Relativistic density functional investigation of UX_6 (X=F, Cl, Br and I)*

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The molecular structures and the vibrational frequencies of uranium hexahalides UX_6 (X=F, Cl, Br and I) molecules are investigated by using local density approximation (LDA) and generalised gradient approximation (GGA) functions (BP, BLYP and RPBE) in combination with two different relativistic methods (scalar and scalar+spin–orbit relativistic effects). The calculated results show that the differences are trivial between scalar and scalar+spin–orbit relativistic methods. The vibrational frequencies are also compared with existing experimental values, and overall, the RPBE approach gives the smallest error. The bond dissociation energies (BDEs) of UX_6 are computed by using the RPBE function, thereby obtaining exact vibrational frequencies. In addition, the calculated magnitudes of the spin–orbit effect on the BDE of UX_6 (X=F, Cl, Br, and I) are found to be approximately –0.3198, –0.3218, –0.3609 and –0.4415 eV, respectively.

Keywords: molecular structure, vibrational frequencies, bond dissociation energy, spin–orbit coupling

PACC: 3310, 3520G

1. Introduction

Because the uranium hexahalides play an important role in nuclear technology, there has been aroused a great interest in the physics and chemistry of actinides.[1,2] The sparsity and the radioactivity of uranium hexahalides implies that it is very difficult to study these compounds experimentally. It is not surprising therefore that the available experimental data on physical and chemical properties of these compounds are rather scarce. However, the experimental infrared spectrum of UF_6 was analysed by McDowell *et al.*[3] For UCl_6 only the frequency of T_{2u} mode v_3 was reported from matrix-isolation IR experiments.[4,5] The BDE of UF_6 was also measured in several experiments. Hildenbrand and Lau obtained a BDE (UF_5–F) of 3.0355±0.0867 eV by studying the reduction of UF_6 due to A_g following the equilibrium of the reaction (A_g+UF_6 →A_gF+UF_5).[6] The BDE 2.9921±0.2168 eV of UF_6 was gained by Compton from threshold of F^- formation due to collisions of fast alkali atoms with UF_6.[7] Nikitin and Tsirel'nikov also obtained the BDE of 3.1656 eV by thermochemistry.[8] However, no experimental investigation of UBr_6 and UI_6 has been reported up to now.

It is very difficult to study uranium hexahalides experimentally, so quantum chemical calculation is very useful for studying the physical and chemical properties of these compounds. Because of the importance in nuclear fuel enrichment and abundant experimental data of UF_6, the molecule has been treated as a model to test computational electronic structure method applied to the study of actinide compounds.[9,10] A large number of studies of molecular structures and vibrational frequencies of UF_6 have been performed, and the obtained results are in good agreement with experimental values.[11–23] For example, Hay and Martin[11] calculated the bond lengths and harmonic vibrational frequencies by using their LC-RECPs method, and found that the average deviation for the best function (B3LYP) was only 14 cm^{-1} for the all vibrational frequencies. The good bond lengths and vibrational frequencies of UF_6 were also obtained by Batista *et al.* by using both Hartree-Fock and three density functional theory (DFT) approximations (spin–density approximation, the generalised gradient approximation, and hybrid density approximation).[23] Also the structural and the vibrational properties of UCl_6 were investigated by quantum chemical calculation.[12,14,19,21,24] For example, Han has examined the performance of widely used hybrid functions for calculating the bond lengths and

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the vibrational frequencies of UCl_6 molecule by using small-core relativistic effective core potential and extended basis set.[19] In addition, the BDE of UF_6 was obtained by Batista *et al.* from the relative energy of the fragments [UF_6 $\rightarrow UF_5$+F] by using the DFT in combination with both relativistic effective core potential and all-electron approach.[23] Then they also calculated the BDEs of the UF_n and UCl_n ($n = 1 - 6$) molecules by using the all-electron hybrid density functional method.[25]

The computational results for these molecules in the literature were obtained by using GAUSSIAN program and relativistic effective core potential (RECP) method. The RECP method was also applied to many heavy metal clusters and molecules.[26−29] In the present work, we perform density functional calculations of the bond lengths and vibrational frequencies of UX_6 by using Amsterdam density functional (ADF) program. We also analyse the effects for computing molecular structures and vibrational frequencies from two different levels of approximation: the scalar-relativistic and scalar+spin–orbit relativistic approximations. Certainly, these relativistic effects are introduced via the zeroth-order regular approximation (ZORA) approach to the Dirac equation in the present study. We know that relativistic effects are very important for computing molecules containing heavy metal atoms. Generally, only the use of the RECP for inner electrons of heavy metal atoms is not enough for the reasonable description of their properties, because the relativistic effects of their valence electrons in these heavy metal systems are also important. The ZORA relativistic method could reasonably describe the properties of inner and valence electrons of heavy metal systems, and it proved to be an effective tool for the study of these systems.

The purpose of the work is to examine the performance of the various DFT functions on uranium hexahalides. In particular, we concentrate our attention on the accuracies of these experimental data and our results of UF_6 and UCl_6 molecules. Experimentally unknown geometries and vibrational frequencies of UBr_6 and UI_6 molecules are also presented and discussed. In addition, we calculate the BDE of UX_6 by using the RPBE function, under the scalar and scalar+spin–orbit relativistic approximations separately.

Details of calculation are given in Section 2, and result and discussion are presented in Section 3. The article ends with the summary.

2. Computational details

Our calculations were performed by using the 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 analyse and interpret these in convenient and simple chemical terms.[30] The reason for its popularity and success are easy to understand. In the first place, the DFT approach is exact in principle. In particular, the Kohn–Sham method implies a one-electron picture of the many-electron systems but yields, in principle, the exact electron density and the total energy. In the second place, it preserves at all levels of approximation the appealing one-electron molecular orbital view on chemical reactions and properties. The computed orbits are suitable for the typical molecular orbital-theoretical analyses and interpretations. The Kohn–Sham approach effectively incorporates all correlation effects. In the third place, it is a relatively efficient computational method, and its fundamental scaling properties do not deteriorate when methodological accuracy increases. So it is well suited for computing molecules containing heavy metal atoms.

In this method, scalar and spin–orbit coupling relativistic effects are introduced via the ZORA approach to the Dirac equation.[31−33] For the closed-shell systems, the spin restricted DFT scheme is used. In the present paper, a triple-ζ Slater type basis set augmented with one set of polarisation functions, i.e. the triple-zeta polarised (TZP) basis set, is employed for all atoms (F, Cl, Br, I and U). A frozen core approximation is used. Core electrons (F.1s, Cl.2p, Br.3d, I.4d and U.5d) are frozen for fluorine, chlorine, bromine, iodine and uranium, respectively. Moreover, the calculations are performed by using LDA and GGA (BP, BLYP and RPBE) functions.[34,35]

The ADF program has a fragment oriented approach: the poly-atomic 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 is carried out 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 in advance, and then their properties must be passed to the current calculation. This is done by attaching fragment files which contain the necessary

information. In the present paper, the BDE for U–X bond in the UX_6 between the U and UX_5 radical fragments are obtained by using the fragment approach.

3. Results and discussion

In this section, the calculated results of UX_6 molecules are presented. The quantities calculated for the four molecules are U–X bond lengths, vibrational frequencies, and BDE properties. In addition, with the high computational cost and the absence of analytic forces for our relativistic all-electron calculations, all computations are performed by using the frozen core approximation.

3.1. Structures

For octahedral UX_6, the electronic configurations including all the electrons on U and X atoms are as follows:

UF_6: $(2T_{1u})^6$ $(2E_g)^4$ $(1T_{2g})^6$ $(3T_{1u})^6$ $(3A_{1g})^2$ $(1T_{2u})^6$ $(1T_{1g})^6$ $(4T_{1u})^6$,
UCl_6: $(1T_{1u})^6$ $(2A_{1g})^2$ $(1E_g)^4$ $(2T_{1u})^6$ $(2E_g)^4$ $(3A_{1g})^2$ $(1T_{2g})^6$ $(3T_{1u})^6$ $(1T_{2u})^6$ $(4T_{1u})^6$ $(1T_{1g})^6$,
UBr_6: $(1T_{1u})^6$ $(2A_{1g})^2$ $(1E_g)^4$ $(2T_{1u})^6$ $(3A_{1g})^2$ $(2E_g)^4$ $(1T_{2g})^6$ $(3T_{1u})^6$ $(4T_{1u})^6$ $(1T_{2u})^6$ $(1T_{1g})^6$,
UI_6: $(1T_{1u})^6$ $(2A_{1g})^2$ $(1E_g)^4$ $(2T_{1u})^6$ $(3A_{1g})^2$ $(2E_g)^4$ $(1T_{2g})^6$ $(3T_{1u})^6$ $(4T_{1u})^6$ $(1T_{2u})^6$ $(1T_{1g})^6$,

where the highest occupied molecular orbits of each molecule are indicated.

In the present paper, the geometric parameters of UX_6 have been extensively studied by a variety of methods derived from LDA and GGA (BP, BLYP and RPBE) methods. For the UF_6 and UCl_6 molecules there are also a variety of experimental data.[36–38] Here a comparison is presented between the experimental results and the calculations with DFT accompanied with using the four different functions and two different relativistic methods (scalar and scalar+spin–orbit relativistic effects). The calculated results show that the ground states of UX_6 are singlet states.

The results of geometric structures of UX_6 are reported in Table 1. In the Table, the predicted structures of UF_6 and UCl_6 are also compared with experimental values measured by electron diffraction. It is encouraging that all the calculated structures for all levels are reasonably consistent with experimental data. For example, for the UF_6 molecule a largest difference between the calculated structure and experiment is given by the BLYP function and the scalar relativistic method which overestimates the bond length by only 0.0363 Å or 0.0319 Å (1 Å=0.1 nm). The best prediction of UF_6 molecule is given by the LDA function. The error is less than 0.1%. The errors for UCl_6 in the bond length are only 0.14% for LDA, 0.72% for BP, 2.37% for BLYP, and 1.09% for RPBE, with the scalar relativistic effect taken into account, and only 0.18% for LDA , 0.65% for BP, 1.91% for BLYP, and 1.03% RPBE, with the spin–orbit relativistic effect taken into consideration. From Table 1, we also find that the difference among the calculated results obtained from both scalar and scalar+spin–orbit relativistic effect are trivial, so the spin–orbit coupling effect has a negligible effect on the bond lengths of closed shell UX_6 molecules.

Table 1. Calculated equilibrium geometries of uranium tetrahalides (in Å).

	LDA	BP	BLYP	RPBE	Expt.
R (U–F)					
scalar	1.9975	2.0151	2.0323	2.0272	1.996 (8)[a]
spin–orbit	1.9968	2.0138	2.0309	2.0258	1.999 (2)[b]
R (U–Cl)					
scalar	2.4565	2.4776	2.5082	2.4869	2.46 (1)[c]
spin–orbit	2.4556	2.4761	2.5071	2.4854	
R (U–Br)					
scalar	2.6498	2.6665	2.6869	2.6699	
spin–orbit	2.6486	2.6646	2.6852	2.6684	
R (U–I)					
scalar	2.8987	2.9092	2.9294	2.9163	
spin–orbit	2.8972	2.9067	2.9278	2.9142	

[a]Seip [36], [b]Kimura *et al.*[37], [c]Ezhov *et al.*[38]

3.2. Vibrational frequencies

The octahedral UX_6 molecules each have four normal modes of vibration: $T_{\rm mol} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$, where only the T_{1u} vibrations (v_3 and v_4) are infrared active. The two modes v_3 and v_4 correspond to the asymmetric stretching and bending modes, respectively. The vibrational frequencies of the UF_6 have been studied extensively in the gas phase and matrix spectroscopy. McDowell *et al.* analysed the infrared spectrum of UF_6 and derived a vibrational force field,[3] and Paine *et al.* reported on matrix-isolated UF_6 vibrational spectra.[39] For UCl_6 only the frequency of infrared active T_{1u} mode (v_3) was reported from matrix-isolation infrared active experiments (around 358 cm^{-1}[4,5]). There exists no experimental information about UBr_6 and UI_6 molecules up to now. In the present paper, the vibrational frequencies calculated at the optimised geometries of each molecule by using the LDA and GGA (BP, BLYP and RPBE) functions in combination with both scalar and scalar+spin–orbit relativistic methods are listed in Tables 2–5. As noted in these tables, the differences among the calculated results by the scalar and scalar+spin–orbit relativistic methods are trivial. For example, for the UF_6 molecule the RPBE frequencies obtained by the scalar relativistic method are 669.2797, 533.8869, 623.6415, 181.4717, 191.4623 and 139.7444 cm^{-1} compared with the frequencies of 668.6199, 533.2180, 624.5020, 182.1084, 191.8735 and 139.2524 cm^{-1} obtained by using the scalar +spin–orbit method. Their average difference is only 0.6215 cm^{-1}. In addition, the calculated frequencies obtained by the scalar relativistic method from LDA and GGA (BP and BLYP) density functional approaches are also closer to the spin–orbit relativistic ones. In view of the reason, the details of the analysis are given only by scalar relativistic method in the following.

The six vibrational modes can be separated into U–X stretching modes, v_1, v_2, and v_3, and bending modes, v_4, v_5, and v_6. For all levels treated by the DFT method, the error in the calculated frequencies correlates with the error in bond lengths. For example, the LDA predicts shorter bond lengths and higher frequencies while the RPBE predicts longer bond lengths and lower vibrational frequencies. The last column in Table 2 shows the mean absolute differences between the calculated frequencies and the experimental values. Overall, the RPBE approach gives a small error compared with experimental values. For example, for the strongly IR-allowed v_3 band the RPBE frequency is 623.6415 cm^{-1} for UF_6, compared with the experimental frequency of 626 cm^{-1}. The error is only 0.38%. Thus the comparison of experimental values with the calculated frequencies shows a small error. From Table 3, for UCl_6 only the frequency of the IR active v_3 band of T_{1u} mode is reported from matrix-isolation IR experiments. As noted in the Table, the RPBE approach gives the good results compared with experimental values, and the differences are only 2.1962 cm^{-1} for 358 cm^{-1}, and 2.3962 cm^{-1} for 358.2 cm^{-1}. In the absence of any experimental information about UBr_6 and UI_6 we also predict the vibrational frequencies by using the same method. For the two molecules, we can only assume the deviations to be similar to those found in the case of UF_6 and UCl_6.

Table 2. Calculated vibrational frequencies of UF_6 (in cm^{-1}).

	method	v_1	v_2	v_3	v_4	v_5	v_6	Avg. error
	LDA	696.1482	578.2926	649.3758	173.4284	185.4451	136.9640	21.6632
scalar	BP	681.0371	554.0046	637.8682	176.9287	188.6464	137.0709	12.0440
	BLYP	672.0299	539.4155	629.3342	176.3054	187.8194	135.2047	7.2471
	RPBE	669.2797	533.8869	623.6415	181.4717	191.4623	139.7444	3.5123
	LDA	695.4783	577.6189	650.2430	174.0717	185.8665	136.4623	21.4900
scalar+	BP	680.3829	553.3345	638.7293	177.5686	189.0660	136.5736	11.8733
spin–orbit	BLYP	671.3798	538.7555	630.1846	176.9351	188.2282	134.7178	7.0731
	RPBE	668.6199	533.2180	624.5020	182.1084	191.8735	139.2524	3.2776
expt.[a]		667	534	626	186	200	143	

[a] McDowell *et al.*[3]

Table 3. Calculated vibrational frequencies of UCl_6 (in cm^{-1}).

	method	v_1	v_2	v_3	v_4	v_5	v_6
	LDA	387.5280	338.9911	386.6900	115.8429	123.2404	81.0991
scalar	BP	369.8990	318.6868	368.6664	116.8649	123.7843	81.3351
	BLYP	363.0975	311.8369	363.9037	116.1836	122.5149	79.9801
	RPBE	357.1037	306.4201	355.8038	115.9756	123.1640	81.0992
	LDA	386.8072	338.2958	387.5671	116.5046	123.6798	80.5764
scalar+	BP	369.1894	318.0060	367.5375	116.5227	124.2131	80.8162
spin–orbit	BLYP	362.3873	311.1470	361.7748	116.8293	122.9372	79.4765
	RPBE	356.4014	305.7435	355.6639	116.6319	123.5953	80.5884
expt.				358[a]			
				358.2[b]			

[a]Maier II *et al.*[4], [b]Hunt *et al.* [5]

Table 4. Calculated vibrational frequencies of UBr_6 (in cm^{-1}).

	method	v_1	v_2	v_3	v_4	v_5	v_6
	LDA	249.7461	194.9723	221.0289	78.9217	82.9904	49.3734
scalar	BP	232.1292	179.7578	204.5611	77.2754	81.4022	49.9711
	BLYP	229.2893	174.3493	199.8123	76.3713	80.8811	49.2584
	RPBE	219.5975	170.4607	194.9024	76.0921	81.0751	49.3996
	LDA	248.9727	194.2212	221.9527	79.6362	83.5216	48.7660
scalar+	BP	231.3603	179.0154	205.465	77.9765	81.9309	49.3687
spin–orbit	BLYP	228.5294	173.6104	200.7225	77.0680	81.3994	48.6695
	RPBE	218.8393	169.7238	195.8048	76.7900	81.5954	48.8058

Table 5. Calculated vibrational frequencies of UI_6 (in cm^{-1}).

	method	v_1	v_2	v_3	v_4	v_5	v_6
	LDA	189.8791	140.2647	151.9887	59.0224	63.8712	35.0985
scalar	BP	177.9823	127.8792	139.3476	57.8210	62.6238	35.4562
	BLYP	175.2444	123.1544	136.3645	57.0128	62.2013	34.9782
	RPBE	168.8972	120.6521	131.9145	56.4988	62.3132	35.1107
	LDA	188.8905	139.3724	153.2863	59.8547	64.5198	34.3666
scalar+	BP	177.0024	126.9978	140.5371	58.6469	62.9531	34.7304
spin–orbit	BLYP	174.2665	122.2736	137.5165	57.8317	62.8302	34.2604
	RPBE	167.9262	119.7732	133.0962	57.3198	62.9441	34.3860

3.3. Bonding energy analysis of U–X

The energy decomposition for U–X bonds in UX_6 molecules between X and UX_5 radical fragments has been analysed by using the program package ADF which is based on the methods of Morokuma[40,41] and Ziegler and Rauk.[42–44] The overall bond energy ΔE_e between the fragments UX_5 and X is given by the sum of ΔE_{prep} and ΔE_{int}, i.e.

$$\Delta E_e = \Delta E_{prep} + \Delta E_{int}. \quad (1)$$

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

$$\Delta E_{prep} = E_{total} \text{ (distorted fragments)} - E_{total} \text{ (fragments in the equilibrium structure)}, \quad (2)$$

$\Delta E_{\rm int}$ in Eq. (1) is the instantaneous interaction energy between the two distorted fragments in the molecule. This term can be further decomposed into three main contributions:

$$\Delta E_{\rm int} = \Delta E_{\rm elstat} + \Delta E_{\rm Pauli} + \Delta E_{\rm orb}, \qquad (3)$$

where $\Delta E_{\rm elstat}$ represents the electrostatic interaction energy between the fragments. The term $\Delta E_{\rm Pauli}$ is the Pauli repulsion energy that arises from the closed shell repulsion between both fragments. $\Delta E_{\rm Pauli}$ is calculated by enforcing the Kohn–Sham determinant of X_5U–X, which results from the superimposition of the fragments X and UX_5, to be orthonormal through antisymmetrization and renormalisation. The stabilising orbital interaction term $\Delta E_{\rm orb}$ is the term related to the stabilisation of the system when the densities of the the fragments X and UX_5 are allowed to relax. It contains charge transfer as well as polarisation. This method has been successfully applied to many systems.[45−47]

In the present paper, we try to understand the trends through the detailed analysis of the bonding mechanism in the compounds UX_6. The energy decomposition analyses of U–X bonds in the UX_6 molecules are summarised in Tables 6 and 7. These tables show the values of repulsive term $\Delta E_{\rm Pauli}$, attractive electrostatic term $\Delta E_{\rm elstat}$, orbital interaction term $\Delta E_{\rm orb}$, interaction energy term $\Delta E_{\rm int}$, and preparation energy term $\Delta E_{\rm prep}$, which are calculated by an RPBE DFT method in combination with both the scalar and scalar+spin–orbit relativistic methods with using the TZP basis set. In all systems, there is a net flow of electrons from the U to substituent X_5, resulting in a positive atomic charge on U according to both the VDD and the Hirshfeld method (see Tables 6 and 7).[48,49] In addition, we divide the $\Delta E_{\rm orb}$ term into $\Delta E_{\rm A1g}$, $\Delta E_{\rm g}$, $\Delta E_{\rm T1g}$, $\Delta E_{\rm T2g}$, $\Delta E_{\rm A2u}$, $\Delta E_{\rm T2u}$ and $\Delta E_{\rm T1u}$ in the Table 6. However, in Table 7 the $\Delta E_{\rm orb}$ term separates into $\Delta E_{\rm A1g}$, $\Delta E_{\rm g}$, $\Delta E_{\rm T1g}$, $\Delta E_{\rm T2g}$, $\Delta E_{\rm A2u}$, $\Delta E_{\rm T2u}$, $\Delta E_{\rm T1u}$ and $\Delta E_{\rm spin-orbit}$. From Table 7, we find that the calculated magnitudes of spin–orbit effect on the BDE of UX_6 (X=F, Cl, Br, and I) are found to be approximately −0.3198, −0.3218, −0.3609 and −0.4415 eV respectively. Tables 6 and 7 also show that there are strong Pauli repulsions between U and X atoms. The electrostatic attraction $\Delta E_{\rm elstat}$ is always smaller than the orbital interaction $\Delta E_{\rm orb}$. The calculated data show that BDE of U–F bonds are −3.0989 and −3.2558 eV from Table 6 and Table 7 respectively, which are in agreement with the observed values. In addition, we also find that the results of BDE of U–Cl are also in agreement with the experimental values.

Table 6. Energy decomposition analyses of U–X bonds in UX_6 molecules with the scalar relativistic method (in eV).

Term	X=F	X=Cl	X=Br	X=I
$\Delta E_{\rm A1g}$	–0.3580	–0.4458	–0.3658	–0.3452
$\Delta E_{\rm A2g}$	0.00	0.00	0.00	0.00
$\Delta E_{\rm g}$	–2.6009	–2.1325	–1.8937	–1.5788
$\Delta E_{\rm T1g}$	–0.8550	–0.6390	–0.5904	–0.5189
$\Delta E_{\rm T2g}$	–1.6634	–1.3840	–1.2393	–1.0217
$\Delta E_{\rm A2u}$	0.1766	0.1692	0.1726	0.1606
$\Delta E_{\rm Eu}$	0.00	0.00	0.00	0.00
$\Delta E_{\rm T2u}$	–0.5860	–0.3373	–0.2542	–0.1710
$\Delta E_{\rm T1u}$	–2.0690	–1.3990	–1.2178	–0.9854
$\Delta E_{\rm orb}$	–7.9557	–6.1684	–5.3886	–4.4604
$\Delta E_{\rm Pauli}$	6.7331	6.1066	5.6648	5.0034
$\Delta E_{\rm elstat}$	–1.8928	–2.1182	–2.2196	–2.1013
$\Delta E_{\rm int}$	–3.1154	–2.1800	–1.9434	–1.5583
$\Delta E_{\rm prep}$	0.0165	0.0180	0.0185	0.0216
ΔE(BDE)	–3.0989	–2.1620	–1.9249	–1.5367
Expt.	3.0355±0.0867[a]	2.1856		
Expt.	2.9921±0.2168[b]			
Expt.	3.1656[c]			
Hirshfeld (U)	0.99	0.48	0.34	0.20
VDD[‡] (U)	0.49	0.45	0.39	0.22

[‡]VDD stands for Voronoi deformation density.

[a]Hildenbrand and Lau[6], [b]Compton[7], [c]Nikitin and Tsirelnikov[8].

Table 7. Energy decomposition analyses of U–X bonds in UX_6 molecules with the spin–orbit relativistic method (in eV).

term	X=F	X=Cl	X=Br	X=I
$\Delta E_{\rm A1g}$	–0.3603	–0.4511	–0.3586	–0.3371
$\Delta E_{\rm A2g}$	0.00	0.00	0.00	0.00
$\Delta E_{\rm g}$	–2.6141	–2.1499	–1.7981	–1.5647
$\Delta E_{\rm T1g}$	–0.8556	–0.6391	–0.5795	–0.5102
$\Delta E_{\rm T2g}$	–1.6726	–1.4011	–1.1749	–1.0136
$\Delta E_{\rm A2u}$	0.1748	0.1666	0.1615	0.1475
$\Delta E_{\rm Eu}$	0.00	0.00	0.00	0.00
$\Delta E_{\rm T2u}$	–0.5950	–0.3442	–0.2326	–0.1670
$\Delta E_{\rm T1u}$	–1.9182	–1.2449	–0.9857	–0.7770
$\Delta E_{\rm spin-orbit}$	–0.3198	–0.3218	–0.3609	–0.4415
$\Delta E_{\rm orb}$	–8.1608	–6.3855	–5.3288	–4.6636
$\Delta E_{\rm Pauli}$	6.7972	6.1880	5.3288	4.9808
$\Delta E_{\rm elstat}$	–1.9099	–2.1458	–2.0707	–2.0918
$\Delta E_{\rm int}$	–3.2735	–2.3433	–2.0707	–1.7746
$\Delta E_{\rm prep}$	0.0177	0.0188	0.0204	0.0221
ΔE (BDE)	–3.2558	–2.3245	–2.0503	–1.7525
Expt.	3.0355±0.0867[a]	2.1856		
Expt.	2.9921±0.2168[b]			
Expt.	3.1656[c]			
Hirshfeld (U)	0.99	0.48	0.37	0.19
VDD (U)	0.49	0.45	0.41	0.22

[‡]VDD stands for Voronoi deformation density.

[a]Hildenbrand and Lau[6], [b]Compton[7], [c]Nikitin and Tsirelnikov[8].

4. Summary

We compare the performances of the widely used LDA and GGA functions (BP, BLYP and RPBE) for calculating the bond lengths and the vibrational frequencies of UX_6 with using the TZP basis set under two different levels of approximation: the scalar and the scalar+spin–orbit relativistic approximation. We find that the spin–orbit coupling has little effect on bond lengths and vibrational frequencies for closed shell UX_6. The LDA predicts shorter bond lengths and higher frequencies. The vibrational properties of UX_6 are well reproduced by the BP, BLYP and RPBE functions. However, the best match with experimental values is found in the RPBE method. For example, the calculated asymmetric stretching and bending modes (v_3 and v_4) of UF_6 molecule are in accordance with the experimental data within 2.3585 cm^{-1} and 4.5183 cm^{-1} for the scalar relativistic method, and within 1.4980 and 3.8916 cm^{-1} for the scalar+spin–orbit relativistic method. After the vibrational frequencies are obtained, the BDEs of UX_6 are investigated by using the RPBE method, thereby obtaining exact vibrational frequencies. Calculated data show that there are strong Pauli repulsions between X and UX_5 fragments. The electrostatic attractions are always smaller than the orbital interactions. The trend in U–X BDEs for the substituent X shows the order $UF_6 > UCl_6 > UBr_6 > UI_6$. In addition, the calculated magnitudes of spin–orbit effect on the BDE of UX_6 (X=F, Cl, Br, and I) are found to be approximately −0.3198, −0.3218, −0.3609 and −0.4415 eV respectively.

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