H	11.371860	-0.723895	4.674046	f=Th
C	5.901495	-1.245931	3.574189	f=Th	H	11.859943	-2.295894	5.321670	f=Th
C	5.120501	-1.993551	4.449196	f=Th	H	10.178051	-2.011493	4.885263	f=Th
C	4.665589	-3.253578	4.113293	f=Th	H	10.210704	-4.050631	3.345842	f=Th
C	4.984336	-3.792908	2.881007	f=Th	H	11.880578	-4.342493	3.833882	f=Th
C	5.771922	-3.098067	1.968828	f=Th	H	11.473106	-4.206509	2.117891	f=Th
C	11.477026	1.884262	-0.478818	f=Th	H	13.309291	-2.456498	1.935134	f=Th
C	12.059239	-0.237780	-1.675428	f=Th	H	13.597312	-2.600926	3.665640	f=Th

A.1. Geometries from the Chapter Coordination of Alkyl cations  $[(XA_2)X(CH_2Y)]$   
 ( $X = Th, U$  or  $Zr$ ;  $Y = SiMe_3, H$ ) with an arene for Ethylene polymerisation: 129  
 Exploration of the bonding

H	13.271260	-1.015787	2.970150 f=Th	H	2.023116	-0.304910	-5.332371 f=Th
H	9.199021	1.578924	-7.715184 f=Th	H	2.243110	1.837275	-4.151726 f=Th
H	7.893633	1.023996	-6.669715 f=Th	H	5.063609	2.682650	-1.880322 f=Th
H	9.466364	0.215883	-6.620761 f=Th	H	5.530565	3.525093	-4.146533 f=Th
H	9.062271	4.227903	-5.067339 f=Th	H	4.697625	4.751023	-3.187300 f=Th
H	7.655977	3.403263	-5.749219 f=Th	H	3.809476	3.834332	-4.408152 f=Th
H	8.965376	3.925969	-6.808159 f=Th	H	2.134978	3.306497	-2.516800 f=Th
H	11.356882	3.110821	-5.130232 f=Th	H	3.146004	4.070953	-1.299125 f=Th
H	11.126408	2.794355	-6.846933 f=Th	H	2.654951	2.379898	-1.114592 f=Th
H	11.522107	1.462210	-5.765337 f=Th	H	6.764722	-1.670735	-2.924705 f=Th
H	4.864216	-1.577139	5.416301 f=Th	H	4.858407	-3.246758	-2.382183 f=Th
H	4.059349	-3.818053	4.812273 f=Th	H	6.244384	-4.041422	-3.146204 f=Th
H	4.622356	-4.781875	2.630661 f=Th	H	4.792273	-3.702770	-4.080098 f=Th
H	6.371557	-2.996093	-0.078895 f=Th	H	6.129983	-2.365536	-5.824199 f=Th
H	8.282693	-3.938901	1.161342 f=Th	H	7.578559	-2.842665	-4.933536 f=Th
H	7.739590	-5.044894	-0.107411 f=Th	H	7.280938	-1.136547	-5.283185 f=Th
H	7.318435	-5.360952	1.580171 f=Th	H	4.495565	2.496989	0.419390 f=Th
H	4.910659	-5.557293	0.732995 f=Th	H	5.041364	1.824459	1.953486 f=Th
H	5.353072	-5.041284	-0.881110 f=Th	H	7.682408	3.350048	-1.117148 f=Th
H	4.108492	-4.159270	0.015172 f=Th	H	7.903993	4.941016	-0.388200 f=Th
H	6.796481	0.623345	3.140931 f=Th	H	6.366284	4.528934	-1.135367 f=Th
H	7.115790	-0.498071	5.960250 f=Th	H	4.873490	5.305651	1.443879 f=Th
H	7.798398	1.020792	5.373451 f=Th	H	6.416696	5.787062	2.151182 f=Th
H	8.348981	-0.508823	4.691395 f=Th	H	5.373528	4.646483	3.003464 f=Th
H	4.368458	0.995917	3.876609 f=Th	H	7.785475	2.771763	3.196918 f=Th
H	5.564066	2.007833	4.701832 f=Th	H	8.793504	3.816215	2.204449 f=Th
H	4.873618	0.614392	5.519097 f=Th	H	8.582200	2.121517	1.760960 f=Th
H	3.769718	-2.019910	-5.111020 f=Th				

Optimised geometry of  $\eta^1$ -6-Th-vertical and the name of the fragment f in the  
 ETS-NOCV in which each atom belongs

C	4.078764	1.565437	-3.050514 f=Th	C	5.852038	-1.814352	-3.616612 f=Th
C	5.030930	0.527165	-2.946449 f=Th	C	5.228428	-3.148810	-3.215530 f=Th
C	4.836050	-0.691409	-3.642015 f=Th	C	4.293886	2.930944	-2.434616 f=Th
C	3.684864	-0.846600	-4.403004 f=Th	C	4.639183	3.956515	-3.515604 f=Th
C	2.734396	0.156473	-4.485450 f=Th	C	5.620042	2.325287	1.011215 f=Th
C	2.934893	1.347033	-3.815138 f=Th	Si	6.938723	3.661012	1.147061 f=Th
N	6.162369	0.670264	-2.095322 f=Th	C	6.222560	5.169963	2.007215 f=Th
C	7.430896	0.913081	-2.610829 f=Th	C	8.392545	3.044094	2.163031 f=Th
C	8.483694	0.653722	-1.732622 f=Th	C	7.541505	4.189147	-0.550068 f=Th
C	9.810616	0.795029	-2.047467 f=Th	C	12.987905	-2.087212	2.931452 f=Th
C	10.084329	1.280235	-3.332383 f=Th	C	11.232233	-1.700966	4.634799 f=Th
C	9.084245	1.583530	-4.246690 f=Th	C	10.891620	2.283058	-5.885091 f=Th
C	7.749982	1.380733	-3.874439 f=Th	C	8.824362	1.189687	-6.703267 f=Th
O	8.040745	0.213266	-0.491716 f=Th	C	5.280708	1.189373	4.600252 f=Th
C	8.977886	-0.343145	0.370068 f=Th	C	5.014271	-4.569271	0.268321 f=Th
C	10.329551	-0.273421	0.150201 f=Th	C	6.557403	-1.948440	-4.966379 f=Th
C	10.913483	0.456930	-1.052797 f=Th	C	3.093561	3.407109	-1.620197 f=Th
C	11.136795	-0.894597	1.111143 f=Th	H	12.208586	-0.853680	0.980892 f=Th
C	10.612384	-1.557060	2.212713 f=Th	H	8.780525	-2.116841	3.216411 f=Th
C	9.222070	-1.594250	2.376417 f=Th	H	6.945245	1.587587	-4.569907 f=Th
C	8.383198	-0.984963	1.457557 f=Th	H	11.117635	1.425217	-3.613421 f=Th
Th	5.636555	0.132242	0.028979 f=Th	H	10.853809	2.414681	-0.087310 f=Th
N	6.993453	-0.939845	1.471774 f=Th	H	12.011851	2.297453	-1.419600 f=Th
C	6.220227	-1.657165	2.427791 f=Th	H	12.375117	1.540513	0.138528 f=Th
C	5.896511	-1.074947	3.675143 f=Th	H	12.777492	-0.666422	-1.048109 f=Th
C	5.097548	-1.794245	4.558420 f=Th	H	12.406044	0.081888	-2.590747 f=Th
C	4.613341	-3.046480	4.235518 f=Th	H	11.523895	-1.364632	-2.082675 f=Th
C	4.921946	-3.608331	3.009891 f=Th	H	11.427004	-0.626483	4.671786 f=Th
C	5.725620	-2.942906	2.090410 f=Th	H	11.881587	-2.188819	5.366067 f=Th
C	11.577514	1.758740	-0.574766 f=Th	H	10.200708	-1.869758	4.950247 f=Th
C	11.964343	-0.428668	-1.734546 f=Th	H	10.142049	-3.960210	3.481174 f=Th
C	11.502358	-2.263437	3.234948 f=Th	H	11.810755	-4.286365	3.951852 f=Th
C	11.185153	-3.763964	3.223550 f=Th	H	11.377434	-4.197386	2.239015 f=Th
C	9.392734	2.134550	-5.638229 f=Th	H	13.261049	-2.512648	1.962659 f=Th
C	8.743624	3.515727	-5.788870 f=Th	H	13.576756	-2.604336	3.691920 f=Th
C	6.407116	0.283407	4.103825 f=Th	H	13.284984	-1.035580	2.945536 f=Th
C	7.480844	0.158208	5.185059 f=Th	H	9.043208	1.575581	-7.702110 f=Th
C	6.103149	-3.642394	0.798155 f=Th	H	7.740150	1.087110	-6.621436 f=Th
C	7.408332	-4.425175	0.961629 f=Th	H	9.267039	0.193917	-6.621330 f=Th

H	9.127029	4.212860	-5.040090	f=Th	H	2.794779	2.680269	-0.859331	f=Th
H	7.658080	3.468032	-5.680088	f=Th	H	6.615762	-1.562552	-2.874836	f=Th
H	8.959433	3.926795	-6.778373	f=Th	H	4.691691	-3.081667	-2.266555	f=Th
H	11.354732	2.977804	-5.180085	f=Th	H	6.004046	-3.911970	-3.115653	f=Th
H	11.056027	2.679185	-6.889378	f=Th	H	4.521149	-3.503737	-3.968456	f=Th
H	11.412924	1.324563	-5.821879	f=Th	H	5.844227	-2.205432	-5.753937	f=Th
H	4.853451	-1.362474	5.522080	f=Th	H	7.308716	-2.740665	-4.924660	f=Th
H	3.993886	-3.589217	4.940224	f=Th	H	7.058284	-1.022465	-5.249815	f=Th
H	4.537993	-4.591784	2.770733	f=Th	H	4.747326	2.800377	0.530224	f=Th
H	6.292596	-2.874550	0.033839	f=Th	H	5.297204	2.117033	2.045484	f=Th
H	8.235989	-3.781799	1.258826	f=Th	H	7.979068	3.367171	-1.122148	f=Th
H	7.677063	-4.916187	0.023104	f=Th	H	8.307811	4.962700	-0.444202	f=Th
H	7.287128	-5.199781	1.723594	f=Th	H	6.732680	4.618500	-1.147378	f=Th
H	4.897848	-5.451873	0.900632	f=Th	H	5.381798	5.586728	1.445801	f=Th
H	5.283562	-4.928152	-0.726187	f=Th	H	6.974278	5.957904	2.109915	f=Th
H	4.042611	-4.074482	0.202487	f=Th	H	5.861564	4.923797	3.009556	f=Th
H	6.869724	0.754782	3.234024	f=Th	H	8.099523	2.844076	3.197231	f=Th
H	7.081457	-0.328732	6.078620	f=Th	H	9.175338	3.807654	2.193349	f=Th
H	7.839505	1.148091	5.477433	f=Th	H	8.837228	2.130146	1.760861	f=Th
H	8.338687	-0.417041	4.837217	f=Th	F	3.345025	-1.481475	-0.490926	f=F
H	4.450282	1.244452	3.892156	f=Th	C	2.119049	-1.320570	0.075798	f=F
H	5.655793	2.202610	4.762568	f=Th	C	1.980962	-0.294753	0.983390	f=F
H	4.876331	0.840262	5.553245	f=Th	C	0.784881	-0.050183	1.611934	f=F
H	3.529299	-1.770865	-4.947950	f=Th	C	-0.288853	-0.875503	1.301136	f=F
H	1.842714	0.012878	-5.084808	f=Th	C	-0.149713	-1.908246	0.384984	f=F
H	2.198488	2.137326	-3.904363	f=Th	C	1.067182	-2.143236	-0.243382	f=F
H	5.157083	2.863906	-1.768336	f=Th	H	-1.243297	-0.704784	1.782551	f=F
H	5.536758	3.669606	-4.065705	f=Th	H	0.701750	0.763088	2.321850	f=F
H	4.818721	4.936989	-3.067869	f=Th	F	3.078675	0.469421	1.224273	f=F
H	3.820816	4.060831	-4.232634	f=Th	H	1.200370	-2.939922	-0.964282	f=F
H	2.222873	3.591417	-2.253632	f=Th	H	-0.996023	-2.541678	0.151729	f=F
H	3.327995	4.346190	-1.113450	f=Th					

### Optimised geometry of $\eta^6$ -6-Th-exo and the name of the fragment f in the ETS-NOCV in which each atom belongs

Th	-0.281113	17.831764	4.911994	f=Th	C	5.026606	12.343647	1.875173	f=Th
C	-0.248155	16.989317	7.160963	f=Th	C	0.02478	11.756221	3.883116	f=Th
Si	-0.24196	15.23722	7.860108	f=Th	C	0.017556	12.207192	1.419024	f=Th
C	-1.754947	14.280659	7.296585	f=Th	C	-3.951601	17.358069	6.598062	f=Th
O	-0.164173	15.574553	3.903963	f=Th	C	-3.92761	18.122359	7.918485	f=Th
C	-1.318106	14.91378	3.501055	f=Th	C	-2.748502	18.370494	1.721278	f=Th
C	-1.312083	13.649344	2.969776	f=Th	C	-1.914368	19.539057	1.205064	f=Th
C	-0.022972	12.855171	2.808123	f=Th	C	2.075338	18.957791	1.92197	f=Th
C	1.179131	13.774005	2.984742	f=Th	C	2.849176	18.099312	0.918023	f=Th
C	1.054975	15.034538	3.512378	f=Th	C	3.497213	17.389482	6.607388	f=Th
C	-2.464197	15.689364	3.676764	f=Th	C	3.326807	18.101479	7.948185	f=Th
C	-3.676546	15.142323	3.290531	f=Th	C	1.303546	14.318728	7.321671	f=Th
C	-3.741652	13.848166	2.76099	f=Th	C	-0.260035	15.312201	9.736378	f=Th
C	-2.562585	13.130362	2.612753	f=Th	C	-6.001784	13.209024	3.609237	f=Th
C	2.47734	13.379133	2.641788	f=Th	C	-5.75538	14.166961	1.313112	f=Th
C	3.57822	14.209343	2.802916	f=Th	C	5.493951	14.7054	1.283616	f=Th
C	3.380938	15.488882	3.334663	f=Th	C	5.927876	13.874592	3.600798	f=Th
C	2.115015	15.92237	3.69658	f=Th	C	-3.751143	17.921202	0.658789	f=Th
C	-5.100945	13.269596	2.369893	f=Th	C	-5.146988	16.401185	6.586023	f=Th
C	-4.988055	11.860749	1.793468	f=Th	C	4.750558	16.514524	6.649415	f=Th
N	-2.241223	16.948176	4.2235	f=Th	C	1.699775	20.283493	1.26817	f=Th
C	-3.245783	17.954284	4.205437	f=Th	H	-2.602629	12.130476	2.205642	f=Th
C	-3.991708	18.246676	5.372253	f=Th	H	-4.575276	15.736566	3.404082	f=Th
C	-4.865779	19.330257	5.345308	f=Th	H	4.215594	16.169515	3.451285	f=Th
C	-5.040672	20.088579	4.20115	f=Th	H	2.619199	12.38852	2.234932	f=Th
C	-4.347868	19.763923	3.048091	f=Th	H	-0.004211	12.18446	4.886884	f=Th
C	-3.44775	18.704281	3.022264	f=Th	H	0.941742	11.170719	3.788102	f=Th
N	1.76643	17.166117	4.218433	f=Th	H	-0.826733	11.080924	3.775273	f=Th
C	2.732905	18.210672	4.294504	f=Th	H	-0.826217	11.530886	1.280256	f=Th
C	2.856484	19.118901	3.212685	f=Th	H	0.923554	11.614261	1.292158	f=Th
C	3.778295	20.154575	3.317757	f=Th	H	-0.012956	12.961481	0.630822	f=Th
C	4.572619	20.301384	4.440955	f=Th	H	-5.559367	12.580722	4.385874	f=Th
C	4.452285	19.408963	5.488504	f=Th	H	-6.975508	12.7884	3.345799	f=Th
C	3.542185	18.356762	5.444033	f=Th	H	-6.174942	14.199875	4.034494	f=Th
C	4.986747	13.778283	2.395037	f=Th	H	-5.927582	15.178463	1.687297	f=Th

A.1. Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 131  
Exploration of the bonding

H	-6.724998	13.756196	1.020849	f=Th	H	4.698659	15.819438	7.490939	f=Th
H	-5.133574	14.236883	0.41727	f=Th	H	5.649484	17.123481	6.775975	f=Th
H	-4.378992	11.838134	0.886366	f=Th	H	4.211344	18.687144	8.208871	f=Th
H	-5.982982	11.496944	1.52869	f=Th	H	3.177128	17.372161	8.74767	f=Th
H	-4.564572	11.157096	2.514345	f=Th	H	2.471649	18.781537	7.948544	f=Th
H	6.502625	14.412677	0.981197	f=Th	H	1.146756	18.416474	2.151127	f=Th
H	5.535299	15.746676	1.61056	f=Th	H	1.201931	20.969888	1.955569	f=Th
H	4.848104	14.652528	0.403747	f=Th	H	1.030363	20.104885	0.425196	f=Th
H	5.581759	13.242885	4.422376	f=Th	H	2.577412	20.795753	0.868861	f=Th
H	6.012054	14.898128	3.971398	f=Th	H	3.796011	18.582884	0.6631	f=Th
H	6.931326	13.545533	3.319558	f=Th	H	2.273597	17.98332	-0.003543	f=Th
H	4.695699	11.626595	2.630632	f=Th	H	3.068113	17.106852	1.310168	f=Th
H	6.052482	12.084893	1.605048	f=Th	H	0.643776	17.48359	7.584048	f=Th
H	4.412005	12.215142	0.980827	f=Th	H	-1.114091	17.499365	7.62023	f=Th
H	-5.44129	19.570313	6.231481	f=Th	H	1.42187	14.278972	6.235756	f=Th
H	-5.734165	20.921685	4.202689	f=Th	H	1.26273	13.288474	7.687351	f=Th
H	-4.512585	20.344411	2.147274	f=Th	H	2.206297	14.771139	7.740047	f=Th
H	-2.075264	17.529096	1.904839	f=Th	H	0.612141	15.845947	10.123696	f=Th
H	-4.329667	17.060317	0.996199	f=Th	H	-0.251521	14.307574	10.168866	f=Th
H	-3.228245	17.638182	-0.257597	f=Th	H	-1.152619	15.823456	10.107362	f=Th
H	-4.449483	18.723644	0.408664	f=Th	H	-2.677746	14.715474	7.688992	f=Th
H	-2.535591	20.406589	0.971254	f=Th	H	-1.698561	13.255714	7.675054	f=Th
H	-1.388597	19.255214	0.29084	f=Th	H	-1.84645	14.226011	6.208844	f=Th
H	-1.166225	19.866104	1.933001	f=Th	H	0.595273	20.216477	7.644759	f=F
H	-3.04863	16.747082	6.536484	f=Th	H	-1.724150	19.942888	6.795392	f=F
H	-6.088161	16.956609	6.613188	f=Th	H	-2.381466	20.956813	4.618841	f=F
H	-5.118174	15.746689	7.460443	f=Th	F	1.674463	22.764851	4.116384	f=F
H	-5.147701	15.77017	5.697109	f=Th	H	2.239873	21.564320	6.332672	f=F
H	-3.117166	18.853664	7.974199	f=Th	C	1.226557	21.414600	5.981901	f=F
H	-3.797397	17.424474	8.748503	f=Th	C	0.310571	20.648822	6.693492	f=F
H	-4.862626	18.657729	8.09746	f=Th	C	-0.983923	20.477976	6.209266	f=F
H	3.886251	20.857989	2.502037	f=Th	C	-1.370641	21.058694	4.999987	f=F
H	5.29168	21.110866	4.493911	f=Th	C	-0.455906	21.828848	4.306887	f=F
H	5.088496	19.52232	6.358975	f=Th	C	0.834873	22.010228	4.799450	f=F
H	2.640493	16.729379	6.457757	f=Th	F	-0.797031	22.418000	3.173317	f=F
H	4.861795	15.92641	5.738864	f=Th					

Optimised geometry of  $\eta^6$ -6-Th-side and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	3.5195	18.3662	5.4188	f=Th	C	-5.1084	13.2624	2.3482	f=Th
C	2.7095	18.2118	4.2703	f=Th	C	-5.7586	14.1606	1.2894	f=Th
C	2.8311	19.1136	3.1830	f=Th	C	4.9781	13.7740	2.3931	f=Th
C	3.7529	20.1500	3.2812	f=Th	C	5.9169	13.8740	3.6005	f=Th
C	4.5473	20.3045	4.4031	f=Th	C	-3.9619	17.3294	6.5874	f=Th
C	4.4278	19.4196	5.4563	f=Th	C	-5.1780	16.3993	6.5659	f=Th
N	1.7483	17.1617	4.2002	f=Th	C	-2.7521	18.3861	1.7234	f=Th
C	2.1015	15.9165	3.6854	f=Th	C	-3.7733	17.9355	0.6788	f=Th
C	1.0439	15.0252	3.5055	f=Th	C	2.0465	18.9466	1.8950	f=Th
C	1.1700	13.7640	2.9799	f=Th	C	1.6891	20.2710	1.2282	f=Th
C	2.4691	13.3710	2.6379	f=Th	C	3.4768	17.4061	6.5883	f=Th
C	3.5684	14.2038	2.7982	f=Th	C	4.7386	16.5444	6.6435	f=Th
C	3.3687	15.4847	3.3259	f=Th	C	-0.2605	16.9679	7.1552	f=Th
O	-0.1754	15.5628	3.8986	f=Th	Si	-0.2301	15.2151	7.8508	f=Th
C	-1.3279	14.9029	3.4919	f=Th	C	-0.2439	15.2851	9.7273	f=Th
C	-1.3210	13.6386	2.9604	f=Th	C	-1.7380	14.2495	7.2880	f=Th
C	-0.0314	12.8436	2.8055	f=Th	C	1.3214	14.3103	7.3068	f=Th
C	-2.5709	13.1211	2.5989	f=Th	C	-4.9949	11.8536	1.7718	f=Th
C	-3.7499	13.8398	2.7440	f=Th	C	-6.0135	13.2023	3.5845	f=Th
C	-3.6857	15.1336	3.2747	f=Th	C	5.0210	12.3385	1.8760	f=Th
C	-2.4739	15.6793	3.6644	f=Th	C	5.4858	14.6999	1.2809	f=Th
Th	-0.2921	17.8204	4.9105	f=Th	C	-3.9160	18.0764	7.9167	f=Th
N	-2.2490	16.9363	4.2129	f=Th	C	-1.9251	19.5511	1.1880	f=Th
C	-3.2448	17.9495	4.2049	f=Th	C	2.8050	18.0674	0.8976	f=Th
C	-3.9851	18.2377	5.3762	f=Th	C	3.2900	18.1265	7.9222	f=Th
C	-4.8335	19.3418	5.3692	f=Th	H	-2.6107	12.1214	2.1914	f=Th
C	-4.9881	20.1259	4.2400	f=Th	H	-4.5845	15.7280	3.3870	f=Th
C	-4.3056	19.8036	3.0799	f=Th	H	4.2016	16.1677	3.4402	f=Th
C	-3.4329	18.7221	3.0337	f=Th	H	2.6132	12.3799	2.2330	f=Th
C	0.0141	11.7507	3.8868	f=Th	H	-0.0171	12.1846	4.8881	f=Th
C	0.0124	12.1876	1.4204	f=Th	H	0.9315	11.1650	3.7971	f=Th

H	-0.8370	11.0745	3.7809 f=Th	H	5.2607	21.1187	4.4541 f=Th
H	-0.8307	11.5099	1.2838 f=Th	H	5.0586	19.5444	6.3287 f=Th
H	0.9189	11.5942	1.2991 f=Th	H	2.6277	16.7359	6.4386 f=Th
H	-0.0167	12.9370	0.6276 f=Th	H	4.8622	15.9527	5.7367 f=Th
H	-5.5740	12.5737	4.3626 f=Th	H	4.6885	15.8534	7.4885 f=Th
H	-6.9866	12.7823	3.3178 f=Th	H	5.6304	17.1633	6.7727 f=Th
H	-6.1875	14.1932	4.0093 f=Th	H	4.1622	18.7316	8.1793 f=Th
H	-5.9312	15.1721	1.6633 f=Th	H	3.1508	17.4015	8.7276 f=Th
H	-6.7276	13.7508	0.9939 f=Th	H	2.4232	18.7914	7.9122 f=Th
H	-5.1337	14.2303	0.3957 f=Th	H	1.1103	18.4218	2.1321 f=Th
H	-4.3829	11.8306	0.8667 f=Th	H	1.2185	20.9737	1.9187 f=Th
H	-5.9893	11.4907	1.5037 f=Th	H	1.0044	20.0966	0.3965 f=Th
H	-4.5744	11.1494	2.4939 f=Th	H	2.5718	20.7599	0.8112 f=Th
H	6.4953	14.4079	0.9806 f=Th	H	3.7592	18.5336	0.6379 f=Th
H	5.5253	15.7418	1.6060 f=Th	H	2.2269	17.9526	-0.0226 f=Th
H	4.8413	14.6446	0.4001 f=Th	H	3.0088	17.0751	1.2979 f=Th
H	5.5705	13.2427	4.4223 f=Th	H	0.6127	17.4848	7.5906 f=Th
H	5.9981	14.8982	3.9699 f=Th	H	-1.1450	17.4551	7.6034 f=Th
H	6.9216	13.5467	3.3216 f=Th	H	1.4371	14.2727	6.2205 f=Th
H	4.6902	11.6223	2.6323 f=Th	H	1.2899	13.2794	7.6716 f=Th
H	6.0478	12.0809	1.6080 f=Th	H	2.2214	14.7699	7.7231 f=Th
H	4.4080	12.2073	0.9810 f=Th	H	0.6247	15.8256	10.1133 f=Th
H	-5.4020	19.5802	6.2602 f=Th	H	-0.2251	14.2796	10.1573 f=Th
H	-5.6589	20.9772	4.2577 f=Th	H	-1.1399	15.7876	10.1021 f=Th
H	-4.4601	20.4018	2.1888 f=Th	H	-2.6624	14.6777	7.6842 f=Th
H	-2.0765	17.5446	1.8987 f=Th	H	-1.6749	13.2235	7.6626 f=Th
H	-4.3453	17.0747	1.0272 f=Th	H	-1.8319	14.1982	6.2003 f=Th
H	-3.2672	17.6520	-0.2468 f=Th	H	0.7754	20.6094	7.8893 f=F
H	-4.4764	18.7380	0.4422 f=Th	H	-1.4835	19.9474	7.0719 f=F
H	-2.5505	20.4168	0.9573 f=Th	H	-2.2297	20.6287	4.7985 f=F
H	-1.4146	19.2622	0.2668 f=Th	F	2.4289	22.0678	6.5455 f=F
H	-1.1636	19.8763	1.9027 f=Th	F	1.6304	22.8049	4.0976 f=F
H	-3.0725	16.7000	6.5137 f=Th	C	0.8392	22.0435	4.8297 f=F
H	-6.1068	16.9744	6.6065 f=Th	C	1.2567	21.6582	6.1014 f=F
H	-5.1589	15.7307	7.4298 f=Th	C	0.4416	20.8740	6.8934 f=F
H	-5.1966	15.7825	5.6673 f=Th	C	-0.8098	20.4888	6.4165 f=F
H	-3.0985	18.7999	7.9661 f=Th	C	-1.2303	20.8749	5.1448 f=F
H	-3.7823	17.3685	8.7376 f=Th	C	-0.3931	21.6493	4.3456 f=F
H	-4.8436	18.6188	8.1124 f=Th	H	-0.7026	21.9890	3.3647 f=F
H	3.8599	20.8493	2.4619 f=Th				

### Optimised geometry of $\eta^6$ -6-Th-endo and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	3.477468	20.142211	3.344767 f=Th	C	-3.998495	15.106810	3.446703 f=Th
C	2.559315	19.088440	3.248252 f=Th	C	-2.768903	15.653939	3.822391 f=Th
C	2.482665	18.150969	4.324976 f=Th	C	4.665638	13.622946	2.401651 f=Th
C	3.333864	18.289348	5.460652 f=Th	C	5.123397	14.525285	1.234421 f=Th
C	4.236242	19.361504	5.493746 f=Th	C	-0.305112	11.726233	4.290288 f=Th
C	4.311560	20.280776	4.452927 f=Th	C	-0.342346	11.923108	1.778110 f=Th
C	3.333017	17.302216	6.618655 f=Th	C	-5.456847	13.221585	2.555470 f=Th
C	3.195237	17.995976	7.984193 f=Th	C	-6.400777	13.241116	3.777006 f=Th
N	1.507918	17.101124	4.268571 f=Th	N	-2.524870	16.943124	4.311358 f=Th
Th	-0.533459	17.819405	4.989196 f=Th	C	-3.538014	17.954380	4.283612 f=Th
C	-0.494988	17.083987	7.276719 f=Th	C	-4.366001	18.182676	5.421733 f=Th
Si	-0.482609	15.376207	8.107996 f=Th	C	-5.277176	19.246833	5.381445 f=Th
C	1.053759	14.398616	7.607217 f=Th	C	-5.396175	20.061272	4.258568 f=Th
C	1.723698	18.942337	1.979396 f=Th	C	-4.606308	19.814617	3.137509 f=Th
C	2.406115	18.000503	0.967958 f=Th	C	-3.674510	18.768702	3.118195 f=Th
C	1.839100	15.830115	3.779553 f=Th	C	-4.347827	17.272961	6.641699 f=Th
C	0.764358	14.932286	3.667148 f=Th	C	-4.218406	18.042000	7.965791 f=Th
C	0.862964	13.644140	3.174496 f=Th	C	-2.895131	18.496221	1.837869 f=Th
C	2.153385	13.234344	2.784401 f=Th	C	-2.320864	19.768224	1.198120 f=Th
C	3.270364	14.073159	2.868375 f=Th	C	-6.060843	14.091922	1.431800 f=Th
C	3.097551	15.377150	3.372513 f=Th	C	-5.366143	11.775274	2.044181 f=Th
C	-0.357375	12.718472	3.099807 f=Th	C	5.671972	13.748004	3.565123 f=Th
C	-1.643475	13.546403	3.203586 f=Th	C	4.678044	12.165473	1.914569 f=Th
C	-1.631659	14.839892	3.690900 f=Th	C	-5.608046	16.387822	6.677836 f=Th
O	-0.453344	15.498655	4.083853 f=Th	C	-3.770275	17.744425	0.816452 f=Th
C	-2.908630	13.037519	2.847794 f=Th	C	1.404077	20.277556	1.293683 f=Th
C	-4.084463	13.788390	2.958177 f=Th	C	4.604262	16.433185	6.610385 f=Th

A.1. Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 133  
Exploration of the bonding

C	-0.471427	15.585210	9.985197 f=Th	H	-3.333090	18.693837	7.984412 f=Th
C	-2.017073	14.385438	7.627230 f=Th	H	-4.131997	17.337331	8.805462 f=Th
H	-2.965340	12.018332	2.472338 f=Th	H	-5.100231	18.669656	8.161716 f=Th
H	-4.892167	15.726996	3.527480 f=Th	H	3.552629	20.866310	2.533384 f=Th
H	3.942490	16.064544	3.428851 f=Th	H	5.023729	21.106360	4.500254 f=Th
H	2.277808	12.224434	2.400483 f=Th	H	4.896917	19.474033	6.355028 f=Th
H	-0.316346	12.256778	5.252441 f=Th	H	2.471925	16.631763	6.484291 f=Th
H	0.611233	11.120656	4.242804 f=Th	H	4.703074	15.863125	5.678533 f=Th
H	-1.170897	11.049255	4.261408 f=Th	H	4.576344	15.713996	7.442063 f=Th
H	-1.198757	11.239206	1.722583 f=Th	H	5.505725	17.052042	6.733456 f=Th
H	0.560458	11.303783	1.703258 f=Th	H	4.085104	18.594790	8.226879 f=Th
H	-0.376553	12.593115	0.908300 f=Th	H	3.085498	17.244483	8.779482 f=Th
H	-5.993828	12.638059	4.601693 f=Th	H	2.327291	18.668415	8.030274 f=Th
H	-7.382474	12.827017	3.503170 f=Th	H	0.762601	18.463715	2.257426 f=Th
H	-6.565281	14.261486	4.151325 f=Th	H	0.978739	21.022373	1.982710 f=Th
H	-6.206624	15.133379	1.752528 f=Th	H	0.685747	20.118055	0.478692 f=Th
H	-7.043305	13.696531	1.133970 f=Th	H	2.301666	20.722697	0.841236 f=Th
H	-5.412471	14.096060	0.543285 f=Th	H	3.378129	18.416970	0.663404 f=Th
H	-4.733420	11.693771	1.148039 f=Th	H	1.786247	17.895722	0.065420 f=Th
H	-6.370083	11.421296	1.770411 f=Th	H	2.577976	17.000976	1.384641 f=Th
H	-4.974774	11.091044	2.811444 f=Th	H	0.392815	17.627078	7.669152 f=Th
H	6.122432	14.220084	0.889252 f=Th	H	-1.378263	17.622782	7.686297 f=Th
H	5.182168	15.581774	1.532878 f=Th	H	1.156048	14.285857	6.517678 f=Th
H	4.431354	14.450383	0.382782 f=Th	H	1.002177	13.388115	8.041568 f=Th
H	5.364892	13.132712	4.423394 f=Th	H	1.974959	14.864700	7.986421 f=Th
H	5.774933	14.786671	3.909533 f=Th	H	0.415108	16.143120	10.322337 f=Th
H	6.667068	13.408945	3.241206 f=Th	H	-0.461987	14.607667	10.491441 f=Th
H	4.383026	11.463745	2.708743 f=Th	H	-1.360338	16.131884	10.334409 f=Th
H	5.695385	11.895208	1.598171 f=Th	H	-2.938335	14.847574	8.011473 f=Th
H	4.015051	12.013435	1.050113 f=Th	H	-1.954808	13.378425	8.068246 f=Th
H	-5.921687	19.429277	6.243422 f=Th	H	-2.127379	14.263890	6.539381 f=Th
H	-6.118018	20.879785	4.249134 f=Th	C	-0.440917	20.878248	4.959267 f=F
H	-4.726458	20.442717	2.253369 f=Th	C	0.686687	20.974758	5.795315 f=F
H	-2.051979	17.829057	2.091184 f=Th	C	0.499284	21.108800	7.167083 f=F
H	-4.140740	16.794486	1.221944 f=Th	C	-0.795351	21.136173	7.709972 f=F
H	-3.192679	17.525278	-0.093460 f=Th	C	-1.910581	21.033135	6.885139 f=F
H	-4.637390	18.357142	0.527336 f=Th	C	-1.736120	20.905798	5.501965 f=F
H	-3.113966	20.430876	0.823727 f=Th	H	1.701367	20.979875	5.391659 f=F
H	-1.691045	19.505138	0.336729 f=Th	F	1.549265	21.222137	7.989030 f=F
H	-1.708584	20.351708	1.901867 f=Th	H	-0.298818	20.869337	3.875138 f=F
H	-3.478377	16.606637	6.545334 f=Th	F	-0.939957	21.259180	9.032545 f=F
H	-6.517675	16.999610	6.772797 f=Th	H	-2.904213	21.072415	7.331658 f=F
H	-5.569561	15.706669	7.540479 f=Th	H	-2.612225	20.862404	4.852201 f=F
H	-5.700417	15.775681	5.771744 f=Th				

Optimised geometry of  $\eta^2$ -E-Th and the name of the fragment f in the ETS-NOCV  
in which each atom belongs

C	21.847110	13.218075	0.029437 f=Th	C	20.293051	16.664835	-4.434125 f=Th
C	22.243178	14.460897	-0.521528 f=Th	C	21.190648	15.893936	-3.741004 f=Th
C	22.901704	15.420206	0.287493 f=Th	O	22.379862	15.435881	-4.295372 f=Th
C	23.187838	15.096854	1.609350 f=Th	C	19.143598	17.044362	-3.730178 f=Th
C	22.835709	13.868886	2.140739 f=Th	C	18.922276	16.683373	-2.407646 f=Th
C	22.165940	12.947590	1.356963 f=Th	C	19.886205	15.908000	-1.752104 f=Th
N	22.070791	14.724384	-1.905604 f=Th	C	21.032539	15.497390	-2.411557 f=Th
Th	23.908423	14.003799	-2.987916 f=Th	C	24.479529	17.580554	-9.093641 f=Th
C	23.084229	11.927646	-3.860379 f=Th	C	25.658547	18.491474	-8.730240 f=Th
Si	21.697883	11.549284	-5.081391 f=Th	C	20.194110	18.526593	-6.103935 f=Th
C	20.052949	12.186872	-4.439322 f=Th	C	19.611404	16.186171	-6.780334 f=Th
C	23.247791	16.804657	-0.217781 f=Th	C	17.663067	17.102832	-1.650041 f=Th
C	24.701966	17.176531	0.052609 f=Th	C	16.725998	17.950498	-2.506254 f=Th
C	21.020343	12.216908	-0.746789 f=Th	C	26.189652	14.692150	-4.883797 f=Th
C	19.548569	12.316697	-0.339403 f=Th	C	26.690753	13.547550	-5.549312 f=Th
N	24.791161	14.944346	-4.836444 f=Th	C	28.059350	13.297847	-5.510715 f=Th
C	24.132397	15.719102	-5.786060 f=Th	C	28.925987	14.138571	-4.840708 f=Th
C	22.797790	16.006050	-5.492148 f=Th	C	28.434409	15.256543	-4.190849 f=Th
C	21.977409	16.778136	-6.274645 f=Th	C	27.077603	15.560784	-4.195965 f=Th
C	22.546441	17.274150	-7.453608 f=Th	C	25.807251	12.610126	-6.342315 f=Th
C	23.863218	17.019077	-7.812680 f=Th	C	25.981023	12.834353	-7.845391 f=Th
C	24.651912	16.234930	-6.962407 f=Th	C	26.608574	16.837360	-3.524103 f=Th
C	20.526660	17.045459	-5.891159 f=Th	C	27.441588	17.220654	-2.305338 f=Th

C	21.556337	9.693661	-5.327932	f=Th	H	23.969559	18.773129	-10.809929	f=Th
C	22.046343	12.342433	-6.747187	f=Th	H	23.110702	19.262915	-9.353352	f=Th
C	16.899678	15.851437	-1.200520	f=Th	H	29.988937	13.926889	-4.827043	f=Th
C	18.057876	17.924322	-0.417095	f=Th	H	23.086883	16.821504	-1.300458	f=Th
C	22.313323	17.851305	0.391058	f=Th	H	29.126347	15.909962	-3.675236	f=Th
C	21.505198	10.778902	-0.582707	f=Th	H	19.148036	13.314623	-0.520607	f=Th
C	24.982946	16.428185	-9.970074	f=Th	H	19.422387	12.085167	0.721474	f=Th
C	23.480451	18.397508	-9.908823	f=Th	H	18.947403	11.606121	-0.911614	f=Th
C	26.593957	18.005753	-4.513307	f=Th	H	25.724413	13.853382	-8.134541	f=Th
C	26.067152	11.141571	-6.010772	f=Th	H	25.334249	12.155574	-8.406482	f=Th
H	18.403131	17.640124	-4.243753	f=Th	H	27.012710	12.640642	-8.150600	f=Th
H	25.689493	16.036231	-7.202942	f=Th	H	23.686132	15.824214	2.239806	f=Th
H	21.930287	17.876857	-8.104671	f=Th	H	28.453622	12.429123	-6.024642	f=Th
H	19.750293	15.620154	-0.716474	f=Th	H	21.083964	12.484010	-1.803559	f=Th
H	23.993529	11.452306	-4.266859	f=Th	H	17.163515	18.234697	0.128871	f=Th
H	22.845056	11.369858	-2.937494	f=Th	H	18.608267	18.823708	-0.703960	f=Th
H	19.153008	18.731197	-5.853497	f=Th	H	18.680543	17.350762	0.272926	f=Th
H	20.329780	18.810298	-7.147745	f=Th	H	20.066910	13.256462	-4.213680	f=Th
H	20.828381	19.166539	-5.488042	f=Th	H	19.737427	11.657622	-3.536595	f=Th
H	15.846936	18.224247	-1.919149	f=Th	H	19.279202	12.019808	-5.194489	f=Th
H	16.374447	17.407263	-3.386815	f=Th	H	22.484145	9.270753	-5.722601	f=Th
H	17.201168	18.877693	-2.836083	f=Th	H	20.756016	9.451336	-6.033046	f=Th
H	26.437082	17.952507	-8.185970	f=Th	H	21.334188	9.182422	-4.387272	f=Th
H	25.330448	19.329205	-8.109954	f=Th	H	25.940680	17.813661	-5.363341	f=Th
H	26.111410	18.899364	-9.637442	f=Th	H	27.603240	18.189088	-4.891442	f=Th
H	18.563102	16.361530	-6.529147	f=Th	H	26.250345	18.917060	-4.017965	f=Th
H	19.820358	15.122552	-6.649563	f=Th	H	27.553807	16.398692	-1.593680	f=Th
H	19.759717	16.436451	-7.832991	f=Th	H	26.974557	18.057049	-1.783747	f=Th
H	25.760654	15.846775	-9.470707	f=Th	H	28.442603	17.549106	-2.592028	f=Th
H	25.410792	16.820870	-10.895857	f=Th	H	22.925911	11.905868	-7.227014	f=Th
H	24.168582	15.749217	-10.233900	f=Th	H	22.201166	13.422959	-6.683780	f=Th
H	15.991836	16.137915	-0.663641	f=Th	H	21.198410	12.170292	-7.416715	f=Th
H	17.496537	15.229778	-0.529840	f=Th	H	22.547077	18.843158	-0.002793	f=Th
H	16.608551	15.239948	-2.057803	f=Th	H	22.425484	17.886803	1.477719	f=Th
H	23.068753	13.636711	3.173546	f=Th	H	21.269054	17.635469	0.163155	f=Th
H	25.312561	10.509711	-6.484817	f=Th	H	24.933030	18.145381	-0.394781	f=Th
H	26.043652	10.945384	-4.935711	f=Th	H	25.399094	16.440821	-0.357896	f=Th
H	27.039597	10.810052	-6.381602	f=Th	H	24.906711	17.257959	1.122191	f=Th
H	24.769399	12.841190	-6.093934	f=Th	C	26.471504	12.963033	-1.559296	f=F
H	25.570389	16.689314	-3.194245	f=Th	C	25.496519	12.651090	-0.702519	f=F
H	21.868676	12.000128	1.790645	f=Th	H	25.203156	13.312913	0.108506	f=F
H	22.572295	10.671456	-0.794024	f=Th	H	24.991800	11.689823	-0.748135	f=F
H	20.961852	10.120369	-1.263992	f=Th	H	26.798991	12.274123	-2.333134	f=F
H	21.331968	10.403863	0.428502	f=Th	H	27.024737	13.894649	-1.485349	f=F
H	22.624717	17.796978	-10.227329	f=Th					

## A.1.5 Optimised geometries of Alkyl cations containing Uranium

### Optimised geometry of $\eta^6$ -2-U

U	26.800801	13.592814	-5.510886	H	27.657731	14.009038	-8.081075
C	25.491564	16.354392	-4.125418	H	25.897664	14.000468	-8.066364
C	27.859184	16.450443	-4.100940	C	22.962081	17.231350	-3.514712
C	25.374046	17.619561	-3.607720	C	26.545780	19.064114	-1.941638
C	26.584983	18.512217	-3.372946	H	25.642966	19.653100	-1.776663
C	27.866905	17.717483	-3.576799	H	27.397400	19.719182	-1.754472
O	26.704269	15.785651	-4.471938	H	26.566917	18.256036	-1.208279
Si	26.748725	16.263684	-8.357543	C	21.519420	19.128052	-2.641993
C	24.072324	18.040990	-3.315238	H	20.489393	19.409663	-2.413867
H	23.936071	19.035812	-2.915692	H	21.897596	19.839603	-3.380282
C	30.220188	16.219437	-3.954170	H	22.099150	19.239753	-1.722441
H	31.115029	15.624078	-4.087968	C	32.345398	17.198517	-2.025562
C	29.126541	18.236029	-3.254768	H	32.506732	16.185276	-2.399907
H	29.177043	19.237272	-2.851155	H	31.744232	17.133317	-1.115349
C	23.154197	15.944873	-4.031913	H	33.322367	17.608172	-1.757125
H	22.310559	15.281382	-4.176239	C	29.805556	13.442668	-4.839113
C	28.996215	15.672194	-4.305170	C	26.552193	19.680812	-4.371123
N	28.755425	14.406473	-4.835895	H	25.642392	20.270138	-4.239342
C	30.300529	17.515419	-3.430218	H	26.579185	19.320344	-5.401177
C	24.425166	15.485274	-4.344659	H	27.409759	20.339120	-4.217147
C	26.778469	14.516861	-7.642928	C	32.544149	18.151328	-4.327783

A.1. Geometries from the Chapter Coordination of Alkyl cations [(XA<sub>2</sub>)X(CH<sub>2</sub>Y)]  
(X = Th, U or Zr; Y = SiMe<sub>3</sub>, H) with an arene for Ethylene polymerisation: 135  
Exploration of the bonding

H	32.714518	17.158779	-4.749780	H	32.100533	11.991274	-6.874219
H	33.520806	18.578219	-4.086297	C	23.020567	13.949256	-7.211135
H	32.083187	18.772426	-5.099434	H	23.864406	14.626238	-7.063852
C	20.657882	17.624523	-4.411195	C	20.969504	16.776983	-2.080826
H	19.651565	17.978086	-4.173094	H	19.956329	17.094454	-1.821588
H	20.564615	16.604010	-4.787757	H	21.577117	16.810911	-1.173131
H	21.055466	18.248659	-5.215074	H	20.915606	15.738034	-2.413315
C	31.669022	18.093653	-3.070331	C	25.184386	17.157574	-7.836846
C	21.547648	17.694299	-3.165275	H	25.071592	17.224607	-6.752064
C	21.808269	11.226944	-4.874431	H	24.291556	16.669657	-8.236224
H	21.050588	10.451720	-4.879614	H	25.197361	18.177318	-8.232864
C	30.412511	13.398266	-8.542697	N	24.768544	14.225881	-4.841291
H	30.335210	14.119434	-9.359476	C	23.752146	13.222525	-4.857619
H	29.540937	12.743199	-8.604023	C	26.772624	16.154835	-10.232090
H	31.297555	12.788620	-8.737350	H	27.672651	15.648994	-10.592301
C	30.049640	12.697456	-3.662349	H	26.752358	17.151948	-10.681267
C	30.510203	14.133732	-7.209000	H	25.907894	15.604016	-10.612132
H	29.627020	14.765887	-7.098002	C	30.341608	13.507969	-1.308866
C	30.576414	13.219479	-6.001855	H	30.864947	14.397379	-1.661677
C	23.567820	12.412978	-3.712184	H	31.088627	12.748095	-1.066251
C	29.348920	12.993585	-2.351449	H	29.819117	13.767429	-0.385121
H	28.623463	13.791967	-2.528938	C	28.592478	11.784703	-1.807714
C	21.980390	12.037195	-5.980298	H	27.835621	11.426989	-2.509936
H	21.345209	11.894524	-6.847401	H	28.086699	12.042829	-0.874627
C	23.250793	13.168848	-8.503801	H	29.266299	10.951369	-1.594781
H	24.144407	12.542989	-8.454812	C	28.248346	17.245122	-7.805123
H	23.369329	13.856229	-9.344718	H	29.176377	16.814151	-8.189238
H	22.404839	12.517532	-8.736037	H	28.336417	17.315384	-6.718361
C	31.569684	19.504055	-2.494917	H	28.180909	18.263558	-8.199184
H	31.131538	20.206564	-3.208142	C	23.549502	13.464920	-1.433089
H	32.570526	19.867326	-2.252717	H	24.129666	13.627673	-0.521457
H	30.980681	19.529486	-1.574720	H	22.627970	12.946131	-1.155389
C	31.712367	11.412966	-4.857821	H	23.281318	14.437698	-1.844433
H	32.446786	10.615850	-4.869923	C	24.782199	11.321412	-1.764336
C	24.350617	12.624722	-2.430434	H	25.438511	11.534204	-0.918324
H	25.254524	13.194362	-2.679122	H	25.317446	10.663177	-2.451053
C	31.003709	11.687375	-3.700574	H	23.927313	10.767982	-1.370276
H	31.202326	11.107937	-2.805781	C	25.594100	9.997042	-5.377091
C	21.762270	14.806669	-7.349048	H	24.761453	9.589362	-4.817891
H	21.603122	15.430853	-6.469947	C	27.942134	10.519101	-5.548983
H	20.874611	14.185137	-7.491402	H	28.943723	10.506546	-5.135160
H	21.846915	15.466632	-8.215871	C	25.379494	10.515147	-6.646812
C	31.732670	15.055063	-7.232214	H	24.382527	10.508200	-7.068628
H	31.802451	15.653685	-6.324210	C	27.728898	11.028977	-6.828773
H	31.674671	15.740739	-8.080969	H	28.572872	11.381829	-7.408480
H	32.654880	14.476800	-7.331643	C	26.446421	11.034485	-7.375398
C	22.592172	11.423751	-3.750368	H	26.290706	11.407912	-8.380757
H	22.432412	10.798651	-2.879927	C	26.871514	10.003360	-4.827268
C	22.937241	13.048575	-5.996127	H	27.039543	9.581841	-3.843284
C	31.505942	12.182604	-5.988417				

### A.1.6 Optimised geometries of Alkyl cations containing Zirconium

Optimised geometry of  $\eta^6$ -2'-Zr and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	6.765617	8.543203	16.019925	f=B	C	8.051034	12.749072	20.103447	f=Z
C	7.594672	9.346129	15.246965	f=B	C	8.280057	9.255044	20.402336	f=Z
C	7.196142	10.639722	14.906181	f=B	C	8.560596	8.286726	21.368180	f=Z
C	5.972804	11.130791	15.343249	f=B	C	9.155616	8.635298	22.577247	f=Z
C	5.154178	10.338319	16.152808	f=B	C	9.478542	9.973302	22.811748	f=Z
C	5.548108	9.046473	16.486256	f=B	C	8.253111	14.586079	21.549236	f=Z
H	8.549431	8.971886	14.901321	f=B	C	7.383513	15.319339	20.747801	f=Z
Zr	7.388531	10.680855	17.780436	f=Z	C	6.858483	14.724108	19.597930	f=Z
C	9.476823	11.030952	17.040068	f=Z	C	7.181169	13.414049	19.256415	f=Z
O	8.269054	11.440735	19.704398	f=Z	C	9.461558	7.595019	23.654881	f=Z
C	8.628986	10.555301	20.706789	f=Z	C	8.743402	7.979213	24.954065	f=Z
C	9.220970	10.971548	21.878665	f=Z	N	7.666527	9.057113	19.160128	f=Z
C	9.596177	12.436971	22.049428	f=Z	C	7.320155	7.685229	18.917442	f=Z
C	8.610252	13.271948	21.243984	f=Z	C	8.292561	6.787389	18.441989	f=Z



C	7.924372	5.462894	18.219243 f=Z	H	5.172311	9.157319	19.494083 f=Z
C	6.643436	4.992255	18.459809 f=Z	H	4.263650	8.778327	21.763931 f=Z
C	5.709381	5.895833	18.955297 f=Z	H	4.844233	7.109950	21.721998 f=Z
C	6.015533	7.228151	19.204871 f=Z	H	5.999277	8.447249	21.711694 f=Z
N	6.709354	12.678854	18.161878 f=Z	H	2.848548	8.577403	19.718800 f=Z
C	5.793790	13.422420	17.343529 f=Z	H	3.416166	7.685328	18.303492 f=Z
C	4.404791	13.321505	17.575246 f=Z	H	3.185581	6.861806	19.839551 f=Z
C	3.544369	14.075971	16.786534 f=Z	H	9.805655	8.271329	18.334010 f=Z
C	3.998873	14.939301	15.795797 f=Z	H	10.463436	6.757366	20.182720 f=Z
C	5.368096	15.023748	15.598507 f=Z	H	10.664756	5.426295	19.035438 f=Z
C	6.282390	14.286679	16.346818 f=Z	H	11.720952	6.837195	18.946788 f=Z
C	6.966115	16.747203	21.102858 f=Z	H	9.493775	7.335754	16.002418 f=Z
C	7.652049	17.254159	22.368855 f=Z	H	11.168315	7.277577	16.559820 f=Z
C	9.607344	12.844484	23.519379 f=Z	H	10.188352	5.815982	16.549550 f=Z
C	11.005365	12.649569	21.462693 f=Z	H	7.184001	3.061091	17.813897 f=Z
C	9.729930	7.193328	18.175972 f=Z	H	6.703419	2.902632	20.248589 f=Z
C	10.162820	6.891034	16.741693 f=Z	H	5.000618	3.260531	19.943677 f=Z
C	6.288478	3.546344	18.210695 f=Z	H	5.711505	1.773855	19.315796 f=Z
C	5.181821	3.405791	17.165219 f=Z	H	5.459866	3.884216	16.223342 f=Z
C	4.956975	8.131120	19.814740 f=Z	H	4.980056	2.351711	16.961921 f=Z
C	3.531246	7.793075	19.385413 f=Z	H	4.248396	3.858345	17.510703 f=Z
C	3.825036	12.445980	18.672675 f=Z	H	2.477136	13.996342	16.958363 f=Z
C	2.467497	11.840098	18.322728 f=Z	H	5.739936	15.694090	14.829888 f=Z
C	3.041172	15.761244	14.966304 f=Z	H	4.528812	11.622897	18.844284 f=Z
C	2.250963	16.743154	15.828516 f=Z	H	3.282134	12.555753	20.767863 f=Z
C	7.760670	14.445703	16.047375 f=Z	H	4.659292	13.580684	20.346768 f=Z
C	8.070690	14.297339	14.557208 f=Z	H	3.025055	14.059450	19.876922 f=Z
C	7.326302	17.694915	19.953681 f=Z	H	2.442099	11.371183	17.335437 f=Z
C	5.450141	16.785160	21.331705 f=Z	H	2.196899	11.083883	19.062567 f=Z
C	10.974200	7.554671	23.903527 f=Z	H	1.676357	12.592999	18.339442 f=Z
C	9.003939	6.193832	23.258062 f=Z	H	8.292559	13.658651	16.586978 f=Z
H	8.284576	7.261235	21.171217 f=Z	H	9.365763	15.875988	16.298718 f=Z
H	6.168539	15.273180	18.970894 f=Z	H	7.783310	16.618070	16.050233 f=Z
H	8.665378	15.040704	22.437342 f=Z	H	8.190092	15.901656	17.615256 f=Z
H	10.337666	12.256421	24.076020 f=Z	H	9.150252	14.237740	14.400297 f=Z
H	9.905766	13.887622	23.627945 f=Z	H	7.611651	13.408930	14.117843 f=Z
H	8.628259	12.712520	23.983202 f=Z	H	7.711329	15.156260	13.986028 f=Z
H	11.735101	12.043939	22.004695 f=Z	H	3.648979	16.346516	14.267533 f=Z
H	11.044661	12.367011	20.408760 f=Z	H	2.662673	14.200154	13.495038 f=Z
H	11.293617	13.699933	21.544630 f=Z	H	1.457407	14.279404	14.785979 f=Z
H	8.401770	17.687980	19.759981 f=Z	H	1.460087	15.495549	13.509926 f=Z
H	6.813361	17.427730	19.027610 f=Z	H	2.914448	17.396077	16.399301 f=Z
H	7.035820	18.717484	20.207501 f=Z	H	1.611544	17.370887	15.203804 f=Z
H	4.897447	16.481220	20.440229 f=Z	H	1.605797	16.217401	16.537449 f=Z
H	5.160581	16.122475	22.150918 f=Z	H	9.985759	10.086449	16.820017 f=Z
H	5.134555	17.799495	21.588964 f=Z	H	9.526360	11.652714	16.141655 f=Z
H	8.739628	17.275510	22.263279 f=Z	H	10.043300	11.537249	17.825413 f=Z
H	7.323190	18.274893	22.574635 f=Z	C	5.027882	8.119345	21.344000 f=Z
H	7.399525	16.647924	23.242254 f=Z	C	10.696641	6.513226	19.146332 f=Z
H	11.356428	8.520654	24.239192 f=Z	C	5.906079	2.831771	19.505962 f=Z
H	11.208964	6.817641	24.675722 f=Z	C	3.698954	13.206581	19.994957 f=Z
H	11.514543	7.277311	22.995038 f=Z	C	8.302917	15.788679	16.537731 f=Z
H	7.925012	6.149437	23.088775 f=Z	C	2.104801	14.880875	14.142108 f=Z
H	9.510072	5.835066	22.358283 f=Z	H	9.943884	10.244620	23.749566 f=Z
H	9.238419	5.494863	24.063640 f=Z	H	7.845085	11.258052	14.300136 f=B
H	7.661076	8.015551	24.807948 f=Z	H	5.659133	12.132494	15.081835 f=B
H	8.955785	7.241210	25.731701 f=Z	H	4.209622	10.729768	16.504973 f=B
H	9.064587	8.953571	25.326710 f=Z	H	4.914149	8.421604	17.099425 f=B
H	8.671252	4.766910	17.849489 f=Z	H	7.065048	7.538292	16.286669 f=B
H	4.706281	5.543943	19.166778 f=Z				

Optimised geometry of  $\eta^6$ -2-Zr and the name of the fragment f in the ETS-NOCV in which each atom belongs

;lkjhgfdsrftghjklp;

Optimised geometry of  $\eta^6$ -3'-Zr-exo and the name of the fragment f in the ETS-NOCV in which each atom belongs

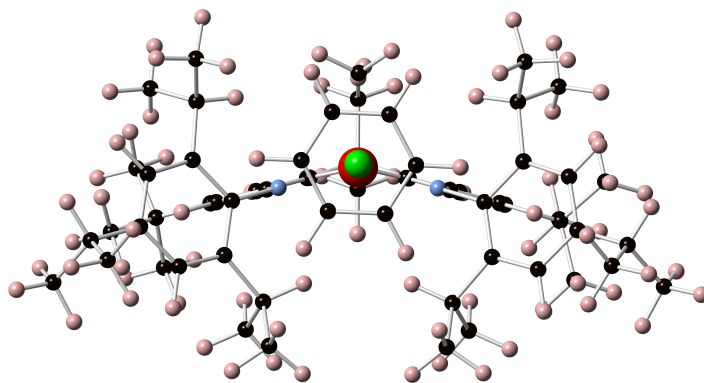


FIGURE A.1: 2'-Zr-a molecule. Green: Pu; red: O; blue: N; black: C; pink: H

Zr	7.241484	8.778722	15.728818	f=Z	C	4.449933	15.454959	15.065231	f=Z
O	8.37604	10.43795	14.725539	f=Z	H	3.796974	14.761958	14.528403	f=Z
N	6.041734	10.575997	15.687056	f=Z	H	4.45103	15.179758	16.12301	f=Z
N	8.580454	7.966974	14.257685	f=Z	H	4.006296	16.449677	14.986067	f=Z
C	7.847188	13.982576	14.065712	f=Z	C	5.76314	15.919013	13.014691	f=Z
H	8.340867	14.845178	13.639288	f=Z	H	5.176693	15.205728	12.430227	f=Z
C	6.548546	14.119205	14.559059	f=Z	H	5.276267	16.895079	12.945114	f=Z
C	5.915737	13.007942	15.107004	f=Z	H	6.74679	16.005144	12.549168	f=Z
H	4.908206	13.088679	15.487045	f=Z	C	4.660025	10.709227	16.060997	f=Z
C	6.560912	11.770446	15.170919	f=Z	C	4.300172	11.057838	17.376605	f=Z
C	9.457686	8.790449	13.542351	f=Z	C	2.948951	11.216177	17.674901	f=Z
C	10.396445	8.399063	12.592137	f=Z	H	2.66217	11.480989	18.686918	f=Z
H	10.488642	7.34834	12.351078	f=Z	C	1.946728	11.061465	16.728534	f=Z
C	11.196338	9.338666	11.937741	f=Z	C	2.332178	10.732959	15.4356	f=Z
C	11.05044	10.685071	12.256195	f=Z	H	1.569189	10.618426	14.672579	f=Z
H	11.667627	11.41714	11.757684	f=Z	C	3.662998	10.560343	15.074594	f=Z
C	9.964387	12.575135	13.6375	f=Z	C	3.983874	10.251212	13.623686	f=Z
C	8.529419	12.771957	14.104719	f=Z	H	5.052405	10.026627	13.558602	f=Z
C	7.843191	11.714965	14.662143	f=Z	C	3.714556	11.460192	12.726124	f=Z
C	9.369295	10.147382	13.80374	f=Z	H	3.984213	11.233569	11.691628	f=Z
C	10.125937	11.125106	13.204583	f=Z	H	2.654716	11.7277	12.743193	f=Z
C	10.323614	13.539776	12.511312	f=Z	H	4.290299	12.330043	13.043208	f=Z
H	10.230982	14.57351	12.846571	f=Z	C	3.214969	9.042157	13.093204	f=Z
H	11.362163	13.407536	12.206714	f=Z	H	3.522626	8.822293	12.068282	f=Z
H	9.684256	13.397917	11.638253	f=Z	H	3.37927	8.142452	13.691201	f=Z
C	10.903549	12.832114	14.832205	f=Z	H	2.13874	9.22657	13.073153	f=Z
H	10.79525	13.860951	15.182735	f=Z	C	5.328534	11.294083	18.46876	f=Z
H	10.678964	12.163515	15.665722	f=Z	H	6.224168	10.726947	18.197704	f=Z
H	11.942768	12.671409	14.536719	f=Z	C	5.738926	12.766197	18.558806	f=Z
C	12.1962	8.858842	10.88479	f=Z	H	6.185356	13.124851	17.63257	f=Z
C	13.185709	7.877959	11.52368	f=Z	H	4.868977	13.389582	18.783206	f=Z
H	13.742256	8.35351	12.335036	f=Z	H	6.466102	12.906057	19.362746	f=Z
H	12.682995	6.997693	11.929344	f=Z	C	4.866663	10.833415	19.850879	f=Z
H	13.905614	7.533028	10.77715	f=Z	H	4.443631	9.825299	19.853821	f=Z
C	11.440193	8.149451	9.754941	f=Z	H	5.707009	10.851923	20.549002	f=Z
H	10.888694	7.279704	10.118005	f=Z	H	4.105157	11.499925	20.261716	f=Z
H	10.727811	8.825013	9.275063	f=Z	C	0.49476	11.25608	17.095625	f=Z
H	12.143268	7.802524	8.993403	f=Z	H	0.467841	11.506463	18.16191	f=Z
C	12.993337	10.009111	10.27525	f=Z	C	-0.127385	12.421453	16.329699	f=Z
H	13.583338	10.540351	11.026303	f=Z	H	0.430775	13.346411	16.488697	f=Z
H	13.68955	9.613599	9.532765	f=Z	H	-0.148137	12.222629	15.25485	f=Z
H	12.348039	10.729747	9.766824	f=Z	H	-1.15738	12.585655	16.654351	f=Z
C	5.86003	15.481822	14.481236	f=Z	C	-0.31574	9.977254	16.898486	f=Z
C	6.682208	16.512038	15.264871	f=Z	H	0.102675	9.146664	17.471432	f=Z
H	7.691833	16.618366	14.863564	f=Z	H	-1.348565	10.125093	17.221968	f=Z
H	6.201045	17.49216	15.215714	f=Z	H	-0.339518	9.682131	15.845967	f=Z
H	6.76683	16.228464	16.316794	f=Z	C	8.723797	6.578796	13.92012	f=Z

C	7.933199	6.024248	12.890256	f=Z	H	10.030744	2.030424	13.44568	f=Z
C	8.114705	4.686552	12.560278	f=Z	C	7.974383	1.609377	13.067519	f=Z
H	7.505573	4.258712	11.772254	f=Z	H	7.66456	1.673585	14.113085	f=Z
C	9.050226	3.878302	13.195526	f=Z	H	7.142472	1.954414	12.447563	f=Z
C	9.811753	4.450824	14.202076	f=Z	H	8.147306	0.557217	12.83032	f=Z
H	10.54556	3.832723	14.709134	f=Z	C	9.68957	2.29021	11.356487	f=Z
C	9.67749	5.783626	14.583113	f=Z	H	10.606795	2.852447	11.169614	f=Z
C	6.901207	6.83332	12.125691	f=Z	H	9.878672	1.241744	11.115352	f=Z
H	6.596811	7.667998	12.76726	f=Z	H	8.925386	2.65484	10.664915	f=Z
C	7.484733	7.440819	10.84804	f=Z	C	8.68459	9.195491	17.393953	f=Z
H	6.719476	8.012559	10.316729	f=Z	H	8.219318	9.763178	18.20611	f=Z
H	8.322596	8.105118	11.055649	f=Z	H	9.140681	8.301301	17.826483	f=Z
H	7.835466	6.650299	10.178958	f=Z	H	9.489988	9.810183	16.983148	f=Z
C	5.65189	6.030165	11.767412	f=Z	C	6.399183	7.241748	18.048942	f=t
H	5.258706	5.453637	12.608836	f=Z	C	7.042913	6.322772	17.208383	f=t
H	4.865322	6.699292	11.412636	f=Z	H	7.925389	5.808493	17.567453	f=t
H	5.84912	5.321333	10.960095	f=Z	C	6.563710	6.045666	15.934283	f=t
C	10.571936	6.31737	15.685831	f=Z	H	7.070384	5.316600	15.317068	f=t
H	10.126239	7.246935	16.047122	f=Z	C	5.443818	6.721495	15.442507	f=t
C	11.974768	6.651486	15.173733	f=Z	H	5.069741	6.508599	14.449781	f=t
H	12.597962	7.01566	15.994496	f=Z	C	4.796711	7.643354	16.260262	f=t
H	12.454898	5.759762	14.761196	f=Z	H	3.923633	8.176336	15.908099	f=t
H	11.955385	7.417182	14.399607	f=Z	C	5.277655	7.904809	17.543025	f=t
C	10.700352	5.354788	16.866994	f=Z	H	4.761421	8.632196	18.154469	f=t
H	11.163343	5.863011	17.716054	f=Z	C	6.846925	7.436240	19.457397	f=t
H	9.740565	4.947067	17.192041	f=Z	H	6.599208	8.430215	19.827540	f=t
H	11.338864	4.502893	16.622291	f=Z	H	6.335326	6.708595	20.095550	f=t
C	9.235178	2.430524	12.807497	f=Z	H	7.918576	7.273051	19.566346	f=t

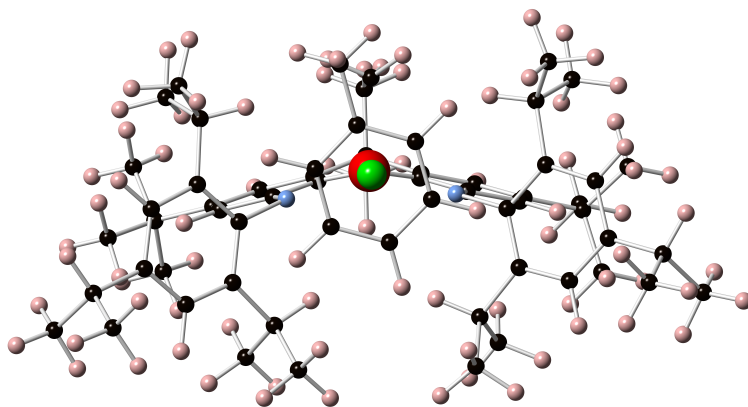


FIGURE A.2: 3'-Zr-a molecule. Green: Pu; red: O; blue: N; black: C; pink: H

Optimised geometry of  $\eta^6$ -4'-Zr-exo and the name of the fragment f in the ETS-  
 NOCV in which each atom belongs

Zr	7.199815	10.734381	18.139199 f=Z	H	5.078085	16.678940	20.703242 f=Z
C	9.010617	10.914767	16.901978 f=Z	H	5.353573	16.328814	22.414726 f=Z
N	6.732466	12.730258	18.505216 f=Z	H	5.389765	17.997863	21.830443 f=Z
C	7.237468	13.496107	19.551206 f=Z	H	8.978854	17.347302	22.450513 f=Z
C	8.127030	12.821728	20.372407 f=Z	H	7.605515	18.403378	22.766366 f=Z
C	8.721761	13.342691	21.493135 f=Z	H	7.634193	16.787180	23.463695 f=Z
C	8.396184	14.670369	21.785527 f=Z	H	11.481180	8.547794	24.412880 f=Z
C	7.524385	15.414368	20.995482 f=Z	H	11.336491	6.842235	24.839879 f=Z
C	6.946060	14.813874	19.871378 f=Z	H	11.599238	7.313721	23.155124 f=Z
C	9.704397	12.492366	22.289867 f=Z	H	8.008385	6.200588	23.340154 f=Z
C	9.311673	11.029192	22.120943 f=Z	H	9.571459	5.886366	22.562140 f=Z
C	8.686371	10.623636	20.964629 f=Z	H	9.346346	5.533664	24.271503 f=Z
O	8.317457	11.509919	19.963324 f=Z	H	7.799523	8.057223	25.076170 f=Z
C	9.579950	10.018531	23.040570 f=Z	H	9.115235	7.271574	25.959908 f=Z
C	9.237008	8.684177	22.809422 f=Z	H	9.220736	8.985946	25.562437 f=Z
C	8.598960	8.345833	21.617138 f=Z	H	8.642841	5.106947	17.584314 f=Z
C	8.306896	9.327319	20.674377 f=Z	H	4.626910	5.794792	18.793041 f=Z
C	7.167156	16.862897	21.330599 f=Z	H	5.112218	9.310802	19.632402 f=Z
C	7.546677	17.770764	20.155282 f=Z	H	4.198509	8.703377	21.840827 f=Z
C	9.727690	12.896902	23.760780 f=Z	H	4.778847	7.046900	21.632469 f=Z
C	11.111337	12.689274	21.693133 f=Z	H	5.934886	8.377892	21.760609 f=Z
C	9.566489	7.636205	23.872515 f=Z	H	2.790275	8.686098	19.768697 f=Z
C	11.085089	7.586506	24.080001 f=Z	H	3.400996	7.992781	18.260272 f=Z
N	7.644696	9.178804	19.459128 f=Z	H	3.146781	6.973663	19.676032 f=Z
C	7.301602	7.866091	19.023120 f=Z	H	9.817991	8.479446	18.595735 f=Z
C	8.278702	7.025886	18.452638 f=Z	H	10.369122	6.720232	20.257812 f=Z
C	7.894025	5.760398	18.020840 f=Z	H	10.596780	5.547755	18.953528 f=Z
C	6.592132	5.296211	18.127032 f=Z	H	11.678799	6.934698	19.093796 f=Z
C	5.647580	6.144083	18.697171 f=Z	H	9.557871	7.853322	16.157331 f=Z
C	5.968379	7.413734	19.158565 f=Z	H	11.216259	7.708092	16.749054 f=Z
C	9.729745	7.432499	18.297428 f=Z	H	10.232977	6.266238	16.526185 f=Z
C	10.204199	7.309467	16.849433 f=Z	H	7.128336	3.464428	17.235543 f=Z
C	6.219295	3.912676	17.651095 f=Z	H	6.509414	2.972740	19.594376 f=Z
C	5.172435	3.956146	16.540569 f=Z	H	4.833399	3.416440	19.254391 f=Z
C	4.900485	8.250931	19.839466 f=Z	H	5.550776	2.017132	18.456356 f=Z
C	3.486824	7.958775	19.349525 f=Z	H	5.511448	4.556798	15.693363 f=Z
C	5.818481	13.331859	17.592169 f=Z	H	4.961723	2.948284	16.176307 f=Z
C	6.296126	14.043585	16.472427 f=Z	H	4.230448	4.379850	16.898827 f=Z
C	5.368049	14.582774	15.588096 f=Z	H	2.487351	13.695155	17.075037 f=Z
C	3.997794	14.463192	15.772887 f=Z	H	5.727005	15.132477	14.723720 f=Z
C	3.554159	13.780257	16.900238 f=Z	H	4.661308	11.961003	19.520064 f=Z
C	4.428366	13.215366	17.819975 f=Z	H	3.029932	13.102346	20.980549 f=Z
C	7.770942	14.284981	16.222982 f=Z	H	4.246706	14.234883	20.382954 f=Z
C	8.199296	13.914005	14.804881 f=Z	H	2.626260	14.221795	19.674087 f=Z
C	3.860042	12.547012	19.056172 f=Z	H	2.962441	10.853683	17.994139 f=Z
C	2.702071	11.603131	18.746028 f=Z	H	2.393472	11.080161	19.653509 f=Z
C	3.026833	15.075727	14.791992 f=Z	H	1.827210	12.143424	18.378647 f=Z
C	2.190181	16.173872	15.445218 f=Z	H	8.332240	13.659450	16.919845 f=Z
C	9.091935	6.239915	23.478514 f=Z	H	9.208527	15.898556	16.339156 f=Z
C	8.885200	8.015287	25.192833 f=Z	H	7.596570	16.419022	15.841223 f=Z
C	5.658166	16.967870	21.582322 f=Z	H	7.916864	16.023364	17.535131 f=Z
C	7.893314	17.367613	22.574818 f=Z	H	9.283159	14.004305	14.706426 f=Z
C	10.641991	6.609766	19.208002 f=Z	H	7.923962	12.890358	14.544636 f=Z
C	5.753994	3.030976	18.808193 f=Z	H	7.751567	14.578374	14.061905 f=Z
C	4.963593	8.089279	21.359540 f=Z	H	3.625286	15.539494	14.000316 f=Z
C	3.419369	13.590835	20.084049 f=Z	H	2.723240	13.248947	13.642200 f=Z
C	2.133956	14.020750	14.143082 f=Z	H	1.496131	13.530410	14.883314 f=Z
C	8.140054	15.742239	16.505820 f=Z	H	1.480029	14.480297	13.398746 f=Z
H	10.071961	10.277875	23.968308 f=Z	H	2.821821	16.947082	15.887089 f=Z
H	8.301516	7.325759	21.416671 f=Z	H	1.540080	16.647416	14.706258 f=Z
H	6.249845	15.363208	19.249527 f=Z	H	1.552126	15.768846	16.235125 f=Z
H	8.838922	15.129311	22.656782 f=Z	H	9.538701	9.964884	16.794549 f=Z
H	10.454037	12.299617	24.312854 f=Z	H	8.710989	11.257021	15.903437 f=Z
H	10.037240	13.936769	23.869874 f=Z	H	9.711156	11.650599	17.307009 f=Z
H	8.749465	12.774499	24.228994 f=Z	C	5.335433	10.773110	15.476623 f=t
H	11.837963	12.074331	22.228760 f=Z	C	5.525781	9.667681	16.313699 f=t
H	11.138670	12.408082	20.638483 f=Z	C	6.337495	8.606945	15.891653 f=t
H	11.412788	13.735928	21.774913 f=Z	C	6.980050	8.669311	14.667198 f=t
H	8.616436	17.170773	19.940983 f=Z	C	6.796046	9.782767	13.856071 f=t
H	7.003500	17.507786	19.245230 f=Z	C	5.974804	10.831879	14.249578 f=t
H	7.306609	18.810306	20.392142 f=Z	Br	7.661406	9.865988	12.196192 f=t

H	7.603622	7.850533	14.332358 f=t	H	4.901991	9.545096	17.202458 f=t
H	5.824671	11.681194	13.596222 f=t	H	6.442404	7.722144	16.508373 f=t
H	4.670173	11.577534	15.768395 f=t				

### Optimised geometry of $\eta^6\text{-}4'\text{-Zr}$ -horizontal and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	1.148781	9.601211	14.619544 f=Z	H	-3.481685	8.002451	20.725676 f=Z
C	0.673990	10.683643	15.398187 f=Z	H	-2.721743	11.308468	22.317984 f=Z
C	0.555205	11.967135	14.828107 f=Z	H	-1.884428	12.019301	20.931235 f=Z
C	0.877636	12.126313	13.484817 f=Z	H	-3.630742	11.745886	20.858792 f=Z
C	1.327173	11.081041	12.694370 f=Z	H	-4.814205	12.222189	15.792557 f=Z
C	1.468641	9.831507	13.288947 f=Z	H	-3.856136	11.467314	14.511872 f=Z
N	0.323648	10.458942	16.760571 f=Z	H	-5.608424	11.293276	14.514456 f=Z
C	-1.008264	10.342883	17.141844 f=Z	H	-3.591101	8.922962	14.445997 f=Z
C	-1.188772	10.200101	18.510549 f=Z	H	-4.421655	7.921366	15.642244 f=Z
C	-2.393944	10.021929	19.139171 f=Z	H	-5.349713	8.781375	14.405696 f=Z
C	-3.509981	9.995356	18.296186 f=Z	H	-6.104176	10.751811	17.455766 f=Z
C	-3.405406	10.133943	16.915083 f=Z	H	-6.769737	9.868012	16.084993 f=Z
C	-2.140558	10.314812	16.342525 f=Z	H	-5.951323	8.986084	17.369386 f=Z
C	-2.457356	9.925330	20.660457 f=Z	H	-1.091241	8.920483	25.153255 f=Z
C	-1.117508	9.409622	21.175998 f=Z	H	0.029522	8.159731	26.282824 f=Z
C	0.025033	9.602267	20.435973 f=Z	H	0.551367	9.547839	25.317974 f=Z
O	0.018714	10.206175	19.189549 f=Z	H	2.279856	6.559147	23.817026 f=Z
C	1.293988	9.186109	20.798453 f=Z	H	2.544634	8.139139	24.579362 f=Z
C	1.438173	8.561830	22.032834 f=Z	H	1.905476	6.795820	25.521025 f=Z
C	0.325322	8.354522	22.847404 f=Z	H	-0.093701	5.700011	23.458299 f=Z
C	-0.930438	8.773471	22.401611 f=Z	H	-0.347239	5.912075	25.196225 f=Z
C	-4.628998	10.060579	16.001102 f=Z	H	-1.475559	6.629163	24.046163 f=Z
C	-5.931041	9.908045	16.783116 f=Z	H	6.581655	9.877803	21.384232 f=Z
C	-3.601916	9.017999	21.106840 f=Z	H	5.502852	6.211410	19.515345 f=Z
C	-2.686008	11.339441	21.226728 f=Z	H	2.039379	7.291088	18.762551 f=Z
Zr	1.952082	10.409557	18.036020 f=Z	H	1.760770	4.985668	19.592276 f=Z
C	0.441767	7.673773	24.211278 f=Z	H	3.368241	5.036358	20.324017 f=Z
C	-0.421839	6.406751	24.224502 f=Z	H	2.086880	6.095926	20.927566 f=Z
N	2.273716	9.444370	19.846307 f=Z	H	2.647700	5.450121	17.288330 f=Z
C	3.601394	8.966923	20.053222 f=Z	H	3.785214	6.776571	17.002139 f=Z
C	4.557828	9.769887	20.707707 f=Z	H	4.274163	5.369710	17.944581 f=Z
C	5.842125	9.265130	20.878495 f=Z	H	3.218604	11.391398	20.957663 f=Z
C	6.211278	7.996550	20.455108 f=Z	H	3.475617	10.342469	23.183313 f=Z
C	5.244122	7.216088	19.832223 f=Z	H	5.182185	10.804157	23.217997 f=Z
C	3.946550	7.664689	19.622511 f=Z	H	3.929394	12.048709	23.226782 f=Z
C	4.223933	11.126257	21.290369 f=Z	H	5.264702	12.251528	19.730738 f=Z
C	4.200484	11.071998	22.818928 f=Z	H	4.852313	13.192887	21.171175 f=Z
C	7.607960	7.475617	20.699160 f=Z	H	6.193719	12.056591	21.214065 f=Z
C	7.598198	6.285850	21.656917 f=Z	H	8.169420	8.284706	21.178501 f=Z
C	2.934903	6.713715	19.015303 f=Z	H	7.113650	6.539612	22.601786 f=Z
C	2.511977	5.648498	20.028610 f=Z	H	7.065800	5.434335	21.224844 f=Z
C	0.088374	13.177657	15.608518 f=Z	H	8.618643	5.962380	21.874307 f=Z
C	-1.290949	13.651900	15.151491 f=Z	H	8.377564	7.982089	18.725182 f=Z
C	1.650904	11.297224	11.235080 f=Z	H	9.345603	6.793343	19.601906 f=Z
C	3.129182	11.053835	10.939911 f=Z	H	7.815359	6.307713	18.875731 f=Z
C	1.255845	8.195331	15.184761 f=Z	H	1.828258	9.006228	12.687072 f=Z
C	-0.107129	7.502395	15.213686 f=Z	H	0.773115	13.108742	13.035497 f=Z
C	2.117158	12.537237	18.628359 f=Z	H	1.592295	8.269404	16.233328 f=Z
C	-4.726407	11.336766	15.158261 f=Z	H	-0.015899	6.498803	15.636409 f=Z
C	-4.484491	8.850128	15.070011 f=Z	H	-0.840265	8.054894	15.800117 f=Z
C	-0.048212	8.634482	25.301440 f=Z	H	-0.493622	7.403323	14.195809 f=Z
C	1.877829	7.273990	24.539736 f=Z	H	3.245736	7.783301	14.375911 f=Z
C	5.187094	12.214211	20.819768 f=Z	H	2.377135	6.368399	14.985307 f=Z
C	8.324365	7.122831	19.398196 f=Z	H	1.919015	7.071413	13.447875 f=Z
C	3.442650	6.047997	17.740087 f=Z	H	0.009751	12.888008	16.658622 f=Z
C	1.088070	14.330447	15.505460 f=Z	H	-1.598901	14.525375	15.731253 f=Z
C	2.262699	7.314899	14.455771 f=Z	H	-1.276771	13.941344	14.097500 f=Z
C	0.765447	10.444159	10.329609 f=Z	H	-2.048440	12.879259	15.282607 f=Z
H	-1.791650	8.600673	23.033093 f=Z	H	0.811792	15.132069	16.194099 f=Z
H	2.421050	8.229484	22.337577 f=Z	H	2.107569	14.015674	15.739302 f=Z
H	-2.027091	10.404964	15.269053 f=Z	H	1.101130	14.757085	14.499797 f=Z
H	-4.485716	9.858622	18.738007 f=Z	H	1.437713	12.348742	11.014946 f=Z
H	-3.658924	8.975175	22.194838 f=Z	H	3.767928	11.702558	11.544443 f=Z
H	-4.560578	9.406600	20.762172 f=Z	H	3.405091	10.014849	11.141816 f=Z

A.1. Geometries from the Chapter Coordination of Alkyl cations  $[(XA_2)X(CH_2Y)]$   
 ( $X = Th, U$  or  $Zr$ ;  $Y = SiMe_3, H$ ) with an arene for Ethylene polymerisation: 141  
 Exploration of the bonding

H	3.347912	11.254404	9.888684 f=Z	C	6.668704	7.903664	15.667402 f=t
H	-0.293501	10.631874	10.517600 f=Z	C	6.662601	7.965837	14.281666 f=t
H	0.968350	10.665448	9.279369 f=Z	C	5.963600	8.971677	13.630088 f=t
H	0.949810	9.377701	10.484074 f=Z	C	5.262890	9.923889	14.357237 f=t
H	3.036382	12.746366	19.183090 f=Z	H	5.960261	9.024021	12.547885 f=t
H	2.073659	13.210702	17.768137 f=Z	H	7.208921	7.228521	13.706043 f=t
H	1.275731	12.787666	19.283410 f=Z	H	4.709335	10.709690	13.860260 f=t
Br	4.407454	11.206023	16.741043 f=t	H	5.988764	8.812140	17.500800 f=t
C	5.293763	9.833134	15.735801 f=t	H	7.217446	7.121333	16.177889 f=t
C	5.981724	8.848467	16.418211 f=t				

Optimised geometry of  $\eta^6$ -5'-Zr-exo and the name of the fragment f in the ETS-  
 NOCV in which each atom belongs

C	5.537644	9.678384	16.311264 f=t	C	7.776121	14.289557	16.220646 f=Z
C	6.329164	8.599653	15.891837 f=t	C	8.144154	15.746347	16.507494 f=Z
C	6.959412	8.638335	14.661669 f=t	C	9.006617	10.913195	16.891880 f=Z
C	6.770844	9.748100	13.854006 f=t	C	8.880950	8.010272	25.188540 f=Z
C	5.973807	10.816795	14.229568 f=t	C	11.084494	7.588027	24.080407 f=Z
C	5.348104	10.777171	15.462709 f=t	C	7.893123	17.369939	22.573133 f=Z
H	7.571843	7.817650	14.310294 f=t	C	7.552894	17.772942	20.152692 f=Z
F	7.367646	9.784202	12.673467 f=t	C	10.205503	7.310334	16.839624 f=Z
H	5.839430	11.651137	13.553299 f=t	C	5.172468	3.955187	16.543854 f=Z
H	4.693620	11.589993	15.755161 f=t	C	3.492982	7.962947	19.345178 f=Z
H	4.912054	9.567614	17.200501 f=t	C	2.701033	11.606301	18.737014 f=Z
H	6.426936	7.721394	16.518662 f=t	C	2.198950	16.179353	15.443691 f=Z
C	6.301309	14.046565	16.468613 f=Z	C	8.205701	13.923379	14.801733 f=Z
C	5.823385	13.333500	17.587476 f=Z	H	10.067514	10.277122	23.969450 f=Z
C	4.432990	13.214396	17.813007 f=Z	H	8.305760	7.325812	21.411116 f=Z
C	3.559163	13.779248	16.892915 f=Z	H	6.254774	15.366510	19.244677 f=Z
C	4.003208	14.465242	15.767567 f=Z	H	8.835735	15.130606	22.657789 f=Z
C	5.373509	14.586207	15.584190 f=Z	H	10.438410	12.298455	24.321038 f=Z
N	6.736627	12.732991	18.501777 f=Z	H	10.022798	13.935857	23.878013 f=Z
C	7.240378	13.498687	19.548519 f=Z	H	8.733977	12.772169	24.228646 f=Z
C	8.127616	12.823494	20.371745 f=Z	H	11.833525	12.077313	22.243597 f=Z
C	8.719851	13.343995	21.494008 f=Z	H	11.142146	12.412485	20.650162 f=Z
C	8.394694	14.672015	21.785492 f=Z	H	11.409181	13.739091	21.789734 f=Z
C	7.525627	15.416832	20.993315 f=Z	H	8.622978	17.710981	19.940590 f=Z
C	6.949279	14.816662	19.867997 f=Z	H	7.011054	17.510916	19.241567 f=Z
O	8.318138	11.511676	19.962765 f=Z	H	7.314248	18.812943	20.388970 f=Z
C	8.686274	10.624969	20.963944 f=Z	H	5.081491	16.683658	20.695175 f=Z
C	9.308959	11.029850	22.121915 f=Z	H	5.352531	16.335012	22.407664 f=Z
C	9.699312	12.493265	22.294236 f=Z	H	5.392095	18.003396	21.821754 f=Z
C	9.577314	10.018302	23.040606 f=Z	H	8.978940	17.347873	22.451581 f=Z
C	9.236923	8.683736	22.807174 f=Z	H	7.606483	18.406241	22.763508 f=Z
C	8.601174	8.346100	21.613473 f=Z	H	7.630845	16.790308	23.461608 f=Z
C	8.309031	9.328402	20.671661 f=Z	H	11.477744	8.549562	24.415918 f=Z
Zr	7.200536	10.736097	18.137230 f=Z	H	11.335605	6.843003	24.839637 f=Z
N	7.648668	9.180079	19.455337 f=Z	H	11.601518	7.317890	23.156354 f=Z
C	7.305780	7.867236	19.019609 f=Z	H	8.012671	6.196405	23.331187 f=Z
C	8.282386	7.028363	18.446250 f=Z	H	9.578092	5.887344	22.555793 f=Z
C	7.898096	5.762522	18.015136 f=Z	H	9.350275	5.531005	24.264075 f=Z
C	6.597061	5.296615	18.124920 f=Z	H	7.795475	8.050015	25.069251 f=Z
C	5.653105	6.143085	18.698077 f=Z	H	9.110716	7.265899	25.955056 f=Z
C	5.973519	7.413241	19.158489 f=Z	H	9.213449	8.981120	25.560398 f=Z
C	9.714604	12.895924	23.765852 f=Z	H	8.646520	5.110020	17.576524 f=Z
C	11.109096	12.692277	21.705024 f=Z	H	4.633080	5.792613	18.796756 f=Z
C	9.566310	7.634770	23.869297 f=Z	H	5.120969	9.309471	19.640278 f=Z
C	9.095842	6.238076	23.471827 f=Z	H	4.199801	8.692424	21.843070 f=Z
C	7.169310	16.865846	21.327293 f=Z	H	4.776612	7.035665	21.627247 f=Z
C	5.659852	16.972833	21.575316 f=Z	H	5.935612	8.363186	21.765294 f=Z
C	9.732527	7.436883	18.287811 f=Z	H	2.796710	8.689492	19.766203 f=Z
C	10.647309	6.618527	19.199803 f=Z	H	3.410948	8.003339	18.255863 f=Z
C	6.224645	3.912821	17.649377 f=Z	H	3.149482	6.976848	19.664960 f=Z
C	5.766506	3.029187	18.807865 f=Z	H	9.819225	8.484878	18.582882 f=Z
C	4.905830	8.249180	19.841030 f=Z	H	10.376230	6.732724	20.249673 f=Z
C	4.964562	8.079041	21.360366 f=Z	H	10.602694	5.555521	18.949375 f=Z
C	3.864048	12.543749	19.047736 f=Z	H	11.683557	6.944138	19.082454 f=Z
C	3.430556	13.585624	20.080671 f=Z	H	9.555955	7.849040	16.146453 f=Z
C	3.032499	15.080256	14.787970 f=Z	H	11.215834	7.712571	16.736349 f=Z
C	2.136596	14.028098	14.138760 f=Z	H	10.238110	6.266049	16.520170 f=Z

H	7.132587	3.466715	17.229142 f=Z	H	9.212542	15.903925	16.341530 f=Z
H	6.525946	2.971328	19.590185 f=Z	H	7.600308	16.424500	15.844586 f=Z
H	4.847569	3.412804	19.259047 f=Z	H	7.920571	16.024505	17.537478 f=Z
H	5.563128	2.015392	18.455984 f=Z	H	9.289211	14.018285	14.703534 f=Z
H	5.506041	4.557714	15.695795 f=Z	H	7.934759	12.899217	14.538856 f=Z
H	4.962473	2.947307	16.179249 f=Z	H	7.755577	14.587825	14.060289 f=Z
H	4.231125	4.376134	16.906999 f=Z	H	3.631026	15.543844	13.996236 f=Z
H	2.492292	13.692200	17.066114 f=Z	H	2.723559	13.255896	13.635752 f=Z
H	5.732714	15.137895	14.721184 f=Z	H	1.498770	13.537821	14.879016 f=Z
H	4.663630	11.952345	19.507924 f=Z	H	1.482549	14.490207	13.396134 f=Z
H	3.040624	13.095507	20.976064 f=Z	H	2.832812	16.950538	15.885919 f=Z
H	4.261410	14.224740	20.380348 f=Z	H	1.548995	16.655395	14.706215 f=Z
H	2.639533	14.221750	19.674652 f=Z	H	1.561048	15.774498	16.233811 f=Z
H	2.955123	10.859998	17.979873 f=Z	H	9.529982	9.961519	16.777541 f=Z
H	2.394102	11.079667	19.642905 f=Z	H	8.702572	11.261323	15.896745 f=Z
H	1.826796	12.152215	18.376552 f=Z	H	9.712619	11.644496	17.295639 f=Z
H	8.337490	13.662454	16.916066 f=Z				

### Optimised geometry of $\eta^6$ -5'-Zr-horizontal and the name of the fragment f in the ETS-NOCV in which each atom belongs

C	4.956835	9.670408	15.943967 f=t	C	0.880813	11.904527	13.405515 f=Z
C	6.074845	9.090378	16.485056 f=t	C	1.247849	10.824287	12.618656 f=Z
C	7.174465	8.969835	15.644581 f=t	C	1.330568	9.576793	13.227951 f=Z
C	7.111237	9.424195	14.334801 f=t	C	1.033743	9.384055	14.570482 f=Z
C	5.948883	10.003554	13.846154 f=t	C	0.190685	13.027025	15.528276 f=Z
C	4.831654	10.137945	14.661571 f=t	C	1.189759	14.166133	15.321952 f=Z
H	5.901550	10.355603	12.822990 f=t	C	1.082086	7.981728	15.150044 f=Z
H	7.975236	9.326106	13.689307 f=t	C	2.095292	7.071836	14.465544 f=Z
H	3.905863	10.575787	14.308477 f=t	C	1.563285	11.007138	11.152977 f=Z
F	3.840492	9.798254	16.789883 f=t	C	0.697886	10.117671	10.264513 f=Z
H	6.086304	8.748216	17.513100 f=t	C	1.835201	7.353448	24.602246 f=Z
H	8.082719	8.517133	16.023156 f=t	C	-0.507519	6.590262	24.338905 f=Z
Zr	1.957971	10.200814	17.974402 f=Z	C	-4.579021	8.838280	15.177185 f=Z
C	2.450817	12.321618	18.285107 f=Z	C	-5.952936	10.016339	16.871308 f=Z
N	0.315954	10.318194	16.720485 f=Z	C	4.146719	11.063438	22.780140 f=Z
C	-1.011543	10.271017	17.131581 f=Z	C	7.604667	6.117442	21.585506 f=Z
C	-1.171727	10.201249	18.508356 f=Z	C	2.492683	5.577057	20.061481 f=Z
C	-2.372519	10.104767	19.162902 f=Z	C	-0.300668	7.328617	15.131634 f=Z
C	-3.503793	10.083021	18.340215 f=Z	C	3.048064	10.783840	10.871098 f=Z
C	-3.418946	10.150087	16.952844 f=Z	C	-1.210755	13.506898	15.148438 f=Z
C	-2.158107	10.250734	16.353050 f=Z	H	-1.784182	8.809318	23.093551 f=Z
C	-2.414460	10.086404	20.687169 f=Z	H	2.398468	8.220895	22.368177 f=Z
C	-1.094992	9.523728	21.203745 f=Z	H	-2.060312	10.288158	15.274929 f=Z
C	0.045315	9.636727	20.444364 f=Z	H	-4.475842	10.007903	18.804166 f=Z
O	0.049582	10.193124	19.171042 f=Z	H	-3.637572	9.284335	22.286909 f=Z
C	-0.923093	8.920918	22.448425 f=Z	H	-4.540647	9.693696	20.849303 f=Z
C	0.316192	8.456899	22.894700 f=Z	H	-3.543061	8.230137	20.867002 f=Z
C	1.428025	8.588118	22.063395 f=Z	H	-2.569304	11.561846	22.277407 f=Z
C	1.298852	9.180478	20.811920 f=Z	H	-1.721569	12.156096	20.843054 f=Z
C	-4.660352	10.088124	16.062613 f=Z	H	-3.481472	11.977436	20.813764 f=Z
C	-4.723246	11.334359	15.172732 f=Z	H	-4.771581	12.245514	15.773948 f=Z
C	-3.598816	9.268753	21.197396 f=Z	H	-3.856965	11.409659	14.512300 f=Z
C	-2.553448	11.537445	21.185548 f=Z	H	-5.614584	11.298342	14.541448 f=Z
C	0.416176	7.812628	24.277364 f=Z	H	-3.696604	8.853189	14.533858 f=Z
C	-0.013382	8.828766	25.342488 f=Z	H	-4.539262	7.930397	15.783949 f=Z
N	2.279183	9.365119	19.844578 f=Z	H	-5.459315	8.776705	14.532308 f=Z
C	3.602887	8.884245	20.073960 f=Z	H	-6.083436	10.892918	17.510817 f=Z
C	4.559056	9.695379	20.717595 f=Z	H	-6.804828	9.978996	16.189225 f=Z
C	5.838225	9.184165	20.910376 f=Z	H	-5.996068	9.120695	17.495837 f=Z
C	6.205662	7.909449	20.505403 f=Z	H	-1.043128	9.160480	25.196734 f=Z
C	5.241759	7.127195	19.879657 f=Z	H	0.053360	8.380801	26.337169 f=Z
C	3.947203	7.578453	19.657898 f=Z	H	0.629775	9.711947	25.324439 f=Z
C	4.236476	11.073988	21.253058 f=Z	H	2.193092	6.598726	23.897115 f=Z
C	5.250411	12.123041	20.799128 f=Z	H	2.543733	8.185712	24.608442 f=Z
C	7.604569	7.393801	20.748203 f=Z	H	1.851726	6.903954	25.597245 f=Z
C	8.361292	7.188359	19.437332 f=Z	H	-0.223123	5.845359	23.591642 f=Z
C	2.938576	6.628517	19.043934 f=Z	H	-0.445128	6.122409	25.324658 f=Z
C	3.457552	5.950739	17.779368 f=Z	H	-1.551308	6.858166	24.164962 f=Z
C	0.642687	10.501407	15.345133 f=Z	H	6.577157	9.800951	21.411715 f=Z
C	0.582503	11.782891	14.758700 f=Z	H	5.501027	6.120475	19.570066 f=Z

A.1. Geometries from the Chapter Coordination of Alkyl cations  $[(XA_2)X(CH_2Y)]$   
 ( $X = Th, U$  or  $Zr$ ;  $Y = SiMe_3, H$ ) with an arene for Ethylene polymerisation: 143  
 Exploration of the bonding

H	2.048391	7.208580	18.775639 f=Z	H	-0.255199	6.325269	15.562157 f=Z
H	1.741317	4.915783	19.623133 f=Z	H	-1.034834	7.907335	15.691802 f=Z
H	3.340064	4.961611	20.374783 f=Z	H	-0.655608	7.236020	14.101757 f=Z
H	2.060793	6.038582	20.950412 f=Z	H	3.087826	7.524191	14.405501 f=Z
H	2.667536	5.347381	17.326643 f=Z	H	2.181156	6.133199	15.014659 f=Z
H	3.804223	6.672452	17.035804 f=Z	H	1.780248	6.815210	13.451781 f=Z
H	4.288866	5.276447	17.995905 f=Z	H	0.180323	12.771817	16.590235 f=Z
H	3.254720	11.357955	20.868128 f=Z	H	-1.465301	14.406413	15.714133 f=Z
H	3.380245	10.372287	23.133446 f=Z	H	-1.261269	13.757330	14.085456 f=Z
H	5.100957	10.770871	23.225949 f=Z	H	-1.969342	12.753304	15.358050 f=Z
H	3.897163	12.060816	23.150004 f=Z	H	0.976357	14.981680	16.016172 f=Z
H	5.400559	12.111028	19.716994 f=Z	H	2.222481	13.848661	15.479827 f=Z
H	4.912857	13.121865	21.084551 f=Z	H	1.123783	14.577055	14.311841 f=Z
H	6.225484	11.966685	21.266337 f=Z	H	1.332488	12.049227	10.906964 f=Z
H	8.132546	8.165908	21.318123 f=Z	H	3.669203	11.463874	11.459654 f=Z
H	7.080004	6.262356	22.531896 f=Z	H	3.343392	9.757665	11.107987 f=Z
H	7.121261	5.292248	21.056099 f=Z	H	3.268400	10.956848	9.815282 f=Z
H	8.628428	5.809061	21.808642 f=Z	H	-0.365186	10.282906	10.450359 f=Z
H	8.421725	8.117606	18.865025 f=Z	H	0.894563	10.327083	9.210776 f=Z
H	9.380852	6.848170	19.632193 f=Z	H	0.908182	9.058313	10.433046 f=Z
H	7.873536	6.433073	18.814542 f=Z	H	3.378294	12.432557	18.853548 f=Z
H	1.627538	8.723499	12.630716 f=Z	H	2.581884	12.812227	17.314974 f=Z
H	0.821798	12.885097	12.944358 f=Z	H	1.660679	12.854688	18.822414 f=Z
H	1.376605	8.056921	16.208835 f=Z				

Optimised geometry of  $\eta^2$ -E'-Zr-horizontal and the name of the fragment f in the  
 ETS-NOCV in which each atom belongs

C	7.558282	8.854639	16.089291 f=Z	C	14.890901	11.374616	16.931186 f=Z
C	8.153290	9.648401	15.078342 f=Z	C	12.093599	5.792469	16.850034 f=Z
C	7.667009	10.948369	14.824314 f=Z	C	11.071509	5.339423	17.887842 f=Z
C	6.595211	11.412500	15.579647 f=Z	C	15.049059	7.523058	15.529803 f=Z
C	5.996834	10.658307	16.576170 f=Z	C	15.873489	6.243283	20.655511 f=Z
C	6.502170	9.383756	16.816629 f=Z	C	5.490044	8.228339	10.911512 f=Z
N	9.263475	9.130158	14.357418 f=Z	C	6.642649	6.379226	9.734524 f=Z
Zr	11.046520	9.240895	15.415755 f=Z	C	16.115175	4.337158	13.529685 f=Z
C	11.761421	11.267041	14.913923 f=Z	C	16.371435	5.037955	11.167085 f=Z
C	8.251683	11.859960	13.765859 f=Z	C	7.297567	12.033327	12.582954 f=Z
C	8.608811	13.234999	14.332718 f=Z	C	3.568930	10.375914	17.146084 f=Z
C	4.833615	11.202755	17.369227 f=Z	C	7.469596	6.462294	15.319809 f=Z
C	5.162448	11.310860	18.856453 f=Z	C	12.891823	4.584485	16.354046 f=Z
C	8.021682	7.434911	16.362634 f=Z	C	13.963181	7.583101	21.601655 f=Z
C	7.684915	6.937324	17.762502 f=Z	C	16.315403	9.728787	15.700392 f=Z
N	12.807960	8.160428	15.283434 f=Z	H	9.300203	7.312590	9.451316 f=Z
C	13.331354	7.589170	14.131490 f=Z	H	7.014344	8.789188	12.761740 f=Z
C	12.535474	7.769066	13.008069 f=Z	H	15.143495	6.712897	14.837603 f=Z
C	12.792276	7.252753	11.764618 f=Z	H	14.241837	6.108341	10.691156 f=Z
C	13.984352	6.528825	11.651876 f=Z	H	11.121463	6.537547	8.811728 f=Z
C	14.845998	6.335662	12.727576 f=Z	H	12.767650	6.128993	9.230043 f=Z
C	14.505337	6.869671	13.976416 f=Z	H	11.431404	5.428841	10.157404 f=Z
C	11.836420	7.522869	10.606950 f=Z	H	11.664110	8.989793	9.010334 f=Z
C	10.453085	7.833021	11.170998 f=Z	H	12.387851	9.636361	10.489558 f=Z
C	10.322002	8.335418	12.444128 f=Z	H	13.335656	8.577165	9.436234 f=Z
O	11.397449	8.502465	13.300421 f=Z	H	17.378093	7.326077	12.316590 f=Z
C	9.261147	7.697449	10.461613 f=Z	H	17.267394	6.793030	13.998486 f=Z
C	8.019357	8.037219	11.003266 f=Z	H	18.269786	5.897727	12.858675 f=Z
C	7.961072	8.536759	12.304033 f=Z	H	16.019334	4.636078	14.575743 f=Z
C	9.127244	8.691326	13.045804 f=Z	H	15.280057	3.675013	13.288308 f=Z
C	16.148550	5.547313	12.588662 f=Z	H	17.040300	3.762981	13.435112 f=Z
C	17.331273	6.447567	12.964526 f=Z	H	16.438687	5.856158	10.445809 f=Z
C	11.783222	6.330474	9.653169 f=Z	H	17.312842	4.486385	11.123910 f=Z
C	12.337245	8.760653	9.839429 f=Z	H	15.578884	4.356799	10.847533 f=Z
C	6.760947	7.848753	10.155921 f=Z	H	7.723304	8.473041	8.292195 f=Z
C	6.857185	8.730396	8.904859 f=Z	H	5.964159	8.605085	8.287268 f=Z
C	13.411749	7.977729	16.555700 f=Z	H	6.937805	9.786527	9.173617 f=Z
C	14.365857	8.901124	17.037096 f=Z	H	5.348799	7.616794	11.806337 f=Z
C	14.863913	8.727117	18.323159 f=Z	H	5.485975	9.280829	11.206290 f=Z
C	14.475519	7.675444	19.141992 f=Z	H	4.623708	8.068808	10.266280 f=Z
C	13.560933	6.760006	18.632358 f=Z	H	6.570689	5.725488	10.607146 f=Z
C	13.022924	6.876392	17.358909 f=Z	H	5.745205	6.234887	9.127837 f=Z
C	14.899885	10.037793	16.191982 f=Z	H	7.498702	6.053457	9.140850 f=Z



H	6.211869	12.408856	15.384529	f=Z	H	13.472425	4.149515	17.171953	f=Z
H	6.045477	8.783068	17.593069	f=Z	H	10.526037	6.176114	18.329495	f=Z
H	9.120999	7.403883	16.264222	f=Z	H	10.345594	4.666380	17.426089	f=Z
H	7.825124	5.447897	15.516291	f=Z	H	11.541648	4.786226	18.703527	f=Z
H	6.377479	6.450296	15.365866	f=Z	H	14.258463	10.128337	15.313193	f=Z
H	7.762023	6.737305	14.306907	f=Z	H	16.686876	10.548867	15.081445	f=Z
H	8.152145	5.967058	17.934455	f=Z	H	17.002729	9.605699	16.541405	f=Z
H	8.020314	7.623258	18.544698	f=Z	H	16.344102	8.818135	15.101172	f=Z
H	6.609110	6.794469	17.885221	f=Z	H	15.145093	12.185008	16.244738	f=Z
H	9.167373	11.395839	13.392369	f=Z	H	13.916206	11.599404	17.371727	f=Z
H	7.071788	11.081971	12.101429	f=Z	H	15.626395	11.394079	17.738594	f=Z
H	6.356118	12.486056	12.904716	f=Z	H	15.723516	8.371150	20.690010	f=Z
H	7.744535	12.691525	11.834239	f=Z	H	13.390397	8.511226	21.539646	f=Z
H	9.210494	13.167229	15.241638	f=Z	H	13.264611	6.747531	21.506611	f=Z
H	9.172013	13.810845	13.595138	f=Z	H	14.408551	7.527417	22.597292	f=Z
H	7.713058	13.810680	14.576578	f=Z	H	16.669865	6.206345	19.909492	f=Z
H	4.640890	12.214298	16.995999	f=Z	H	16.331861	6.182525	21.644996	f=Z
H	3.311987	10.317290	16.086547	f=Z	H	15.249334	5.355276	20.525444	f=Z
H	3.691240	9.355654	17.519418	f=Z	H	10.939087	11.982021	14.833614	f=Z
H	2.724733	10.822073	17.676332	f=Z	H	12.458811	11.627763	15.678074	f=Z
H	6.046331	11.929730	19.026742	f=Z	H	12.296647	11.265589	13.958929	f=Z
H	4.327298	11.759011	19.399157	f=Z	C	10.924368	9.553377	18.192012	f=t
H	5.348561	10.326569	19.294609	f=Z	C	10.128037	10.543560	17.768890	f=t
H	13.264375	5.918623	19.248369	f=Z	H	10.525372	11.530788	17.554392	f=t
H	15.595102	9.433720	18.701999	f=Z	H	9.054213	10.413600	17.672924	f=t
H	11.548122	6.192245	15.987721	f=Z	H	10.518402	8.584812	18.471925	f=t
H	12.216789	3.813811	15.974068	f=Z	H	11.988135	9.695550	18.360094	f=t
H	13.579450	4.855213	15.553094	f=Z					

## A.2 Geometries from the Chapter Thermodynamic properties and electronic structures of Plutonium Oxides in Angstrom

### A.2.1 Molecules containing Plutonium

$\text{PuO}_2(\text{OH})_2$  coordinates in Å

Label	x	y	z
Pu	0.000000	0.967853	0.000000
O	-0.017474	0.880968	1.740764
O	0.017474	0.880968	-1.740764
O	1.676305	2.238293	0.001209
O	-1.676305	2.238293	-0.001209
H	2.063158	2.697914	0.750904
H	-2.063158	2.697914	-0.750904

$\text{PuO}_3$  coordinates in Å

Label	x	y	z
Pu	0.000000	0.000000	0.000000
O	1.934000	0.000000	0.000000

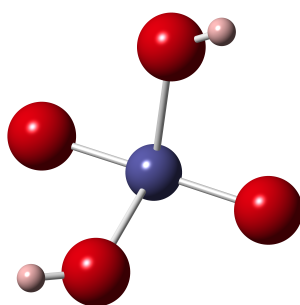


FIGURE A.3:  $\text{PuO}_2(\text{OH})_2$  molecule. Blue: Pu; red: O; pink: H.

0	-0.118952	0.000000	1.762992
0	-0.118952	0.000000	-1.762992

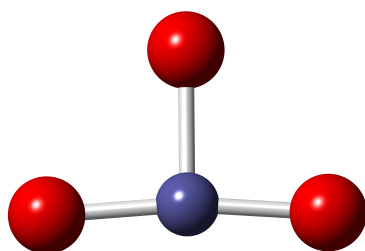
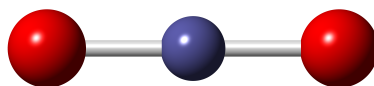


FIGURE A.4:  $\text{PuO}_3$  molecule. Blue: Pu; red: O.

#### $\text{PuO}_2$ coordinates in Å

Label	x	y	z
Pu	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.808000
O	0.000000	0.000000	-1.808000

FIGURE A.5: PuO<sub>2</sub> molecule. Blue: Pu; red: O.

## A.2.2 Organic Molecules

### H<sub>2</sub>O<sub>2</sub> coordinates in Å

Label	x	y	z
O	-0.275341	-0.185870	0.687291
O	-0.213172	0.301727	-0.678278
H	0.365257	0.397493	1.116183
H	0.173256	-0.463349	-1.125197

### H<sub>2</sub>O coordinates in Å

Label	x	y	z
O	0.000000	0.000000	0.000000
H	0.521742	0.000000	0.823124
H	0.521742	0.000000	-0.823124

### O<sub>2</sub> coordinates in Å

Label	x	y	z
O	0.000000	0.000000	0.603760
O	0.000000	0.000000	-0.603760

**OH coordinates in Å**

Label	x	y	z
O	0.000000	0.000000	0.975370
H	0.000000	0.000000	0.000000

**H<sub>2</sub> coordinates in Å**

Label	x	y	z
H	0.000000	0.000000	0.372000
H	0.000000	0.000000	-0.372000



## Appendix B

# Electronic levels of Plutonium and Plutonium oxydes

TABLE B.1: Electronic levels (cm-1) of the plutonium atom and analysis of the various states obtained with the ano-cc-TZVP.

J-value	E (cm-1)	Character
0	0	54% $^7F$ , 38% $^5D$ , 7% $^3P$
1	1806	64% $^7F$ , 32% $^5D$
2	4208	82% $^7F$ , 17% $^5D$
3	6353	88% $^7F$ , 10% $^5D$
4	8091	93% $^7F$
5	9552	90% $^7F$
6	11010	85% $^7F$ , 10% $^5G$
0	12499	44% $^7F$ , 21% $^5D$ , 8% $^3P$
1	13612	66% $^9H$ , 9% $^7F$ , 7% $^7G$
2	14399	82% $^9H$ , 14% $^7G$
1	14845	38% $^5D$ , 20% $^7F$ , 9% $^9G$
3	15551	89% $^9H$ , 8% $^7G$
4	17026	86% $^9H$ , 6% $^7G$
1	17032	66% $^9D$ , 29% $^7P$

TABLE B.2: Energy electronic states ( $E < 16\,000\text{ cm}^{-1}$ ) of  $\text{PuO}_2(\text{OH})_2$  at SF-CASPT2 and SO-CASPT2 levels obtained with the ano-cc-TZVP.

Term Symbol	Character : % [orbital(number of electron)]	E ( $\text{cm}^{-1}$ )
SF $^3B(1)$	49% $2a/\Phi_u(1)$ , $1b/\delta_u(1)$ 48% $1a/\delta_u(1)$ , $2b/\Phi_u(1)$	0
$^3A(1)$	41% $1a/\delta_u(1)$ , $2a/\Phi_u(1)$ 59% $1b/\delta_u(1)$ , $2b/\Phi_u(1)$	889
$^3B(2)$	75% $1a/\delta_u(1)$ , $1b/\delta_u(1)$ 20% $2a/\Phi_u(1)$ , $2b/\Phi_u(1)$	2136
$^3A(2)$	59% $1a/\delta_u(1)$ , $2a/\Phi_u(1)$ 41% $1b/\delta_u(1)$ , $2b/\Phi_u(1)$	4698
$^3B(3)$	52% $2a/\Phi_u(1)$ , $1b/\delta_u(1)$ 46% $1a/\delta_u(1)$ , $2b/\Phi_u(1)$	5351
$^1A(1)$	58% $1b/\delta_u(1)$ , $2b/\Phi_u(\bar{1})$ 30% $1a/\delta_u(1)$ , $2a/\Phi_u(\bar{1})$ 5% $2a/\Phi_u(2)$	5764
$^1B(1)$	50% $1a/\delta_u(1)$ , $1b/\delta_u(\bar{1})$ 28% $2a/\Phi_u(1)$ , $2b/\Phi_u(\bar{1})$ 16% $1a/\delta_u(1)$ , $2b/\Phi_u(\bar{1})$	7444
$^1A(2)$	39% $1a/\delta_u(1)$ , $2a/\Phi_u(\bar{1})$ 29% $2a/\Phi_u(2)$ 13% $1b/\delta_u(1)$ , $2b/\Phi_u(\bar{1})$ 10% $1a/\delta_u(2)$ 7% $2a/\Phi_u(2)$	9626
$^1A(3)$	44% $1b/\delta_u(2)$ 33% $2a/\Phi_u(2)$ 12% $2b/\Phi_u(2)$ 9% $1a/\delta_u(2)$	10184
$^1B(2)$	66% $2a/\Phi_u(1)$ , $2b/\Phi_u(\bar{1})$ 26% $1a/\delta_u(1)$ , $2b/\Phi_u(\bar{1})$ 8% $1a/\delta_u(1)$ , $1b/\delta_u(\bar{1})$	10287
SO X	46.1% $^3A(1)$ , 41.4% $^3B(1)$ , 6.4% $^3B(2)$	0
a	45.3% $^3B(1)$ , 44.8% $^3A(1)$ , 6.3% $^3B(2)$	323
b	34.9% $^3B(2)$ , 24.7% $^3B(1)$ , 14.4% $^1A(1)$ , 12.5% $^3A(2)$ , 10.1% $^3B(3)$	2222
c	40.3% $^3A(2)$ , 25.4% $^3B(2)$ , 18.8% $^1B(1)$ , 7.1% $^3B(1)$ , 6.1% $^3A(1)$	3757
d	35.5% $^3B(3)$ , 34.3% $^3B(2)$ , 14.3% $^1A(2)$ , 11.1% $^3B(1)$ ,	4158
e	63.5% $^3B(1)$ , 30.1% $^3B(2)$	7268
f	92.8% $^3A(1)$	7575
g	32.4% $^1A(1)$ , 28.1% $^3B(3)$ , 27.8% $^3A(2)$ , 6.3% $^3B(2)$ ,	10041
h	41.1% $^3A(2)$ , 24.1% $^3B(3)$ , 15.3% $^3B(2)$ , 10.5% $^3B(1)$ , 6.1% $^1B(1)$	10142
i	33.5% $^3A(2)$ , 26.3% $^3B(2)$ , 13.8% $^3B(3)$ , 13.1% $^1B(1)$ , 8.2% $^3B(1)$	10343
j	29.3% $^3B(2)$ , 25.6% $^3B(3)$ , 22.0% $^3B(1)$ , 16.6% $^1A(2)$	11089
k	26.3% $^3B(3)$ , 22.9% $^3A(1)$ , 17.0% $^3B(1)$ , 16.6% $^3A(2)$ , 13.0% $^3B(2)$	12269
l	26.1% $^3A(2)$ , 23.6% $^3A(1)$ , 21.3% $^3B(3)$ , 15.4% $^3B(2)$ , 9.6% $^3B(1)$	12311
m	27.5% $^3B(3)$ , 24.6% $^3A(2)$ , 22.2% $^3A(1)$ , 12.1% $^3B(1)$ , 9.7% $^3B(2)$	13782
n	34.8% $^3B(3)$ , 21.8% $^3A(2)$ , 17.7% $^3A(1)$ , 13.0% $^3B(1)$ , 8.5% $^3B(2)$	13783
o	40.9% $^1A(1)$ , 19.7% $^1A(3)$ , 15.4% $^3B(2)$ , 7.3% $^3B(4)$ ,	15696

TABLE B.3: Vertical transitions in  $\text{cm}^{-1}$  of the low-energy ( $E < 16000 \text{ cm}^{-1}$ ) electronic states of  $\text{PuO}_3$  at SF-CASPT2 and SO-CASPT2 levels obtained with the ANO-RCC-TZVP. Orbitals  $1a_1$ ,  $2a_1/\pi_u$ ,  $3a_1$  always doubly occupied and do not appear in the following table.

SF	Term Symbol	Character: % [orbital(number of electron)]	E ( $\text{cm}^{-1}$ )
$^3B_2(1)$		36% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$	0
		21% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(1)]$	
		22% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$	
$^3A_2(1)$		43% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$	3161
		23% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(0)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(1)]$	
$^3B_1(1)$		17% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$	
		38% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	4663
		12% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
$^1A_1(1)$		12% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 1b_1/\Phi_u(1), 2b_1/\pi_u(2), 1b_2/p^{(0)}(2)]$	7239
		32% $[4a_1/p^{(0)}(2), 1b_2/p^{(0)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(\bar{1}), 1a_2/\delta_u(2)]$	
		28% $[4a_1/p^{(0)}(2), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(2)]$	
$^3A_2(2)$		11% $[4a_1/p^{(0)}(1), 5a_1/\Phi_u(\bar{1}), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 1a_2/\delta_u(2)]$	7287
		20% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(1), 2b_2/\sigma_u(2), 3b_2/\delta_u(2)]$	
		18% $[4a_1/p^{(0)}(1), 5a_1/\Phi_u(\bar{1}), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
$^3B_1(2)$		17% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	8038
		31% $[4a_1/p^{(0)}(1), 5a_1/\Phi_u(\bar{1}), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$	
		11% $[4a_1/p^{(0)}(2), 5a_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 3b_2/\delta_u(1)]$	
$^5B_2(1)$		10% $[4a_1/p^{(0)}(2), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(2), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$	
		10% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(1), 2b_1/\pi_u(1), 1b_2/p^{(0)}(\bar{1}), 2b_2/\sigma_u(2), 1a_2/\delta_u(1)]$	
		47% $[4a_1/p^{(0)}(2), 1b_1/\Phi_u(\bar{1})(1), 1b_2/p^{(0)}(2), 2b_2/\sigma_u(1), 3b_2/\delta_u(1), 1a_2/\delta_u(1)]$	8962



Table B.3 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
<sup>3</sup> A <sub>1</sub> (1)	41% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ )(1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 39% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ )(1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 11% [4(2), 1b <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ )(1), 8(1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	9645
<sup>3</sup> B <sub>2</sub> (2)	15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 15% [4a <sub>1</sub> /p <sup>(O)</sup> (1), 5a <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ ), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 12% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ ), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	9731
<sup>1</sup> A <sub>2</sub> (1)	26% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 11( $\bar{1}$ ), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 24% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 18% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 16% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	10293
<sup>1</sup> B <sub>2</sub> (1)	30% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 22% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ ), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 16% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (2)]	10604
<sup>5</sup> A <sub>1</sub> (1)	27% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 12% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 26% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> ( $\bar{1}$ ), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 17% [4a <sub>1</sub> /p <sup>(O)</sup> (1), 5a <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ ), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	10662
<sup>3</sup> B <sub>1</sub> (3)	34% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 18% [4a <sub>1</sub> /p <sup>(O)</sup> (1), 5a <sub>1</sub> /Φ <sub>u</sub> ( $\bar{1}$ ), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )] 17% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	11567
<sup>1</sup> B <sub>1</sub> (1)	36% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	11632
<sup>5</sup> B <sub>1</sub> (1)	36% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> ( $\bar{1}$ )]	12017

Table B.3 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
<sup>5</sup> A <sub>2</sub> (1)	15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	12017
	36% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>3</sup> B <sub>2</sub> (3)	15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	12023
	24% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>3</sup> A <sub>2</sub> (3)	11% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (2)]	12940
	17% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (2)]	
<sup>1</sup> A <sub>1</sub> (2)	15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	13213
	21% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (2), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>3</sup> A <sub>1</sub> (2)	10% [4a <sub>1</sub> /p <sup>(O)</sup> (1), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (2)]	13421
	10% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (2), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2)]	
<sup>3</sup> B <sub>1</sub> (4)	44% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	13518
	29% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> A <sub>1</sub> (2)	29% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 2b <sub>1</sub> /π <sub>u</sub> <sup>*</sup> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	13575
	15% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> B <sub>1</sub> (2)	13% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 2b <sub>1</sub> /π <sub>u</sub> <sup>*</sup> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (2)]	13970
	11% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> <sup>*</sup> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> A <sub>1</sub> (2)	29% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	13970
	14% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> B <sub>1</sub> (2)	13% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	13970
	12% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 1a <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> B <sub>1</sub> (2)	30% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	13970
	20% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>1</sub> /Φ <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>u</sub> (2), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	
<sup>5</sup> B <sub>1</sub> (2)	16% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	13970
	16% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>u</sub> (1), 2b <sub>1</sub> /π <sub>u</sub> (1), 1b <sub>2</sub> /p <sup>(O)</sup> (2), 2b <sub>2</sub> /σ <sub>u</sub> (1), 3b <sub>2</sub> /δ <sub>u</sub> (1)]	



Table B.3 – Continued from previous page

SO	X	Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
			11% [4a <sub>1</sub> /p <sup>(O)</sup> (2), 5a <sub>1</sub> /Φ <sub>it</sub> (2), 1b <sub>2</sub> /p <sup>(O)</sup> (1), 2b <sub>2</sub> /σ <sub>it</sub> (2), 1a <sub>2</sub> /δ <sub>it</sub> (1)]	
				0
	a		47.15% <sup>3</sup> B <sub>2</sub> (1), 24.15% <sup>3</sup> A <sub>2</sub> (1), 14.14% <sup>3</sup> B <sub>1</sub> (1)	1235
	b		58.72% <sup>3</sup> B <sub>2</sub> (1), 24.89% <sup>3</sup> A <sub>2</sub> (1)	1783
	c		73.37% <sup>3</sup> B <sub>2</sub> (1)	3777
	d		51.22% <sup>3</sup> A <sub>2</sub> (1)	5660
	e		23.54% <sup>3</sup> B <sub>1</sub> (1), 18.35% <sup>1</sup> A <sub>1</sub> (1), 16.73% <sup>3</sup> A <sub>2</sub> (2), 10.23% <sup>3</sup> B <sub>1</sub> (2)	6658
	f		49.43% <sup>3</sup> B <sub>1</sub> (1), 22.12% <sup>3</sup> A <sub>1</sub> (1)	7062
	g		43.87% <sup>3</sup> B <sub>1</sub> (1), 19.21% <sup>3</sup> A <sub>1</sub> (1), 11.3% <sup>3</sup> B <sub>1</sub> (2)	7929
	h		23.47% <sup>3</sup> B <sub>2</sub> (1), 17.68% <sup>3</sup> A <sub>2</sub> (1), 17.17% <sup>3</sup> B <sub>1</sub> (2)	7973
	i		26.14% <sup>3</sup> A <sub>2</sub> (1), 21.08% <sup>5</sup> B <sub>2</sub> (1), 18.73% <sup>3</sup> A <sub>2</sub> (2)	8675
	j		32.2% <sup>3</sup> A <sub>2</sub> (2), 24.4% <sup>3</sup> A <sub>2</sub> (1), 15% <sup>5</sup> B <sub>2</sub> (1)	9096
	k		28.2% <sup>3</sup> A <sub>2</sub> (1), 22.38% <sup>3</sup> B <sub>1</sub> (1), 11.46% <sup>5</sup> B <sub>2</sub> (1)	9345
	l		28.45% <sup>3</sup> A <sub>2</sub> (1), 26.41% <sup>3</sup> B <sub>2</sub> (1)	9399
	m		30.77% <sup>3</sup> B <sub>1</sub> (2), 19% <sup>3</sup> B <sub>1</sub> (1)	9690
	n		16.69% <sup>3</sup> B <sub>2</sub> (1), 14.81% <sup>5</sup> B <sub>2</sub> (1)	9879
	o		28.51% <sup>3</sup> B <sub>1</sub> (2), 11.78% <sup>3</sup> A <sub>1</sub> (2), 10.3% <sup>3</sup> B <sub>1</sub> (1)	10224
	p		24.08% <sup>3</sup> A <sub>2</sub> (2), 15.86% <sup>5</sup> B <sub>1</sub> (1), 13.35% <sup>3</sup> B <sub>2</sub> (2)	10235
	q		25.31% <sup>3</sup> A <sub>2</sub> (2), 14.83% <sup>3</sup> B <sub>2</sub> (2), 9.57% <sup>5</sup> B <sub>1</sub> (1)	10342
	r		23.29% <sup>5</sup> B <sub>2</sub> (1), 13.35% <sup>5</sup> B <sub>1</sub> (3)	10686
	s		29.37% <sup>5</sup> B <sub>1</sub> (1), 24.74% <sup>5</sup> A <sub>1</sub> (1), 10.19% <sup>5</sup> B <sub>2</sub> (1), 10.05% <sup>5</sup> A <sub>1</sub> (2)	10749
			23.12% <sup>3</sup> B <sub>2</sub> (2), 20.68% <sup>3</sup> B <sub>1</sub> (3), 15.13% <sup>3</sup> B <sub>1</sub> (2)	

Table B.3 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
t	25.96% <sup>5</sup> B <sub>1</sub> (1), 20.75% <sup>5</sup> A <sub>1</sub> (1), 15.44% <sup>5</sup> B <sub>2</sub> (1)	10768
u	23.74% <sup>5</sup> B <sub>2</sub> (1), 11.62% <sup>3</sup> B <sub>1</sub> (3), 10.37% <sup>5</sup> A <sub>1</sub> (1)	11022
v	24.63% <sup>5</sup> B <sub>2</sub> (1), 21.07% <sup>5</sup> A <sub>1</sub> (1), 12.44% <sup>3</sup> B <sub>1</sub> (1)	11207
w	14.48% <sup>3</sup> A <sub>1</sub> (1), 10.17% <sup>3</sup> A <sub>1</sub> (2)	11616
x	36.43% <sup>5</sup> A <sub>1</sub> (1), 12.09% <sup>3</sup> B <sub>1</sub> (2)	12429
y	20.5% <sup>3</sup> A <sub>2</sub> (2)	12567
z	11.52% <sup>1</sup> A <sub>1</sub> (1), 10.25% <sup>3</sup> B <sub>1</sub> (3), 10.04% <sup>3</sup> B <sub>2</sub> (3)	12693
aa	14.11% <sup>1</sup> A <sub>2</sub> (1)	12794
ab	29.09% <sup>3</sup> B <sub>2</sub> (2), 24.21% <sup>3</sup> A <sub>2</sub> (3)	12873
ac	16.43% <sup>3</sup> A <sub>1</sub> (3), 15.09% <sup>5</sup> B <sub>1</sub> (2), 14.7% <sup>3</sup> A <sub>1</sub> (1), 10.89% <sup>5</sup> B <sub>1</sub> (1)	13058
ad	30.37% <sup>3</sup> A <sub>2</sub> (3), 13.89% <sup>1</sup> A <sub>1</sub> (1),	13309
ae	20.38% <sup>5</sup> B <sub>1</sub> (2), 13.23% <sup>5</sup> A <sub>1</sub> (3), 9.98% <sup>5</sup> B <sub>2</sub> (2)	13341
af	34.08% <sup>3</sup> B <sub>2</sub> (3), 16.97% <sup>1</sup> A <sub>2</sub> (1), 11.74% <sup>1</sup> A <sub>2</sub> (2)	13488
ag	24.73% <sup>3</sup> A <sub>1</sub> (1), 12.48% <sup>5</sup> B <sub>1</sub> (2), 11.36% <sup>5</sup> B <sub>1</sub> (1)	13582
ah	18.48% <sup>5</sup> B <sub>1</sub> (2), 15.12% <sup>5</sup> A <sub>1</sub> (3)	13814
ai	27.31% <sup>5</sup> B <sub>2</sub> (1), 14.88% <sup>1</sup> B <sub>2</sub> (1), 12.3% <sup>3</sup> A <sub>1</sub> (1)	13936
aj	28.12% <sup>5</sup> B <sub>2</sub> (1), 19.38% <sup>5</sup> A <sub>1</sub> (1), 10% <sup>5</sup> B <sub>1</sub> (2)	13996
ak	17.59% <sup>5</sup> B <sub>1</sub> (2), 14.15% <sup>5</sup> B <sub>1</sub> (3), 11.94% <sup>5</sup> A <sub>1</sub> (2), 11.41% <sup>5</sup> A <sub>1</sub> (1)	14024
al	53.19% <sup>1</sup> B <sub>1</sub> (1), 12.49% <sup>3</sup> A <sub>2</sub> (3)	14216
am	22.79% <sup>5</sup> A <sub>1</sub> (2), 12.86% <sup>5</sup> B <sub>1</sub> (3), 10.57% <sup>3</sup> B <sub>1</sub> (3)	14257
an	31.62% <sup>5</sup> B <sub>2</sub> (1), 10.41% <sup>3</sup> A <sub>1</sub> (2)	14680
ao	19.07% <sup>5</sup> B <sub>1</sub> (1), 17.32% <sup>5</sup> B <sub>1</sub> (2), 16.76% <sup>5</sup> A <sub>1</sub> (3)	14724
ap	21.09% <sup>5</sup> A <sub>1</sub> (1), 10.26% <sup>5</sup> A <sub>1</sub> (2), 10% <sup>5</sup> B <sub>1</sub> (3)	14750

Table B.3 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
aq	16.59% <sup>5</sup> B <sub>1</sub> (3) , 13.06% <sup>5</sup> B <sub>1</sub> (2) , 9.69% <sup>5</sup> A <sub>1</sub> (2)	14874
ar	16.33% <sup>5</sup> B <sub>1</sub> (1)	15129
as	20.39% <sup>5</sup> A <sub>1</sub> (2) , 20.07% <sup>5</sup> B <sub>1</sub> (1) , 12.66% <sup>5</sup> B <sub>1</sub> (3) , 10.85% <sup>3</sup> B <sub>1</sub> (3) , 9.82% <sup>5</sup> A <sub>1</sub> (1)	15141
at	28.7% <sup>3</sup> B <sub>2</sub> (2) , 12.63% <sup>5</sup> B <sub>2</sub> (1)	15375
au	15.53% <sup>3</sup> A <sub>1</sub> (2) , 12.26% <sup>5</sup> B <sub>1</sub> (3) , 10.67% <sup>5</sup> B <sub>1</sub> (1) , 9.55% <sup>3</sup> B <sub>2</sub> (2)	15439
av	25.7% <sup>3</sup> B <sub>2</sub> (3) , 10.77% <sup>3</sup> B <sub>2</sub> (2) , 10.04% <sup>5</sup> A <sub>1</sub> (2)	15494
aw	23.7% <sup>5</sup> B <sub>1</sub> (3) , 12.34% <sup>3</sup> A <sub>1</sub> (2) , 11.09% <sup>3</sup> B <sub>1</sub> (3)	15616
ay	12.56% <sup>5</sup> A <sub>1</sub> (3) , 11.67% <sup>3</sup> B <sub>1</sub> (2) , 10.58% <sup>3</sup> A <sub>1</sub> (3) , 10.25% <sup>3</sup> A <sub>2</sub> (3)	15708
az	15.14% <sup>5</sup> B <sub>1</sub> (3) , 10.79% <sup>3</sup> B <sub>1</sub> (3)	15906
ba	18.56% <sup>3</sup> B <sub>2</sub> (3) , 16.95% <sup>5</sup> B <sub>1</sub> (3)	15948

TABLE B.4: Vertical transitions in  $\text{cm}^{-1}$  of the low-energy ( $E < 16\,000\text{ cm}^{-1}$ ) electronic states of  $\text{PuO}_3$  at SF-CASPT2 and SO-CASPT2 levels obtained with the ANO-RCC-TZVP. Orbitals  $1a_1$ ,  $2a_1/\pi_u$ ,  $3a_1$  always doubly occupied and do not appear in the following table.

Term	Symbol	Character : % [orbital(number of electron)]	E ( $\text{cm}^{-1}$ )
SF	$^5A_g(1)$	84% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]	0
	$^5A_g(2)$	45% [ $1a_u/\delta_u(1)$ , $3b_{2u}/\pi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]	4798
	$^5B_{3u}(1)$	45% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\pi_u(1)$ ]	5421
	$^5B_{2u}(1)$	85% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]	5421
	$^5B_{3g}(1)$	44% [ $2b_{2u}/\Phi_u(1)$ , $3b_{2u}/\pi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]	6019
	$^5B_{2g}(1)$	44% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{3u}/\pi_u(1)$ , $3b_{3u}/\pi_u(1)$ ]	6019
	$^5A_g(3)$	45% [ $1a_u/\delta_u(1)$ , $3b_{2u}/\pi_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ ]	6067
	$^5B_{1g}(1)$	44% [ $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{3u}/\pi_u(1)$ , $2b_{1u}/\delta_u(1)$ ]	6158
	$^3B_{3u}(1)$	59% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ ]	6855
	$^3B_{2u}(1)$	19% [ $3a_g(1)$ , $1a_u/\delta_u(1)$ , $2b_{2u}/\Phi_u(1)$ , $2b_{1u}/\delta_u(1)$ ]	6855
	$^5B_{1g}(2)$	44% [ $1a_u/\delta_u(1)$ , $2b_{1u}/\delta_u(1)$ , $2b_{3u}/\Phi_u(1)$ , $3b_{3u}/\pi_u(1)$ ]	7293

Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
<sup>5</sup> A <sub>u</sub> (1)	79% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	7452
<sup>5</sup> B <sub>1u</sub> (1)	80% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> 0(1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	7462
<sup>5</sup> B <sub>3g</sub> (2)	37% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	7637
	33% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> 3(1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
	12% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	
<sup>5</sup> B <sub>2g</sub> (2)	37% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> 6(1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	7637
	33% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
	12% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	
<sup>3</sup> B <sub>1u</sub> (1)	51% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	9586
	68% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
<sup>3</sup> A <sub>u</sub> (1)	51% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	9614
	17% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
<sup>3</sup> B <sub>3g</sub> (1)	38% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	10101
	36% [1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
<sup>3</sup> B <sub>2g</sub> (1)	38% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	10101
	36% [1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
<sup>3</sup> B <sub>1g</sub> (1)	24% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1)]	10308
	24% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (2)]	
	19% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
	16% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	
<sup>5</sup> A <sub>u</sub> (2)	23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1)]	11344
	23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	
	20% [3a <sub>g</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	



Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
$^5B_{1u}(2)$	20% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 23% [3a <sub>g</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 23% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1)] 19% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 19% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 11(1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	11347
$^3B_{3g}(2)$	35% [1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	11467
$^3B_{2g}(2)$	33% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	11467
$^3B_{1g}(2)$	35% [1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 33% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	12812
$^3A_g(1)$	34% [1a <sub>u</sub> /δ <sub>u</sub> (2), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 33% [3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	12815
$^3B_{1u}(2)$	51% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 17% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	13398
$^3A_u(2)$	20% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1)] 20% [3a <sub>g</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 15% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 15% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	13402
$^5B_{3g}(3)$	15% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1)] 15% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 14% [3a <sub>g</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 14% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 46% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 45% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	13460

Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
<sup>5</sup> B <sub>2g</sub> (3)	46% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 45% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	13460
<sup>3</sup> B <sub>1g</sub> (3)	34% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (2)] 34% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1)]	13638
<sup>3</sup> A <sub>g</sub> (2)	47% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1̄)] 17% [1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1̄), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	13659
<sup>5</sup> B <sub>3u</sub> (2)	45% [2a <sub>g</sub> /δ <sub>u</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (6)] 42% [1b <sub>1g</sub> /δ <sub>u</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (0), 2b <sub>1u</sub> /δ <sub>u</sub> (1)]	14688
<sup>5</sup> B <sub>2u</sub> (2)	45% [2a <sub>g</sub> /δ <sub>u</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 42% [1b <sub>1g</sub> /δ <sub>u</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1)]	14688
<sup>3</sup> B <sub>3u</sub> (2)	30% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1̄)] 22% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 22% [3a <sub>g</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	15060
<sup>3</sup> B <sub>2u</sub> (2)	11% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1̄), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1)] 34% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1̄), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 22% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>2u</sub> /Φ <sub>u</sub> (1)] 22% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (3)]	15062
<sup>1</sup> B <sub>3u</sub> (1)	11% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1̄), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 32% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 21% [3a <sub>g</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	15336
<sup>1</sup> B <sub>2u</sub> (1)	21% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 3b <sub>2u</sub> /π <sub>u</sub> (1)] 32% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 21% [3a <sub>g</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)]	15336

Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
<sup>3</sup> B <sub>3u</sub> (3)	21% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 3b <sub>2u</sub> /π <sub>u</sub> (1)] 29% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1)] 24% [3a <sub>g</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)]	15370
<sup>3</sup> B <sub>2u</sub> (3)	37% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 24% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (3)] 23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>2u</sub> /Φ <sub>u</sub> (1)]	15382
<sup>5</sup> A <sub>g</sub> (4)	64% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 20% [2b <sub>2u</sub> /Φ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 23% [1a <sub>u</sub> /δ <sub>u</sub> (1), 3b <sub>2u</sub> /π <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 14% [2b <sub>2u</sub> /Φ <sub>u</sub> (2), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 3b <sub>3u</sub> /π <sub>u</sub> (1)] 10% [2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (2), 3b <sub>3u</sub> /π <sub>u</sub> (1)]	15800
<sup>1</sup> B <sub>3u</sub> (2)	41% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 13(1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 23% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)] 23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>2u</sub> /Φ <sub>u</sub> (1)]	15850
<sup>1</sup> B <sub>2u</sub> (2)	41% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (1), 2b <sub>3u</sub> /Φ <sub>u</sub> (1)] 23% [3a <sub>g</sub> (1), 2b <sub>2u</sub> /Φ <sub>u</sub> (1), 2b <sub>1u</sub> /δ <sub>u</sub> (2)] 23% [3a <sub>g</sub> (1), 1a <sub>u</sub> /δ <sub>u</sub> (2), 2b <sub>2u</sub> /Φ <sub>u</sub> (1)]	15850
SO 0 <sub>g</sub> <sup>-</sup>	48% <sup>5</sup> A <sub>g</sub> (1), 22.45% <sup>3</sup> B <sub>1g</sub> (1)	0
1 <sub>g</sub>	67% <sup>5</sup> A <sub>g</sub> (1), 14.59% <sup>3</sup> B <sub>1g</sub> (1)	2462
1 <sub>u</sub>	27% <sup>5</sup> B <sub>2u</sub> (1), 26.81% <sup>5</sup> B <sub>3u</sub> (1), 13.24% <sup>5</sup> A <sub>u</sub> (1), 12.77% <sup>5</sup> B <sub>1u</sub> (1)	5851
2 <sub>g</sub>	85.58% <sup>5</sup> A <sub>g</sub> (1)	5904

Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
2 <sub>u</sub>	24.14% <sup>5</sup> A <sub>u</sub> (1), 21.34% <sup>5</sup> B <sub>2u</sub> (1), 21.31% <sup>5</sup> B <sub>3u</sub> (1)	6266
3 <sub>u</sub>	38.85% <sup>5</sup> B <sub>3u</sub> (1), 24.97% <sup>3</sup> B <sub>2u</sub> (1)	7197
a <sub>g</sub>	49.54% <sup>5</sup> A <sub>g</sub> (2), 36.86% <sup>5</sup> B <sub>1g</sub> (1)	7240
b <sub>g</sub>	31.53% <sup>5</sup> A <sub>g</sub> (3), 23.96% <sup>5</sup> B <sub>1g</sub> (2), 18.11% <sup>3</sup> B <sub>3g</sub> (2), 18.11% <sup>3</sup> B <sub>2g</sub> (2)	7595
c <sub>u</sub>	22.24% <sup>3</sup> B <sub>2u</sub> (1), 21.61% <sup>3</sup> B <sub>3u</sub> (1), 12.23% <sup>3</sup> A <sub>u</sub> (1), 10.77% <sup>5</sup> B <sub>2u</sub> (1), 10.68% <sup>5</sup> B <sub>3u</sub> (1)	7911
d <sub>g</sub>	47.71% <sup>5</sup> A <sub>g</sub> (2), 28.33% <sup>5</sup> B <sub>1g</sub> (1), 15.29% <sup>5</sup> B <sub>2g</sub> (1)	8738
e <sub>g</sub>	32.7% <sup>5</sup> A <sub>g</sub> (3), 23.46% <sup>5</sup> B <sub>1g</sub> (2), 18.02% <sup>5</sup> A <sub>g</sub> (1), 12.56% <sup>3</sup> B <sub>2g</sub> (2), 12.56% <sup>3</sup> B <sub>3g</sub> (2)	8971
f <sub>g</sub>	49.36% <sup>5</sup> B <sub>2g</sub> (1), 49.3% <sup>5</sup> B <sub>3g</sub> (1)	9610
g <sub>g</sub>	72.76% <sup>5</sup> A <sub>g</sub> (2)	10193
h <sub>g</sub>	44.58% <sup>5</sup> A <sub>g</sub> (3), 22.96% <sup>5</sup> B <sub>1g</sub> (2), 17.34% <sup>5</sup> B <sub>3g</sub> (2)	10763
i <sub>g</sub>	63.19% <sup>5</sup> B <sub>1g</sub> (1), 10.62% <sup>5</sup> B <sub>2g</sub> (1), 10.62% <sup>5</sup> B <sub>3g</sub> (1)	11038
j <sub>u</sub>	44.22% <sup>5</sup> A <sub>u</sub> (2), 43.57% <sup>5</sup> B <sub>1u</sub> (2)	11105
k <sub>u</sub>	48.86% <sup>5</sup> A <sub>u</sub> (1), 43.03% <sup>5</sup> B <sub>1u</sub> (1)	11239
l <sub>u</sub>	29.76% <sup>5</sup> B <sub>3u</sub> (1), 29.64% <sup>5</sup> B <sub>2u</sub> (1)	11362
m <sub>u</sub>	21.94% <sup>5</sup> A <sub>u</sub> (1), 21.78% <sup>5</sup> B <sub>1u</sub> (1), 18.43% <sup>5</sup> B <sub>3u</sub> (1), 18.4% <sup>5</sup> B <sub>2u</sub> (1)	11700
n <sub>g</sub>	19.12% <sup>5</sup> B <sub>2g</sub> (2), 19.07% <sup>5</sup> B <sub>3g</sub> (2), 17.44% <sup>3</sup> B <sub>1g</sub> (1), 14.82% <sup>1</sup> A <sub>g</sub> (1)	11817
o <sub>u</sub>	42.88% <sup>3</sup> B <sub>2u</sub> (1), 31.88% <sup>5</sup> B <sub>3u</sub> (1)	11850
p <sub>g</sub>	36.81% <sup>5</sup> B <sub>2g</sub> (1), 36.81% <sup>5</sup> B <sub>3g</sub> (1), 9.67% <sup>5</sup> A <sub>g</sub> (3)	12253
q <sub>g</sub>	30.81% <sup>5</sup> B <sub>1g</sub> (1), 23.75% <sup>5</sup> A <sub>g</sub> (2), 17.24% <sup>3</sup> B <sub>2g</sub> (1), 10.5% <sup>5</sup> B <sub>3g</sub> (1)	12345
r <sub>u</sub>	36.84% <sup>5</sup> B <sub>1u</sub> (1), 14.5% <sup>3</sup> B <sub>3u</sub> (1), 14.32% <sup>3</sup> B <sub>2u</sub> (1), 9.93% <sup>3</sup> A <sub>u</sub> (3)	12539
s <sub>u</sub>	26.69% <sup>3</sup> A <sub>u</sub> (2), 26.67% <sup>3</sup> B <sub>1u</sub> (2), 21.97% <sup>5</sup> A <sub>u</sub> (2), 21.84% <sup>5</sup> B <sub>1u</sub> (2)	12545
t <sub>g</sub>	53.19% <sup>5</sup> B <sub>1g</sub> (2), 14.79% <sup>5</sup> B <sub>2g</sub> (2), 14.79% <sup>5</sup> B <sub>3g</sub> (2)	12687
u <sub>u</sub>	25.54% <sup>5</sup> A <sub>u</sub> (1), 19.8% <sup>3</sup> B <sub>1u</sub> (1), 19.02% <sup>5</sup> B <sub>1u</sub> (1)	13216

Table B.4 – Continued from previous page

Term Symbol	Character : % [orbital(number of electron)]	E (cm <sup>-1</sup> )
$v_u$	43.47% <sup>3</sup> A <sub>u</sub> (1), 24.48% <sup>3</sup> B <sub>1u</sub> (1)	13241
$w_g$	28.83% <sup>5</sup> B <sub>1g</sub> (2), 20.15% <sup>5</sup> B <sub>2g</sub> (2), 19.79% <sup>5</sup> A <sub>g</sub> (3), 12.91% <sup>5</sup> B <sub>3g</sub> (2), 12.71% <sup>5</sup> B <sub>2g</sub> (1)	13394
$x_g$	58.26% <sup>5</sup> B <sub>2g</sub> (1)	13728
$y_g$	34.24% <sup>5</sup> B <sub>1g</sub> (1), 21.57% <sup>3</sup> B <sub>3g</sub> (1), 21.56% <sup>3</sup> B <sub>2g</sub> (1), 20.21% <sup>5</sup> A <sub>g</sub> (2)	14074
$z_g$	45.19% <sup>5</sup> B <sub>3g</sub> (2), 38.99% <sup>5</sup> B <sub>2g</sub> (2)	14162
$aa_u$	47.44% <sup>3</sup> B <sub>1u</sub> (1), 14.08% <sup>1</sup> A <sub>u</sub> (1), 12.08% <sup>5</sup> A <sub>u</sub> (1)	14253
$ab_g$	32.6% <sup>5</sup> B <sub>3g</sub> (1), 32.6% <sup>5</sup> B <sub>2g</sub> (1), 17.93% <sup>3</sup> B <sub>1g</sub> (2), 10.46% <sup>5</sup> A <sub>g</sub> (2)	14698
$ac_g$	35.2% <sup>5</sup> B <sub>3g</sub> (2), 35.19% <sup>5</sup> B <sub>2g</sub> (2), 11.61% <sup>3</sup> B <sub>3g</sub> (2), 11.61% <sup>3</sup> B <sub>2g</sub> (2)	14747
$ad_g$	27.69% <sup>5</sup> B <sub>3g</sub> (1), 27.69% <sup>5</sup> B <sub>2g</sub> (1), 16.03% <sup>3</sup> A <sub>g</sub> (1), 13.05% <sup>5</sup> B <sub>1g</sub> (1)	14862
$ae_u$	48.62% <sup>5</sup> A <sub>u</sub> (3), 48.07% <sup>5</sup> B <sub>1u</sub> (3)	14968
$af_g$	24.6% <sup>5</sup> B <sub>2g</sub> (1), 24.55% <sup>5</sup> B <sub>3g</sub> (1), 14.87% <sup>3</sup> B <sub>1g</sub> (2), 12.76% <sup>3</sup> A <sub>g</sub> (1)	15217
$ag_g$	57.87% <sup>5</sup> B <sub>3g</sub> (2), 12.24% <sup>3</sup> B <sub>2g</sub> (2)	15786
$ah_u$	32.7% <sup>5</sup> B <sub>3u</sub> (2), 32.65% <sup>5</sup> B <sub>2u</sub> (2), 15.35% <sup>5</sup> B <sub>3u</sub> (1), 14.96% <sup>5</sup> B <sub>2u</sub> (1)	15843
$ai_g$	35.75% <sup>5</sup> B <sub>2g</sub> (3), 35.52% <sup>5</sup> B <sub>3g</sub> (3), 12.29% <sup>5</sup> B <sub>1g</sub> (1)	15851

## Appendix C

# **Additional ETS-NOCV Results**

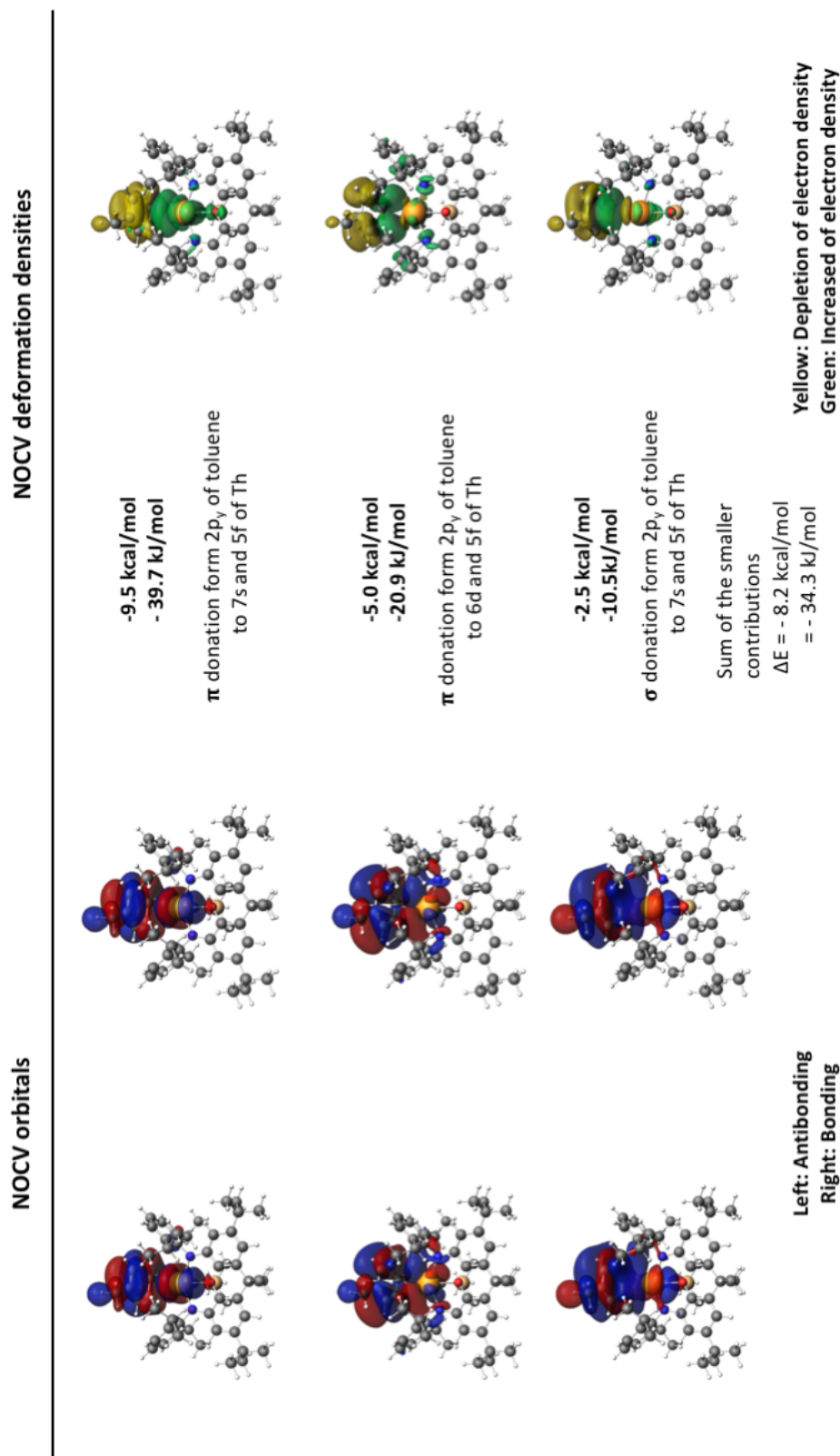


FIGURE C.1: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -3-Th-down.

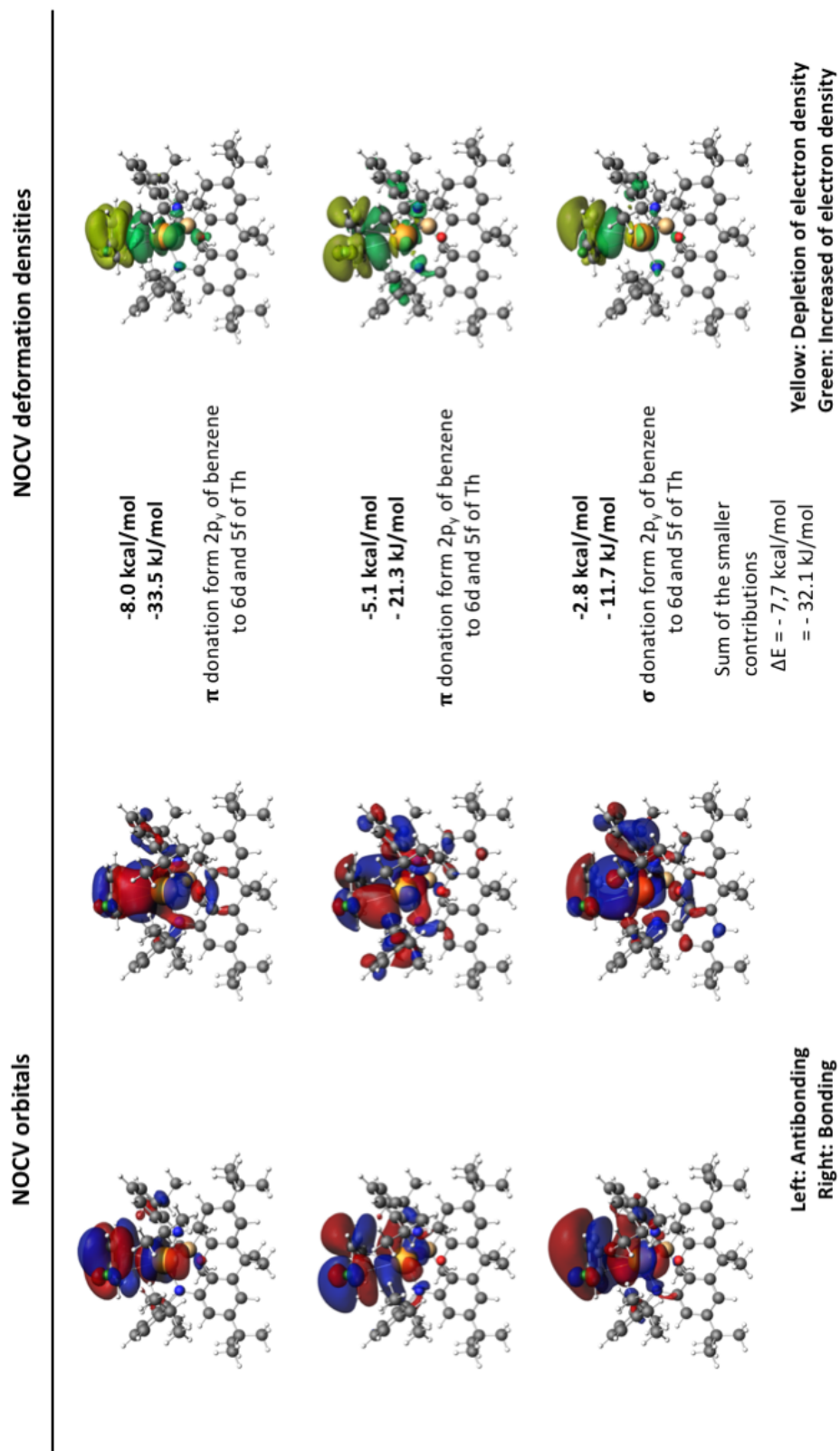


FIGURE C.2: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -5-Th-endo.



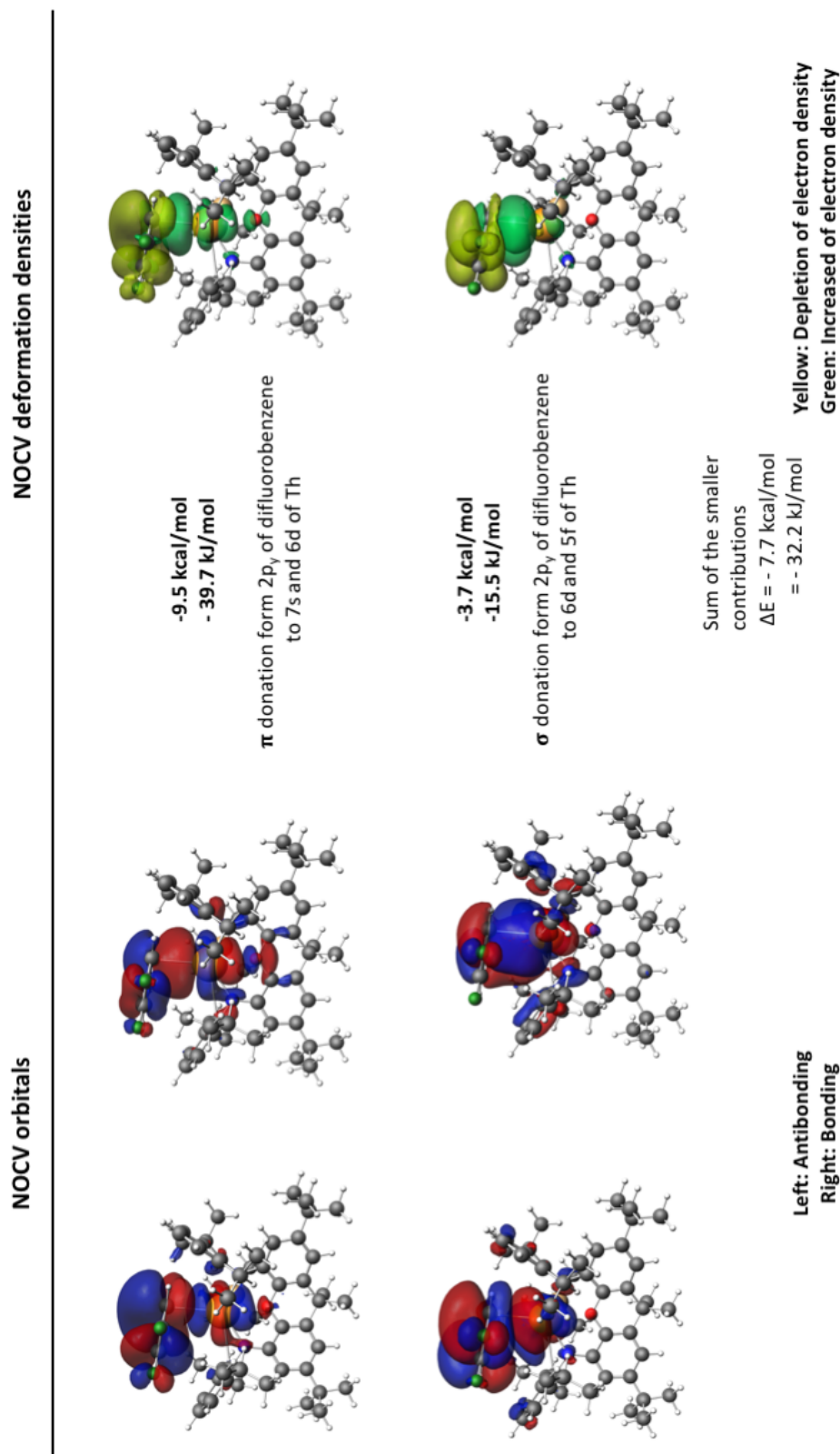


FIGURE C.3: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -**6-Th-exo**.

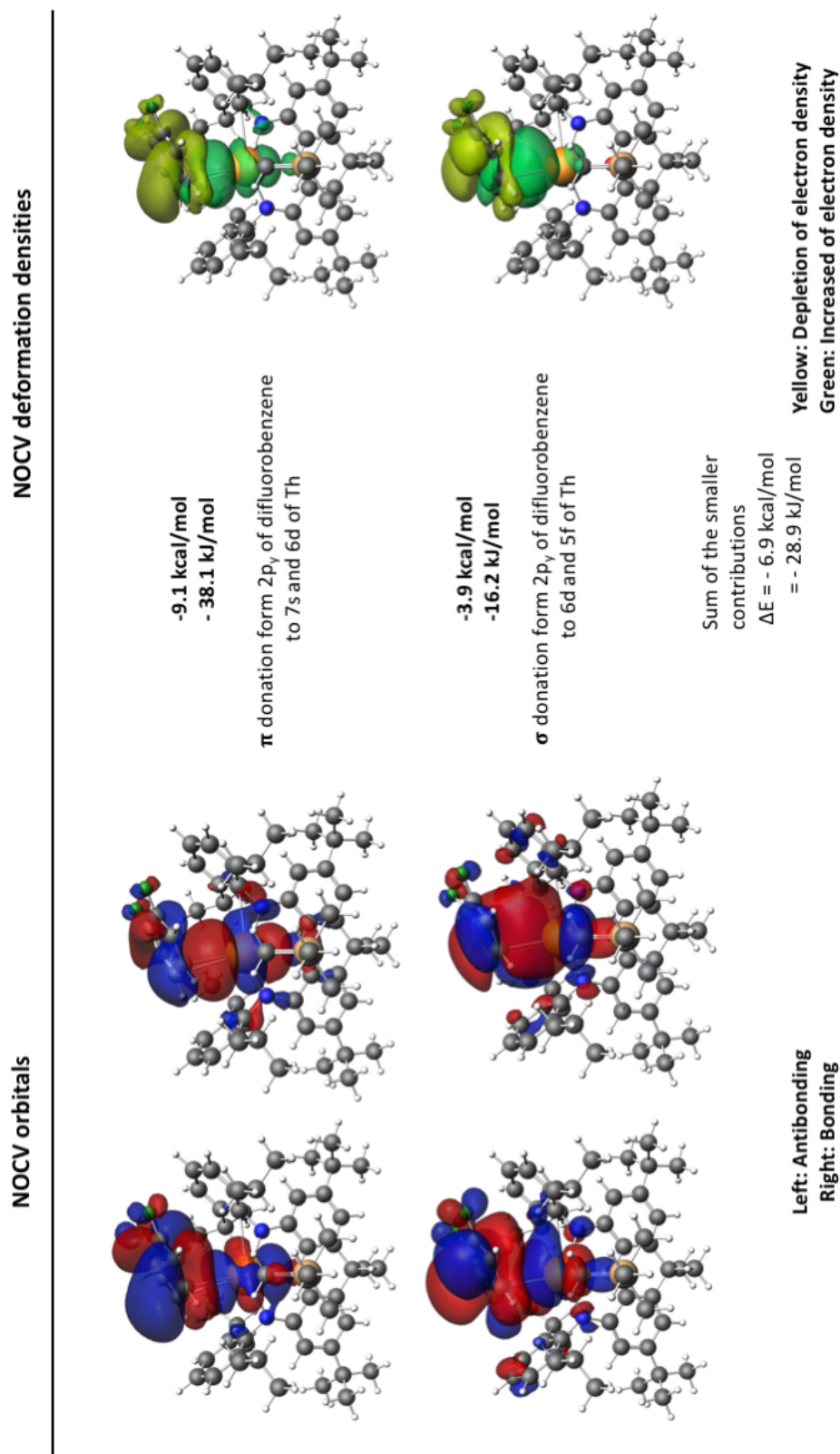


FIGURE C.4: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -6-Th-side.

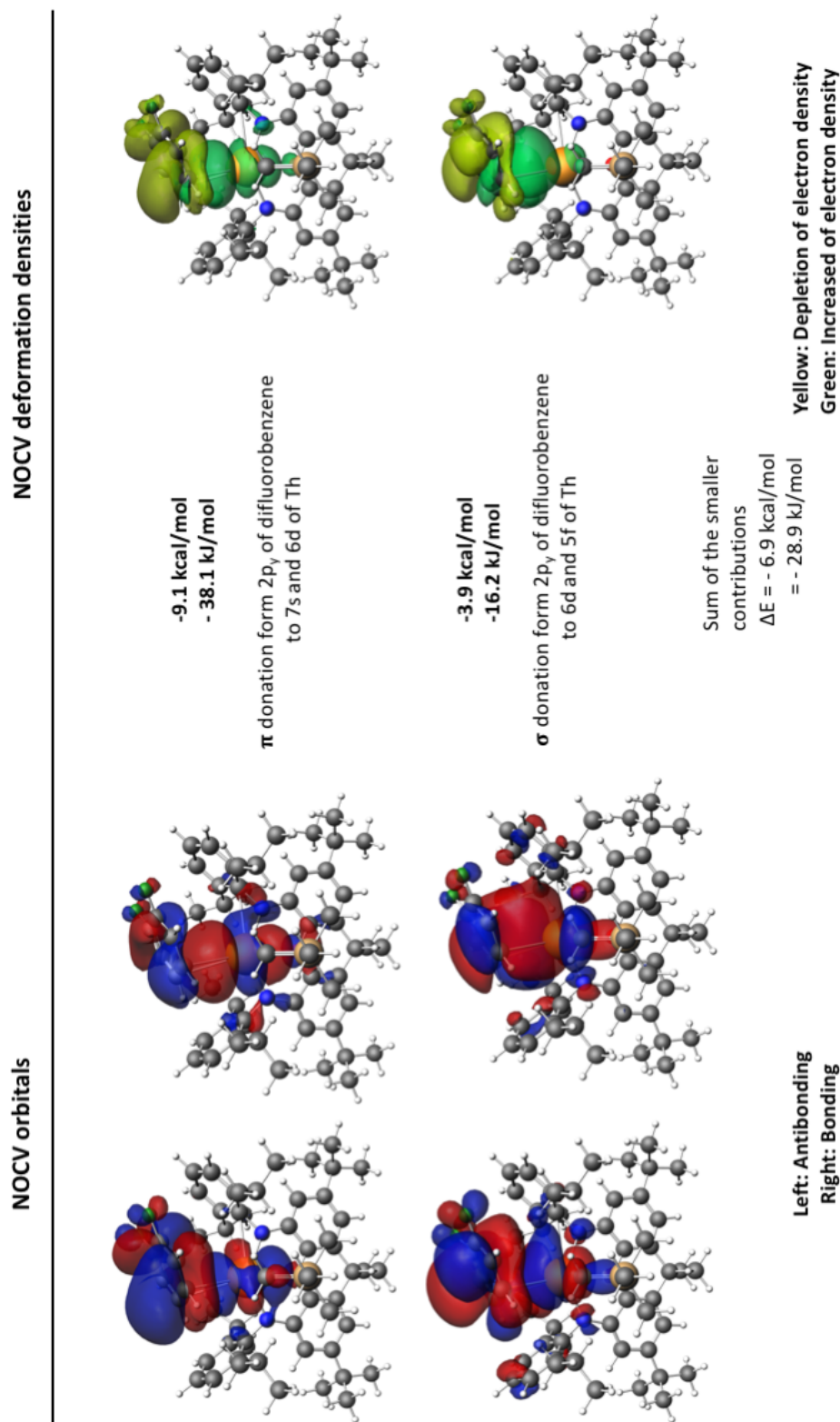


FIGURE C.5: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6$ -6-Th-endo.

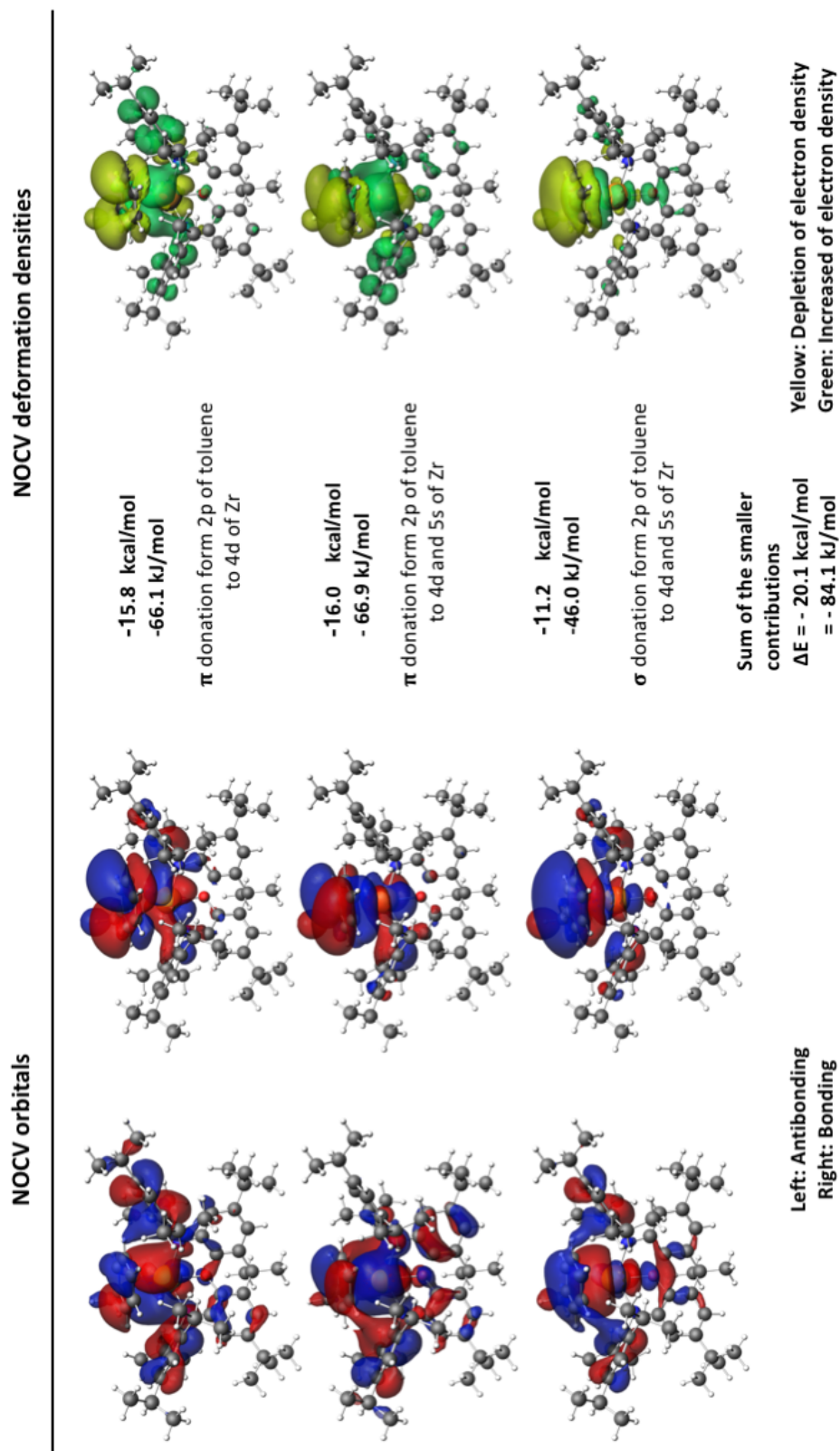


FIGURE C.6: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^2\text{-E-Zr}$ .



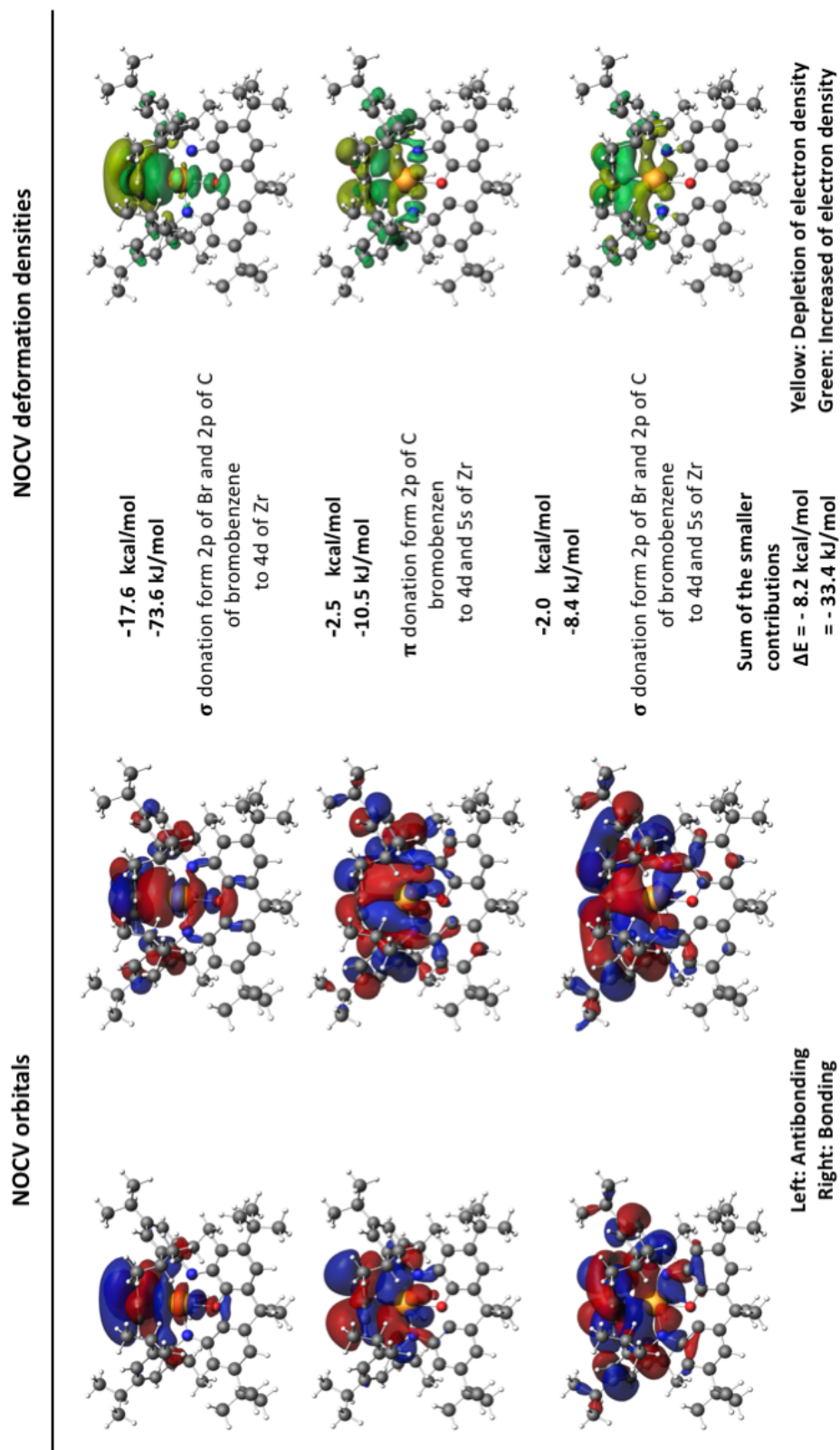


FIGURE C.7: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6\text{-4'-Zr-exo}$ .



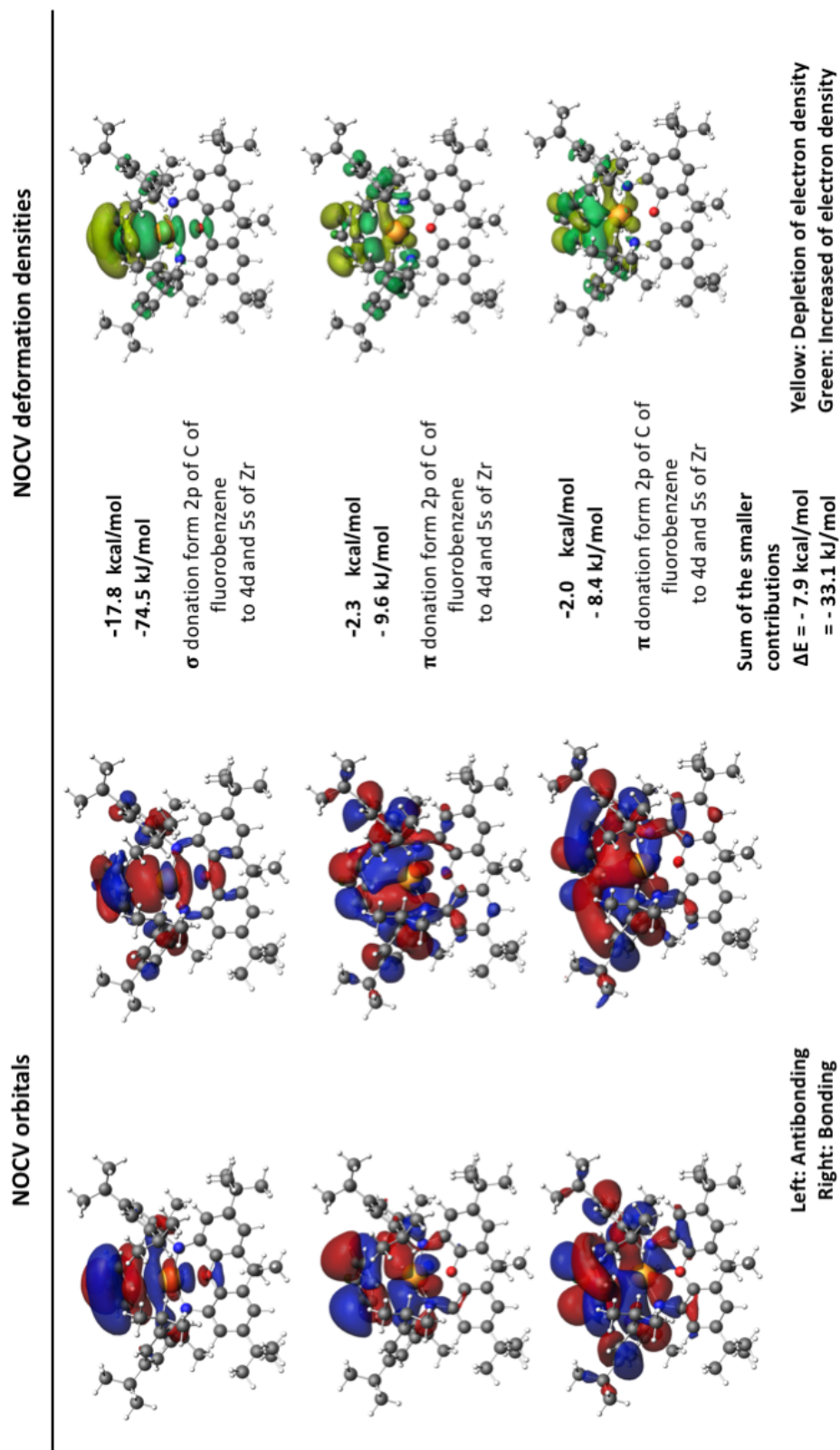


FIGURE C.9: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^6\text{-5'-Zr-exo}$ .

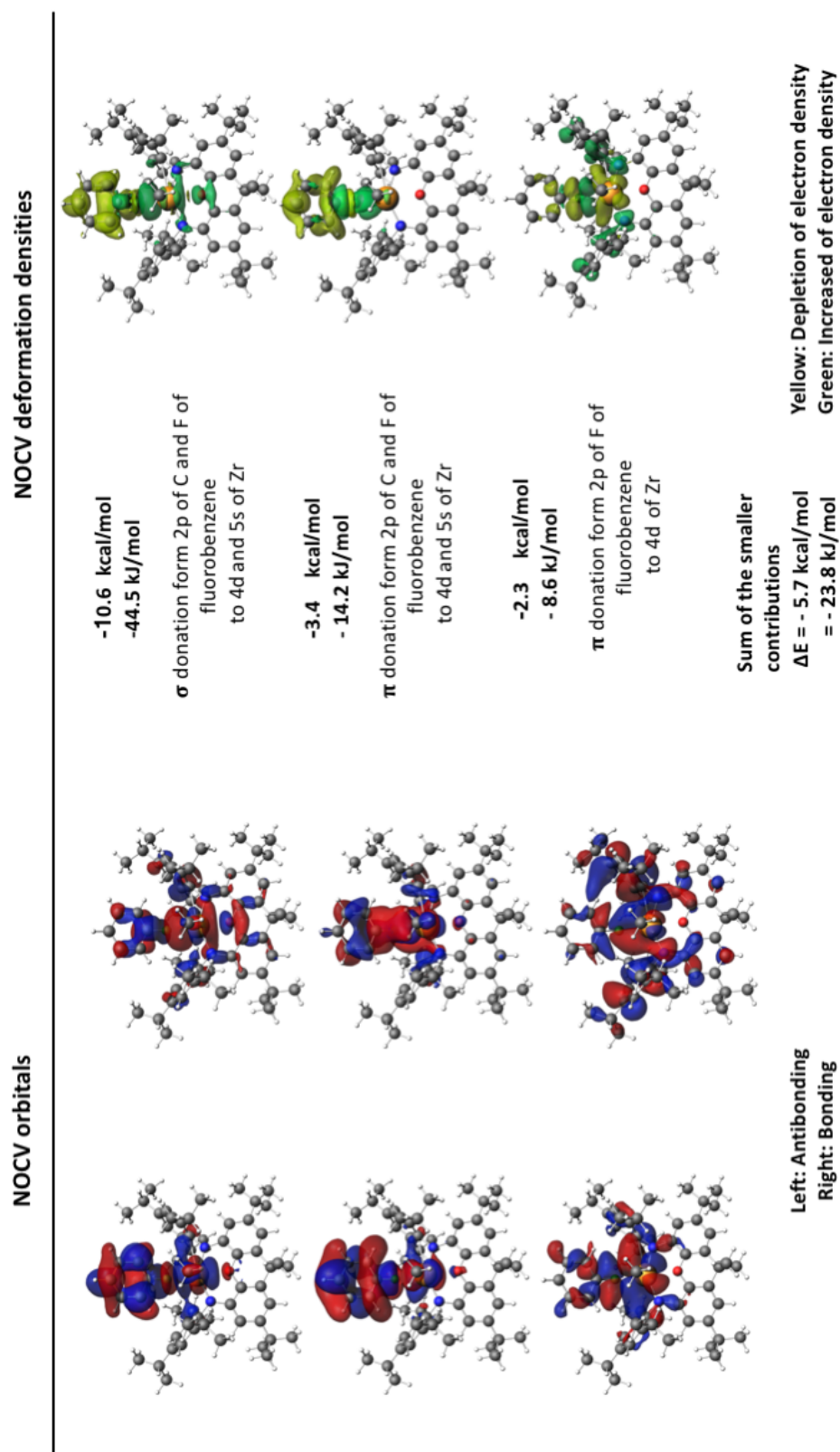


FIGURE C.10: On the left hand side: the NOCV Orbitals (with isosurfaces set to 0.01) and on the right hand side ETS-NOCV deformation density contributions, Increased (green) and decreased (yellow) electron density is presented relative to that in the isolated fragments (isosurfaces are set to 0.0001) for the molecule  $\eta^1\text{-5'-Zr-horizantal}$ .





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