

## Theoretical Study of the Structure and Reactions of Uranium Fluorides

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### Abstract:

Uranium is an actinide metal mostly known for its use as fuel at nuclear power plants. Once the amount of fissile isotope ( $^{235}\text{U}$ ) in nature is not enough for a chain reaction, uranium must be enriched in order to achieve roughly 4% of the 235 isotope. Therefore, it is converted into  $\text{UF}_6$ , a gaseous compound, which can be used in isotope separation techniques (being centrifugation the most used and laser enrichment a promising one) <sup>1</sup>. Currently  $\text{UF}_6$  is made by  $\text{UF}_4(\text{s})$  fluorination, a reaction which presents sub-products. An example of related reaction is  $\text{UF}_6$  successive reduction by hydrogen, leading to lower uranium fluorides and  $\text{HF}$  <sup>2,3</sup>.

In this work, a DFT study has been performed on 3 uranium fluorides and their reactions in gas phase, covering the most stable equilibrium geometry and spin multiplicities. We used the basis sets TZP-DKH for fluorine and hydrogen and LANL2DZ/ECP for uranium. The DFT functional chosen was the hybrid one PBE0.

Initial optimization calculations lead to two isomers ( $C_{2v}$  and  $D_{2d}$ ) for  $\text{UF}_4$ ;  $C_{4v}$  symmetry for  $\text{UF}_5$  and  $O_h$ , for  $\text{UF}_6$ . After that, it has been investigated possible transition states (TS) for  $\text{UF}_6$  formation via reaction between  $\text{UF}_4$  and  $\text{F}_2$ . It has been employed a Linear Least Motion (LLM) analysis for this TS search, followed by geometry optimizations. Two TS had been obtained, been one of them the structure which connects the minima  $\text{UF}_4 + \text{F}_2$  and  $\text{UF}_6$ . This reaction mechanism has been studied in detail using Intrinsic Reaction Coordinate (IRC) calculations.

Another reaction studied was  $\text{UF}_6$  synthesis via  $\text{UF}_4$  and  $\text{HF}$ , a reaction that occurs in two steps and presents  $\text{UF}_5$  as intermediate compound. In the calculations performed, it has been found a TS which consists of a  $\text{UF}_5$  ( $D_{3h}$ ) molecule and a hydrogen atom as a ligand. IRC calculations showed a different product, the complex  $\text{UF}_5\text{H}$ , which had been observed by Eerkens <sup>4</sup>. Besides this, it has been obtained the infrared spectra of this product, which had not been theoretically or experimentally observed yet.

Vibrational frequency calculations have also been performed for the fluorides and they present good agreement with experimental data available. Finally, we have performed



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an investigation on possible isotopic shifts at the vibrational spectra of 6  $\text{UF}_6$  isotopologues, i.e., compounds whose compositions differ by an isotope. As a result, it has been found isotopic shifts for the frequencies  $\nu_3$  and  $\nu_4$ , which may be used in uranium isotopic separation, since all species presented slightly different frequencies, mainly at  $\nu_3$ . Same calculations have been performed for  $\text{UF}_5\text{H}$  and shifts were found at  $\nu_{10}$ .

**Key-words:**  $\text{UF}_6$ . DFT. potential energy surface. isotopic shift.

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