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Density functional investigations of the properties and thermochemistry of UF_n and UCl_n ($n=1,...,6$)

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The structural properties and thermochemistry of the UF_n and UCl_n ($n=1,...,6$) molecules have been investigated using hybrid density functional theory and a small-core (60 electrons) relativistic effective core potential for the uranium atom. For the first time Bond dissociation energies for this whole series are computed and shown to be in good agreement with experiment. The geometry and electronic structure of each molecule was characterized. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1811607]

I. INTRODUCTION

While uranium hexafluoride UF_6 is one of the most extensively studied actinide molecules,[1] both experimentally and theoretically, very few computational studies have been reported on the rest of the fluoride series UF_n or on the uranium chlorides UCl_n.

From the experimental side full thermodynamics data is available for both series,[2,3] except for UCl_6. Experimental thermochemical information on both series is also available.[4–7] The structure of a few of these molecules has been studied experimentally via electron diffraction[8–10] (UF_6,UCl_4), x-ray diffraction[11,12] (UCl_6), and estimated from spectroscopic data[3] (UCl_3). Some other structural properties have been estimated from spectroscopic data[3] such as the product of the three principal moments of inertia and vibrational frequencies of the UCl_n molecules for $n=1,...,5$.

Theoretical studies of the full series UF_n and UCl_n are not available. For the UF_n series, only studies on UF_6, UF_4, and UF_3 have been carried out. The UF_6 molecule, even though it is the largest and has the most electrons, is the easiest one to study with *ab initio* calculations because of its closed shell nature. This molecule has been studied by many authors with a variety of computational techniques[1,13–18] so that it has become a testing benchmark for computational methods aimed at actinide molecules. A study of the electronic structure of UF_4 has been reported using Hartree-Fock-Slater type calculations[19] with scalar relativistic pseudopotentials. Finally, the structural and vibrational frequencies of the UF_3 molecule were studied in detail by Joubert and Maldivi[20] using a number of computational techniques, including the MP2 perturbative approach and DFT techniques. The theoretical studies of UCl_n are much less abundant than those for the UF_n series. The photoelectron spectra of UCl_6 has been reported using $X\alpha$ calculations.[21] The other molecule of this series that has been analyzed theoretically, UCl_3, was studied via Hartree–Fock–Slater calculations.[19]

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Because the previous studies of the molecules composing the UF_n and UCl_n series have been isolated studies of one of the molecules at a time, and only a few of the molecules have been studied, this paper presents a systematic *ab initio* study of both series for $n=1,...,6$. Based on previous experience in comparing the bond dissociation energy of UF_6 with different DFT functionals,[18] the hybrid DFT functionals B3LYP and PBE0 were chosen in combination with a 60-electron relativistic effective core potential for uranium. Spin-orbit interactions, which accounted for less than 4 kcal/mol in the bond dissociation energy of UF_6, were ignored in the present study and will be addressed in future work.

This approach yields reasonably good agreement between the computed quantities and the available experimental data, such as thermodynamics, bond energies, and structural properties. This gives confidence in our predictions of the electronic ground state, vibrational frequencies, and other structural properties.

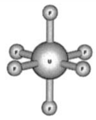
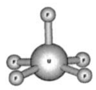
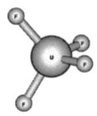
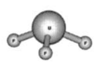
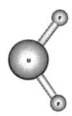
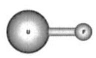
II. COMPUTATIONAL METHODS

The electronic ground state of all the molecules were calculated using two forms of hybrid density functionals: PBE0 (Ref. 22) and B3LYP (Refs. 23 and 24) containing 25% and 20% Hartree–Fock exchange, respectively.

In all the calculations the basis set used for fluorine and chlorine atoms was a double ζ basis with polarization and diffuse functions, 6-31+G*. For the uranium atom the Stuttgart basis set[25] $(25s16p15d7f)/[7s6p5d3f]$ was used in combination with the 60-electron relativistic effective core potential (RECP).[26] This small-core RECP replaces the 60 electrons in the inner shells 1 through 4, leaving the explicit treatment of the $n=5$ shell ($5s$, $5p$, $5d$, and $5f$), and also the $6s$, $6d$, $6p$, and $7s$ valence electrons.

The two hybrid DFT functionals used in this work, together with this RECP were shown to be the best at reproducing molecular properties of UF_6 and UF_5 as well as the bond dissociation energy of UF_6 ($UF_6 \rightarrow UF_5 + F$).[18] For this reason other functionals will not be reported in this work. The 60-electron RECP constitutes a balance between the relativistic corrections introduced via the RECP and the explicit treatment of the valence electrons. As was previously

TABLE I. Geometry of the UF_n molecules.

Molecule	Geometry	Symmetry	Bonds (B3LYP)	Bonds (PBE0)	Expt.
UF_6		O_h	U–F = 2.013 Å	U–F = 1.994 Å	U–F = 1.999(3) Å[a] U–F = 1.996(8) Å[b]
UF_5		C_{4v}	$U–F_{ax}$ = 2.030 Å $U–F_{eq}$ = 2.032 Å $\angle F_{ax}–U–F_{eq}$ = 98.3°	$U–F_{ax}$ = 2.014 Å $U–F_{eq}$ = 2.015 Å $\angle F_{ax}–U–F_{eq}$ = 98.3°	C_{4v} symm.[c]
UF_4		T_d	U–F = 2.069 Å	U–F = 2.053 Å	2.059[d]
UF_3		C_{3v}	U–F = 2.085 Å ∠F–U–F = 107°	U–F = 2.069 Å ∠F–U–F = 105°	
UF_2		C_{2v}	U–F = 2.074 Å ∠F–U–F = 107.9°	U–F = 2.055 Å ∠F–U–F = 106.8°	
UF		$C_{\infty v}$	U–F = 2.041 Å	U–F = 2.024 Å	

[a]Reference 8.
[b]Reference 28.
[c]Reference 29.
[d]Reference 30.

shown, in order to obtain good bond dissociation energies the $5s$, $5p$, and $5d$ electrons must be treated explicitly, even though they constitute closed shells.[18]

The geometry of the molecules was optimized with and without symmetry constraints and the lowest energy obtained is the one reported. In all cases the symmetry group of the optimized molecule was identified.

All the calculations were performed using GAUSSIAN 03 (Ref. 27) suite of codes for quantum chemistry.

III. RESULTS

A. Structure of UF_n and UCl_n

Tables I and II summarize the geometry of the optimized UF_n and UCl_n molecules, respectively. The scarce experimental data available on the structure of these molecules has been included in the last column of the tables. Tabulated are the structure parameters obtained with two different hybrid DFT functionals, B3LYP and PBE0, which were shown to work remarkably well for UF_6 and UF_5 in a previous publication.[18] Notice that the bond length calculated with B3LYP is systematically longer than the ones predicted by PBE0 by 0.8%.

1. UF_6, UF_5, UCl_6, and UCl_5

The structure of the UF_6 and UF_5 molecules and the infrared active modes were shown to be in good agreement with experiments.[18] Those results are included here for the sake of completeness.

TABLE II. Geometry of the UCl_n molecules.

Molecule	Symmetry	Bonds (B3LYP)	Bonds (PBE0)	Expt.
UCl_6	O_h	U–Cl = 2.472 Å	U–Cl = 2.441 Å	U–Cl = 2.42 Å[a]
UCl_5	C_{4v}	$U–Cl_{ax}$ = 2.467 Å	$U–Cl_{ax}$ = 2.439 Å	
		$U–Cl_{eq}$ = 2.492 Å	$U–Cl_{eq}$ = 2.464 Å	
		$\angle F_{ax}–U–Cl_{eq}$ = 101.2°	$\angle F_{ax}–U–Cl_{eq}$ = 98.1°	
UCl_4	T_d	U–Cl = 2.513 Å	U–Cl = 2.494 Å	U–Cl = 2.51 Å[b]
UCl_3	C_{3v}	U–Cl = 2.567 Å	U–Cl = 2.553 Å	U–Cl = 2.549 ± 0.008 Å[c]
		∠Cl–U–Cl = 111.2°	∠Cl–U–Cl = 108.2°	∠Cl–U–Cl = (95 ± 3)°[c]
UCl_2	C_{2v}	U–Cl = 2.566 Å	U–Cl = 2.534 Å	
		∠Cl–U–Cl = 117.0°	∠Cl–U–Cl = 118.1°	
UCl	$C_{\infty v}$	U–Cl = 2.523 Å	U–Cl = 2.496 Å	

[a]Bond length in crystal environment (Refs. 11 and 12).
[b]Reference 10. Measurement at 900 K.
[c]Reference 31.

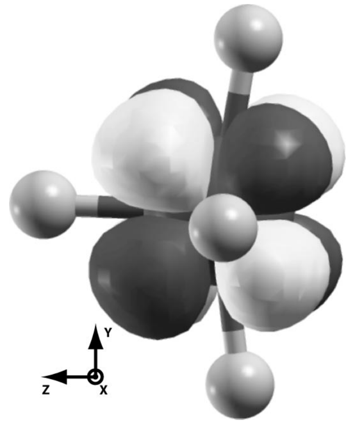


FIG. 1. Natural orbital of the only unpaired electron of UF_5. The unpaired electron occupies an f_{xyz} orbital with $^2B_2$ symmetry.

The electronic state of UF_6 is a formally f^0 singlet state. The optimal geometry of UF_6 has O_h symmetry and the calculated U–F bond length agrees with the experimental value to less than 1%. The main stretch band $\nu_3(t_{1u})$ was predicted at 631 cm^{-1} with PBE0 and 613 cm^{-1} with B3LYP, in good agreement with the experimental value 626 cm^{-1}.[32] The main bend band $\nu_4(t_{1u})$ was predicted to be at 186 cm^{-1} with both functionals in exact agreement with the experimental measurement.[32] The infrared intensities were also found in reasonable agreement with experimental values. The IR intensity of the main stretch mode, ν_3 was predicted at 685 km/mole by B3LYP and 735 km/mole by PBE0, in close agreement with the experimental value 750 km/mole.[29] The intensity for the main bend mode ν_4 was predicted at 41 km/mole by B3LYP and 40 km/mole by PBE0, in good agreement with the experimental value 37.5 km/mole.[29]

The electronic structure of UF_5, calculated with both hybrid functionals, is a doublet described as a $^2B_2$ state, with the unpaired electron in a $5f_{xyz}$ orbital (see Fig. 1). The optimal geometry of UF_5 has C_{4v} symmetry as expected from the IR spectrum.[29] The U–F_{ax} bond length to the axial fluorine was obtained to be 2.014 Å with PBE0 and 2.030 Å with B3LYP. The U–F_{eq} bond length to the equatorial fluorine atoms is slightly longer than the axial bond: 2.015 Å for PBE0 and 2.032 Å for B3LYP. As was shown in Ref. 18, Hartree-Fock underestimates the bond length while DFT-GGA overestimates them. The larger amount of Hartree-Fock exchange in PBE0 causes this functional to yield slightly shorter bonds than B3LYP, as shown in UF_6 and UF_5. The angle between the axial bond and the equatorial bonds is 98.26° in the optimal PBE0 calculation and 98.23° at the optimal B3LYP configuration. The IR frequencies of UF_5 ν_1, ν_2, and ν_7 were predicted in good agreement with the experimental values 646 cm^{-1}, 561 cm^{-1}, and 584 cm^{-1}. The PBE0 functional predicts 660 cm^{-1}, 581 cm^{-1}, and 600 cm^{-1}, respectively, while B3LYP predicts 643 cm^{-1}, 569 cm^{-1}, and 586 cm^{-1}. The frequencies predicted by B3LYP are slightly smaller than those predicted by PBE0 because the bond length is slightly longer.

Far less experimental data are available on the UCl_n molecules. In the crystalline state, the U–Cl bond length of UCl_6 has been measured via x-ray diffraction to be 2.42 Å.[11,12] The calculations in gas phase give an optimal structure with O_h symmetry and a bond length of 2.47 Å with B3LYP and 2.44 Å with PBE0, which is between 1% and 2% longer than the experimentally known bond length. That is the same magnitude of error as in UF_6 and it might be due to intrinsic problems in the computational methodology and to the fact that the experimental bond length was not measured in gas phase but in the solid. The structure of UCl_5 parallels that of UF_5. At its optimal geometry UCl_5 has C_{4v} symmetry while the D_{3h} structure was found to be only 1.36 kcal/mol higher in energy.

Based on spectroscopic data, Gurvich and Dorofeeva estimated the frequencies of vibration of UCl_5 as well as the product of the its three principal moments of inertia.[3] The experimentally estimated product $I_aI_bI_c$ is 180×10^{-113} $g^3\,cm^6$ while the predicted value, based on the geometries calculated via hybrid DFT, is 166×10^{-113} $g^3\,cm^6$ for the optimal geometry predicted by B3LYP and 155×10^{-113} $g^3\,cm^6$ for the geometry obtained with PBE0. The slight disagreement between the molecular constants estimated by Gurvich and Dorofeeva and the ones presented here are not totally understood because the details of their calculation have not been published. We suppose that the difference comes from their estimation of the low lying electronic states and assumptions about the geometry of the molecule.

2. UF_4 and UCl_4

The structure of UF_4 has been the subject of some debate in the literature.[5,19,30,33] Boerrigter *et al.*[19] performed Hartree-Fock-Slater calculations on UF_4 optimizing the geometry of the molecule constrained to a tetrahedral symmetry T_d group. They found an electronic ground state t_2^2, which is triply degenerate and suggested that this degeneracy would induce a molecular deformation due to the Jahn-Teller effect, not included in their calculations. Experimental evidence that the UF_4 molecule was deformed away from the tetrahedral geometry was reported by Hildenbrand and Lau based on comparisons of the entropy measured for crystalline UF_4 with the entropy calculated based on force constants extracted from calculations.[5] More recent infrared spectroscopy, however, showed that the vibrational frequencies of UF_4 were considerably lower than the estimated ones[30,33] and this has weakened the evidence for a structure distorted away from the T_d symmetry group.

The calculations using hybrid DFT presented here found that, within the accuracy of the methodology, the structure of UF_4 has tetrahedral symmetry with the geometrical parameters shown in Table I. The electronic state was found to be a triplet state, $^3T_1:(t_2)^2$, with the unpaired electrons in the $5f_{x^3}$ and $5f_{y^3}$ orbitals (see Fig. 2). The UF_4 singlet $5f^2$ state $1/\sqrt{2}(|5f_{x^3}\alpha,5f_{y^3}\beta\rangle-|5f_{y^3}\alpha,5f_{x^3}\beta\rangle)$ was found to lie 17.52 kcal/mol higher in energy than the triplet state. This energy gap was obtained by doubling the energy gap between the ground state triplet state $(|5f_{x^3}\alpha,5f_{y^3}\alpha\rangle)$ and the the singlet broken symmetry spin state $(|5f_{x^3}\alpha,5f_{y^3}\beta\rangle)$. This approach was justified by obtaining almost no spin mixing in the bro-

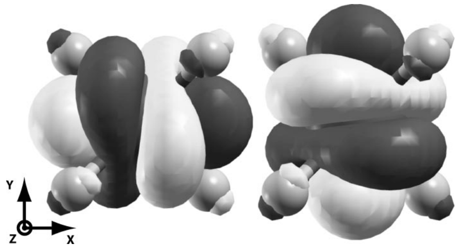


FIG. 2. Natural orbitals of the unpaired electrons of UF_4. The unpaired electrons occupy an f_{x^3} (left) and a f_{y^3} (right) orbitals.

TABLE III. Infrared active vibrational frequencies for UF_4 calculated with the B3LYP and PBE0 hybrid DFT functionals and experimental values for asymmetric stretching and bending modes. All the frequencies are given in cm^{-1}.

Mode	T_d(B3LYP)	T_d(PBE0)	D_{2d}	Expt.[a]
ν_3	111	98	97	
	114	120	116	114
ν_4	540	555	544	539
	549	557	597	

[a]Reference 30.

ken symmetry spin state; the eigenvalue of S^2 was 1.0009. The singlet $|5f_{x^3}\alpha,5f_{x^3}\beta\rangle$ state was found 36.5 kcal/mol higher than the triplet state.

When allowed to optimize the geometry in a lower symmetry group, a D_{2d} state was identified with an energy only 0.5 kcal/mol lower than the T_d structure, the same U–F bond length, and F–U–F angles of 106° and 116°. The difference in vibrational frequencies between the T_d and the D_{2d} states, is not significant. The asymmetric bending mode was calculated at 114.1 cm^{-1} in the T_d geometry, in good agreement with the experimental value of 114 cm^{-1},[30] while the infrared bending mode in the D_{2d} structure is 115.8 cm^{-1}. The asymmetric stretch mode was calculated to be 540 cm^{-1} in the T_d geometry, in good agreement with the experimental value of 539,[30] while the infrared stretching mode in the D_{2d} structure was calculated to be 544 cm^{-1}. The vibrational frequencies calculated with PBE0 give a softer-than-experimental asymmetric bend, 98 cm^{-1}, and a harder-than-experiment asymmetric stretch, 556 cm^{-1}. All the infrared active vibrational frequencies for UF_4 in both geometries are listed in Table III. These differences are sufficiently small that it is not possible to make a definitive conclusion about the geometry of the molecule.

Experimental measurements of the structure of UCl_4 have been carried out by Haaland and co-workers[10] via electron diffraction in gas molecules at 900 K. The experiments were found to be consistent with a tetrahedrally symmetric molecule T_d with a U–Cl bond length of 2.51 Å and infrared active modes at 71.7 cm^{-1} (asymmetric bend) and 337.4 cm^{-1} (asymmetric stretch). The hybrid DFT computed structure for UCl_4 is in close agreement with the experiments. Like the structure of UF_4, the optimal geometry of UCl_4 was found to have tetrahedral symmetry with a U–Cl bond length of 2.513 Å (B3LYP) and 2.494 Å (PBE0). The electronic state of UCl_4, like that of UF_4, is a triplet state, $^3T_1:(t_2)^2$, while the singlet f^2 state ($|5f_{x^3}\alpha,5f_{x^3}\beta\rangle$) was found to be 38.6 kcal/mol higher in energy. The two unpaired electrons were again found to occupy the $5f_{x^3}$ and $5f_{y^3}$ orbitals. The ground state is a triply degenerate state since the empty orbital $5f_{z^3}$, could be exchanged with any of the two occupied ones. Because we are doing unrestricted open shell calculations, the symmetry between $5f_{x^3}$, $5f_{y^3}$, and $5f_{z^3}$ is broken. This also breaks the symmetry among the vibrational modes, giving for the infrared active vibrations one doubly degenerate asymmetric bend frequency plus one extra frequency slightly shifted from the degenerate mode, and the same pattern for the asymmetric stretch. The frequencies for the IR active modes as well as the intensities are shown in Table IV.

The product of the three principal moments of inertia of UCl_4 has been estimated by Gurvich and Dorofeeva[3] based on spectroscopic data and assuming a C_{2v} structure. Their estimated value is 100×10^{-113} g^3 cm^6 which compares well with the predicted values by B3LYP, 93×10^{-113} g^3 cm^6, and PBE0, 89×10^{-113} g^3 cm^6 in a C_{4v} geometry. The small difference might be due to the difference in molecular symmetry assumed by Gurvich and Dorofeeva.

3. UF_3 and UCl_3

Although complete thermodynamic data has been measured for UF_3, as far as the authors could find the structure of this molecule has not been measured. Joubert and Maldivi[20] have published a theoretical study of uranium(III) molecules with a number of computational techniques including B3LYP and PBE0 hybrid DFT. They employed a 78-electron RECP. Their results are similar to the structure presented here computed with the small-core RECP (60 electrons). The UF_3 molecule was found to have C_{3v} symmetry, with U–F bond length of 2.085 Å and 2.069 Å, for B3LYP and PBE0, respectively. The F–U–F angle was calculated to be 107° (B3LYP) and 105° (PBE0). The planar molecule, with D_{3h} symmetry, lies 5 kcal/mol higher in energy than the C_{3v} structure, which has the uranium atom outside the plane determined by the fluorine atoms. The electronic configura-

TABLE IV. Infrared active vibrational frequencies and intensities, in parentheses, for UCl_4 calculated with the B3LYP and PBE0 hybrid DFT functionals. The degeneracy of each frequency is also tabulated and it is already taken into account in the intensities. All the frequencies are given in cm^{-1} and the intensities in km/mole.

Mode	Degen.	B3LYP		PBE0		Expt.[a]
ν_3	2	60	(12)	59	(11)	71.7
	1	62	(6)	60	(6)	
ν_4	1	338	(107)	346	(118)	337.4
	2	340	(225)	344	(225)	

[a]Reference 10.

TABLE V. Infrared active vibrational frequencies and intensities for UF_3 calculated with the B3LYP and PBE0 hybrid DFT functionals. All the frequencies are given in cm^{-1} and the intensities in km/mole.

Mode	B3LYP	I	PBE0	I
ν_2	125	7	101	15
ν_4	144	5	103	21
ν	159	23	106	12
ν_3	528	196	524	262
ν_1	534	197	530	241
ν	543	79	553	89

TABLE VI. Infrared active vibrational frequencies and intensities for UCl_3 calculated with the B3LYP and PBE0 hybrid DFT functionals. All the frequencies are given in cm^{-1} and the intensities in km/mole.

Mode	B3LYP	PBE0	Expt.[a]	Expt.[b]
ν_1	314	329	325 ± 30	300 ± 30
ν_2	47	51	55 ± 10	90 ± 10
ν_3	312(2)	317(2)	315 ± 30	310 ± 30
ν_4	69(2)	71(2)	90 ± 10	90 ± 10

[a]Reference 31.
[b]Reference 3.

tion of UF_3 is a $5f^3$ state. A Mulliken population analysis of the natural orbitals of UF_3 shows that two of the three unpaired electrons have more than 95% uranium f character and the third one is a mixture of 75% uranium f and 25% uranium s character. The infrared active vibrational frequencies of UF_3 are shown in Table V.

The structure of UCl_3 has been measured by Bazhanov and co-workers[31] via electron diffraction at 800 K. Under these conditions it was found that the molecule has C_{3v} symmetry with U–Cl bonds of $r_a = 2.549\pm0.008$ Å and Cl–U–Cl angle of $95\pm3°$. Calculations of the structure of UCl_3 with a variety of computational methods have been published by Joubert and Maldivi,[20] and the calculations presented here agree with their results for small core RECP and hybrid DFT functionals. The lowest energy configuration of UCl_3 was found to have C_{3v} symmetry while the D_{3h} structure was found to lie 4 kcal/mol higher in energy. The U–Cl bond distance at the optimal geometry is 2.567 Å (B3LYP) and 2.553 Å (PBE0). While B3LYP predicts a bond distance slightly longer than the experimental one, the calculation with PBE0 is within the error bar of the experiment. The calculated Cl–U–Cl angle [111° (B3LYP) and 108° (PBE0)] is larger than the experimental one indicating a closer-to-planar structure. This discrepancy could be due to the fact that the electron diffraction measurements were made at high temperatures; the floppy nature of the metal halides and the anharmonicity of the vibrations could render the thermal-average geometry quite different form the equilibrium geometry.[34] As for UF_3, the electronic configuration of UCl_3 is $5f^3$ with the three unpaired electrons occupying uranium $5f$ orbitals. A Mulliken population analysis of the natural orbitals of the unpaired electrons show two of the orbitals having over 97% f character and the third one having 90% f mixed with 8% s character.

Two sets of experimental values for the vibrational modes of UCl_3 are available. Bazhanov and co-workers[31] extracted vibrational frequencies from the vibrational amplitudes measured via electron diffraction. From the same data, a two-force-constant force field was determined yielding f_r and f_θ. The second set of frequencies was estimated by Gurvich and Dorofeeva from spectroscopic constants.[3] Our calculated values are in good agreement with the experimental ones, and are shown in Table VI.

The experimental values for the entropy of UF_3 and UCl_3 have been reported as a function of temperature.[3] At 298 K the experimental entropy of UF_3 is 83.011 cal/(K mol) and the entropy of UCl_3 is 90.874 cal/(K mol). The predicted values, via hybrid DFT, for UF_3 are 82.442 cal/(K mol), using B3LYP, and 84.220 cal/(K mol) using PBE0. For UCl_3 the predicted entropy is 90.972 cal/(K mol) using B3LYP and 90.511 with PBE0, both in very good agreement with the experimental measurement. The estimated product of the three principal moments of inertia for UCl_3, based on spectroscopic data, has been reported to be 37×10^{-113} g^3 cm^6,[3] which compares well with the calculated values 36×10^{-113} g^3 cm^6 with B3LYP and 35×10^{-113} g^3 cm^6 with PBE0. The calculated product of principal moments of inertia for UF_3 is 1.7×10^{-113} g^3 cm^6 calculated with B3LYP and 1.8×10^{-113} g^3 cm^6 with PBE0. The agreement between the calculated entropy and moments of inertia with the experimental values and with those estimated based on experimental data indicates a good overall prediction of the structure and vibrational frequencies of UF_3 and UCl_3.

4. UF_2 and UCl_2

The optimal geometry of UF_2, as well as that of UCl_2, is predicted to have C_{2v} symmetry. The linear configurations were found to be higher in energy by 5.8 kcal/mol in UF_2 and 2.4 kcal/mol in UCl_2. The calculated bond length and bond angles are shown in Tables I and II. The electronic state of UF_2 is a quintet state, with the four unpaired electrons in the uranium $5f^37s^1$ configuration. The triplet state $(5f^27s^2)$ was found to be 5.5 kcal/mol higher than the quintet. A Mulliken population analysis of the natural orbitals of UF_2 shows that three of the unpaired electrons have 92%, 96%, and 94% uranium $5f$ character while the fourth unpaired electron has 97% uranium $7s$ character. The electronic state of UCl_2 is also a quintet (four unpaired electrons) with the triplet state 6 kcal/mol higher. A Mulliken population analysis for the natural orbitals of the four unpaired electrons shows them occupying uranium orbitals. Three of the unpaired electrons have 93%, 98%, and 98% populations in the uranium $5f$ orbitals and the fourth electron is mostly uranium $7s$ in character (86%), with a 20% uranium $6d$ character and -10% fluorine s.

The vibrational frequencies for UF_2 and UCl_2 are shown in Table VII. The only experimental quantities available for UF_2 and UCl_2 are the specify heat C_p and the entropy S^o as functions of the temperature.[3] Good agreement between the computed and the experimental values were obtained for the total entropy of UF_2 and UCl_2. Since the entropy depends on the moments of inertia and the vibrational frequencies of the molecule, this quantity gives an idea of the over all quality of the predictions. At 298 K the measured entropy of UF_2 and

TABLE VII. Vibrational frequencies for UF_2 and UCl_2 calculated with the B3LYP and PBE0 hybrid DFT functionals. All the frequencies are given in cm^{-1} and the intensities in km/mole.

	UF_2		UCl_2		
Mode	B3LYP	PBE0	B3LYP	PBE0	Exp.[d]
ν_1[a]	554	567	306	324	310
ν_2[b]	96	101	45	46	75
ν_3[c]	529	541	300	305	295

[a]Symmetric stretch mode.
[b]Asymmetric stretch mode.
[c]Bend mode.
[d]Reference 3.

UCl_2 are 75.453 cal/(K mol) and 81.047 cal/(K mol),[3] respectively. The entropy calculated from the predicted structure and frequencies of UF_2 is 74.343 cal/(K mol), predicted by B3LYP, and 74.146 cal/(K mol) with PBE0. For UCl_2 the predicted total entropy is 80.688 cal/(K mol) (B3LYP) and 80.402 cal/(K mol) (PBE0). In both molecules the difference with the experimental value is less than 0.5 cal/(K mol). The estimated product of the three principal moments of inertia[3] for UCl_2 is 7×10^{-113} $g^3\,cm^6$ in agreement with the value calculated based on the geometries predicted via hybrid DFT, 6×10^{-113} $g^3\,cm^6$. The calculated product of the three principal moments of inertia for UF_2 is 0.37×10^{-113} $g^3\,cm^6$. The admittedly small amount of experimental data on UF_2 and UCl_2, entropy and estimated inertia moments, is in good agreement with the calculated one.

5. UF and UCl

The U–F bond length was calculated to be 2.041 Å (B3LYP) and 2.024 Å (PBE0), with a vibrational frequency of 576 cm^{-1} (B3LYP) and 599 cm^{-1} (PBE0). For the UCl molecule the bond length was predicted to be 2.523 Å (B3LYP) and 2.496 Å (PBE0). The longer bond length of UCl, versus UF, leads to a lower vibrational frequency of 320 cm^{-1} (B3LYP) and 331 cm^{-1} (PBE0). The estimated vibrational frequency for UCl based on spectroscopic data is 350 cm^{-1},[3] which is in good agreement with the calculated frequencies presented here.

The electronic state of these two molecules is a quartet, with three unpaired electrons in the $5f$ orbitals of uranium; $5f^3\,7s^2$. A Mulliken population analysis of the natural orbitals shows that the three unpaired electrons of UF have more than 95% uranium f character. A similar analysis on the natural orbitals of the unpaired electrons of UCl reveals all three electrons to have more than 98% uranium f character.

The sextet states were also identified and found to be considerably higher in energy than the quartet ones. For UF the sextet state was found to be 19 kcal/mol higher in energy than the quartet, while in the UCl molecule the sextet state was found 16 kcal/mol higher than the quartet. In both molecules, the lowest energy sextet has an electronic configuration $5f^3\,7s\,6d$.

For the UF and UCl molecules the available experimental information includes the specific heat and entropy, the enthalpy of formation and the estimation of the vibrational frequency of UCl, based on spectroscopic data, by Gurvich and Dorofeeva.[3]

The calculated total entropy at 298 K using hybrid DFT is 61.288 cal/(K mol) (B3LYP) and 61.225 cal/(K mol) (PBE0) which is in good agreement with the value reported by Hildenbrand *et al.*[2] of 60.156 cal/(K mol). For UCl the predicted entropy at 298 K is 65.264 cal/(K mol) (B3LYP) and 65.259 cal/(K mol) (PBE0) also in good agreement with the experimental value 63.495 cal/(K mol).[2]

B. Bond dissociation energy of UF_n and UCl_n

The bond dissociation energy (BDE) of the UF_n ($n=1,...,6$) and UCl_n ($n=1,...,5$) series have been measured by thermochemical studies of reaction equilibrium via effusion-beam mass spectrometry.[4,5] The enthalpies of formation of all the species were determined and from there the BDEs were obtained.

The only published theoretical BDEs for these molecules is the one reported by the authors for UF_6.[18] A related calculation was published by De Jong and Nieuwpoort[35] where they calculated the formation energy of UF_6 from the constituent atoms via Dirac-Hartree-Fock-CI[35] and obtained an energy of -524.2 kcal/mol. The experimental value of the enthalpy of formation of UF_6 at 298 K is -513.1 ± 0.5 kcal/mol,[4] which in terms of the BDEs corresponds to the sum of all the BDEs of the UF_n molecules for $n=1,...,6$ plus the enthalpy of formation of the uranium atom and six times the enthalpy of formation of fluorine.

The BDE of UX_k (X=F,Cl) at 298 K was defined as the difference between the enthalpies of UX_k and the sum of the enthalpies of the fragments UX_{k-1} and X,

$$\mathrm{BDE}_{UX_k}=[H(UX_{k-1})+H(X)]-H(UX_k), \quad (1)$$

where H is the total electronic energy plus the zero-point energy of the molecules plus the vibrational, rotational, and translational energies

$$H=E_0+E_{\mathrm{vib}}+E_{\mathrm{rot}}+E_{\mathrm{trans}}+RT. \quad (2)$$

The values calculated for the BDE in UF_n and UCl_n are shown in Fig. 3 and summarized in Table VIII.

C. Trends in bond length and vibrational frequencies

A few trends are interesting to note in these molecules. Similar behavior was observed for the UCl_n molecules as for the UF_n ones, therefore only the latter ones are discussed in this section.

Table IX summarizes of structural and electronic properties calculated with the B3LYP functional for the UF_n mol-

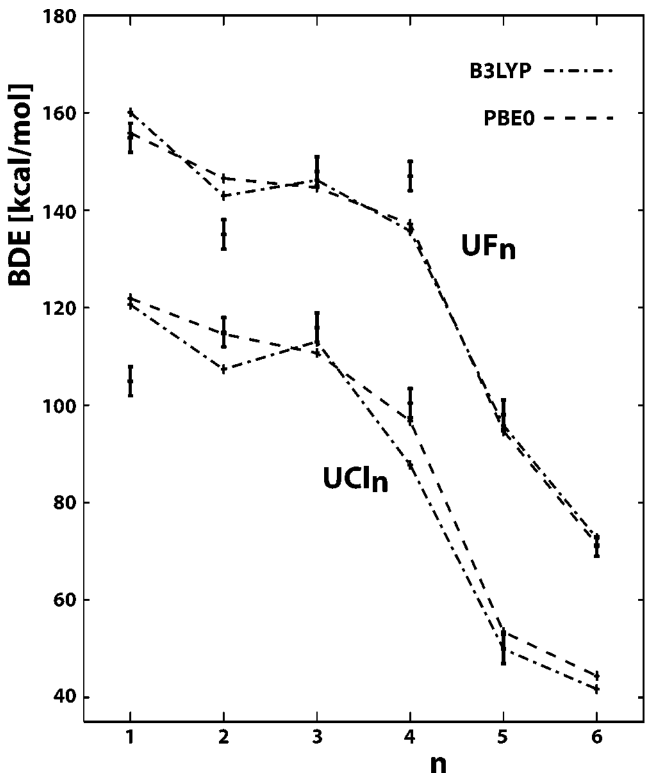


FIG. 3. Bond dissociation energy of the UF_n and UCl_n molecules as function of the number of fluorine atoms. Two sets of calculated values are shown, one for B3LYP and the other calculated with PBE0, against the experimental values from Ref. 4. The error bars were estimated from the errors of ΔH_f shown in Ref. 4 for UF_n and the same error bars were used for the BDE of the UCl_n molecules.

ecules with $n=0,...,6$. The electronic state of UF_6 is a closed shell. As atoms are removed from the UF_6 molecule, the unpaired electrons occupy the uranium $5f$ orbitals; UF_5 has one unpaired electron in an $5f^1$ state, the ground state of UF_4 is a triplet $5f^2$ state with the singlet state considerably higher in energy and the ground state of UF_3 is the quartet $5f^3$ with the doublet much higher in energy. As expected from the energy levels of the uranium atom, as one reaches UF_2 the fourth unpaired electron occupies a $7s$ state forming a quintet state. So far the multiplicity of the state of the molecule has monotonically increased from one to five. The UF molecule breaks this trend by pairing two $7s$ electrons in a $7s^2$ state and the resulting ground state is a quartet. The ground state of the uranium atom is a quintet state with four unpaired electrons in a $5f^3 7s^2 6d$ configuration. In an unrestricted DFT calculation the up-spin orbital energies are arranged as $E(5f)<E(7s)<E(6d)$. In an ionic picture, one can view successive bonds in the UF_n series starting with the U atom as arising from the removal of the highest energy electron on the uranium to form an F^- ion. As can be seen in the discussion above, in the UF molecule a formal U^+-F^- bond is formed by ionization of a $6d$ electron of the uranium atom leaving the unpaired electrons in a $5f^3 7s^2$ configuration. The formation of UF_2 molecule involves the $6d$ and one of the $7s$ electrons and UF_3 involves both $7s$ electrons in the bonding leaving a $5f^3$ state. The UF_4, UF_5, and UF_6 molecules involve one, two, and three of the $5f$ electrons, respectively.

TABLE IX. Trends in various characteristics of the UF_n ($n=1,...,6$) molecules. Bond dissociation energy in kcal/mol bond length in angstroms and vibrational frequency in cm^{-1}. These values were calculated using the B3LYP hybrid DFT functional.

Molecule	BDE	Bond length	ν[a]	Elect. state
UF_6	73	2.012	656	$5f^0$
UF_5	97	2.031	642	$5f^1$
UF_4	137	2.069	598	$5f^2$
UF_3	147	2.085	543	$5f^3$
UF_2	144	2.074	554[b]	$5f^3\,7s^1$
UF	161	2.041	576	$5f^3\,7s^2$
U				$5f^3\,7s^2\,6d$

[a]Frequency of breathing mode.
[b]Symmetric stretch mode.

The separation from the trend by UF is also observed in the other columns of Table IX. The BDE of the molecules monotonically increases up to UF_3, then it decreases for UF_2 and it increases again for UF. This decrease in the BDE of UF_2 is due to the extra stabilization of the UF molecule after pairing the two $7s$ electrons. Because of that the relative energy between UF_2 and the fragments UF and F is lower than that of the molecules with more fluorine atoms. If the ground state of the UF molecule were to be the sextet state, the BDE of UF_2 would have been 170 kcal/mol and that of UF would have been 135 kcal/mol.

To compare the stiffness of the vibrational modes, the main stretching mode—the breathing mode—has been tabulated. A good correlation between bond length and vibrational frequency can be observed; as would be expected, the longer the bond length the lower the vibrational frequency. While UF follows this trend, it is slightly off as one can see comparing the UF vibrational frequency with that of UF_4.

TABLE VIII. Bond dissociation energies at 298 K for UF_n and UCl_n ($n=1,...,6$) molecules. Calculated and experimental values are presented as function of the number of halide atoms. All energies are given in kcal/mol.

n	$UF_n^{(expt.)}$ [a]	$UF_n^{(B3LYP)}$	$UF_n^{(PBE0)}$	$UCl_n^{(expt.)}$ [b]	$UCl_n^{(B3LYP)}$	$UCl_n^{(PBE0)}$
1	154.0	160.1	155.9	104.9	120.7	121.9
2	135.0	143.0	146.6	115.0	107.4	114.6
3	147.9	146.2	144.7	115.9	113.1	110.7
4	147.0	135.7	137.2	100.4	87.7	96.7
5	98.0	95.8	94.6	50.0	50.0	53.4
6	71.0	72.7	71.4		41.7	44.4

[a]Experimental data from Ref. 4.
[b]Experimental data from Ref. 5.

One unexpected trend in the series is given by the BDE as function of the bond length. While it is usually expected that the BDE increases for a shorter bond length, in the case of the UF_n and UCl_n molecules the opposite correlation is observed. In each series, the molecules with stronger BDE have longer bond length. This is due to the reorganization energy since the BDEs were calculated after removing a fluorine atom and relaxing the molecule. On the other hand, if one compares UF_x with UCl_x, for the same number 'x' of halide atoms the expected Badger-rule type behavior is observed: the UCl_x molecule has a longer bond length and a weaker bond energy than UF_x.

IV. CONCLUSIONS

In the present paper the full series of UF_n and UCl_n molecules, with $n=1,...,6$, was systematically analyzed using hybrid DFT computational techniques using two different functionals (B3LYP and PBE0) combined with with a 60-electron relativistic effective core potential for the description of the uranium ion. Geometries, vibrational frequencies, and bond energies were presented.

The only correction missing, for a full DFT treatment, is the energy term due to spin-orbit interaction. The spin-orbit correction to the BDE of UF_6 was shown to be on the order of 4 kcal/mol (Ref. 18) which is smaller than the error that we observe in the BDE of the smaller molecules. Comparing with the available experimental data on these molecules it was found that this methodology predicts the molecular properties with reasonable accuracy.

The computed BDEs for these molecules are presented and they are in reasonably good agreement with the experimental values. The average difference between the computed and experimental BDEs are 5 kcal/mol in UF_n and 7 kcal/mol in UCl_n. As the number of unpaired electrons increases the disagreement becomes larger. This may be due to the lack of a multi configurational wavefunction in DFT to properly describe the multiplet behavior of those states as well as to inherent limitations of the hybrid functionals.

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