

All-Electron Hybrid Density Functional Calculations on UF_n and UCl_n ($n = 1-6$)

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Abstract: We calculate the bond dissociation energies of the series UF_n and UCl_n ($n = 1-6$) using the all-electron third-order Douglas-Kroll-Hess approximation in combination with hybrid density functionals. The spin-orbit (SO) operator is included self-consistently using the nuclear-only SO and the screened-nuclear SO approximations. Results are in very good agreement with experimental values, with the exception of the smallest molecules of each series, UF and UCl. By shifting the one-electron orbital energies of UF_6 and UCl_6 to match the HOMO level with the ΔSCF calculated value of the first ionization energy, we are able to reproduce the main features of the photoelectron spectrum of these two molecules.

1. Introduction

The uranium hexafluoride molecule (UF_6) has been a prototype to test computational electronic structure methods for actinide complexes for a quarter of a century.^{1,2} The reasons are that experimental data for UF_6 is abundant, and, in addition, UF_6 presents a closed shell electronic ground state, which simplifies the calculations. The rest of the fluoride series, UF_n ($n = 1-5$), and the uranium chlorides, UCl_n ($n = 1-6$), are by far less studied from a computational point of view, even though similar experimental data exists for most of the species on both series.³⁻⁸

In a recent paper,⁹ we have studied the structural properties of UF_6 and UF_5 and the bond dissociation energy (BDE) of UF_6 ($\text{UF}_6 \rightarrow \text{UF}_5 + \text{F}$) using density functional theory (DFT) in combination with both relativistic effective core potentials (RECPs) and an all-electron approach based on the Douglas-Kroll-Hess (DKH) approximation.¹⁰⁻¹⁴ In that study, the hybrid density functionals (i.e., those containing a portion of Hartree-Fock type exchange) B3LYP^{15,16} and PBEh (hybrid PBE, also refer to as PBE0¹⁷ and PBE1PBE¹⁸ in the literature) were found to perform notably better than the local spin-density approximation (LSDA), the generalized-gradient approximation (GGA), and the Hartree-Fock approximation.

In the same paper,⁹ the calculated spin-orbit (SO) effect to the BDE of UF_6 using the all-electron approach was found to be approximately -4 kcal/mol. In a subsequent paper, Batista et al.¹⁹ performed a systematic study of structural properties and BDEs of the series UF_n and UCl_n ($n = 1-6$) using hybrid DFT and RECPs.

In this work, we complete the study of the BDEs of UF_n and UCl_n ($n = 1-6$) using the all-electron DKH approximation and hybrid density functionals. To this end, we analyze three different levels of approximation: the scalar-relativistic (i.e., without the SO operator), including the nuclear-only SO operator, and including the screened-nuclear spin-orbit approximation (SNSO).²⁰ In the latter two cases, the corresponding SO operator is fully included in the self-consistent procedure by using a generalized Kohn-Sham approach (GKS).

2. Computational Details

Relativistic effects are taken into account through the third-order DKH (DKH3) approximation. Using a fourth-order Hamiltonian (DKH4) does not change the calculated BDEs in the first decimal figure. Scalar relativistic calculations are carried out using the unrestricted Kohn-Sham approximation, i.e., the electronic ground state is represented by a single unrestricted determinant. When the spin-orbit operator is included in the calculation, we have used the GKS approach. In this scheme, the electronic ground state is represented by

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a single determinant built up from two-component spinors. To guarantee the rotational invariance of the total energy we have employed a noncollinear generalization of the spin-density functional energy and potential.²¹ Two flavors of the SO operator are considered: the third-order nuclear-only (denoted as SO) and the SNSO operator, which includes the electron–electron SO interaction in an approximate way.²⁰ The SNSO approximation has been shown to effectively take into account the electron–electron interaction in atoms and molecules with a marginal increase in computational cost.²² For more details on the implementation the reader is referred to ref 21.

Two different hybrid density functionals are employed: PBEh^{17,18} and the B3LYP functional.^{16,15} The equilibrium molecular structures are taken from ref 19. We have employed the universal Gaussian basis set (UGBS) of Malli and co-workers²³ for the U atom, which consists of an uncontracted (32s29p20d17f) set, and the 6-31+G* basis for fluorine and chlorine. We have checked the impact of using a larger triple- ζ basis set for F and Cl and the basis set superposition error (BSSE) in our results (see next section). The BDEs at the equilibrium geometries are calculated as

$$E(UX_n) = E(UX_{n-1}) + E(X) - E(UX_n) \quad (1)$$

Finite temperature effects and zero-point energy correction are rather small¹⁹ and not included in this study.

The population analysis reported here has been carried out using the scalar relativistic DKH3 Hamiltonian and the PBEh functional. The presence of the SO operator (either nuclear-only or SNSO) as well as the choice of the functional produces only minor changes in the population analysis, and therefore its qualitative meaning remains the same.

All calculations were carried out with the development version of the *Gaussian*²⁴ suite of codes.

3. Results and Discussion

As pointed out in ref 19, the bonding in UF_n and UCl_n can be approximately seen as $U^{+n}F_n^-$ and $U^{+n}Cl_n^-$, respectively. This ionic picture arises from the ionization of the U valence orbitals to the 2p orbitals of F or 3p orbitals of Cl. To obtain a more accurate picture of the bonding nature of the UF_n and UCl_n complexes, we have performed an atomic electron population analysis of the U atom using the natural population analysis (NPA).²⁵ The NPA has recently been shown to achieve the best performance among several orbital based partitioning schemes.²⁶

In Table 1, we show the natural valence electron configuration and the natural charge of the U center for the series UF_n and UCl_n . As suggested by Clark and co-workers, the NPA of the U orbitals is chosen such that the valence space is composed of the 5f, 6d, and 7s orbitals.²⁶ Inspection of the U electron configuration of the UF_n indicates that the electron donation from the U to the F atoms is not uniform along the series. For UF, the total charge donated by the U center is $+0.74e^-$, indicating a strong ionic character. The total charge donated, per fluorine atom, systematically decreases as the number of F atoms increases: $+0.69e^-$ (UF_2), $+0.66e^-$ (UF_3), $+0.59e^-$ (UF_4), $+0.46e^-$ (UF_5), and

Table 1: Natural Electron Configuration and Natural Charge of the Uranium Atom from Natural Population Analysis

molecule	configuration				U charge	molecule	configuration				U charge
	5f	6d	7s				5f	6d	7s		
UF	2.94	0.47	1.85		+0.74	UCl	3.07	0.40	1.87		+0.65
UF_2	3.09	0.67	0.84		+1.38	UCl_2	3.14	0.77	0.84		+1.21
UF_3	3.04	0.69	0.28		+1.97	UCl_3	3.18	0.92	0.23		+1.62
UF_4	2.55	0.99	0.05		+2.35	UCl_4	2.69	1.58	0.23		+1.38
UF_5	2.36	1.17	0.09		+2.29	UCl_5	2.91	1.98	0.30		+0.65
UF_6	2.31	1.42	0.14		+2.08	UCl_6	3.39	2.41	0.38		−0.24

Table 2: All-Electron Bond Dissociation Energies for the UF_n Series (in kcal/mol)

	B3LYP			PBEh			exp ⁵
	scalar	SO	SNSO	scalar	SO	SNSO	
UF	165.1	168.5	172.7	164.1	166.1	172.7	154.9
UF_2	142.3	142.6	143.6	146.1	145.2	146.4	135.0
UF_3	148.3	147.3	148.2	146.5	146.7	147.2	147.9
UF_4	139.0	137.8	139.9	140.8	138.7	140.5	147.0
UF_5	99.7	94.7	98.6	98.2	92.5	96.8	98.0
UF_6	76.0	72.2	75.7	74.5	70.8	74.4	71.0

Table 3: All-Electron Bond Dissociation Energies for the UCl_n Series (in kcal/mol)

	B3LYP			PBEh			exp ⁶
	scalar	SO	SNSO	scalar	SO	SNSO	
UCl	121.0	124.8	129.2	123.8	126.0	132.9	104.9
UCl_2	106.3	105.1	105.1	115.2	114.3	114.7	115.1
UCl_3	114.7	111.5	113.0	116.6	113.2	113.8	116.3
UCl_4	89.3	91.3	92.7	92.7	94.7	96.4	100.9
UCl_5	46.7	44.7	48.6	49.6	47.3	51.3	50.4
UCl_6	48.5	37.9	41.0	51.1	40.4	43.6	

$+0.35e^-$ (UF_6). It is worth commenting that the total charge on U increases from $+0.74e^-$ for UF to $+2.35e^-$ for UF_4 , mainly due to changes in the population of the 6d and 7s orbitals, while the population of the 5f remains unchanged. Further fluorination, $UF_4 \rightarrow UF_5 \rightarrow UF_6$, leads to a redistribution of the charge among the U orbitals, with very little decrease of the total charge of the U atom.

The picture that emerges for the first 3 molecules of the UCl_n series ($n = 1-3$) is similar to that of their analogues UF_n (Table 1), although the total charge on U is slightly smaller, indicating a weaker charge donation to the Cl atoms. Addition of more Cl atoms, $UCl_3 \rightarrow UCl_6$, yields a different situation when compared with UF_n ; the total charge on U decreases from $+1.62e^-$ for UCl_3 , to $+1.38e^-$ for UCl_4 , to $+0.65e^-$ for UCl_5 , and to $-0.24e^-$ for UCl_6 . If we express this decrease in terms of the charge per Cl atom, we obtain $+0.54e^-$ for UCl_3 , $+0.35e^-$ for UCl_4 , $+0.13e^-$ for UCl_5 , and $-0.04e^-$ for UCl_6 , which represents a progressive loss of the ionic character of the U–Cl bonds.

In Tables 2 and 3 we show the all-electron BDEs calculated using the B3LYP and the PBEh functionals and three different relativistic Hamiltonians: scalar, SO, and SNSO, as described above, as well as the experimental

Table 4: One-Electron Energy Levels of the Highest Occupied Molecular Orbitals of UF₆ Using the All-Electron DKH3 Hamiltonian and the PBEh Functional^b

	scalar relativistic	spinor	SO	SNSO ^a
t_{1u}	-12.18	γ_{8u}	-11.80	-13.95
		γ_{6u}	-12.94	-15.09
t_{1g}	-12.79	γ_{8g}	-12.79	-14.94
		γ_{6g}	-12.80	-14.95
t_{2u}	-13.70	γ_{8u}	-13.70	-15.85
		γ_{7u}	-13.70	-15.85
a_{1g}	-13.75	γ_{6g}	-13.76	-15.91
t_{1u}	-14.18	γ_{8u}	-14.17	-16.32
		γ_{6u}	-14.20	-16.35
t_{2g}	-14.59	γ_{7g}	-14.55	-16.70
		γ_{8g}	-14.62	-16.77
e_g	-15.19	γ_{8g}	-15.19	-17.34
t_{1u}	-27.40	γ_{8u}	-25.43	-27.58
		γ_{6u}	-31.73	-33.88
a_{1g}	-33.77	γ_{6g}	-33.77	-35.92
e_g	-34.30	γ_{8g}	-34.31	-36.46
t_{1u}	-35.81	γ_{8u}	-35.44	-37.59
		γ_{6u}	-38.47	-40.62

^a The orbital energy levels are shifted by 2.15 eV to match the HOMO with the Δ SCF calculated value of the first ionization energy.

^b All values in eV.

values. The two hybrid functionals employed here give similar BDEs; the largest difference (10 kcal/mol) occurs for the UCl₂ molecule.

We have tested the effect of BSSE on our results. Using the counterpoise method, the effect of BSSE on calculated BDEs (with PBEh and the scalar relativistic Hamiltonian) is -0.9 kcal/mol for UF₆ and -0.5 kcal/mol for UCl₆. We have also tested the quality of the basis chosen for F and Cl. Using the larger triple- ζ 6-311+G(3df) basis, the BDEs for UF₆ and UCl₆ change by 0.5 and 1.2 kcal/mol, respectively.

The effect of the nuclear-only SO on the BDEs (columns labeled as "SO" in Tables 2 and 3) is rather small for UF_n. For instance, using PBEh, the SO contribution to the BDEs is about +2 kcal/mol for UF, and decreasing when increasing n , with a SO effect on the BDE of UF₆ of -4 kcal/mol. On the other hand, the effect of the electron-electron SO interaction included through the SNSO approximation (columns labeled as "SNSO" in Tables 2 and 3) is positive along

Table 5: One-Electron Energy Levels of the Highest Occupied Molecular Orbitals of UCl₆ Using the All-Electron DKH3 Hamiltonian and the PBEh Functional^b

	scalar relativistic	spinor	SO	SNSO ^a
t_{1g}	-9.46	γ_{8g}	-9.44	-11.08
		γ_{6g}	-9.49	-11.13
t_{1u}	-10.22	γ_{8u}	-10.00	-11.64
		γ_{6u}	-10.63	-12.27
t_{2u}	-10.43	γ_{7u}	-10.40	-12.04
		γ_{8u}	-10.42	-12.06
t_{1u}	-10.76	γ_{8u}	-10.49	-12.13
		γ_{6u}	-10.84	-12.48
t_{2g}	-11.56	γ_{7u}	-11.50	-13.14
		γ_{8u}	-11.60	-13.24
a_{1g}	-11.72	γ_{6g}	-11.73	-13.37
e_g	-12.10	γ_{8g}	-12.10	-13.74
t_{1u}	-22.56	γ_{8u}	-22.01	-23.65
		γ_{6u}	-23.21	-24.85
e_g	-23.72	γ_{8g}	-23.72	-25.36
a_{1g}	-23.85	γ_{6g}	-23.85	-25.49
t_{1u}	-29.52	γ_{8u}	-27.65	-29.29
		γ_{6u}	-35.91	-37.55

^a The orbital energy levels are shifted by 1.64 eV to match the HOMO with the Δ SCF calculated value of the first ionization energy.

^b All values in eV.

the series. The SNSO tends to compensate the effect of the nuclear-only SO for $n = 2-6$, while for UF they operate in the same direction.

The effect of the nuclear-only SO on the UCl_n BDEs follows the same trend as for UF_n, although its magnitude for UCl₆ is larger (approximately 10 kcal/mol). The SNSO correction to the BDEs of UCl_n is similar to that of the UF_n series. As a consequence, we obtain a SO effect for UCl₆ of about -7 kcal/mol, while for the rest of the series ($n = 2-6$), the effect increases when decreasing n up to +9 kcal/mol for UCl.

It is interesting to relate the trend in the BDEs along both series of UF_n and UCl_n to the change of the ionic character (as reflected by the NPA charge on the U atom). According to our calculations, the larger the ionic character is, the larger the BDE. This suggests that even though the nature of the U-F and U-Cl bonds is a mixture of ionic and covalent character, the trend in the BDEs is given mainly by its ionic component.

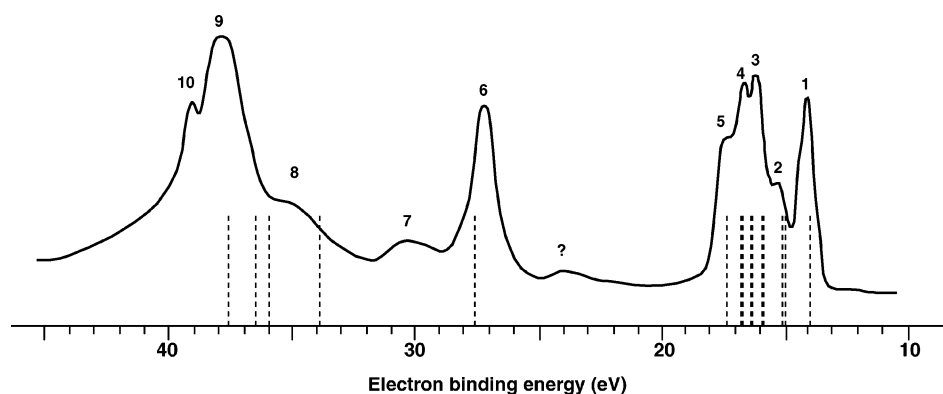


Figure 1. Photoelectron spectrum of UF₆ from ref 29 (solid line) and calculated orbital energies (dashed lines). The orbital energies have been shifted so that the HOMO matches the Δ SCF calculation of the first ionization potential.

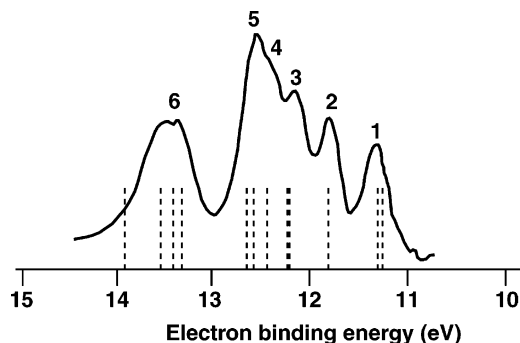


Figure 2. Photoelectron spectrum of UCl_6 from ref 31 and calculated orbital energies. The orbital energies have been shifted so that the HOMO matches the ΔSCF calculation of the first ionization potential.

Our scalar relativistic BDE are in fairly good agreement with those from ref 19 using scalar relativistic effective core potentials. The largest discrepancy corresponds to UCl_6 , where the difference is approximately 7 kcal/mol.

There is an overall good performance of both hybrid functionals for $n = 2-6$, although there is a noticeable worse performance for the BDEs of UF and UCl. This could be attributed to the unsuitability of the approximation employed here to describe systems with a large number of unpaired electrons.²⁷ This observation is in line with the findings of a previous paper.¹⁹ It is worth mentioning that although the total SO effect for UF and UCl is the largest along both series it does not improve the agreement with experiment, making the error associated with the neglect of multiplet interaction in DFT even more dramatic.

There are also large spin-orbit effects on the first ionization energy (IE) of these systems. For example, at the ΔSCF level of approximation, the scalar relativistic first IE of UF_6 is 14.30 eV with PBEh, and 13.96 eV when the SNSO is included. The experimental value is 14.14 eV.^{28,29} This error is of the order of the mean absolute error in the predicted IEs in the G3 data set (0.20 eV).³⁰ A similar analysis for UCl_6 yields a first IE of 11.08 eV, also in good agreement with the experimental value, 11.26 eV.³¹ Tables 4 and 5 present the valence orbital symmetries, the Kohn-Sham orbital eigenvalues, and a set of adjusted energies where the first eigenvalue has been adjusted to the ΔSCF value and the remaining shifted accordingly. The latter are compared with experimental photoemission spectra in Figures 1 and 2. The agreement with experiment is quite good. In fact, the calculation helps identify the features labeled as 7 and “?”²⁹ in UF_6 as artifacts not associated with the molecular ionization spectrum. Our assignments for UF_6 are consistent with previous studies,^{1,32,33} and those for UCl_6 differ only slightly from the pioneering work of Thornton et al.³¹ (the order of the a_{1g} and t_{2g} states in the 11 eV range differs in the present work).

4. Conclusions

The BDEs of the series UF_n and UCl_n ($n = 1-6$) have been calculated using the all-electron third-order DKH approximation in combination with the hybrid density functionals PBEh and B3LYP. The spin-orbit operator is included

self-consistently using the nuclear-only and the SNSO approximation. Results are in very good agreement with experimental values, with the exception of the smallest molecules of each series, UF and UCl, where the deviation from experiment is 18 and 28 kcal/mol, respectively. These systems represent a challenge for computational methods, and they may need to be studied using accurate multireference approaches.

Population analysis reveals a larger ionic character for the U-F bonds than for the U-Cl bonds as well as an increase of the ionicity when decreasing the number of halogen atoms.

The ΔSCF first ionization energies of UF_6 and UCl_6 calculated using PBEh and the SNSO approximation are in good agreement with available experimental data. By shifting the one-electron orbital energies to match the HOMO level with the ΔSCF calculated value of the first ionization energy, we are able to reproduce the main features of the UF_6 and UCl_6 photoelectron spectrum.

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