Investigation of the Reaction Path from UO₂ to UF₆ using Density-functional Theory

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Abstract

A detailed investigation of the reaction mechanism for UO_2 reacting with F_2 to form UF_6 is performed by using density functional theory (DFT). We divide the whole reaction chain into four main steps, $\text{UO}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_2$, $\text{UO}_2\text{F}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_4$, $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$ and $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$. Contrary to what has been mostly expected that F_2 molecule should directly replace two O atoms in UO_2 molecule, two F_2 atoms actually combine with UO_2 successively in the first two steps. The third step is relatively complex and one F atom in UO_2F_4 molecule plays a key role of carrying an O atom close to the other O atom. In last step, F-F bond in F_2 molecule fractures and two F atoms are bonding with U atom in UF_4 molecule successively. Spin-flip appears in two elementary reactions owing to the existence of heavy atom U.

1. Introduction

Uranium, which is the important nuclear fuel nowadays, has drawn considerable interest of investigators. In nuclear industry production, the process from UO_2 to UF_6 is called uranium conversion [1–3]. Uranium conversion is not only an essential step for nuclear fuel processing, but also a key step for the whole nuclear fuel cycle. In general, uranium conversion includes the following two reactions.

In past decades, plentiful experiments were performed by different researchers to analyze multifarious characters for uranium oxides and uranium fluorides. For example, Konings et al. figured structure parameters and vibrational frequencies for UF_4 via gas-phase electron diffraction method and high-temperature infrared spectroscopy, respectively [4]. Before this work, structure parameters for UF_6 have been measured by Seip [5] and Weinstock et al. [6] using electron diffraction method in 1965. Afterwards, infrared and Raman spectra of UF_6 have been gauged using long-path absorption cells and multiple-reflection Raman cells [7]. In recent years, the increasing number of investigators studied the properties of uranium oxides and uranium fluorides by using kinds of quantum chemical packages, along with the rapid development of computational chemistry. For instance, Majumdar et al. calculated structure parameters and vibrational frequencies for UO_2 using Gaussian and Gamess, by employing various functional [8]. The bonding nature of UF_4 was studied by Wang et al. using Gaussian package [9]. Hay et al. calculated the structure and vibrational frequencies of UF_6 using relativistic effective core potentials with Hartree-Fock and density functional methods [10].

Albeit various natures for uranium oxides and uranium fluorides have been studied, few researchers devote their effort on the reaction path about uranium conversion. Until recently, Peluzo et al. investigated the reaction mechanism of UF_4 to UF_6 in 2018 [11]. However, few information about whole reaction chain

of UO_2 to UF_6 and in the present work, we investigated this subject by employing the density functional theory (DFT) [12].

2. Computational Method

Elementary reaction, which is also called simple reaction, refers to a reaction that is directly converted into a product in one step. In most cases, the chemical reaction formula cannot explain the reaction process, because most reactions require several steps to complete in reality [13]. Therefore, in order to figure out a whole reaction chain, we must start from the elementary reaction. Moreover, the reaction barrier and reaction rate can be gained via the elementary reaction [14]. The key step to figure out an elementary reaction is to find the transition state (TS) [15] of this reaction, the energy peak of reaction path on the potential energy surface. It connects reactant with product via minimum energy path. If this minimum energy path is considered under the mass weight coordinate, it also called intrinsic reaction coordinate (IRC) [16, 17]. Therefore, IRC calculations are also taken to verify the reliability of TSs and observe the energy change of reactions.

Take the computational accuracy and elapsed time into consideration comprehensively, here the hybrid functional PBE0 [18], which is shown to have high accuracy on system related to actinide elements [19–22], is adopted to optimize molecular structures, conduct vibration analysis, find TSs and calculate IRCs from beginning to the end.

The Gaussian-type orbital all electron triple-zeta splitting basis set 6-311+G(d) [23, 24] is adopted for O and F atoms, while the Stuttgart/Dresden (SDD) basis set with a matching scalar relativistic effective core potential²⁵ is extensively adopted for U atom, which is immensely popular in calculating the actinide elements for combining accuracy with elapsed time [19–22, 26].

All of the above calculations are carried out with Gaussian16 package [27].

3. Results And Discussion

3.1 structures and vibrational frequencies

When it comes to calculate TSs and IRCs, it is essential to gain molecular ground state structures and conduct vibrational analyses. Therefore, we optimized a number of structures about reactants as well as products and calculated their vibrational frequencies before performing the calculations about TSs and IRCs. At the same time, we compared our results with some experimental and theoretical results, in Tables 1-4.

Table 1
Comparison of some parameters for UO_2 .

Parameters		Bond length/Å	Bond angle/Deg.	Frequencies/cm ⁻¹		
Theo. [8]	MP2	1.795	180.0	896	149	913
	B3LYP	1.764	180.0	880	222	933
Present		1.770	180.0	900	153	951

Table 2
Comparison of some parameters for UO_2F_2 .

Parameters		r(U-O)/ Å	r(U-F)/ Å		O-U-O/ Deg.		F-U-F/ Deg.			
Theo. [28]	B3LYP	1.768	2.075		168		114			
	MP2	1.794	2.070		169		112			
Present		1.743	2.067		171		115			
Parameters		Frequencies/cm ⁻¹								
Theo.[28]	B3LYP	971	903	559	544	240	220	213	203	81
	MP2	942	849	568	555	212	218	182	205	90
Present		1001	934	562	550	248	226	223	199	80

Table 3
Comparison of some parameters for UF_4 .

Parameters	r(U-F)/ Å	Frequencies/cm ⁻¹	
Exp. [4]	2.059	605	537
Theo. [9]	2.070	595	543
Present	2.058	597	557

Table 4
Comparison of some parameters for UF₆.

Parameters	r(U-F)/ Å	Frequencies/cm ⁻¹					
Exp. [5]	1.996						
Exp. [6]	1.999						
Exp. [7]		667	534	626	186	200	143
Theo. [10]	2.014	653	552	647	191	178	150
Present	1.993	669	538	628	186	199	141

The structure parameters and vibrational frequencies for UO₂ molecule are presented in Table 1, including our calculations and results of D. Majumdar et al.[8]. Similarly, Table 2 to Table 4 shows the comparisons of structure parameters and vibrational frequencies for UO₂F₂, UF₄ and UF₆, respectively. Overall, our calculation results are in close agreement with the experimental or theoretical results. Therefore, the functional and basis sets we used are suitable to perform the next calculations.

3.2 Reaction paths

In this section, we focus on the reaction path between UO₂ and F₂. We divide the whole reaction chain into four main steps, UO₂+F₂→UO₂F₂, UO₂F₂+F₂→UO₂F₄, UO₂F₄→UF₄+O₂ and UF₄+F₂→UF₆. Then we divide every reaction into several elementary reactions, meanwhile reactant complexes, TSs, product complexes and IRCs are given in every elementary reaction to clarify reaction mechanism.

3.2.1 UO₂+F₂→UO₂F₂

Fig. 1 presents the IRC curve for the reaction UO₂+F₂→UO₂F₂ and this reaction is an elementary reaction. $\square$ refers to reactant complex of UO₂ and F₂, the number in parenthesis refers to spin multiplicity for this structure (similarly hereinafter), therefore $\square(1)$ indicates singlet state is ground state for complex $\square$. It can be seen that four atoms in complex $\square$ sit in the same plane, while this structure will distort along with the process of reaction. It is clear that four atoms in TS1 don't sit in one plane. In the final product complex $\square$, the O2-U1-O3 plane is perpendicular to the F4-U1-F5 plane. It is observed that two F atoms in F₂ molecule are all added with UO₂ instead of replacing one or two O atoms in UO₂ molecule when F₂ reacts with UO₂.

Figure 2 presents the relative energy change along with the process of step 1. This reaction starts from the formation of reactant complex $\square$, releasing about 813kJ/mol energy. The reaction barrier is just 10kJ/mol, which indicates that this step is easy to complete.

3.2.2 UO₂F₂+F₂→UO₂F₄

Figure 3 presents the IRC for reaction $\text{UO}_2\text{F}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_4$. Influenced by the limitation of two-dimension picture, U1 atom is covered by O2 atom in Figure 3. Actually, U1 atom sits beneath O2 atom. UO_2F_2 and F_2 form the reactant A , the F7-U1 and F6-U1 bond lengths are all 3.04 Å, and angle F6-U1-F7 is 26.4°. The distance between F6 and F7 gets larger while the F7-U1 and F6-U1 bond lengths get diminished. It can be indicated by the structures of TS2 and product B for this reaction. As shown in the figure, the F7-U1 and F6-U1 bond lengths are 2.30 Å in TS2 while 2.03 Å in product B , angle F6-U1-F7 is 50.2° in TS2 while 92.5° in product B . Before the formation of TS2, energy for system is gradually rising because the F6-F7 bond is stretched and the existence of repulsive force between F_2 molecule and UO_2F_2 molecule. After the formation of TS2, energy for system is gradually diminishing because the F6-F7 bond is already fractured and F6 as well as F7 atom is forming new bond with U1 atom, the whole system would change towards a direction of reducing energy. Similarly, this elementary reaction is an addition reaction instead of a substitution reaction.

3.2.3 $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$

Figure 4 shows the IRC for the first elementary reaction of $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$. Similarly, U1 atom sits beneath F6 atom. In this step, F7 atom in reactant A which is formed in last step rotates towards O2 atom in F4-O2-O3 plane. This can be proved by the angle O2-U1-F7, which is 95.5° in reactant A , 66.0° in TS3 while 36.3° in product B . During the process of rotation, the distance between U1 and F7 grows larger, this value, to be specific, is 2.03 Å in A , while 2.16 Å and 2.43 Å in TS4 and B separately. It is worth mentioning that F7 is bonding with O2 in product B . Influenced by F7 atom, O2-U1 bond length also changes. As shown in picture, this value becomes larger, from 1.78 Å in reactant A to 2.13 Å in product B .

Figure 5 shows the IRC for the second elementary reaction of $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$. In this step, O3 and F4 in reactant A rotate towards O2 atom in F4-O2-O3 plane. For example, angle O2-U1-O3 is 158.1° in reactant A , while 125.9° and 91.4° in TS4 and product B respectively. Meanwhile, F7 atom' location also has changed, which is posited in O2-F4-O3 plane in initial moment while is perpendicular to O2-F4-O3 plane in the end.

Figure 6 shows the IRC for the third elementary reaction of $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$, U1 atom sits beneath O2 atom. It can be seen that O2-F7 bond rotate 90 degrees counterclockwise in plane which parallel to O3-F4-F5 plane, from paralleling with U1-F4 bond to paralleling with U1-F5 bond.

Figure 7 shows the IRC for the fourth elementary reaction of $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$. In this step, the distance between O2 and F7 getting bigger while the distance between O2 and O3 getting smaller leads to the broken of O2-F7 bond and the formation of O2-O3 bond. As shown in Fig. 7, the angle O2-U1-O3 is getting smaller along with the process of reaction, to be specific, 79.6°, 56.5° and 32.5° in reactant A , TS6 and product B respectively. During this reaction, the distance between O3 and U1 becomes larger, from 1.74 Å to 2.30 Å, while the distance between F7 and U1 lessens, from 2.70 Å to 2.02 Å. It is worth to mention that the distance between O2 and U1 first decreases and then increases, from 2.15 Å in reactant A to 1.99 Å in TS6 and from 1.99 Å in TS6 to 2.30 Å in product B . This may be caused by the broken of O2-F7 bond and the formation of O2-O3 bond, respectively. In product B , O2 and O3 have already bonded, at the same

time, the distances between U1 and O2 as well as O3 are all 2.30 Å, stretching one third than before. It demonstrates that two O atoms would separate from the product $\square$, that is to say, O_2 molecule would be produced at the end of reaction. Particularly, in this elementary reaction, the ground states for reactant $\square$ and TS6 are all singlet state while the ground state for product $\square$ is triplet state. i.e., spin-flip occurs in this reaction, which mainly caused by spin-orbit coupling of electrons. Spin-flip is more easily appears in system we investigate owing to the existence of heavy atom U, which has a strong relativistic effect.

Through the above analyses, it is observed that the reaction $UO_2F_4 \rightarrow UF_4 + O_2$ can be divided into four elementary reactions. In this process, we highlight the role of F7 atom, carrying O atom. Firstly, F7 breaks away from U1 and binds with O2. Secondly, F7 has an effect on two O atoms closing to each other. Lastly, F7 breaks away from O2 and binds with U1 on the contrary.

Due to the atomic numbers in step 2 keeps the same with the numbers in step 3, the relative energy change diagrams for the reactions $UO_2F_2 + F_2 \rightarrow UO_2F_4$ and $UO_2F_4 \rightarrow UO_4 + O_2$ are presented in Fig. 8 at the same time. In addition, all the energies of reactants, TSs and products relative to the sum energy for the ground state of complex $\square$ and F_2 are calculated. Hence reaction barriers of every elementary reaction can be gained.

3.2.3 $UF_4 + F_2 \rightarrow UF_6$

Figure 9 shows the IRC for the first elementary reaction of $UF_4 + F_2 \rightarrow UF_6$. In this step, F_2 molecule moves towards UF_4 molecule and two F atoms in F_2 molecule gradually separate from each other. To be specific, the distances between two F atoms in F_2 molecule are 1.39 Å and 1.43 Å in reactant $\square$ and TS7, respectively. In product $\square$, the F6-F7 bond has already broken. The distance between F6 and U1 gradually shortens, 2.97 Å in reactant $\square$, 2.68 Å in TS7 and 2.26 Å in product $\square$.

Figure 10 shows the IRC for the second elementary reaction of $UF_4 + F_2 \rightarrow UF_6$, U1 atom sits beneath F4 atom. In this step, the distance between F6 and F7 further increases, F6 is bonding with U1, forming a structure like UF_5 molecule firstly. This can be proven by the distance between F6 and U1, 2.26 Å in reactant $\square$ while 2.01 Å in TS8. While F7 keeps the same distance with U1 basically. Subsequently, F7 atom moves towards UF_5 structure, forming UF_6 molecule. In addition, spin-flip also occurs in this reaction.

We divided the reaction $UF_4 + F_2 \rightarrow UF_6$ into two elementary reactions, in a few words, this reaction can be explained three steps, F6-F7 bond in F_2 molecule fractures and two F atoms are bonding with U1 successively.

Figure 11 presents the relative energy change for the reaction $UF_4 + F_2 \rightarrow UF_6$. As shown in picture, the barriers of two elementary reactions are 5 kJ/mol and 56 kJ/mol, respectively.

4. Conclusion

In this paper, we mainly study the reaction mechanism for UO_2 reacting with F_2 to form UF_6 by using DFT. Before performing the formal calculations, we compare our results of structures and vibration parameters with some experimental and theoretical results, in turns out that our result is reliable. We divide the whole reaction chain into four successive reactions, $\text{UO}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_2$, $\text{UO}_2\text{F}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_4$, $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$ and $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$. There into, the first and second reactions are all elementary reaction and can be regarded as addition reaction. Two F_2 molecules add with UO_2 successively instead of replacing O atom in UO_2 molecule directly when F_2 reacts with UO_2 . Relatively speak, the third reaction is complex, it can be divided into four elementary reactions. In this reaction, one F atom in UO_2F_4 molecule plays a role of carrier, promoting two O atoms in UO_2F_4 molecule closing to and bonding with each other. Then O_2 molecule is formed and separates from the UO_2F_4 molecule in the end. The last reaction in not a simple addition reaction, it can be divided into two elementary reaction. In a word, F-F bond in F_2 molecule fractures and two F atoms are bonding with U atom in UF_4 molecule successively. Spin-flip appears in two elementary reactions owing to the existence of heavy atom U. In addition, energy barriers for every elementary reaction are obtained.

Declarations

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Ethics approval We allow the journal to review all the data, and we confirm the validity of the results. There are no financial relationships. This work was not published previously and it is not submitted to more than one journal. It is also not split up into several parts to submit. No data have been fabricated or manipulated.

Consent to participate All the authors agree to participate in this investigation.

Consent to publication All the authors agree to publish the manuscript.

Conflict of interest The authors declare no competing interests.

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Code availability N/A

Author contribution Jun-kui Wei: calculation, data analysis and writing original draft.

Run-jia Bao: Review, plotting and editing.

Bo-wen Li: Conceptualization, investigation and guidance.

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Figures

Figure 1

IRC of the step 1, reaction $\text{UO}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_2$.

Figure 2

Energy change for the reaction $\text{UO}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_2$.

Figure 3

IRC of the step 2, reaction $\text{UO}_2\text{F}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_4$.

Figure 4

IRC of the first elementary reaction in step 3, reaction $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$.

Figure 5

IRC of the second elementary reaction in step 3, reaction $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$.

Figure 6

IRC of the third elementary reaction in step 3, reaction $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$.

Figure 7

IRC of the fourth elementary reaction in step 3, reaction $\text{UO}_2\text{F}_4 \rightarrow \text{UF}_4 + \text{O}_2$.

Figure 8

Energy change for the reactions $\text{UO}_2\text{F}_2 + \text{F}_2 \rightarrow \text{UO}_2\text{F}_4$ and $\text{UO}_2\text{F}_4 \rightarrow \text{UO}_4 + \text{O}_2$.

Figure 9

IRC of the first elementary reaction in step 4, reaction $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$.

Figure 10

IRC of the second elementary reaction in step 4, reaction $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$.

Figure 11

Energy change for the reactions $\text{UF}_4 + \text{F}_2 \rightarrow \text{UF}_6$.