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A Relativistic Density Functional Study of the U_2F_6 Molecule[*]

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ABSTRACT

All-electronic relativistic density functional theory (DFT) method has been used to study the U_2F_6 molecule. Results from calculations predict the existence of U_2F_6 molecule, which has been found to be stable with a multiply bonded U_2 unit. The calculations also predict that D_{3d} symmetry of U_2F_6 is more stable than D_{3h}. The optimized geometries, vibrational frequencies and infrared intensities are reported for D_{3d} symmetry of U_2F_6 from Becke Three-parameter Lee-Yang-Parr (B3LYP) function with triple zeta valence plus polarization functions basis set (TZP). The bond dissociation energy (BDE) for U-U bond in the U_2F_6 was obtained using the same method. In addition, the entropies of U_2F_6 have been investigated at temperature rang from 0 to 3000 K in 10 steps using the B3LYP method.

Keywords: Molecular Structure; Vibrational Frequency; Bond Dissociation Energy

1. Introduction

The uranium compounds bring a prodigious challenge for investigation from theory and experiment. Still, uranium compounds are not easy to manage in the laboratory. It is very important that we could gain a good understanding of their chemical properties in many areas. Quantum chemistry is now mature enough to compute uranium compounds properties with good accuracy. Gagliardi and Roos have explored how two uranium atoms bind to form the U_2 molecule by multiconfigurational quantum chemistry methods [1,2]. They find that the U_2 chemical bond is more complex than any other known diatomic bond, with summation of the bonding electrons suggesting a quintuple bond. In other words, the uranium atom has the ground-state electronic configuration $(5f)^3 (6d)^1 (7s)^2$ (six valence electrons), and the U-U bond of U_2 molecule is composed of three normal two-electron bonds, four electrons in different bonding orbitals, and two non-bonded electrons leading to a quintuple bond between the two uranium atoms. In addition, its multi-radical nature may support chemical bonds to the framework of diuranium chemistry, such as in $F_3U_2F_3$.

Not much diuranium compounds have been found experimentally. So far, only the molecules OU_2O and $H_2U_2H_2$ [3] have been detected. However, no real inorganic chemistry based on the U_2 unit has been observed. This chemis-

try could occur in solution, analogous to the widely studied transition metal dimmer chemistry. In theory, $Cl_3U_2Cl_3$ molecule has been studied by Complete-Active-Space Self-Consistent-Field (CASSCF)/Complete-Active-Space Second-Order-Perturbation Theory (CASPT2) method, the results from calculation predict to be stable with a multiply bonded U_2 unit [4]. In the paper, All-electronic DFT has been used to show that diuranium compound $F_3U_2F_3$ is stable with a multiple U-U bond. The calculations also predict that D_{3d} symmetry of U_2F_6 is more stable than D_{3h} symmetry. The optimized geometries, BDE and vibrational frequencies are reported for D_{3d} symmetry of U_2F_6 from B3LYP function with TZP basis set [5]. In addition, the entropies of U_2F_6 have been investigated at temperature rang from 0 to 3000 K in 10 steps using the same method.

Methods of calculation are given in the next section, and the Result and Discussion are then presented in Section 3. The article ends with the Summary.

2. Computational Details

Our calculations were performed using the Amsterdam density functional (ADF) program. The underlying theory of the program is the Kohn-Sham approach to the DFT. Kohn-Sham DFT is an important computational method to predict chemical properties accurately and to analyze and interpret these in convenient and simple chemical terms [6]. DFT gives superior accuracy to Hartree-Fock theory and semi-empirical approaches, and it is

well suited for molecules containing heavy metal atoms.

In this method, scalar relativistic effects are introduced via the zeroth-order regular approximation (ZORA) approach to the Dirac equation [7-9], and that spin-orbit coupling is not included in the present study. It will have only a minor effect on the computed structure for singlet electronic state. Certainly, the spin-orbit coupling effect will further lower the energy but has a negligible effect on the geometry. For the close-shell systems, the spin restricted DFT scheme is used. In this paper, a triple-ζ Slater type basis set augmented with one set of polarization functions, *i.e.* the triple-zeta polarized(TZP) basis set is employed for all atoms(F and U). Moreover, the calculations were performed using GGA level to [10,11] DFT: B3LYP function in all-electronic method.

ADF has a fragment oriented approach: the polyatomic system to be computed is conceptually built up from fragments, the molecular orbitals are calculated as linear combinations of fragment orbitals, and final analysis of the bonding energy are in terms of fragment properties. The fragments may be single atoms or larger moieties. When we compute a system in terms of its constituent fragments, these fragments must have been computed before and their properties must be passed on to the current calculation. This is done by attaching fragment files, which contain the necessary information. In the paper, the BDE for U-U bond in the U_2F_6 between the F_3U and UF_3 radical fragments were obtained using the fragment approach.
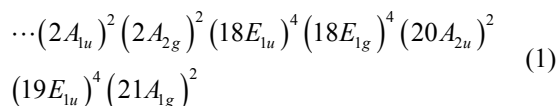
3. Results and Discussion

3.1. Structure and Stability

In a previous study of U_2 molecule [1,2], it was shown that the ground state configuration is $\left(7s\sigma_g\right)^2\left(6d\pi_u\right)^4$ $\left(6d\sigma_g\right)^1\left(6d\delta_g\right)^1\left(5f\delta_g\right)^1\left(5f\pi_u\right)^1\left(5f\phi_u\right)^1\left(5f\phi_g\right)^1$, and that the chemical bond is thus more complex than any other known diatomic bond, with summation of the bonding electrons suggesting a quintuple bond. Its multiradical nature (six electrons are available for binding) may support chemical bonds to $F_3U_2F_3$ molecule. Here we have considered the diuranium compound of U_2F_6. It can have either an eclipsed or a staggered conformation (see **Figures 1** and **2**). Preliminary calculations have indicated that the staggered conformation is lower in energy than the eclipsed form, and the calculations were done under limiting symmetry. Moreover, when the molecular structure of U_2F_6 was optimized under D_{3d} and D_{3h} symmetry respectively (unlimiting symmetry), the final optimum structure was found to be staggered. So the stability of D_{3d} symmetry is better than D_{3h}. We will thus focus our analysis on the staggered structure.

Optimization of the geometry was performed at the

B3LYP level of theory using the TZP basis set. The most stable spin-free electronic state was found to be a singlet state. The U-U bond distance is 2.425 Å, the U-F distance is 1.998 Å, and the U-U-F angle is 120.0°C In addition, we know that scalar relativistic effects are introduced via the ZORA to the Dirac equation, and that spin-orbit coupling is not included in the present study. Certainly, the spin-orbit coupling effect will further lower the energy but has a negligible effect on the geometry.

In the U_2F_6, the formal charge of uranium atom is +3. Thus, 6 of 12 valence electrons remain, and a triple bond can be formed. The electronic configuration for this molecule including all the electrons on U and F atoms is:

$$\cdots\left(2A_{1u}\right)^2\left(2A_{2g}\right)^2\left(18E_{1u}\right)^4\left(18E_{1g}\right)^4\left(20A_{2u}\right)^2$$
$$\left(19E_{1u}\right)^4\left(21A_{1g}\right)^2 \tag{1}$$

where the highest occupied molecular orbitals of each symmetry are indicated.

3.2. Bonding Energy Analysis of F_3U-UF_3

The energy decomposition between the two radical molecular fragments UF_3 in the compound F_3U-UF_3 have been analyzed with the program package ADF which is found on the methods of Morokuma [12,13] and Ziegler and Rauk [14,15]. The overall bond energy ΔE_e between the two fragments UF_3 is given by the summation of ΔE_{prep} and ΔE_{int}.
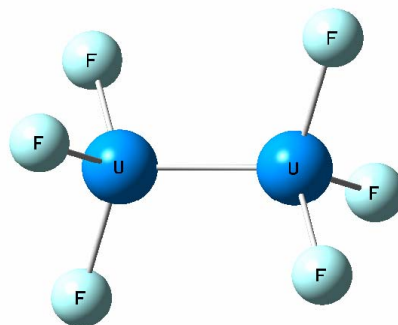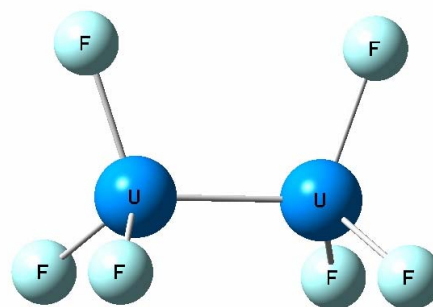

Figure 1. Staggered conformation of U_2F_6.

Figure 2. Eclipsed conformation of U_2F_6.

$$\Delta E_e = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \qquad (2)$$

The preparation energy ΔE_{prep} is the sum total of energy which is necessary associated to the structure distortion of both fragments from their equilibrium geometry to the geometry they have when the complex is formed.

$$\Delta E_{\text{prep}} = E_{\text{total}}(\text{distorted fragments})$$
$$- E_{\text{total}}(\text{fragments in the equilibrium structure}) \qquad (3)$$

ΔE_{int} in Equation (2) is the instantaneous interaction energy between the two distorted fragments in the molecule. This term can be further decomposed into three main contributions:

$$\Delta E_{\text{int}} = \Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{orb}} \qquad (4)$$

ΔE_{elstat} gives the electrostatic interaction energy between the fragments. The term ΔE_{Pauli} is the Pauli repulsion energy that arises from the closed shell repulsion between both fragments. ΔE_{Pauli} is calculated by enforcing the Kohn-Sham determinant of F_3U-UF_3, which results from superimposing two fragments UF_3, to be orthonormal through antisymmetrization and renormalization. The stabilizing orbital interaction term ΔE_{orb} is the term related to the stabilization of the system when the densities of the two fragments UF_3 are allowed to relax. It contains charge transfer as well as polarization. This method has been successfully applied to many systems [16-18].

In the paper, we try to understand the trends through detailed analyses of the bonding mechanism in the compounds F3U2F3. The results of our Kohn-Sham MO analyses are calculated by B3LYP method using TZP basis set. The calculated data shows that the values of the

repulsive term ΔE_{Pauli}, the attractive electrostatic term ΔE_{elstat}, orbital interaction term ΔE_{orb}, and preparation energy term ΔE_{prep} are 250.20 kcal/mol, −63.37 kcal/mol, −205.33 kcal/mol and 1.24 kcal/mol, respectively. From the Equations (2) and (4), the calculational bond dissociation energy of U-U bond is 17.26 kcal/mol. In this molecule, there is a net flow of electrons from the metal to substituent F3, resulting in a positive atomic charge on U according to both the VDD (0.270) and the Hirshfeld (0.722) [19,20]. In addition, we also give the breakdown of the ΔE_{orb} term into contributions of ΔE_{A_1} (−340.48 kcal/mol), ΔE_{A_2} (−2.65 kcal/mol) and ΔE_{E_1} (137.83 kcal/mol). It becomes obvious that the ΔE_{A_1} is much bigger than the other interactions.

The results demonstrate clearly that the atomic partial charges cannot be taken as a measure of the electrostatic interactions between the atoms. The two U atoms in U_2F_6 carry positive charge. Thus, we obtained an innocent conclusion that the electrostatic interactions between two U atoms are repulsive. In addition, we find that there are strong coulomb attractions between two U atoms. The orbital interaction is greater than the electrostatic attraction.

3.3. Frequencies and Thermodynamic Analysis

The fundamental vibrational frequencies of U_2F_6 are obtained from the calculations using B3LYP method with TZP basis set, are reported in **Table 1**. There are not experiments to compare with the computational values up to now. This table also gives the infrared intensities and dipole strength values. Under the D_{3d} symmetry, 12 fundamental vibrational modes of U_2F_6 are classified as the various symmetry species: $3A_{1g} + A_{1u} + 2A_{2u} + 3E_{1g} + 3E_{1u}$. Here, we also give a detailed description of the as

Table 1. Calculated vibrational frequencies and absorption intensity of U_2F_6.

Vib.no	Symmetry	Description[a]	Frequencies	IR.int.
v_1	E_{1u}	v_s UF_3	537.562	226.397
v_2	A_{1g}	v UU	241.901	0.000
v_3	E_{1g}	δ_s UF_3	119.448	0.000
v_4	A_{1u}	τ UU	16.634	0.000
v_5	E_{1g}	v_s UF_3	534.527	0.000
v_6	A_{2u}	δ_s UF_3	146.129	7.402
v_7	A_{2u}	v_{as} UF_3	578.954	365.038
v_8	A_{1g}	δ_{as} UF_3	137.038	0.000
v_9	E_{1g}	ρ UF_3	42.773	0.000
v_{10}	A_{1g}	v_{as} UF_3	602.201	0.000
v_{11}	E_{1u}	δ_{as} UF_3	123.544	6.995
v_{12}	E_{1u}	ρ UF_3	21.983	8.691

[a]The abbreviations used are: v_s, symmetric stretching; v_{as}, antisymmetric stretching; τ, torsion; δ, deformation; ρ, rocking.
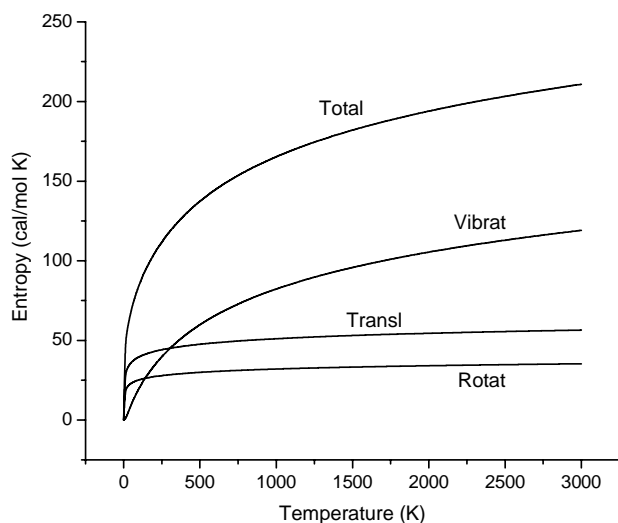
Figure 3. Entropy of U_2F_6 against temperature.

signment of all vibrational modes of U_2F_6 molecule in **Table 1**. Two A_{2u} modes (v_6 and v_7) and three E_{1u} modes (v_1, v_{11} and v_{12}) have only infrared active under D_{3d} symmetry. The five modes v_1, v_6, v_7, v_{11} and v_{12} correspond to the symmetric stretching, deformation symmetric stretching, antisymmetric stretching, deformation antisymmetric stretching and rocking modes, respectively.

After the molecular vibrational frequencies are obtained, some thermodynamic parameters of the U_2F_6 molecule can be calculated. **Figure 3** provide the values of Entropy over a wide temperature range from 0 to 3000 K in 10 steps using a B3LYP method, which obtained good vibrational frequencies. These resulting data, currently not available in the literature, are critical for modeling reaction mechanisms. The entropies are calculated following the anharmonic oscillator approximation. In the calculation, we consider the translational, rotational and vibrational contribution to the molecular entropies, and these calculated results are summarized in **Figure 3**. As noted in the table, the growth rate of vibrational entropy is the fastest with the increase of temperature among the three forms of movement.

4. Summary

The molecular properties of U_2F_6 have been investigated using B3LYP function with TZP basis set. Scalar relativistic effects are introduced via the ZORA to the Dirac equation in the present study. The results from quantum chemical calculations that predict the existence of U_2F_6 molecule, which has been found to be stable with a multiply bonded U_2 unit. The calculation also predicts that D_{3d} symmetry of U_2F_6 is more stable than D_{3h} symmetry. The predicted infrared bands of D_{3d} symmetry at 230.683, 8.289, 373.885, 7.947 and 9.992 cm^{-1} are assigned to the symmetric stretching mode v_1, deformation symmetric

stretching mode v_6, antisymmetric stretching mode v_7, deformation antisymmetric stretching mode v_{11} and rocking mode v_{12}, respectively. After the molecular vibrational frequencies are obtained, the entropies of U_2F_6 have been investigated at temperature rang from 0 to 3000 K in 10 steps using the same method. The growth rate of vibrational entropy is the fastest with the increase of temperature among the three forms of movement. In addition, the BDE for U-U bond in the U_2F_6 molecule was obtained using the B3LYP method.

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