Research Article

Determination of the energy characteristics of the reactions $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$*

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Abstract

Quantum-mechanical methods are used to assess the energy barriers to dissociation and recombination reactions of $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$. The energy characteristics of these reactions are found to be strongly asymmetric: the dissociation reaction barriers exceed the recombination reactions barriers by more than 4 eV. The equilibrium atomic configurations of F_2, UF_4, UF_5 and UF_6 have been determined using precision quantum mechanical calculations. The U-F bond lengths obtained as a result of the calculations are in good agreement with experimental data. It was found that the decay reaction $UF_6 \rightarrow UF_5 + F$ is either barrier-free, or the energy barrier for such a reaction is less than the resolving power of the method (~ 0.1 eV). For the decay of $UF_6 \rightarrow UF_4 + F_2$, there is an energy barrier with a height of about 0.3 eV. An initial approximation was proposed for the arrangement of UF_6 atoms in order to find the saddle points of the UF_6 dissociation reactions. In this initial configuration, all 7 atoms of the UF_6 molecule are located in the same plane. The F atoms are located at the vertices of a regular hexagon, and the U atom is at the center of such a hexagon. The results of this work can be used to determine the constants of thermal reactions of dissociation and recombination $UF_6 \leftrightarrow UF_5 + F$ и $UF_6 \leftrightarrow UF_4 + F_2$. These constants are necessary for modeling the physicochemical processes occurring during the enrichment of spent nuclear fuel (SNF).

Introduction

Closing the fuel cycle requires new approaches to enrichment of reprocessed uranium. Until now, uranium recycle has been limited mainly to recycle of once reprocessed SNF irradiated to relatively low burn-ups. However, the trends in the development of the fuel cycle are such that the stocks of SNF with low burn-up are almost exhausted, but instead of them new ones have been accumulated, already with a higher burn-up in significantly increased volumes. The need to reduce the mass of disposed waste leads to an understanding of the need for multiple recycle of regenerated nuclear materials and, first of all, uranium, which makes up more than 90% of spent nuclear fuel. The physics of multiple recycling of uranium is such that in the sequence of recycles, from the previous one to the next, there is a continuous increase in the ^{236}U isotope content, which, in turn, leads to an increase in the ^{232}U content (Smirnov et al. 2010). This isotope is the main undesirable

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component in the composition of regenerated uranium, which complicates its use due to the presence of daughter products in its decay chain: this decay is accompanied by the emission of high-energy gamma quanta (Matveev and Tsenter 1985). The content of this isotope is limited in the most stringent way at the lowest possible level (Kislov et al. 2012). As the calculation results show, starting from a certain recycle, as a rule, from the second (or, with small burn-up, from the third), there comes a time when, while a certain amount of SNF is being reprocessed, it is not possible to use all the separated regenerate to produce an equivalent amount of fresh fuel. And the main reason for this is precisely ^{232}U due to non-observance of the limitation on the content of this isotope during the enrichment of regenerated uranium. The problem can be solved by using double cascades, which allow for the purification of enriched regenerated uranium. An example of such a cascade is shown in Fig. 1 (Smirnov et al. 2018). Its peculiarity is that, in addition to fuel with the required properties and depleted uranium, at the outlet from the cascade, there is also waste, which consists of uranium with an enrichment of 20% or more, containing a significant fraction of the ^{232}U isotope. This uranium fraction (selection of P_2 in Fig. 1) is small in relative mass, and the ^{232}U concentration in it, depending on the recycle number and enrichment in the second cascade, exceeds by several orders of magnitude the admissible limit on the ^{232}U content in low enriched uranium (LEU).

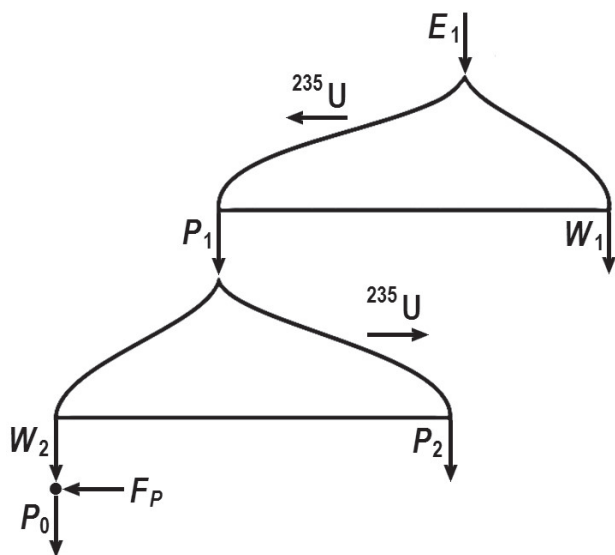In terms of further treatment, this material is, in principle, problematic. The only available method at present is dilution with waste uranium (Vodolazskikh et al. 2006, Mazin et al. 2013), but this method automatically leads to the loss of significant amounts of the ^{235}U isotope. An attempt to prevent these losses is the development of a double cascade with the return of the extraction flow, in which the fraction containing the ^{232}U isotope with a high ^{235}U content is diluted with a new batch of regenerate and again fed to the inlet of the cascade (Smirnov et al. 2019). However, this method requires additional justification, particularly in terms of the radiation resistance of uranium hexafluoride, in which radiolysis reactions occur, caused by an internal source of alpha radiation (Shiflett et al. 1958, Belov et al. 2019). It should be noted that publications of experimental data related to the problem of radiolysis of uranium hexafluoride in open sources are limited, with the exception of the already mentioned work (Shiflett et al. 1958) and two more works by the same authors, where they describe the same experiment.

Dissociation reactions are one of the main reactions that occur with UF$_6$ under the influence of an internal radiation source and thermal influence:

$$UF_6 \rightarrow UF_5 + e^- + F \rightarrow UF_5 + F \text{ and } UF_6 \leftrightarrow UF_4 + F_2.$$

To determine the rates of both thermal and radiation-induced dissociation, energy barriers are of great importance, which must overcome individual atoms of the starting materials in order to achieve a local minimum of potential energy corresponding to the reaction products. Such processes, which underlie chemical kinetics, are currently described using the transition-state theory (Peters 2017).

The experimental determination of such barriers and the atomic geometry corresponding to the transition state causes enormous difficulties associated with the short residence time of atoms near the transition state. Only recently, after the development of the femtochemical infrared spectroscopy method (Zewail 1994), it has become possible to approximately determine the geometry of the transition state by measurement. The use of traditional experimental methods for determining the rates of chemical reactions based on measurements of changes in the amount of reactants and products over time (Avery 1974) is difficult in the case of UF$_6$ dissociation by the presence of a non-thermal radiation-induced contribution.

Thus, theoretical computational methods for determination are extremely important. In quantum chemistry, reliable methods have been developed for calculating the energy characteristics of atoms, molecules, and crystals (Jensen 2007, Lewars Errol 2016). A review of recent applications of quantum chemical methods to the study of transition states is given in (Han and Chu 2013).

In this work, quantum-chemical methods are used to study energy barriers and transition states of reactions.

$$UF_6 \leftrightarrow UF_5 + F \text{ and } UF_6 \leftrightarrow UF_4 + F_2.$$

Figure 1. Scheme of a double cascade for recycling regenerated uranium: E_1 – flow of regenerated uranium; P_1 – flow of selection of the first stage, power supply of the second stage; P_2 – flow of selection of the second cascade (waste of purification from the ^{232}U isotope); W_1 – flow of the dump of the first stage; W_2 – flow of the heavy fraction of the second cascade; F_P – LEU diluent flow; P_0 – final product (commercial LEU).

Table 1. Calculated and experimental values of interatomic distances in F_2, UF_4, UF_5 и UF_6 molecules

Molecule	U-F bond length (F-F for F_2) calculation, pm	U-F bond length (F-F for F_2) experiment, pm	Experiment source
F_2	142.4	144	(Chomaker Verners and Stevenson 1941)
UF_4	207.4	205.6 ± 0.1	(Konings et al. 1996)
UF_5	203.3	200	(Jones Llewellyn and Ekberg Scott 1977)
UF_6	202.4	199.8	(Seip Hans 1965)

Calculation methods and discussion of results

For quantum mechanical calculations, we used the Quantum Espresso program (Giannozzi et al. 2009, 2017) involving pseudopotentials constructed according to the Projected Augmented Waves (PAW) principle (Kresse and Joubert 1999). The exchange-correlation functional in the form of PBE96 was applied (Perdew et al. 1996). The maximum energy of plane waves in basis functions was 520 eV.

Determination of equilibrium geometric configurations of UF_6, UF_4, UF_5 and F_2 molecules

Periodic boundary conditions were used in the calculations. In order to neglect the mutual influence of molecules in neighboring periodic patterns, we selected the size of the unit cell. We used cubic unit cells with an edge length from $d_{min} = 1$ nm to $d_{max} = 2$ nm. We selected the required cell size using the example of the UF_4 molecule. By means of numerical experiments, we determined that with an increase in the unit cell size above $d = 1.6$ nm, the change in the energy of the UF_4 molecule did not exceed 0.01 eV. Subsequently, all the calculations were performed at $d = 1.6$ nm.

To determine the equilibrium geometric configurations, the positions of the atoms were optimized by searching for local minima of the potential energy. The atomic geometries of the F_2, UF_4, UF_5, and UF_6 molecules optimized in this way are shown in Fig. 2.

To determine the accuracy of quantum-chemical methods for calculating the structure of molecules, the bond lengths were compared with the experimental values. The comparison is shown in Table 1. The discrepancy between the calculated and experimental values for all the molecules does not exceed 1%.

Determination of energies of the configurations UF_5 + F and UF_4 + F_2

As a first step to assess the energy barrier of the dissociation reactions $UF_6 \rightarrow UF_5 + F$ and $UF_6 \rightarrow UF_4 + F_2$, we compared the energy of the UF_6 molecule with the sum of the energies of the UF_5 molecule and the F atom and the sum of the energies of the UF_4 and F_2 molecules, respectively. The energies are given in Table 2.

Based on the data in Table 2, we can draw qualitative conclusions about the ratio of the rates of dissociation reactions ($UF_6 \rightarrow UF_5 + F$ and $UF_6 \rightarrow UF_4 + F_2$) and recombination reactions ($UF_5 + F \rightarrow UF_6$ and $UF_4 + F_2 \rightarrow UF_6$).
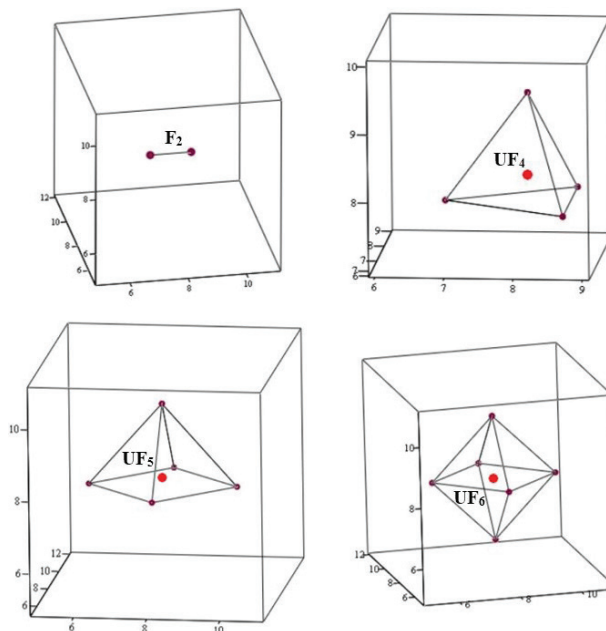
Figure 2. Optimized atomic geometries of the F_2, UF_4, UF_5, and UF_6 molecules.

Table 2. Energies of the UF_6 molecule and the UF_5 + F and UF_4 + F_2 complexes

Configuration	Energy, eV	Energy difference with UF_6, eV
UF_6	–45.732	0
UF_5 + F	–41.227	4.505
UF_4 + F_2	–38.428	7.304

The energy differences between the configurations are very high: 4.505 and 7.304 eV, respectively. At the same time, the energy of the UF_6 molecule is lower. Thus, the rates of the recombination reactions will be much higher than the rates of the dissociation reactions. To quantitatively determine the rates of forward and reverse reactions, it is necessary to determine the energy characteristics of the saddle point between the configurations, the corresponding reactants and reaction products.

Determination of energy barriers to the reactions $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$

Various methods are used to determine the geometry and energy of transition states, for example, the Nudged Elastic Band (NEB) (Henkelman and Jónsson 2000) and the dimer method (Henkelman and Jónsson 1999). The NEB method is mainly used to find potential barriers to diffusion in crystals and at crystal surfaces. In these cases, there are well-defined local potential energy minima corresponding to the movement of the migrating atom over a short distance.

The NEB method is fairly easy to use: it is enough to create several atomic configurations obtained by linear interpolation of atomic configurations corresponding to two minima of potential energy. It is rather difficult to use the NEB method for finding the transition states of chemical reactions, since formally one of the potential energy minima corresponds to the reaction products at infinity, which causes problems with the convergence of numerical algorithms.

However, for a qualitative assessment of the barrier to a chemical reaction, one can use the ideas embodied in the NEB method. For this purpose, several atomic configurations have been constructed by interpolating the atomic positions in the UF_6 molecule and at the extreme positions of the $UF_5 + F$ and $UF_4 + F_2$ complexes. In these extreme positions, the fluorine atom and molecule are at the maximum distances possible, taking into account the chosen size of the simulation volume and periodic boundary conditions, from the atoms included in UF_5 and UF_4, respectively. The extreme atomic configurations corresponding to the maximum distance F from UF_5 and F_2 from UF_4 are shown in Fig. 3.
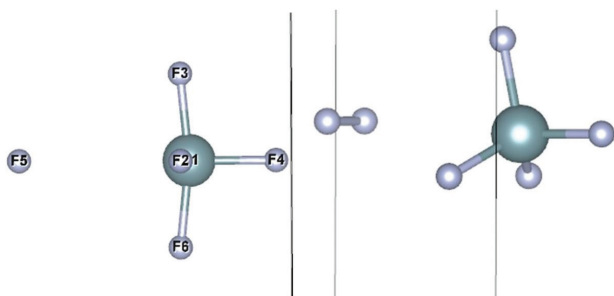

Figure 3. Atomic configurations corresponding to the maximum distance of F from UF_5 (left) and F_2 from UF_4 (right), used to determine the barriers to dissociation and recombination reactions.

For each interpolation configuration between the UF_6 molecule and the extreme positions of the atoms in the complex, the total energy was calculated without relaxation of the atomic positions. The energy dependences of a system of atoms along such interpolation paths are shown in Fig. 4.

For the recombination reaction $UF_4 + F_2 \rightarrow UF_6$, the energy barrier was estimated using this algorithm. This barrier is approximately equal to 0.34 eV. The barrier for the dissociation reaction is 7.64 eV. For the reactions $UF_6 \leftrightarrow UF_5 + F$, it was not possible to estimate the height of the energy barrier due to its low accuracy. However, for pairs of configurations 7-8 and 9-10, the energies are very close. Apparently, the energy barrier can be realized for atomic geometries close to these configurations.

Determination of states for the reactions $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$

The ultimate goal is not only to determine energy reactions, but also to calculate the reaction constants, which will make it possible to calculate the kinetics of the reactions. For this purpose, it is necessary to know not only the height of the energy barrier, but also the vibrational spectra of the initial molecule and the atomic configuration corresponding to the transition state.

The dimer method is used to determine the transition state (Henkelman and Jónsson 1999). In this method, in the presence of an atomic configuration, which is a certain predicted approximation to the geometry of the transition state, the vibrational frequencies of atoms in this configuration are analyzed. As a rule, if the initial approximation is well predicted, one of the natural frequencies is imaginary and the rest are real. The presence of an imaginary frequency in vibrational spectra is an indication of instability.
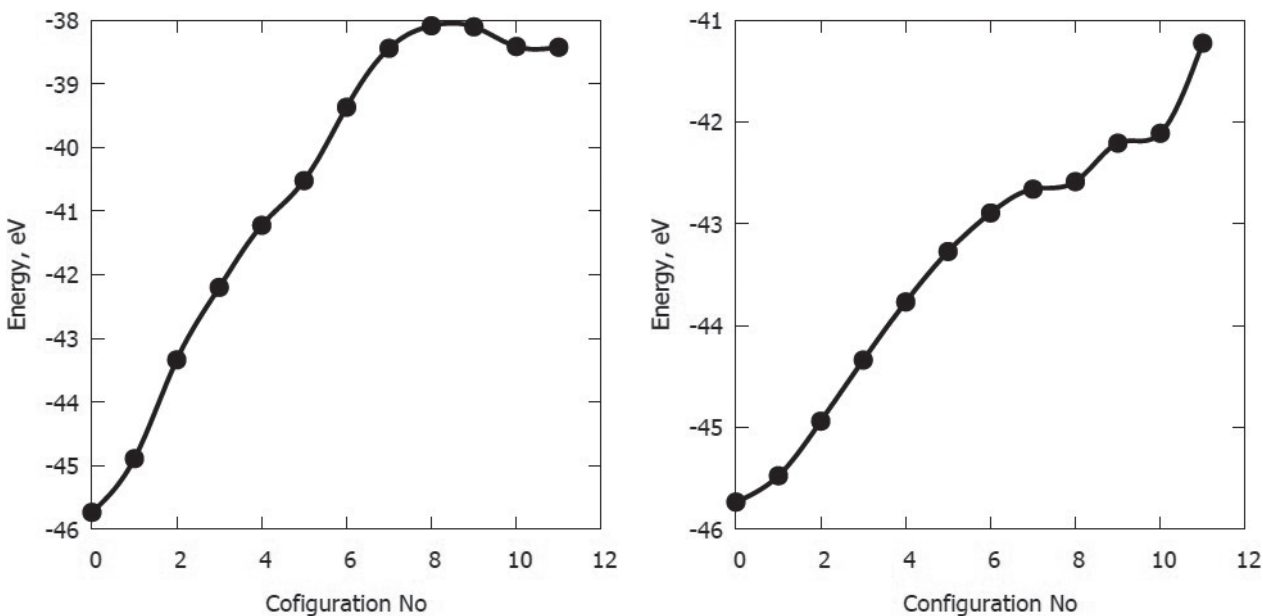

Figure 4. Values for different interpolation configurations of atomic positions of the complex $UF_4 + F_2$ (left) and $UF_5 + F$ (right). Configuration No. 0 corresponds to the UF_6 molecule, Configuration No. 11 corresponds to the most distant atomic positions shown in Fig. 3.
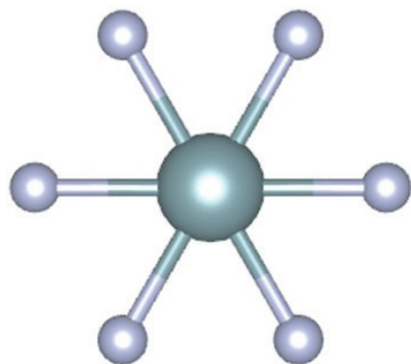
Figure 5. Atomic configuration of the U atom and six F atoms, obtained by minimizing the potential energy when the atoms are located in the same plane. The U atom is in the center of the regular hexagon, and the F atoms are in the vertices of the hexagon.

By displacing the atoms along the eigenvector corresponding to the imaginary natural frequency, in the dimer method, it is possible to adjust the position of the saddle point. As a rule, transition states in chemical reactions correspond to saddle points of the first kind, when only one of the natural frequencies is imaginary. However, there are reports in the literature on the possible existence of saddle points of the second kind, when two natural frequencies are imaginary (Heidrich and Quapp 1986, Minyaev et al. 2004).

A good approximation for starting the search for a saddle point is, apparently, a configuration when all atoms are located in the same plane. Indeed, if we minimize the potential energy of the system under the additional condition that atoms cannot be displaced in one of the directions, then, at least for $2N$ directions in the $3N$ configuration space, where N is the number of atoms, local minima will be observed. The local minima will correspond to positive squares of natural frequencies and, therefore, real natural frequencies.

To search for an initial approximation to the saddle point of the reactions $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$, the positions of atoms in one plane were optimized. The resulting atomic configuration is shown in Fig. 5. As expected, the F atoms are located at the vertices of a regular hexagon with a U atom in the center. In the future, it is planned to use the dimer method to refine the transition state, starting with the configuration shown in Fig. 5.

Note also that the reaction constant for the decay of $UF_6 \rightarrow UF_5 + F$ was estimated experimentally in (Bostick et al. 2020).

Conclusion

With the help of fundamental quantum mechanical methods, a study of the energy barriers to the reactions $UF_6 \leftrightarrow UF_5 + F$ and $UF_6 \leftrightarrow UF_4 + F_2$ has begun. The calculated energy differences between the UF_6 molecule and the $UF_5 + F$ and $UF_4 + F_2$ complexes exceed 5 eV, which indicates strongly different rates of dissociation and recombination reactions. Moreover, the energy of the UF_6 molecule is lower than that of the complexes; therefore, the rate of recombination reactions is expected to be higher than the rate of dissociation reactions. For a more accurate determination of the energy characteristics of these reactions, an initial configuration has been prepared for the search for atomic configurations corresponding to the saddle point. For the recombination reaction $UF_4 + F_2 \rightarrow UF_6$, an energy barrier of 0.34 eV was obtained. For the recombination reaction $UF_5 + F \rightarrow UF_6$ within the framework of the relatively simple approach used, no energy barrier was found. Further research is required. Such studies should include, first of all, calculations of the energy characteristics of the indicated reactions using more accurate, in comparison with those used in this work, exchange-correlation functionals for the electronic subsystem. These calculations will require significant computing resources but can be performed using modern computing clusters.

The results of this work can be used for determining the constants of the considered chemical reactions and, therefore, for the correct parametrization of physico-chemical models describing the kinetics of the processes occurring during the decay of UF_6.

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