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# A Relativistic Density Functional Study on the Uranium Hexafluoride and Plutonium Hexafluoride Monomer and Dimer Species

Laura Gagliardi,<sup>\*,†</sup> Andrew Willetts,<sup>†</sup> Chris-Kriton Skylaris,<sup>†</sup> Nicholas C. Handy,<sup>†</sup> Steven Spencer,<sup>†</sup> Andrew G. Ioannou,<sup>†</sup> and Adrian M. Simper<sup>‡</sup>

Contribution from the Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, U.K., and BNFL, Springfield, Preston, PR4 0XJ, U.K.

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**Abstract:** A study on the UF<sub>6</sub> monomer and dimer was carried out within the density functional method. The U–F distance in the UF<sub>6</sub> monomer was optimized at different levels of theory, pointwise, assuming octahedral geometry, (1) by using an all-electron basis for both U and F in a nonrelativistic calculation; (2) by using a relativistic effective core potential (RECP) on U and nonrelativistic effective core potential (ECP) on the fluorines; and (3) by using RECP on the U atom and an all-electron basis on the F atoms. Atomization energies of 23.11, 33.92, and 35.66 eV were obtained at the three levels, respectively. Relativistic effects lead to about a 50% increase in the atomization energy. For the UF<sub>6</sub> dimer, the potential energy curve, as a function of the intermolecular U–U distance, was computed at level 2, and the rotational barrier between the two monomers was determined. Similar calculations were performed on the corresponding PuF<sub>6</sub> species. Comparisons are made with experiment and other theoretical studies, where available.

## Introduction

There is a great interest in the chemistry and physics of the actinides,<sup>1,2</sup> especially the chemistry of uranium and plutonium, which play a key role in the nuclear industry. The consideration of relativistic effects is essential to the proper understanding of the electronic structure and bonding of systems containing these elements.<sup>3</sup> Uranium hexafluoride (UF<sub>6</sub>) is important for the enrichment process of uranium. It is feed stock for the production of UO<sub>2</sub> ceramic nuclear fuel made by the reaction  $\text{UF}_6 + 2\text{H}_2\text{O} + \text{H}_2 \rightleftharpoons \text{UO}_2 + 6\text{HF}$  via some intermediates that are not well understood. (In the following this reaction will be referred as the key reaction.) For this reason, UF<sub>6</sub> has become a prototype molecule for a considerable amount of experimental<sup>4–8</sup> and theoretical<sup>9–17</sup> work.

Plutonium hexafluoride (PuF<sub>6</sub>) is another important species. Even though it is not currently used in any reprocessing process, it has historically been suggested that the separation of U, Pu, and fission products could be achieved by the same method as <sup>235</sup>U and <sup>238</sup>U separation. For these reasons, it is interesting to investigate the similarities and differences between the two compounds.

UF<sub>6</sub> is described in ref 4 as an octahedral system, with a U–F bond distance of 1.999 Å. With regard to the thermal stability of the molecule, ref 2 reports an atomization energy (*A<sub>e</sub>*) of 32.55 eV. Among the theoretical contributions, two recent papers are of special interest. Malli and Styszynski<sup>16</sup> have performed ab initio all-electron Dirac–Fock, Dirac–Fock–Breit, and Hartree–Fock (HF) calculations for UF<sub>6</sub> at the experimental octahedral geometry. They have determined the spin–orbit splitting for all the ground-state levels and an atomization energy of 13.71, 23.53, and 23.27 eV at the three levels of theory, respectively.

De Jong and Nieuwpoort<sup>17</sup> have studied the electronic structure and bonding of UF<sub>6</sub> with a fully relativistic ab initio code, MOLFDIR.<sup>18</sup> The atomization energy and electron affinity have been calculated at the HF and Dirac–Hartree–Fock (DHF) levels and by introducing the Gaunt interaction as a perturbation to the DHF spinors. These authors have obtained an atomization energy of 9.0, 23.1, and 22.7 eV with the three methods, respectively, at the experimental geometry. They also performed a U–F bond length optimization at the DHF level, which gave a value of 1.994 Å.

The electronic structure of octahedral PuF<sub>6</sub> has been the

\* Corresponding author: Dr. Laura Gagliardi, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK. Tel. ++44 1223 336423. Fax ++44 1223 336362. E-mail: laura@theor.ch.cam.ac.uk.

† University of Cambridge.

‡ BNFL.

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subject of several experimental spectroscopic studies.<sup>19–23</sup> The reactivity and thermal stability of plutonium hexafluoride is described in the paper by Galkin and Tumanov,<sup>5</sup> which reports a value for  $A_e$  of 26.86 eV and a Pu–F bond length of 1.972 Å. On the theoretical side, ligand field models have been used for analyzing the electronic spectra of PuF<sub>6</sub>.<sup>20,24</sup> Koelling, Ellis, and Bartlett<sup>25</sup> performed self-consistent Dirac–Slater (DS) calculations using the discrete variational method.<sup>26</sup> Boring and Hecht<sup>24</sup> performed nonrelativistic calculations on PuF<sub>6</sub> and employed the self-consistent field scattering wave approximation with the  $X\alpha$  exchange potential. The most recent paper, and certainly the first in which ab initio quality calculations have been reported on PuF<sub>6</sub>, is the one by Wadt.<sup>27</sup> An investigation of the 5f spectrum of PuF<sub>6</sub> with the RECP method was reported. The ligand field, spin–orbit coupling, and electron repulsion were included. We were unable to find any previous computational studies of bond properties in the literature.

In this paper, a comprehensive study on the UF<sub>6</sub> monomer is presented. We determined the minimum energy as a function of the U–F distance, by assuming octahedral symmetry, and the atomic energies at the following levels of theory: (1) in an all-electron nonrelativistic calculation, ALL(UF)-nr, by using an all-electron relativistic basis set on U and a nonrelativistic basis set on F; (2) by using a relativistic effective core potential (RECP) on U and a nonrelativistic effective core potential (ECP) on F (RECP(U)-ECP(F)); and (3) by using a RECP on U and an all-electron nonrelativistic basis set on F (RECP(U)-ALL(F)).

The use of analytical first derivatives at level 1 confirmed that the optimized geometry of UF<sub>6</sub> has a octahedral symmetry. Similar calculations have been performed on PuF<sub>6</sub> in order to compare the properties of the two species.

The UF<sub>6</sub> dimer has also been investigated. This species is important since it has been suggested as one of the intermediates that occur in the production of UO<sub>2</sub> ceramic nuclear fuel from UF<sub>6</sub>. We assumed that each monomer maintained  $O_h$  symmetry. We are aware of the fact that, in the real system, the monomers might have a distorted geometry, but for this first investigation we considered the octahedral symmetry of each monomer and the  $D_{2h}$  symmetry of the dimer a reasonable approximation.

Among the possible  $D_{2h}$  structures, we chose the one with a fluorine atom on each monomer pointing against each other (see Figure 1). The potential energy curve as a function of the intermolecular U–U distance has been computed at the RECP(U)-ECP(F) level, and the rotational energy between the two monomers has been determined. Some comparative calculations have been done on the Pu dimer.

We do not claim that this is the lowest-energy structure of the dimer. Other structures could be lower in energy than the one we studied, although the purpose of the study was not to globally examine the potential energy surface, but, given two monomers in a certain orientation one with respect to the other,

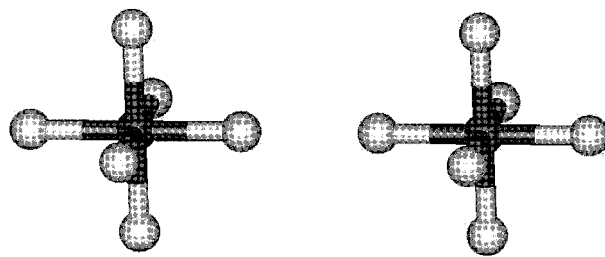


Figure 1. UF<sub>6</sub> dimer structure 1.

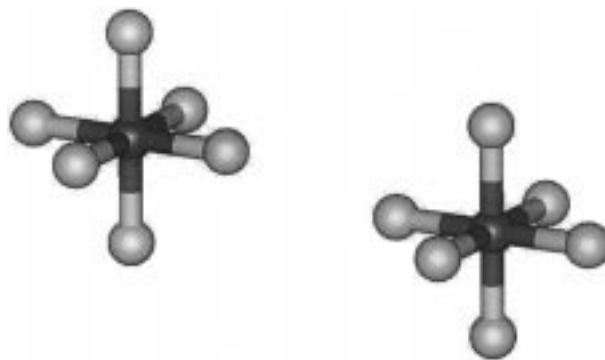


Figure 2. UF<sub>6</sub> dimer structure 2.

we wanted to investigate their interaction. In order to be sure that this did not make any difference, we determined the minimum of a different structure (also  $D_{2h}$  symmetry), in which the square bases of the two monomers do not lie on the same plane, and one side of a monomer points to a side of the other (see Figure 2). The aim of this investigation is to determine the dissociation energy of the dimer and verify if it is present during the key reaction.

In the literature, two studies on UF<sub>6</sub> dimer which use semiempirical methods have been found. In a paper by Zarkova and Pirgov,<sup>28</sup> an effective isotropic ( $n - 6$ ) potential depending on the temperature has been determined for UF<sub>6</sub> gas, and it has been compared with other UF<sub>6</sub>–UF<sub>6</sub> published potentials. In all the potentials discussed in the paper, the U–U equilibrium distance varies between 5 and 6 Å, and the potential depth varies between 0.08 and 0.03 eV approximately.

In a paper by Ursu et al.,<sup>29</sup> the value of the hexadecapole moment for UF<sub>6</sub> is calculated from three different anisotropic potentials. Values of 1.25, 0.88, and  $0.70 \times 10^{-41}$  esu cm<sup>4</sup> are evaluated according to the three potentials.

The results for the monomer species are compared with the experimental and other theoretical estimations, and for the UF<sub>6</sub> dimer some discussion of our results in light of refs 28 and 29 and of the behavior of noble gases is presented.

## Theoretical Approach

The calculations have been performed by using the newly developed MAGIC quantum chemistry code, which provides a means of performing chemically accurate calculations on systems containing many atoms, some of which are heavy. The MAGIC code is described elsewhere,<sup>30</sup> but, in its essentials, it is a code based on the use of Gaussian basis sets that allows density functional calculations within the Kohn–Sham paradigm. In most of the calculations, the LDAX exchange functional<sup>31</sup> was used. Some comparative calculations for the UF<sub>6</sub> monomer and

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**Table 1.** UF<sub>6</sub> Monomer: Some Spectroscopic Properties Computed with the Different Methods<sup>a</sup>

method	$R_{\min}/\text{\AA}$	$E_{\min}/E_h$	$E_{\text{atom}}/E_h$	$A_e/\text{eV}$
ALL(UF)-nr	1.986	-26583.7023	-26582.8530	23.11
RECP(U)-ECP(F)	2.047	-193.0948	-191.8483	33.92
RECP(U)-ECP(F) + BLYP	2.102	-197.1085	-196.1044	27.33
RECP(U)-ALL(F)	2.025	-642.6066	-641.2962	35.66
ref 16				23.27
ref 17	1.994			22.7
experiment <sup>2,4</sup>	1.999			32.55

<sup>a</sup>  $R_{\min}$  is the minimum distance,  $E_{\min}$  the minimum energy, and  $E_{\text{atom}}$  the sum of the atomic energies.  $A_e$  is the difference between  $E_{\text{atom}}$  and  $E_{\min}$ . The RECP(U)-ECP(F) calculation has been repeated with the BLYP exchange correlation term added to LDAX.

dimer were done also at the BLYP level, which includes the nonlocal exchange correction B88X and the LYP correlation functional.<sup>32,33</sup> For the radial quadrature, we followed the scheme by Mura et al.,<sup>34</sup> and for the angular quadrature the scheme by Lebedev.<sup>35</sup> The Coulomb integrals were evaluated by the Rys quadrature,<sup>36</sup> and an auxiliary basis set was used, according to the methods of Dunlap et al.<sup>37</sup> and Eichkorn et al.<sup>38</sup> In addition to the standard, nonrelativistic all-electron scheme, the relativistic effects are considered by an implementation of the RECP of Kahn, Baybutt, and Truhlar.<sup>39</sup>

The RECP employed on the U and Pu atoms and the ECP on the F atom are those reported by Hay.<sup>9,40</sup> The valence basis set used to represent the 6s, 7s, 6p, 7p, 6d, and 5f orbitals of U was the (5s4p3d4f) primitive contracted to [3s3p2d2f], while on F a (4s5p) primitive basis contracted to [2s2p] was employed, as reported in Hay's paper.<sup>9</sup> The all-electron basis used for the F atom was the Dunning DZP,<sup>41</sup> and for the U atom the uncontracted (24s19p16d11f) basis reported in ref 42 was used. The auxiliary basis set for the F atom was the one optimized by Eichkorn et al.<sup>38</sup> for a split valence plus polarization<sup>43</sup> basis. For U and Pu atoms, since specific auxiliary basis sets do not exist, we used the rubidium auxiliary basis, reported in ref 38.

### UF<sub>6</sub> and PuF<sub>6</sub> Monomer Results

The results for the UF<sub>6</sub> monomer at the different levels of theory are reported in Table 1. The minimum energy,  $E_{\min}$ , is obtained by a cubic interpolation of four energies around the minimum. The atomization energy,  $A_e$ , is the difference between  $E_{\min}$  and the sum of the atomic energies,  $E_{\text{atom}}$ . The experimental value for  $A_e$  that we report, 32.55 eV, is the one of Freeman.<sup>2</sup> An estimation of the zero-point energy correction for  $A_e$ , obtained from the force constant of the U–F bond, is done by Galkin and Tumanov,<sup>5</sup> and it is of the order of  $10^{-3}$  eV. We do not include this correction to  $A_e$ .

The minimum bond length,  $R_{\min}$ , decreases on going from the RECP(U)-ECP(F) determination to the ALL(UF)-nr. The RECP(U)-ECP(F) and RECP(U)-ALL(F) methods give a value slightly higher than the experimental one, and this is consistent with the LDAX functional, which is well known to overestimate

**Table 2.** PuF<sub>6</sub> Monomer: Some Spectroscopic Properties Computed with Different Methods<sup>a</sup>

method	$R_{\min}/\text{\AA}$	$E_{\min}/E_h$	$E_{\text{atom}}/E_h$	$A_e/\text{eV}$
RECP(Pu)-ECP(F)	2.014	-213.0325	-211.9456	29.58
RECP(Pu)-ALL(F)	1.995	-662.5276	-661.3935	30.86
experiment <sup>5</sup>	1.972			28.86

<sup>a</sup>  $R_{\min}$  is the minimum distance,  $E_{\min}$  the minimum energy, and  $E_{\text{atom}}$  the sum of the atomic energies.  $A_e$  is the difference between  $E_{\text{atom}}$  and  $E_{\min}$ .

**Table 3.** Comparison between UF<sub>6</sub> and PuF<sub>6</sub> Monomers: Difference between the U–F and Pu–F Minimum Distance and Difference between  $A_e$  for UF<sub>6</sub> and PuF<sub>6</sub> with the Different Methods

method	$\Delta R_{\min}/\text{\AA}$	$\Delta A_e/\text{eV}$
RECP(U,Pu)-ECP(F)	0.033	4.34
RECP(U,Pu)-ALL(F)	0.030	4.80
experiment <sup>2,4,5</sup>	0.027	5.69

the bond length. We repeated the RECP(U)-ECP(F) calculation with the BLYP functional, in order to estimate the functional dependence, and a minimum with a slightly longer bond distance, and an atomization energy of about 7 eV lower than that in the LDAX case was obtained. This indicates that, if LDAX overestimates the bond strength, BLYP underestimates it, and LDAX results seem to be in better agreement with the experiment than BLYP. The fact that BLYP gives a longer bond length than LDAX is not a surprise because this is a common feature of BLYP calculations.

Finally, the ALL(UF)-nr method gives a value for  $R_{\min}$  slightly lower than the experimental one. This can be attributed to the different treatment of the core electrons, and also to the absence of relativistic effects in the all–all case compared to the previous cases. The values of  $A_e$ , obtained with the relativistic methods (only LDAX), are in good agreement with experiment, especially if compared with the other theoretical estimations.<sup>16,17</sup> The inclusion of the relativistic effects with the RECP(U,Pu)-ECP(F) method leads to about a 50% increment in the predicted atomization energy, in agreement with that found in earlier theoretical studies.<sup>16,17</sup>

The results for PuF<sub>6</sub> are reported in Table 2. The minimum distance and energy were determined by a cubic interpolation as described above. The computed values for  $R_{\min}$  are slightly longer than the experimental values, as in the UF<sub>6</sub> case, and a similar trend is shown for  $A_e$ . Apart from the absolute values of the quantities determined, we are interested in the variation of these quantities on going from U to Pu, in order to estimate the relative stability of the U and Pu compounds. In Table 3, the difference between  $R_{\min}(\text{U–F})$  and  $R_{\min}(\text{Pu–F})$  is reported, together with the difference between  $A_e$  values for UF<sub>6</sub> and for PuF<sub>6</sub>. We notice that the theoretical values are in reasonable agreement with the experimental ones.

### UF<sub>6</sub> and PuF<sub>6</sub> Dimer Results

The results for the U and Pu dimers are reported in Table 4, and the potential energy curves as a function of the U–U intermolecular distance are reported in Figures 3 and 4. The potential energy curve was computed at the RECP(U)-ECP(F) level using the monomer-optimized geometry and keeping it fixed during the calculation. The two monomers were only translated, one with respect to the other, without allowing any simultaneous rotation. The minimum energy,  $E_{\text{dimer}}$ , was determined by a cubic interpolation, and  $E_{\infty}$  is twice the energy of the monomer. The curves for the U and Pu dimers have a similar shape, indicating that a very weak interaction occurs between the two monomers, as one would expect.

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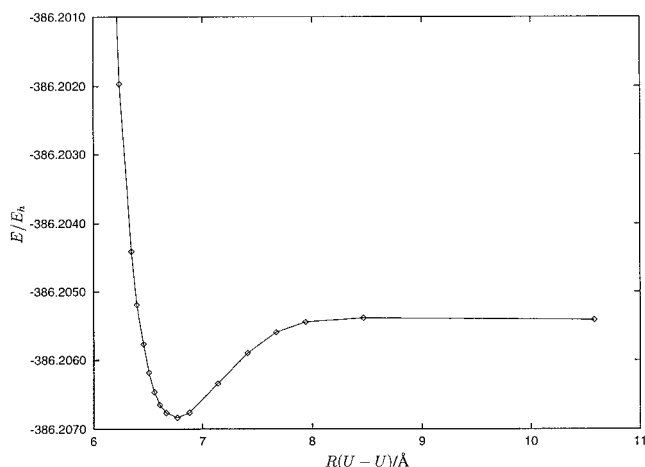
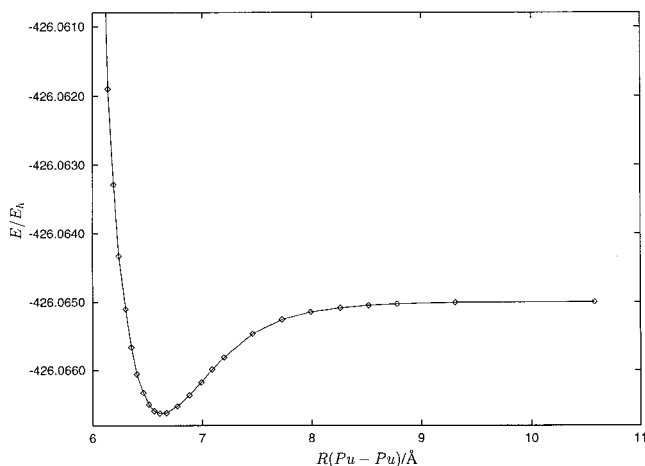
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**Table 4.** UF<sub>6</sub> and PuF<sub>6</sub> Dimers: Some Spectroscopic Properties Determined at the RECP(U,Pu)-ECP(F) Level<sup>a</sup>

functional	$R_{\text{dimer}}/\text{\AA}$	$E_{\text{dimer}}/E_{\text{h}}$	$E_{\infty}/E_{\text{h}}$	$D_e/\text{eV}$
UF <sub>6</sub>				
LDAX	6.761	-386.2068	-386.2054	0.0386
LDAX + BSSE	6.761	-386.2068	-386.2066	0.0068
BLYP	7.091	-394.2173	-394.2171	0.0068
BLYP + BSSE	7.091	-394.2173	-394.2172	0.0028
PuF <sub>6</sub>				
LDAX	6.631	-426.0666	-426.0650	0.0441

<sup>a</sup>  $R_{\text{dimer}}$  is the minimum intermonomer distance and  $E_{\text{dimer}}$  the corresponding energy.  $E_{\infty}$  is twice the energy of the monomer.  $D_e$  is the difference between  $E_{\infty}$  and  $E_{\text{dimer}}$ . In the U case, the LDAX + BSSE, the BLYP, and BLYP + BSSE results are also reported. In both U and Pu calculations, the relative position of the two monomers is the one represented in Figure 1.

**Figure 3.** UF<sub>6</sub> dimer potential energy curve as a function of the distance between the two monomers, with an orientation, one with respect to the other, as shown in Figure 1.**Figure 4.** PuF<sub>6</sub> dimer potential energy curve as a function of the distance between the two monomers, with an orientation, one with respect to the other, as shown in Figure 1.

For the UF<sub>6</sub> dimer, we performed a series of other calculations that we describe below. We did not do the same for PuF<sub>6</sub> since the behaviors of the two dimers are likely to be similar.

We estimated the basis set superposition error (BSSE) that might affect the value of the dissociation energy, according to the counterpoise method,<sup>44</sup> by determining the monomer energy within the basis set of the dimer and using twice this value as the energy of the dimer at infinite distance. The dissociation

energy (see Table 4) is reduced by 1 order of magnitude (from 0.0386 to 0.0068 eV). We repeated the calculations of some points of the curve around the minimum and at infinite distance (twice the monomer energy) with the BLYP functional in order to examine this dependence. The position of the minimum on the curve slightly changes, and the well depth is the same as in the LDAX + BSSE case. We thus estimated the BSSE to the BLYP value, and a final value of 0.0028 eV was obtained. These results indicate that the system is weakly bound, and it is unlikely to exist under the conditions at which the key reaction occurs (in particular,  $T$  above 100 °C).

We are aware of the fact that density functional theory does not reproduce the experimental potential energy curve for weakly bound systems.<sup>45</sup> For this reason, we made an estimation of the dispersion energy,  $E_{\text{disp}}$ , of the system, according to the London formula (see ref 46):

$$E_{\text{disp}} = -\frac{3}{4} \frac{E_{\text{ion}} \alpha^2}{R^6} \quad (1)$$

For the ionization energy,  $E_{\text{ion}}$ , we used the highest occupied molecular orbital energy obtained from our calculation,  $0.12E_{\text{h}}$ , and for the UF<sub>6</sub> polarizability,  $\alpha$ , we used the experimental value, 84 au (1 au =  $4\pi\epsilon_0 a_0^3$ ).<sup>47</sup> (From our DFT calculation we obtain a polarizability of 52 au). With this simple formula, at the equilibrium distance,  $R = 6.761 \text{ \AA}$ , we calculate

$$E_{\text{disp}} = -0.00015E_{\text{h}} = -0.0041 \text{ eV} \quad (2)$$

Therefore, at this geometry, the dispersion energy is of the same order of magnitude as the dissociation energy obtained from the density functional calculation in which BLYP and BSSE are included.

This discussion might be qualified by some considerations regarding the noble gases, which resemble the UF<sub>6</sub> dimer to some extent. From the Pérez-Jordá and Becke paper,<sup>48</sup> it is clear that LDAX overestimates the well depth in systems like He<sub>2</sub>, Ne<sub>2</sub>, and Ar<sub>2</sub>. When a nonlocal correction to exchange is introduced, the potential energy curves for these systems become repulsive. The inclusion of correlation does not change the shape of the curves because the errors arising from the other terms in the Hamiltonian are greater than the correlation effects. In light of these considerations, we computed the potential energy curve for Ne<sub>2</sub> including only exchange effects (LDAX + B88X) and exchange and correlation effects (LDAX + BLYP), and in both cases the curves were repulsive. We then subtracted the two curves point by point and obtained a curve, representing the correlation effects only, which was fitted to  $cR^{-n}$ . The best value of  $n$  was 6. This indicates, to our surprise, that some of the dispersion is described by the correlation term, but it does not come out in an LDAX + BLYP calculation because other terms are dominant. If we now move back to the object of this study, the UF<sub>6</sub> dimer, we can say that the LDAX result, 0.0386 eV, is an overestimation of the well depth, but the fact that BLYP also gives some bond indicates that UF<sub>6</sub> might be slightly bound. However, this does not affect the general conclusion that the dimer is unstable during the key reaction.

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The minimum for the UF<sub>6</sub> dimer was also computed for a different relative orientation of the two monomers (see Figure 2), and the equilibrium distance and dissociation energy did not change to within our quoted precision.

By comparing our results with those reported by Zarkova and Pirgov,<sup>28</sup> we notice that our values for the dissociation energy are in qualitative agreement with those obtained by semiempirical methods; however, we obtained a longer U—U bond.

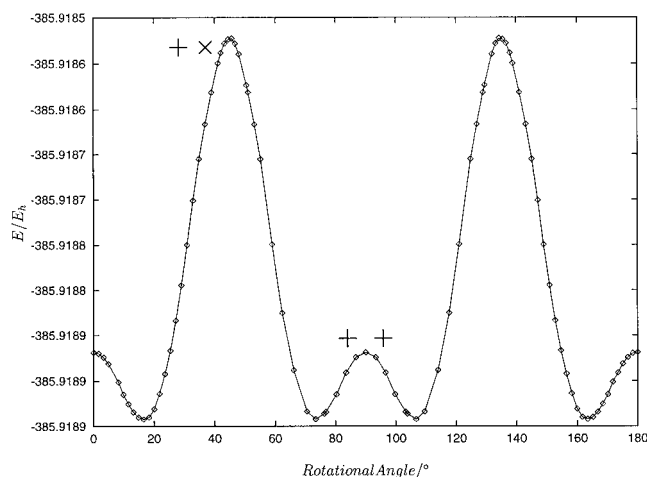
The dissociation energy of the dimer might also be compared to the cohesive energy of the solid. From the vaporization data for UF<sub>6</sub> solid,<sup>1</sup> and by using the Clausius Clapeyron equation, one can work out a value for the enthalpy of formation of the UF<sub>6</sub> crystal of about 22 kJ mol<sup>-1</sup>. If we consider the dissociation energy of the dimer from our calculation, multiply it by the coordination number of the crystal, 4, and divide by 2, we get in the two cases the values for the dissociation energy:

$$0.0386 \text{ eV} \times 2 = 0.0772 \text{ eV} \approx 8 \text{ kJ mol}^{-1} \quad (\text{LDAX}) \quad (3)$$

$$0.0028 \text{ eV} \times 2 = 0.0056 \text{ eV} \approx 0.6 \text{ kJ mol}^{-1} \quad (\text{BLYP} + \text{BSSE}) \quad (4)$$

We note that this is again small for the second case, but a comparison of the dissociation energy of the dimer with the crystal binding energy is very questionable because many other effects should be taken into consideration.

We also examined the rotational effects in the UF<sub>6</sub> dimer at the RECP(U)-ECP(F) level. We used the optimized dimer distance and fixed the intramolecular U—F distances to 3.50 *a*<sub>0</sub>, starting from the structure of Figure 1. One monomer was kept fixed while the other was rotated. The U—U distance remained unchanged during the rotation. The energy curve as a function of the rotational angle is reported in Figure 5. The curve presents a barrier with a height of about 0.25 kcal mol<sup>-1</sup>. The barrier is symmetric, since after a 90° rotation the geometry reproduces itself. A local maximum occurs at 0 (90)° and a global maximum at 45°. This can be explained in terms of simple electrostatic interactions between the two monomers. At 0 (90)°, one F atom of the first monomer points toward one F atom of the second monomer, while at 45°, two F atoms of the first monomer point toward one F atom of the second monomer, giving a stronger repulsive interaction. In other words, we can say that at 0 (90)° there is only one interaction between two F atoms, one on each monomer, while at 45° two F atoms of the second monomer interact, each of them with two F atoms of the first monomer. In Figure 5, a planar projection of the monomer orientation, one with respect to the other, is reported near the global and local maxima. A minimum is present at



**Figure 5.** Rotational barrier for the UF<sub>6</sub> dimer. Near the maxima at 45 and 90°, the planar projection of the two monomers is reported.

about 20 (80)°, between the two maxima, slightly closer to the local maximum, which is reasonable since the local maximum is certainly a less repulsive structure than the global one.

## Conclusions

A relativistic study of the UF<sub>6</sub> monomer and dimer, with some comparisons with the PuF<sub>6</sub> corresponding species, has been presented. The atomization energy of the UF<sub>6</sub> and PuF<sub>6</sub> monomers has been determined using the RECP(U)-ECP(F) method, and values close to the experimental ones have been obtained. A comparison with nonrelativistic calculations shows that relativistic effects are very significant in bonding and lead to about a 50% increment in the predicted atomization energy. In the UF<sub>6</sub> dimer, a weak interaction between the two monomers has been determined at LDAX and BLYP levels, and a rotational barrier has been observed. From these results, the dimer is not sufficiently stable to be present during the key reaction.

This is the first system extensively studied with the new code MAGIC, which will be used from now on to investigate other systems of interest, for which the relativistic effects must be taken into consideration.

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