UNIVERSITAT
ROVIRA i VIRGILI

COMPUTATIONAL STUDY OF THE ADSORPTION OF ACTINIDES ON GRAPHENE

Bachelor's thesis

Bachelor's degree in chemistry - Universitat Rovira i Virgili

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Area of knowledge

Department of Physical and Inorganic Chemistry

2022

ACKNOWLEDGEMENTS

The completion of this thesis could not have been possible without the expertise of Dr. Antonio Rodríguez Fortea. I would like to thank the guidance and the knowledge provided during the period of this thesis.

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1. SUMMARY

Recently a dimetallic actinide endofullerene U_2@C80 has been synthesised and characterized. A long U-U distance of 4 Å has been found, although the interaction between metals is weak. In this work, an actinide dimer adsorbed on a graphene flake system has been computationally developed for the study of the interaction of the metals.

The results show that for actinium, thorium, and uranium, a stronger dimetallic interaction has been obtained. The smaller charge transfer from the metals to the carbonaceous structure results in more electron availability for the formation of intermetallic bonds, so stronger interactions are obtained.

Recentment s'ha sintetitzat i caracteritzat un endofullerè dimetàl·lic d'actínid U_2@C80. S'ha trobat una distància U-U de 4 Å, tot i que la interacció entre metalls és feble. En aquest treball, s'ha desenvolupat mitjançant mètodes computacionals un dímer d'actínid adsorbit en un sistema d'un "flake" de grafè per a l'estudi de la interacció dels metalls.

Els resultats mostren que per a l'actini, el tori i l'urani, s'ha obtingut una interacció dimetàl·lica més forta. La transferència de càrrega dels metalls a l'estructura carbonosa és més baixa que en un ful·lerè, cosa que dona lloc a més disponibilitat d'electrons per a la formació d'enllaços intermetàl·lics, de manera que s'obtenen interaccions més fortes.

2. GOAL

The main objective of this thesis is to give insight on the actinide-actinide bond on carbonaceous surfaces like graphene sheets, modelled by graphene nanoflakes, and compare to the bond found in endohedral diactinidofullerenes. By comparison of the interaction energies of the actinide dimer (or trimer) with the surface at different An-An distances, we estimate the An-An bond energies. The interaction between a single actinide with the nanoflake is the first step of the analysis so that we can learn the formal oxidation state of the actinide to better understand the nature of the An-An bond.

3. THEORETICAL BACKGROUND

3.1. Fullerenes and endohedral fullerenes

Carbon has the capacity of forming allotropes, which are structurally different forms of carbon arrangements, as for example the oldest-known diamond and graphite, or the most recently discovered as fullerenes, nanotubes, nano-onions, or graphene

Fullerenes are closed structures composed by carbon arranged in a way to achieve cages, which are thermodynamically unstable but kinetically stable.[1]

The first discovered fullerene was the so-called "Buckminsterfullerene", which is formed by 60 carbon atoms. This molecule consists of a polygon with 32 faces, 12 of them being pentagonal and 20 hexagonal.[2] In fullerenes, carbon atoms show a sp^2 hybridization, with each atom bonded to its three nearest neighbours.[3] Isolated C_{60} satisfies the so-called Isolated Pentagon Rule (IPR) where the pentagonal faces are surrounded by hexagons and no pentagon-pentagon adjacencies are present, so minimizing the strain.[4]

Afterwards, endohedral metallofullerenes (EMF) were found out by Kroto et al., prepared by vaporization of a $LaCl_3$, resulting in a $La@C_{60}$. Endohedral metallofullerenes are fullerenes with metal atoms trapped inside the cage; they are interesting structures due to the electron transfer from the trapped metal to the cage, what modifies the properties of the fullerene.[5] It was also found out that the encapsulated metal atoms do not react with gases external to the cage, such as hydrogen, oxygen, or ammonia, what leads to the believe that the fullerene protects the encaged atoms from the surroundings.[5] Not only is a single metal atom found inside the cage, but two metals (La_2, Y_2, Gd_2, Dy_2...) or different metal clusters (M_3N, M_2O, M_2C_2, MCN, etc. with M usually being group 3 or lanthanide) have been also encapsulated in the last two decades.[4]

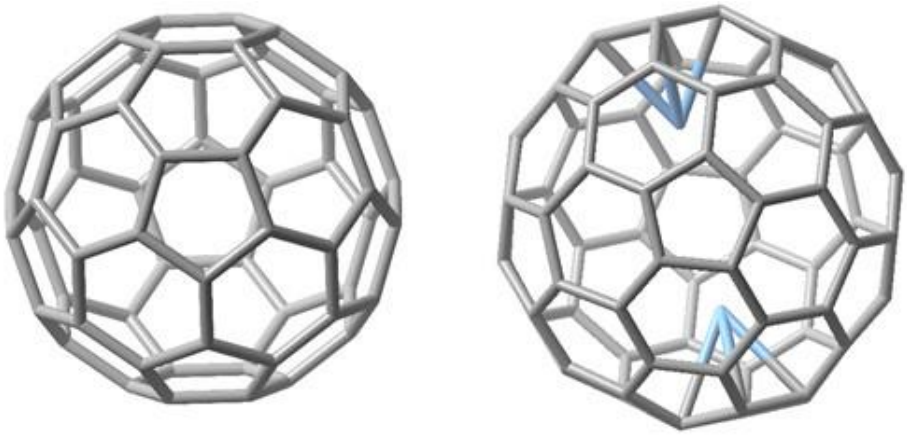


Figure 1 - Fullerene C_{60} and diactinium endohedral metallofullerene, $U_2@C_{80}$.

3.2. Diactinide endohedral metallofullerenes

In 2017, the first metallofullerene containing an actinide, $Th@C_{82}$, was isolated and characterized.[6] Later, other mono-actinidofullerenes as non-IPR U@C80, Th@C80 and U@C76; or IPR U@C82, U@C84 and U@C86 have been also characterized.[7]In these actinide endofullerenes, the actinide tends to act with formal oxidation state +4, which involves an important metal-cage interaction with significant covalent contributions.

In 2018, the first endohedral di-actinidofullerene, $U_2@C_{80}$, was synthesized and characterized.[8] The crystallographic analysis showed that the U-U distance was 3.79 Å (Figure 2). It is known that C_{80} shows preference for the C_{80}^{6-} state,[8] so the U ions inside are formally U^{3+} ($5f^3$ configuration). This oxidation state of +3 was confirmed by X-ray absorption spectroscopy. The electronic ground state is a spin septet with six unpaired electrons, three on each U ion. Even though there is no electron pairing, the authors found, from the topological analysis of the electronic density and the electron localization function, that there exists a weak U-U bond.[8]

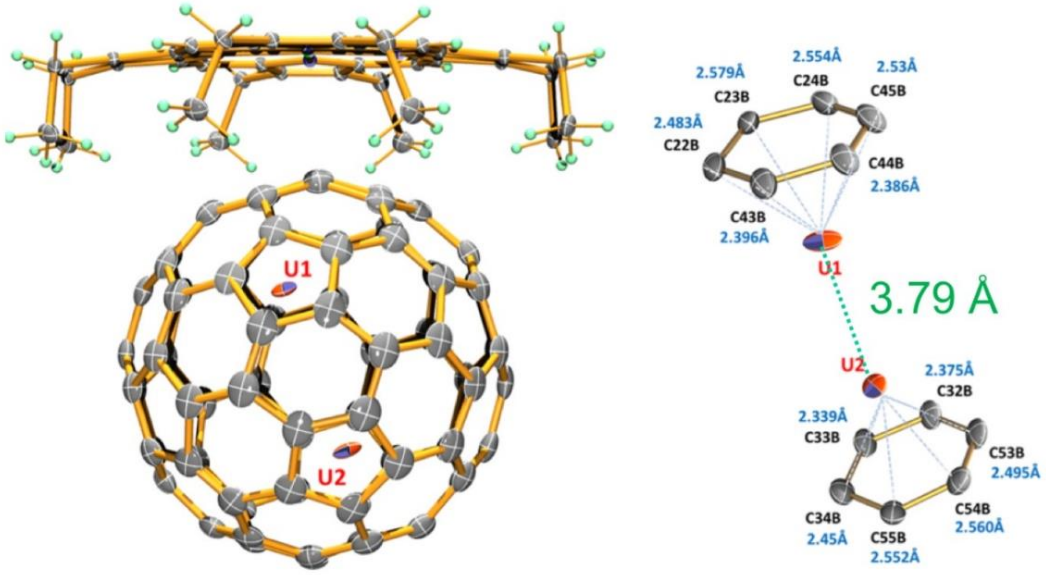


Figure 2 - X-ray structure of U2@C80 showing the U-U and nearest U-C distances[8]

Recently, the C_{80} cage with a thorium dimer inside was synthesized and characterized, and further computational analysis was performed.[9] Thorium is formally Th^{3+}, so there remains one valence electron on each Th ion that can couple to make a bond. Indeed, it was found that a strong covalent bond between the metal atoms is formed, and both the experimental and computed bond Th-Th distance were reported to be 3.816 Å. At such a large distance there still exists a significant overlap between the 7s6d hybrid orbitals on each Th centre, which extend over long distances, that leads to a strong bond that is estimated to have a dissociation energy larger than 40 kcal mol^{-1}.[9] It is worth mentioning that so far, the thorium-thorium interaction encaged inside an EMF is found to be the strongest among all actinide-actinide interactions. Therefore, fullerenes in general, and the C_{80} cage in this case, can be seen as nanocontainers or nanovessels that encapsulate dimers with covalent actinide-actinide bond that cannot be observed outside the fullerene.

At this point, we might wonder why the bond is so different in $Th_2@C_{80}$ compared to $U_2@C_{80}$. The point is that for the former, hybrids 7s6d orbitals overlap effectively whereas for the latter, 5f orbitals are much more localized and the overlap is not so effective. But could it be possible to have a strong U-

U bond inside a fullerene? Recently, in laser vaporization experiments, U_2 dimer has been detected inside small cages, as small as C_{48}.[9] On account of these results, the interaction between uranium atoms was studied in small fullerenes, $U_2@C_{48}$ and $U_2@C_{50}$. Due to the size constraints, the U-U distances were found to be in the range of 2.47 to 2.59 Å, too small to avoid the formation of a metal-metal bond.

Further computational analysis in $U_2@C_{60}$ with a U-U distance of 2.37 Å, revealed that, there exists a strong triple U-U bond, with one sigma and two pi occupied molecular orbitals (Figure 3).

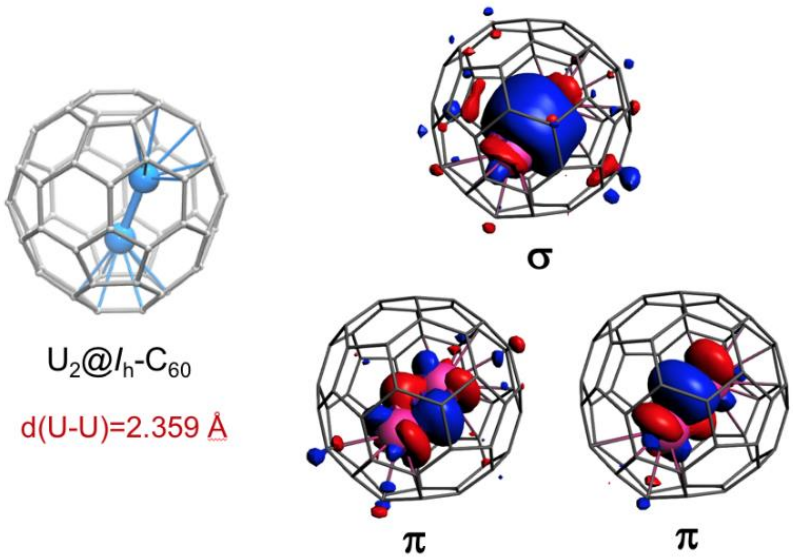


Figure 3 - Computed structure (DFT) of $U_2@C_{60}$ and occupied sigma and pi orbitals that lead to the triple U-U bond.[9]

The authors of this work also found that the U_2 dimer with a short U-U distance (around 2.5 Å), and therefore with a strong triple bond, can be also found in larger cages as in C_{78} and C_{80}, but at somewhat higher energies than the dimers at long distances (around 4 Å).

3.3. Graphene

Graphene is an allotrope of carbon consisting of a single layer of carbon atoms arranged in hexagons. In 2010, the Nobel prize in physics was awarded to Sir Professor Andrei Geim and Sir Professor Kostya Novoselov, for their work on the graphene field. This material has been an essential component for the understanding of the other allotropes of carbon due to the simplicity in its obtention.[10]

Each carbon atom forming the graphene flake is bonded to its three closest neighbours by in-plane covalent bonds (σ-bonds). These are formed by the electrons in the 2s, $2p_x$ and $2p_y$ orbitals, taking part in the hybridization to form sp^2 orbitals. The remaining valence electron is found in the $2p_z$ orbital, oriented perpendicular to the graphene flake, thus, having no interaction with the in-plane σ electrons. The $2p_z$ orbitals from neighbouring carbons overlap, deriving in delocalized π and π* bands.[10]

Graphene is relatively chemically inert, unlike fullerenes and carbon nanotubes which have curved surfaces that induce strain in sp^2 bonds that help facilitate chemical functionalization. However, graphene can adsorb metal atoms, as pristine or chemically modified.

Recently, the catalysis in the electrochemical reduction reaction of N_2 to NH_3 using a uranium Single-Atom Catalyst (SAC) adsorbed on a graphene surface was achieved, obtaining thus an extremely high yield. The preparation of the catalyst comes from a doping of the graphene layer with a nitrogen atom, and the active centre is uranium, which is coordinated by the nitrogen and two carbon atoms ($U@N_1C_2$).[11]

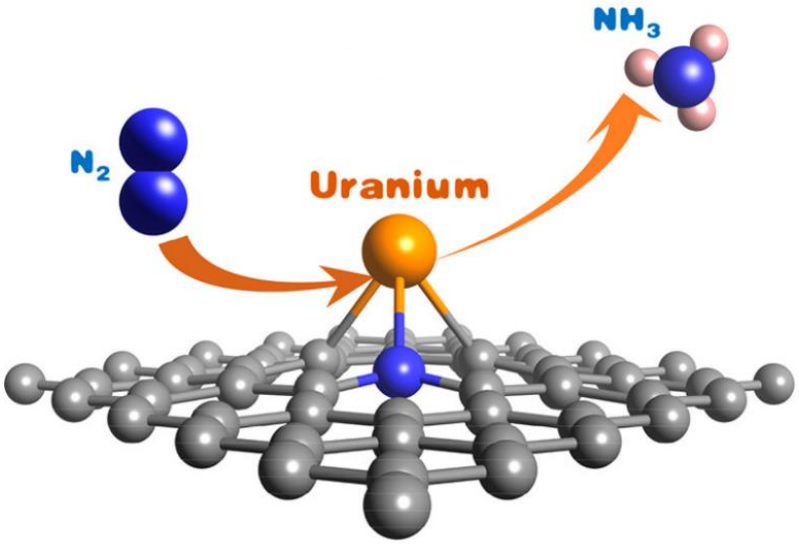


Figure 4 - Scheme of the structure and reaction of U@N1C2 catalytical process.[11]*

The SACs are prone to have desorption and aggregation problems, so the stability of the uranium atom was analysed by a molecular dynamics simulation, which showed that the atom was stable even at 500K. Further computational analysis determined that the d and f electrons of the uranium are fundamental in the catalysis of the nitrogen reduction, all due to the σ-donation and the π-backdonation. Therefore, the work concludes that yields of 3 to 4 orders of magnitude higher than previous catalysis of nitrogen reduction reaction can be achieve by this method, but the most important fact is the promising innovation in the uranium chemistry.[11]

Carbon nanotubes have the same structure as graphene; hexagons with each carbon bonded to three other carbons, but they are not flat. In fact, nanotubes can be seen as rolled graphene sheets capped with half-fullerenes. In 2020, one of these structures was used to study the evolution of a metal-metal bond in a dirhenium molecule at room temperature. At first instance, the length of the Re-Re bond was observed to measure 2.2 Å, having a bond order close to four; through DFT calculations, the same bond length was obtained. The dimer was observed for 553s, and during this lapse of time, the three values for the bond distance that appeared the most were 2.2, 2.5 and 3.0 Å, corresponding to a quadruple, double and single bond, respectively. DFT

calculations were performed to determine the electronic structure of the Re_2 bonded to the nanotube. The binding energy from the ensemble with a quadruple metallic bond was -1.71 eV.[12]

Having put into perspective the topic of single actinides and metallic dimers adsorbed on carbonaceous surfaces, a computational study on the adsorption of diactinides on a graphene sheet will be developed.

4. COMPUTATIONAL DETAILS

4.1. ADF[13]

The calculations of this thesis are based in Density Functional Theory (DFT) and are done by means of the program Amsterdam Density Functional (ADF, 2019 version). We used the Local Density Approximation (LDA), with a Generalized Gradient Approximation (GGA) part and a Hartree-Fock exchange part, leading to a hybrid functional. The specific functional used is PBE0, a hybrid form of PBE.

The basis set used to describe the valence orbitals of the atoms is a triple-zeta basis set with a polarization function (TZP). Furthermore, a large frozen core was selected, what means that internal shell electrons are not taken into account (electrons that do not participate in the bond).

A Becke Grid numerical integration was used, and, of a range from basic to excellent, it was set to good, having thus a balance between a nice accuracy of the results and an acceptable computational time.

Relativistic scalar effects were also needed to be taken into account. The Zero Order Regular Approximation (ZORA) was used as it is the most appropriate approach for the studied systems in this thesis, considering that they are based on heavy elements (actinides).

In order to apply dispersion corrections to the bonding energy, the Grimme D3 method was selected. Bader's Quantum Theory of Atoms In Molecules

(QTAIM) option was selected to perform further analysis. The theory consists of the analysis of the bonds through the topology od the electron density. The presence of bond critical points between two atoms implies that the atoms are bonded.

4.2. Modelling of the graphene flake

Graphene is usually modelled as a finite polyaromatic hydrocarbon, which is capped with hydrogen atoms that bind to its edges. This design has the advantage that the calculation is much more computationally available, although there is an important disadvantage: the electronic density on the system is affected, as the electrons of hydrogen generate a negative electrostatic potential above and below the carbon flake, where the π electron cloud is located. The larger the system size, the lower the hydrogens will affect the system; in an infinite periodic flake of graphene, the quadrupolar potential would completely disappear.[14]

The graphene flake used in the calculations was designed to be able to fit the necessary positions with the less possible interaction from the hydrogens to the metal atoms and taking into account that the lowest computational cost needed to be achieved.

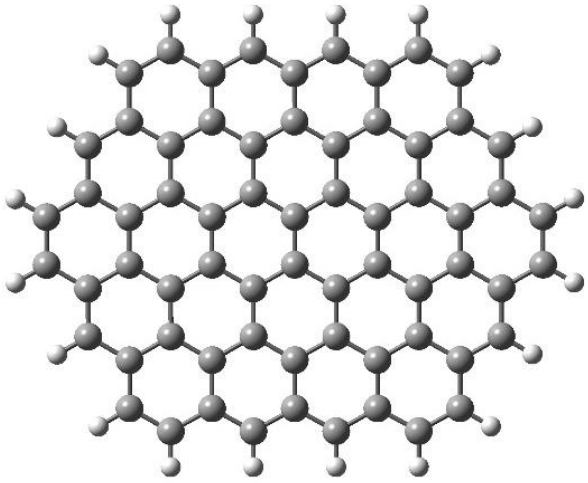


Figure 5 - Designed graphene flake.

4.3. Modelling of the system

The dimetallic graphene system will be studied with three different actinides: uranium, thorium, and actinium. For each of the metals, several cases will be analysed: 1) The interaction of a single metal with the carbon flake considering different spin states; 2) The interaction of a metal dimer with the surface and the possibility of bond formation within the dimer, changing the relative positions of the actinides on the flake and the spin state; 3) The interaction of a metal trimer on the surface and the metal-metal bond formation. The metal atoms will be initially located on the centre of the hollow spaces in some carbon hexagons.

By changing the position of the metals, up to three different dimetallic systems will be selected to be optimized: 1,2 , 1,3 and 1,4 positions, according to the relative position of the hexagons to which the actinides are adsorbed (see Figure 6).

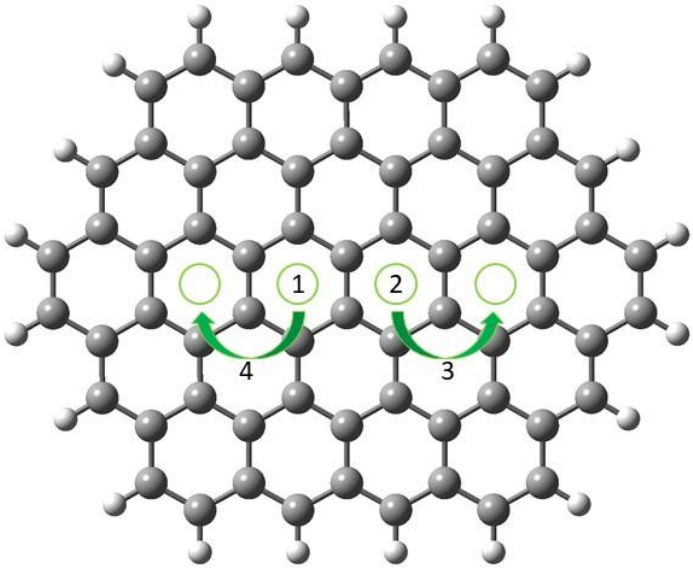


Figure 6 - Representation of the different studied systems.

In the 1,2 positions, the metal atoms are separated originally by 2.5 Å, in the 1,3 systems that distance is around 5 Å, and finally, in the 1,4 systems, the distance is approximately 7.5 Å.

5. RESULTS AND DISCUSSION

At first instance, the objective was to analyse different uranium systems adsorbed on graphene; however, while performing the optimizations, it was found that these systems were taking a lot of time to converge. Therefore, the thorium systems were set to optimize, as it has less valence electrons than uranium, what results in a much shorter computation time for the same type of calculation. Afterwards obtaining the results for the thorium systems, both uranium and actinium systems were proceeded to be optimized.

The objective of the optimizations was to find the interaction or bonding energy between the actinides and the carbon flake. To do that, we take the energy output of the whole system, and we subtract the energy values of the flake and the single metal atom (n = 1, 2 or 3, depending on the systems, single atom, dimer, or trimer)

$$E_{int} = E(whole) - E(flake) - n \cdot E(metal) \quad (5.1)$$

Another parameter that is useful to understand the interactions between actinide atoms is the bond distance between both metals, so we will measure each bond for every different system. Depending on the length, it can be determined if the formation of a bond occurs, or if the distances between metal atoms are too large to be able to create a bond.

Through the molecular orbitals of the systems, we can find the characteristics of the bonds by observing the interactions of the metals with the graphene layer and also of the metal with the other metal.

The metal-metal interaction will be also analysed by means of Bader's Quantum Theory of Atoms In Molecules (QTAIM). This will allow the interpretation of the formation of bonds through bond critical points.

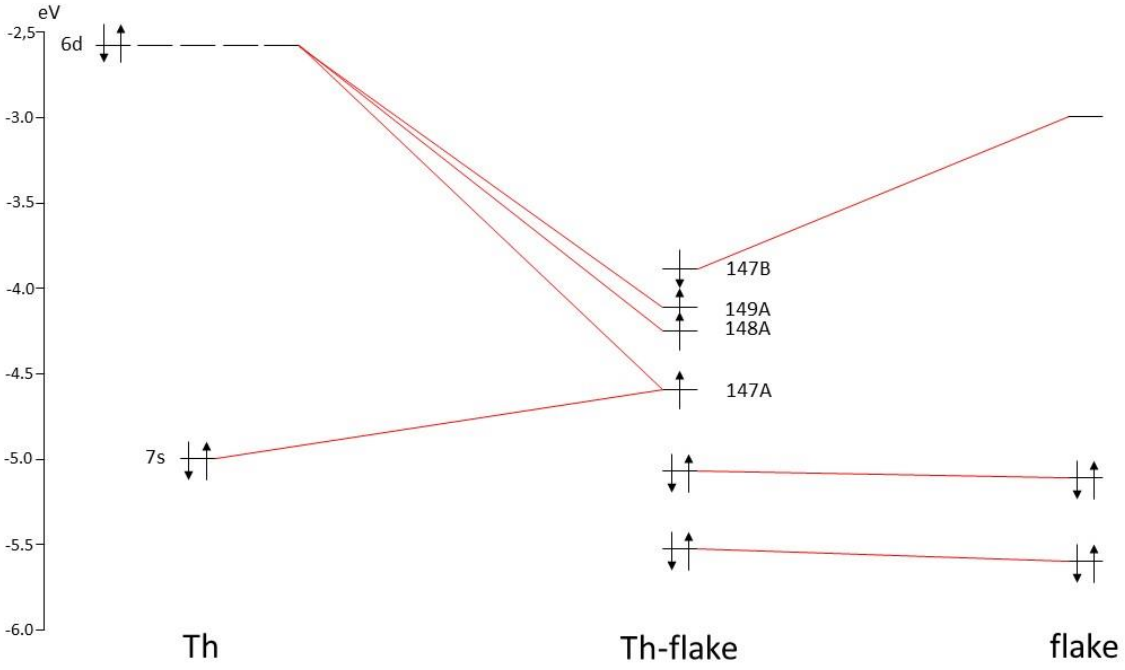
5.1. Single Atom Thorium and Dimer on Graphene

Table 1 – Interaction energies (eV) and Th-Th bond distances (Å) from single atom Th and Th_2 dimers adsorbed on the graphene flake.

System	Spin state	Interaction energy (eV)	Bond distance (Å)
Th	Triplet	-3.36	-
	Quintet	-3.09	-
Th_2 1,2 position	Singlet	-9.33	3.17
	Triplet	-9.09	3.04
	Quintet	-8.39	2.94
	Septet	-6.73	3.10
Th_2 1,3 position	Singlet		
	Triplet	-9.09	3.05
	Quintet	-8.17	3.11
	Septet	-7.32	3.67
Th_2 1,4 position	Singlet	-6.26	7.40
	Triplet	-6.00	7.35
	Quintet	-5.81	7.39
	Septet	-5.95	7.17

As it can be observed in Table 1, the interaction energy for the system in which just one metal is adsorbed on the flake is, for both triplet and quintet states, in between 3.09 and 3.36 eV. That value will be taken as reference

when comparing the different cases, as it defines the energy released when building the basic metal-graphene system.



Scheme 1 - Molecular orbital diagram of Th-flake system based on the interaction of the two fragments, the Th atom, and the flake.

By studying the molecular orbitals diagram of the system (Scheme 1 and Figure 7) and the frontier molecular orbitals compositions, the contributions from the metal show that the formal electron transfer of the thorium atom to the graphene sheet could be said to be 1, what results in a Th^+ ion, having still each metal 3 valence electrons.

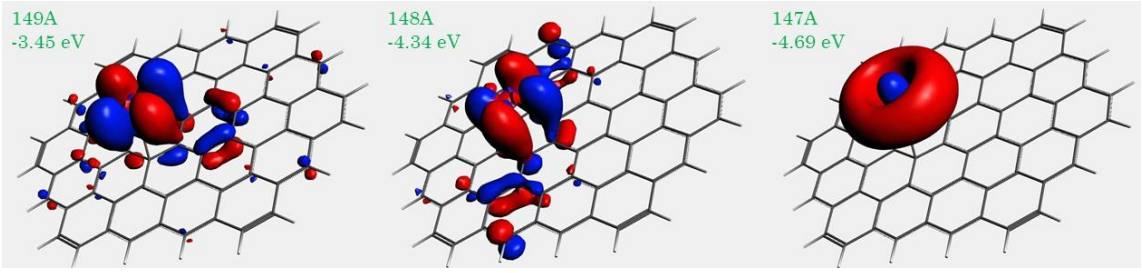


Figure 7 – Singly occupied alpha molecular orbitals for the triplet state of Th-flake system. Three of the four valence electrons of Th formally remain on Th once adsorbed on the flake, so we deduce that it is formally Th^+.

From the data on Table 1 corresponding to the Th_2-1,2 system, it can be determined that, regarding the energies and the Th-Th distances (around 3

Å) a bond should be formed between the metals. The energy is found to be significantly larger than twice the value from the single-Th interaction (9.33 eV *vs* 3.36 eV x 2 = 6.72 eV); this should induce the thinking that the difference in energy should come from the formation of a bond, on condition that the Th-flake interaction is similar in the two cases. If we pay attention to what was said before, the thorium atoms are, formally, transferring just one electron to the graphene flake, but they still have 3 electrons left that can participate in the development of a bond; thus, there is the possibility that a triple bond exists between the metals.

To corroborate that idea, we can take a close look at the molecular orbitals of the singlet state system (Figure 8), which is the most stable one, to find their contributions on the bond making. There is clearly one doubly-occupied σ orbital, one π orbital and one orbital (153A in Figure 8) which is not straight-forward to recognize as σ nor as π.

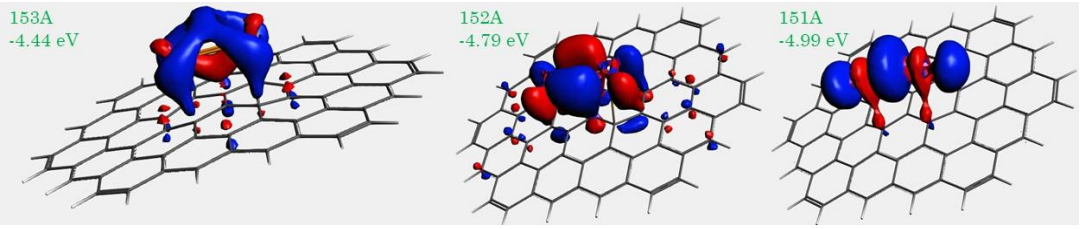


Figure 8 – Doubly-occupied molecular orbitals for the singlet state of the Th_2-1,2 system that describe the formation of a triple Th-Th bond.

To finish confirming that the bond is formed, we can look up to the Bader's QTAIM analysis to find whether there is a bond critical point or not.

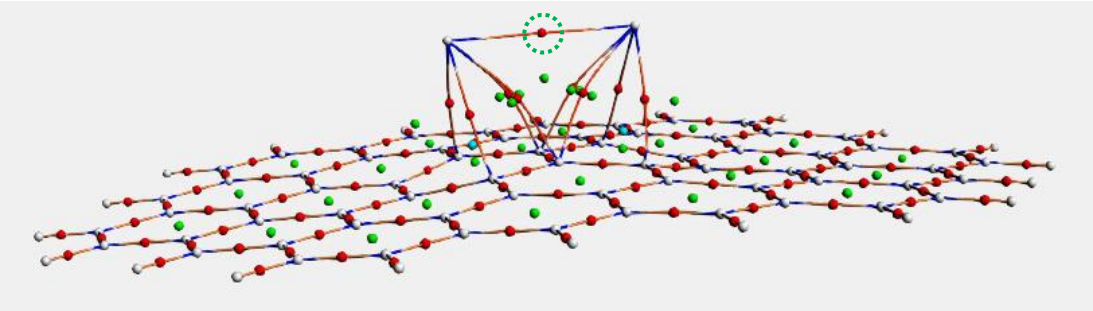


Figure 9 – Critical points (CP) in QTAIM theory found for the singlet state of Th_2-1,2 system. Atom CP in grey, bond CP in red, ring CP in green and cage CP in blue. The bond CP between the two Th atoms is highlighted in green.

In Figure 9, we can see the representation of a bond critical point (red dot) between the thorium atoms. This confirms the existence of a bond, what is in line with the short bond distance (3.07 Å) and the large interaction energy (9.33 eV). We can estimate the Th-Th bond energy on the flake as BE = 9.33 eV – 2 x 3.36 eV = 2.61 eV (60 kcal mol^{-1}).

It is worth also mentioning that, for the thorium atoms to form a bond, the atoms move to a more separated position than the initial one. The distance between both metal atoms before the optimization was 2.5 Å, while after, the atoms have moved to a distance up to 3.17 Å.

Other spin multiplicities different from singlet have been also considered for the Th_2-1,2 system, that is, triplet (S=1), quintet (S=2) and septet (S=3). Triplet and quintet show somewhat smaller interaction energies than singlet state and Th-Th distances that are even slightly shorter (2.94 Å for the quintet). This can be understood by the fact that π orbitals with more effective overlap at shorter distances are occupied in these higher spin states. Finally, the quite low interaction energy found for the septet spin state deserves a comment; in this case, one Th-Th bonding π orbital is doubly occupied and the system, to get a septet spin state, has to open the electronic closed shell of the flake, i.e. make a flake radical.

If we look up again at Table 1, much lower interaction energies are observed for the Th_2-1,4 system in contrast to the previously analysed Th_2-1,2 system. The energies are approximately double the ones from the single thorium system. At such larger distances, no Th-Th bond will be formed, so the computed energy will correspond to just the formation of the system, with no further interactions. Moreover, the energy differences between the spin states are rather small, confirming that the interaction is more of the magnetic type with localized magnetic moments instead of bond formation.

This statement is corroborated by Bader's theory, as no bond critical point is found in the middle of both metals (see Figure 10).

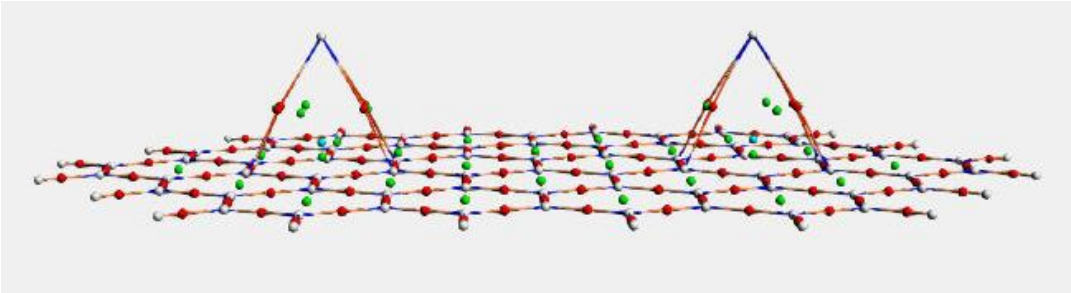


Figure 10 - *Critical points (CP) found for the septet state of Th_2-1,4 system. Atom CP in grey, bond CP in red, ring CP in green and cage CP in blue. No bond CP between the two Th atoms is found.*

The results for the Th_2-1,3 system are very similar to those from the analogous 1,2 system. Observing the optimized geometry (see Figure 11), it is noticed that both metal atoms shift to a closer position, what leads to the possibility of the formation of a bond, which is confirmed by the QTAIM representation by a bcp present between the thorium atoms.

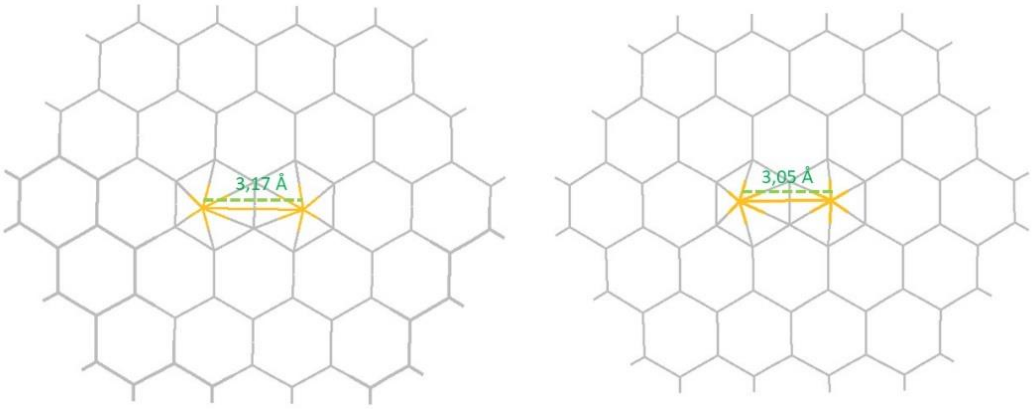


Figure 11 - Th_2-1,2 (left) and Th_2-1,3 (right) optimized systems. Yellow dots are the Th atoms on the graphene flake. The final distances are shown for the singlet state of 1,2 system and the triplet state of 1,3 system.

5.2. Single Atom Actinium and Dimer on Graphene

Table 2 - Interaction energies (eV) and Ac-Ac bond distances (Å) from single atom Ac and Ac_2 dimers adsorbed on the graphene flake.

System	Spin state	Interaction energy (eV)	Bond distance (Å)
Ac	Triplet	-1.95	-
Ac_2 1,2 position	Singlet	-5.92	3.50
Ac_2 1,3 position	Septet	-4.71	3.52
Ac_2 1,4 position	Septet	-4.09	7.31

Diactinium endohedral metallofullerenes show no Ac-Ac bond because the charge transfer to the cage is of 3 electrons from each metal, so no valence electrons are left to form a metal-metal bond.

However, adsorbed on graphene, when analysing the frontier molecular orbitals of the system (Figure 12), and their compositions, the contributions from the actinium show that, again, the formal electron transfer of the metal to the graphene flake is likely to be 1, what leaves formally an Ac^+ ion. This cation has still 2 valence electrons, that can be used to create a double bond between the actinium atoms. Besides, the interaction energy (–1.95 eV**)** is significantly lower than for Th (–3.36 eV).

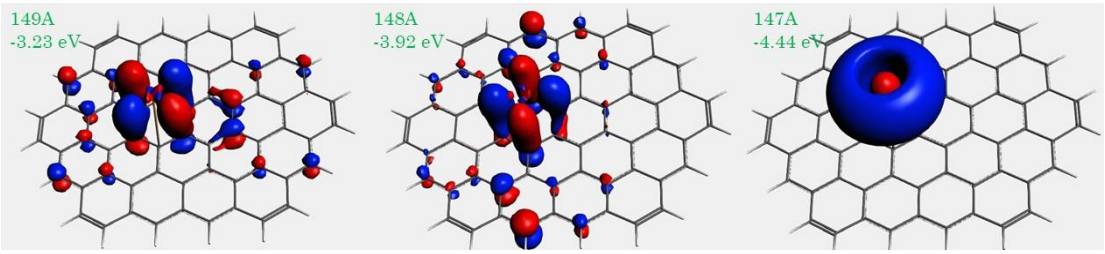


Figure 12 - Singly occupied alpha molecular orbitals for the triplet state of Ac-flake system. Two of the three valence electrons of Ac formally remain on Ac once adsorbed on the flake, so we deduce that it is formally Ac^+.

From Table 2, for the Ac_2-1,2 system, it can be seen that the interaction energy is also lower than for Th (5.92 eV *vs* 9.33 eV), but a similar trend as before is observed. The energy and bond length values for the Ac_2-1,2 system makes one think that, again, a bond should be formed between both metals. There is 2.02 eV of difference between the mentioned dimer and the one that would be considered our reference value, i.e. twice the interaction energy of the single Ac-flake system (5.92 eV vs 2 x 1.95 eV = 3.90 eV). As said previously, this value of 2.02 eV (46 kcal mol^{-1}) could be considered as an estimation of the Ac-Ac bond energy.

The analysis of the molecular orbitals of the system (Figure 13) can give further information on the presence of a bond. Clearly, the first molecular orbital corresponds to a doubly-occupied σ orbital, and the other one to a π orbital.

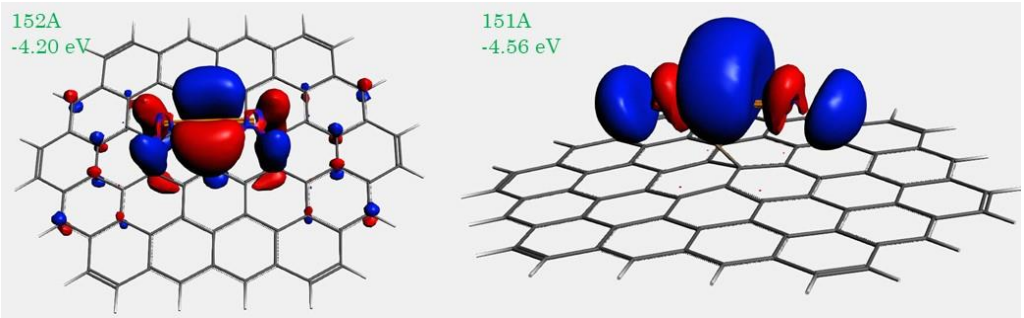


Figure 13 - Doubly-occupied molecular orbitals for the singlet state of the Ac_2-1,2 system that describe the formation of a double Ac-Ac bond.

Finally, the Bader's QTAIM representation of the bond critical points can give a definitive statement on whether there is a bond or not. As it can be seen in Figure 14, a bond critical point (red dot) is present in the middle of the metals, so it is another confirmation that a bond is present, what was hypothesized from the bond distance value (3.50 Å) and the interaction bond energy (2.02 eV). Higher spin multiplicities have not been considered for Ac_2-1,2 system due to lack of time.

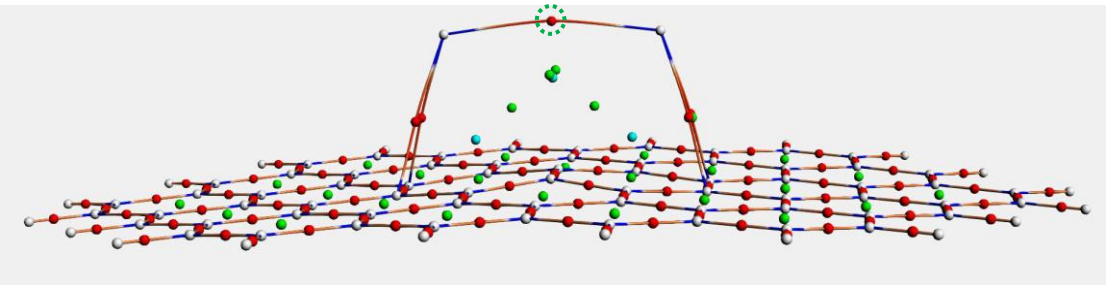


Figure 14 - Critical points (CP) in QTAIM theory found for the singlet state of Ac_2-1,2 system. Atom CP in grey, bond CP in red, ring CP in green and cage CP in blue. The bond CP between the two Ac atoms is highlighted in green.

Finally, for the Ac_2-1,2 system, the metal atoms have also shifted their position with respect to their original placement. The difference between the original M-M distance (2.5 Å) and the one after the optimization (3.5 Å) is of 1 Å. The fact that an Ac-Ac bond has been observed is a novel finding, given the fact that no Ac-Ac bond has been observed for the dimer adsorbed in other carbonaceous systems.

By checking Table 2 again, the Th_2-1,4 system, we see that the same trend is followed as for thorium, being the interaction energy (-4.09 eV) approximately double that of the single Ac-flake system (-1.95 eV x 2 = -3.90 eV). That should give the hint that no M-M bond is formed, because of the large distance separating the actinium atoms (7.31 Å). The computed energy will just indicate the formation of the system with no further significant Ac-Ac interactions.

Finally, the Th_2-1,3 system shows very similar bond distance to that of the previously analysed Th_2-1,2, what means that again the atoms are translated to a closer position, but in this case, the interaction energy is more than 1 eV lower than for the Th_2-1,2 dimer. The reason for such a difference is that what we call Th_2-1,3 system was optimized in a septet state while the 1,2 was done in a singlet state.

5.3. Single Atom Uranium and Dimer on Graphene

Table 3 - Interaction energies (eV) and U-U bond distances (Å) from single atom U and U_2 dimers adsorbed on the graphene flake.

System	Spin state	Interaction energy (eV)	Bond distance (Å)
U	Triplet	-6.04	-
U_2 1,2 position	Singlet	-16.22	2.25
U_2 1,3 position	Singlet	-16.22	2.25
U_2 1,4 position	Septet	-11.51	7.54
	Nonet	-12.61	7.37

From the molecular orbitals analysis (Figure 15), it can be deduced that uranium has a formal exchange of 2 electrons to the graphene flake, so the metal is left with an f^4 configuration that leads to a possible quadruple bond formation.

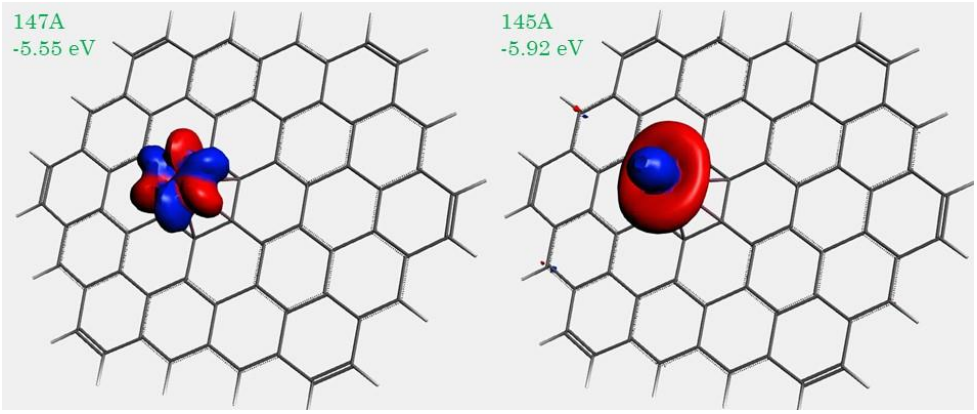


Figure 15 - Singly occupied alpha molecular orbitals for the triplet state of U-flake system. Four of the six valence electrons of U formally remain on U once adsorbed on the flake, so we deduce that it is formally U^{2+}.

As it can be seen in Table 3, in this case, the interaction energies are much more important. For the U_2-1,2 system, the interaction energy is much larger

than our reference value of the single U-flake (16.22 eV vs 6.04 eV x 2 = 12.08 eV). Again, this may indicate that a strong (likely quadruple) bond is being formed, whose bond energy can be estimated as 4.14 eV (95 kcal mol^{-1}).

As previously stated, the uranium atoms, after the exchange of the 2 electrons to the flake, have still 4 valence electrons available for the formation of a bond. As it can be seen in Figure 16, these electrons interact in order to form what is thought to be a quadruple bond.

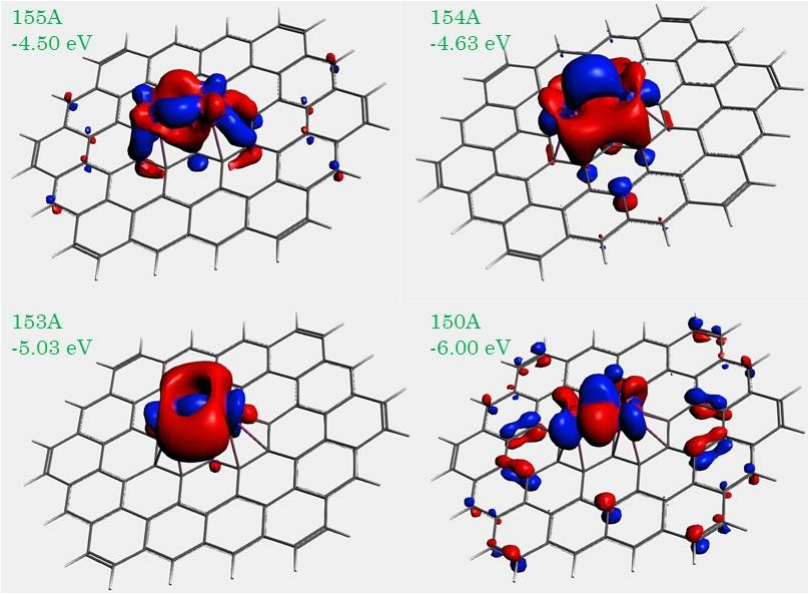


Figure 16 - Doubly-occupied molecular orbitals for the singlet state of the U_2-1,2 system that describe the formation of a quadruple U-U bond.

To have the confirmation of the presence of the bond, we look the Bader's AIM representation (Figure 17) for bond critical points. One of them (red dot) is found between both metal atoms, so the presence of a U-U bond is corroborated.

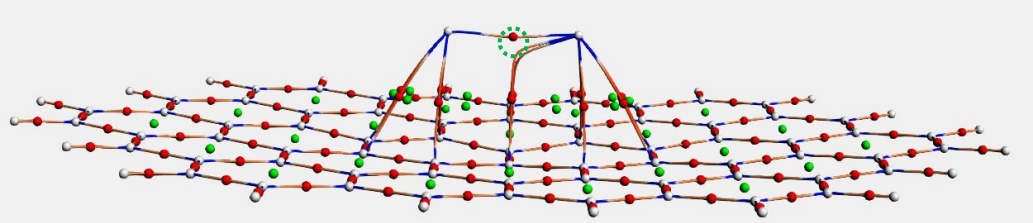


Figure 17 - Critical points (CP) in QTAIM theory found for the singlet state of U_2-1,2 system. Atom CP in grey, bond CP in red, ring CP in green and cage CP in blue. The bond CP between the two U atoms is highlighted in green.

An aspect to highlight here again is that what we initially call U_2-1,3 system, once optimized, leads to the U_2-1,2 system with the U atoms translated to the hollow positions of two contiguous hexagons (see Table 3, same energies and U-U distances, and Figure 18), showing again that such 1,3 disposition of the actinides is not stable.

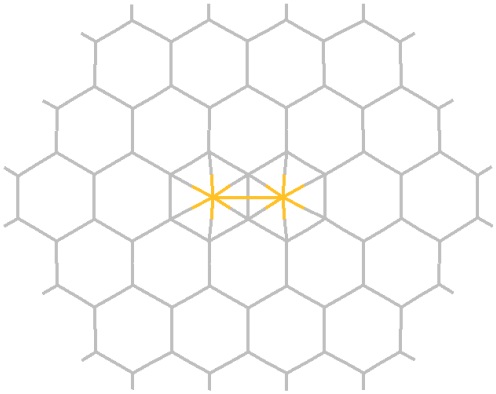


Figure 18 - Optimized geometry representation of what we initially call U_2-1,3 system in its singlet state.

Again, by looking the values of the 1,4 system in Table 3, the values of their energies are approximately double the one for the single atom system, even though the septet (S=3) and the nonet (S=4) give somewhat different values. So, no presence of a U-U bond is expected at such large distances.

5.4. Thorium Trimers on Graphene

Table 4 - Interaction energies (eV) and Th-Th bond distances (Å) for Th_3 trimers adsorbed on the graphene flake.

System	Metals Geometry	Interaction energy (eV)	Bond distance (Å)
Th_3	Triangle	-15.00	3.19 / 3.17 / 3.17
	Linear	-13.05	3.10 / 3.07

The last studied case is the adsorption of three thorium atoms onto the graphene sheet. Two different arrangements have been designed (Figure 19): one in which the three atoms are in a triangular disposition, having the same distance between all of them, and a linear arrangement. Both systems were computed at the singlet state.

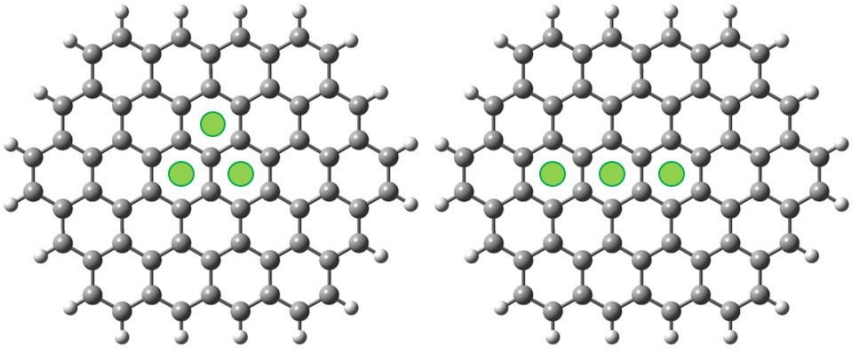


Figure 19 - Representation of the different thorium trimer studied systems: triangular (left) and linear (right).

After the computational optimization of both systems, as it is displayed in Table 4, the triangular geometry is the most energetically stable one, and the bond distances between thorium atoms are very similar to that of the Th_2-1,2 system, while in the linear one the distances are a bit smaller. For the linear arrangement the Th-Th bonding energy could be estimated as BE = 13.05 eV - 3 x 3.36 eV = 2.97 eV; this value corresponds to the formation of two different Th-Th bonds, what leaves a value of 1.49 eV on average per bond. The triangular system shows an interaction energy that is more than 2 eV higher than for the linear case. This can be explained because, as the three atoms are all interacting between them, one more bond is formed. The Th-Th bonding energy now is estimated as BE = 15.00 eV – 3 x 3.36 eV = 4.92 eV. So, each Th-Th bond would have on average a bond energy of 1.64 eV, a value quite similar to that of the linear case. Compared to Th_2 dimers, whose Th-Th bond energy was estimated to be 2.61 eV, for the trimer case we find significantly lower Th-Th bonding energies (by 1 eV). This is most likely because the bond order for each Th-Th bond is lower now since there are on average nine Th electrons (three per atom) that must be shared to form three Th-Th bonds (formally a bond order of 1.5 for the triangular case).

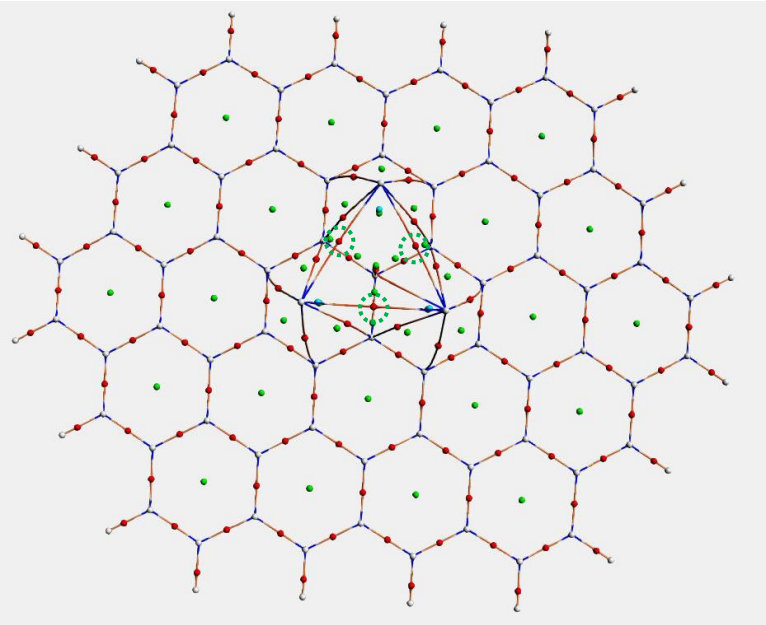


Figure 20 - Critical points (CP) in QTAIM theory found for the singlet state of Th3-triangular system. Atom CP in grey, bond CP in red, ring CP in green and cage CP in blue. The three bond CPs between the three Th atoms are highlighted in green.

The QTAIM topology representation confirms the existence of three bond critical points, ergo, the existence of three Th-Th bonds. By observation of the molecular orbitals, we can find out which are the contributions of each metal to each bond. In Figure 21 we can see three doubly-occupied σ orbitals and a π orbital.

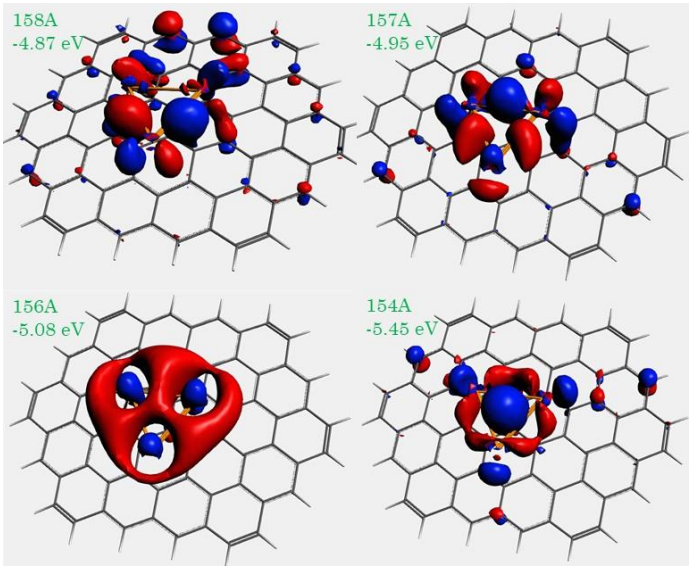


Figure 21 - Doubly-occupied molecular orbitals for the singlet state of the Th3-triangle system that describe the formation of Th-Th bonds.

6. CONCLUSIONS

The results have shown that there exists the possibility that intermetallic bonds are formed on every studied actinide dimers adsorbed in a graphene sheet. Depending on the metal used, different interactions have been observed through molecular orbitals diagrams.

We have observed that thorium dimers adsorbed on graphene, formally transfer two electrons to the flake, what leads to the formation of a triple bond with the resting three valence electrons. We can do a comparison with the case of fullerenes, in which the dimer transfers 6 electrons to the carbon structure and just a single M-M bond is formed. For the case of actinium, it was surprising that a bond was formed, as in fullerenes the dimer transfers all 6 valence electrons, so no bond can be formed.; in the case of graphene just two electrons are transferred, so a double bond can be formed between the metals. Finally, for uranium adsorbed in graphene a quadrupole bond has been observed in contrast to the triple bond that is created in diuranium endohedral fullerenes.

As a general trend, it has been observed that every system studied can form an actinide-actinide bond if both metal atoms are close enough. For systems with a 1,4 relative position, it has been impossible to form any bond, nor for both atoms to shift close enough for them to interact, a situation that actually does happen in the 1,3 case; the atoms are originally separated by nearly 5 Å, although after the optimization, depending on the actinide used, they can shift to a position separated up to 2.25 Å.

To culminate the thesis, this work has successfully achieved to analyse and report the interactions of different actinide dimers and trimers on carbonaceous surfaces, as it is a graphene sheet, by observation of the interaction energies, bond distances, molecular orbitals, and bond critical points from Bader's theory. Thus, it is concluded that the main objective of the thesis has been accomplished.

Els resultats obtinguts en aquest treball han demostrat que existeix la possibilitat que es formin enllaços intermetàl·lics a tots els dímers d'actínids estudiats adsorbits en una làmina de grafè. Segons el metall utilitzat, s'han observat diferents interaccions mitjançant diagrames d'orbitals moleculars.

Hem observat que els dímers de tori adsorbits al grafè, transfereixen formalment dos electrons al "flake", fet que comporta la formació d'un triple enllaç amb els tres electrons de València en repòs. Podem fer una comparació amb el cas dels ful·lerens, on el dímer transfereix 6 electrons a l'estructura de carboni i només es forma un enllaç simple M-M. En el cas de l'actini, va ser sorprenent veure la formació d'un enllaç, ja que en els ful·lerens el dímer transfereix els 6 electrons de València, de manera que no en queda cap per poder formar un enllaç; en el cas del grafè només es transfereixen dos electrons, de manera que es pot formar un doble enllaç entre els metalls. Finalment, per a l'urani adsorbit en el grafè s'ha observat un enllaç quàdruple que contrasta amb el triple enllaç que es crea en els ful·lerens endoèdrics de diurani.

Com a tendència general, s'ha observat que tots els sistemes estudiats poden formar un enllaç actínid-actínid, sempre i quan els dos àtoms metàl·lics estiguin prou a prop. Per als sistemes amb una posició relativa 1,4, ha estat impossible la formació de cap enllaç, ni que els àtoms s'apropin prou perquè interactuïn, una situació que si passa en el cas 1,3; els àtoms estan separats originalment per gairebé 5 Å, encara que després de l'optimització, depenent de l'actínid utilitzat, poden desplaçar-se fins a una posició separada per 2,25 Å.

Per culminar la tesi, aquest treball ha aconseguit analitzar i plasmar amb èxit les interaccions de diferents dímers i trímers d'actínids sobre superfícies carbonàcies (làmina de grafè) mitjançant l'observació de les energies d'interacció, distàncies d'enllaç, orbitals moleculars i punts crítics d'enllaç de la teoria de Bader. D'aquesta forma, es conclou que l'objectiu principal de la tesi s'ha assolit.

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