A density functional study of thorium tetrahalides

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The results of a study on the ground states of thorium tetrahalides using density functional theory are presented. The equilibrium geometries of ThX_4 (X = F, Cl, Br, I) have been optimized and their harmonic frequencies have been calculated. In the geometry optimizations the results were generated by using two different density functional programs, namely GAUSSIAN98 and MAGIC. Both local and non-local functionals were used. This allowed us to benchmark the MAGIC program and check the consistency of the theoretical predictions between different codes. Equilibrium structures, harmonic frequencies and zero-point energies were then calculated for a wider range of methods using GAUSSIAN98. Among these methods Hartree–Fock and Møller–Plesset second-order perturbation theory are included. All the calculated results are compared with experimental values where available. The frequencies of only the v_3 and v_4 vibrational modes have been measured for ThF_4 and only v_3 has been measured for $ThCl_4$, while no vibrational frequencies have been measured for $ThBr_4$ and ThI_4. It is thus important to obtain improved values for all the vibrational frequencies of these molecules. Comparison can then be made with existing values, most of which have been derived from empirical correlations with results from related lighter tetrahalide molecules.

1 Introduction

The equilibrium structures of the uranium and thorium tetrahalides have been the subject of many investigations over the last 40 years.[1-9] While it is clear that the thorium compounds are tetrahedral, considerable uncertainty exists for the uranium compounds with both tetrahedral and distorted tetrahedral geometries being suggested. Unfortunately, no definitive high resolution spectroscopic measurements have been performed on these compounds and existing experimental evidence is drawn from results of electron diffraction experiments and thermochemical treatment of torsion effusion vapor pressure studies.[6] Ref. 10 describes in detail the state-of-the-art of the experimental and theoretical research on these compounds. The situation for the thorium tetrahalides is much clearer than for the uranium tetrahalides. Experimental information from electron-diffraction measurements and thermochemical studies confirm the tetrahedral geometry for these molecules deduced in the first experimental investigations.[10]

Analysis of the torsion effusion vapor pressure results[6] was made using estimated vibrational frequencies that were available at that time. However, more recent gas-phase infrared studies on UCl_4, UF_4 and ThF_4 (ref. 10) showed that the frequencies of the bending modes of these molecules were much lower than the early estimates. Reliable vibrational frequencies of the uranium and thorium tetrahalides are important in evaluating entropies for different geometries and they should be compared with the experimentally derived entropies. While the equilibrium structures of the ThX_4 molecules are not in doubt, being established as tetrahedral, the equilibrium structures of the UX_4 molecules are not well established. The best

available estimates have been deduced from the second law of entropy of sublimation supported by computed entropies, derived from available vibrational frequencies.[6] Experimental work on thorium tetrahalides is currently being performed by Hildenbrand's group[10] and Dyke's group.[11]

In the present study, the equilibrium geometries of ThX_4 molecules in their ground states were determined with density functional theory (DFT) methods. At these geometries, the DFT harmonic vibrational frequencies were then computed, providing a test of the measured vibrational frequencies, and providing values for the other modes that have not yet been measured. Two DFT programs were used, namely GAUSSIAN98[12] and MAGIC.[13] Comparative calculations were performed at both the Hartree–Fock (HF) and Møller–Plesset (MP2) second-order perturbation levels of theory with the GAUSSIAN98 code.

In Section 2 the theoretical methods and computational details are described. Section 3 reports the results of the calculations and finally in Section 4 some conclusions are presented.

2 Theoretical methods and computational details

The newly developed MAGIC quantum chemistry code is aimed at providing a means of performing chemically accurate calculations on systems containing many atoms, some of which are heavy. It is described elsewhere,[13-19] but, briefly, it is a code based on the use of Gaussian basis sets that allows density functional calculations to be performed within the Kohn–Sham paradigm. MAGIC allows energies and optimized geometries to be calculated. In the MAGIC calculations

performed in this work, two functionals were used. The first functional was the local spin density approximation (LSDA) which includes uniform electron gas exchange[20] and the Vosko–Wilk–Nussair (VWN)[21] correlation functional. The second functional was the gradient-corrected BLYP functional which includes the uniform electron gas exchange, the Becke 88 correction to exchange[22] and the Lee–Yang–Parr correlation functional.[23]

MAGIC employs the RI–J method to calculate the Coulomb energy,[24] which is roughly an order of magnitude faster than the conventional approach. Auxiliary basis sets for fitting the density are required for this purpose. The auxiliary basis set of Ahlrichs et al.[24,25] was used on the halogen atoms and a "working auxiliary" basis set[26] was used on the thorium atom. The Gaussian and MAGIC approaches are thus not identical because of the difference by which the Coulomb energy is determined and this paper allows a comparison between the two different approaches.

In the MAGIC calculations the geometries of ThX_4 compounds were optimized without any symmetry restrictions. The gradient tolerance was set to 10^{-4} on the largest component of the Cartesian gradient in order to converge bond lengths to the third decimal and angles to the first decimal. An ultrafine grid was used, within the so-called Log3 scheme for the radial part of the grid by Mura and Knowles.[27]

Several functionals were tested in the GAUSSIAN98 calculations. The LSDA and BLYP calculations were repeated to benchmark the MAGIC code. Calculations using the B3LYP functional and HF method were also performed. Equilibrium geometries and harmonic frequencies were computed. Comparative geometry optimizations and harmonic frequency calculations were also performed using MP2.

Gaussian calculations were performed using the ultrafine (99, 590) grid having 99 radial shells and 590 angular points per shell, which is recommended for computing very low frequency modes. At the same time the weighting scheme of Becke has been used for numerical integrations and very tight thresholds have been enforced both for the self-consistent and optimization convergence criteria. The gradient tolerance was the default one in Gaussian which is set to be 10^{-6} on the largest component of the Cartesian gradient.

In both the GAUSSIAN98 and MAGIC calculations, the relativistic effects due to the high atomic number of the thorium atom are taken into account implicitly through the use of effective core potentials (ECPs) derived from high accuracy relativistic calculations on atoms. The energy-adjusted thorium ECPs of Küchle et al. were used for this purpose.[28] The accompanying basis sets of the thorium ECPs were used to describe the valence electron density.[28] This basis includes 30 valence electrons on Th. This was augmented by two g functions with exponents of 0.52 and 0.22 to describe the valence electron density. On the fluorine and chlorine atoms the 6-311G** (ref. 29) all-electron basis set was used. On bromine and iodine the energy-adjusted ECPs of Bergner et al.[30] were used. The B3LYP calculations on ThF_4 and $ThCl_4$ were repeated also by using the energy-adjusted ECPs on the halogens of Bergner et al.[30] A polarization d function was added to the halogen basis with the exponent of 1.75, 0.75, 0.389 and 0.266 for F, Cl, Br and I, respectively. The accompanying basis sets of the Br and I ECPs were used to describe the valence electron density[28] and they include seven valence electrons on the halogens. The basis sets used are Spherical. The convergence of the results with the basis set was investigated by a number of B3LYP computations on ThF_4. These results are discussed in the next section.

3 Results and discussion

The full optimization predicts a tetrahedral structure for all the thorium tetrahalides with both GAUSSIAN98 and MAGIC. This is confirmed by the harmonic frequency calculations, which give real harmonic frequencies for all the thorium tetrahalides at a tetrahedral geometry.

In Table 1 a comparison between GAUSSIAN98 (standard DFT) and MAGIC (DFT with RI–J) results is reported. The equilibrium distances Th–X for the tetrahedral structures have been obtained at the LSDA and BLYP level of theory. An overall agreement between the two sets of results can be seen. Differences are at the level of the convergence tolerance in the optimization used in the MAGIC calculations. The experimental equilibrium bond distances are those listed in ref. 6 and 10 and are obtained from gas-phase electron diffraction measurements on the thorium tetrahalides where the experimental error is at least ± 0.005 Å.

In Tables 2–5 the DFT, HF and MP2 equilibrium bond distances, harmonic frequencies and zero-point energies for ThF_4, $ThCl_4$, $ThBr_4$ and ThI_4, respectively, are reported.

Inspection of Table 2 shows that for the equilibrium bond length of ThF_4, the HF value is too low, as expected, with all the density functional values also being too low, apart from the BLYP result which is slightly too high. The B3LYP bond length with the ECPs basis on fluorine is slightly shorter than the bond length with the all electron basis 6-311G** on fluorine. The MP2 value for the equilibrium bond distance is very close to the B3LYP and HF values. As regards the frequencies, only the v_3 (t_2) and v_4 (t_2) frequencies have been measured for ThF_4, as these are the only modes which are infrared active. The $v_1(a_1)$ mode was estimated from a correlation between v_1 and v_3 in a series of lighter tetrahedral tetrafluoride molecules. Similarly, $v_2(e)$ was estimated from a correlation between v_2 and the M–F bond length in these tetrafluorides. From these correlations, the measured values of v_3, v_4 and R(Th–F) were used to estimate v_2 and v_1 in ThF_4. If initially only the computed frequency values are considered, overall the MP2 frequencies are slightly lower than the HF frequencies, and slightly higher than the B3LYP and BLYP frequencies.

The basis set convergence was investigated in some B3LYP calculations on ThF_4. The inclusion of g orbitals on thorium increases the Th–F equilibrium bond distance by 0.007 Å and on going from a double to a triple zeta basis on the fluorine the Th–F equilibrium bond distance increases by 0.01 Å. In agreement with previous studies,[31,32] doubling the polarization functions and addition of diffuse functions or f functions

Table 1 GAUSSIAN98 (standard DFT) vs. MAGIC (DFT with RI–J) results[a]

	$R_{Th–X}$	
ThF_4	GAUSSIAN98	MAGIC
LSDA	2.1067	2.103
BLYP	2.1433	2.140
Experiment	2.14	
$ThCl_4$	GAUSSIAN98	MAGIC
LSDA	2.5433	2.544
BLYP	2.5966	2.598
Experiment	2.567	
$ThBr_4$	GAUSSIAN98	MAGIC
LSDA	2.7049	2.706
BLYP	2.7545	2.763
Experiment	2.73	
ThI_4	GAUSSIAN98	MAGIC
LSDA	2.9242	2.926
BLYP	2.9795	2.981
Experiment	2.91	

[a] Th–X equilibrium distance (Å) in tetrahedral ThX_4, computed using LSDA and BLYP. Basis sets used: ECPs on thorium;[28] 6-311G** on fluorine and chlorine; ECPs on bromine and iodine.[30] Experimental values from refs. 6 and 10 are affected by an error which is at least ± 0.005 Å.

Table 2 ThF$_4$: equilibrium distance, harmonic frequencies (their relative intensities in parentheses), and zero-point energy[a]

	$R_{\text{Th–F}}$/Å	$v_1(a_1)$/cm^{-1}	$v_2(e)$/cm^{-1}	$v_3(t_2)$/cm^{-1}	$v_4(t_2)$/cm^{-1}	ZPE/kcal mol^{-1}
B3LYP	2.1300	581.6(0)	109.3(0)	533.6(218.0)	106.2(32.7)	3.89
ECPs on F	2.1267	580.9(0)	108.5(0)	528.6(211.8)	106.4(33.9)	3.86
BLYP	2.1433	562.7(0)	102.9(0)	519.3(170.4)	99.3(29.9)	3.75
LSDA	2.1067	593.2(0)	104.3(0)	548.2(179.0)	99.1(28.0)	3.92
HF	2.1340	595.3(0)	126.5(0)	544.2(218.0)	126.7(43.5)	4.09
MP2	2.1304	592.6(0)	116.7(0)	546.8(192.8)	113.6(31.9)	4.01
Experiment	2.14	[618] ± 10	[121] ± 5	520 ± 3	116 ± 3	

[a] Basis set: ECPs on thorium,[28] 6-311G** on fluorine. The B3LYP calculation has been repeated by using ECPs on fluorine.[30] Experimental values from ref. 10. Values in [ ] have been extrapolated.

has a negligible effect in DFT, while the role of high angular momentum basis functions is significantly larger for methods such as MP2. For instance, removal of Th g functions increases the bond length of ThF$_4$ by 0.02 Å at the MP2 level. However, since this paper is essentially a DFT study, we have reached convergence at DFT level with the basis set.

For ThCl$_4$ similar comparisons can be made, but only the Th–Cl bond length and v_3 have been measured. As regards the bond length, the HF, BLYP and B3LYP values are slightly higher than the experimental value, while the LSDA and MP2 values are slightly lower. Comparing the R(Th–Cl) and v_3 measured values in Table 3 with the computed values, the closest results to the experimental values are the B3LYP results. The MP2 value for v_3 is too high and overall MP2

frequencies are larger than B3LYP and BLYP frequencies. The use of a ECPs basis on chlorine, instead of a 6-311G** basis, has little effect on the results.

For ThBr$_4$ and ThI$_4$ only the equilibrium bond lengths have been measured. For ThBr$_4$ (Table 4) the B3LYP equilibrium bond distance is the closest result to the experimental value, the BLYP and HF values being too high, and the LSDA and MP2 too low. For ThI$_4$ (Table 5), the LSDA equilibrium bond distance is the closest to the experimental value.

In order to investigate the overall agreement of the methods used in this study with experimental values, we compared the computed and experimental values for the quantities that have been measured, namely the Th–halogen equilibrium bond distance for the four molecules, v_3 and v_4 for ThF$_4$, and v_3 for

Table 3 ThCl$_4$: equilibrium distance, harmonic frequencies (their relative intensities in parentheses), and zero-point energy[a]

	$R_{\text{Th–Cl}}$/Å	$v_1(a_1)$/cm^{-1}	$v_2(e)$/cm^{-1}	$v_3(t_2)$/cm^{-1}	$v_4(t_2)$/cm^{-1}	ZPE/kcal mol^{-1}
B3LYP	2.5802	340.3(0)	62.0(0)	330.4(119.3)	61.8(8.6)	2.35
ECPs on Cl	2.5834	339.1(0)	63.2(0)	330.5(114.4)	62.9(8.8)	2.35
BLYP	2.5966	325.6(0)	57.2(0)	318.8(107.3)	56.9(8.0)	2.24
LSDA	2.5433	348.8(0)	52.8(0)	344.6(107.5)	47.0(7.0)	2.33
HF	2.5964	351.4(0)	72.9(0)	337.6(140.2)	75.4(12.1)	2.48
MP2	2.5474	368.9(0)	72.3(0)	364.0(122.6)	67.4(6.9)	2.58
Experiment	2.567	[325] ± 10	[60] ± 5	335 ± 3	[70] ± 10	

[a] Basis set: ECPs on thorium,[28] 6-311G** on chlorine. The B3LYP calculation has been repeated by using ECPs on chlorine.[30] Experimental values from ref. 10. Values in [ ] have been extrapolated.

Table 4 ThBr$_4$: equilibrium distance, harmonic frequencies (their relative intensities in parentheses), and zero-point energy[a]

	$R_{\text{Th–Br}}$/Å	$v_1(a_1)$/cm^{-1}	$v_2(e)$/cm^{-1}	$v_3(t_2)$/cm^{-1}	$v_4(t_2)$/cm^{-1}	ZPE/kcal mol^{-1}
B3LYP	2.7377	207.8(0)	40.4(0)	227.0(60.1)	44.6(2.5)	1.58
BLYP	2.7545	198.7(0)	37.6(0)	219.1(53.8)	41.8(2.4)	1.51
LSDA	2.7049	211.9(0)	34.4(0)	236.1(51.4)	34.7(1.9)	1.56
HF	2.7569	213.8(0)	45.9(0)	231.1(72.2)	51.9(3.8)	1.65
MP2	2.7096	223.0(0)	44.0(0)	247.8(61.1)	44.9(2.0)	1.70
Experiment	2.73	[220] ± 10	[50] ± 5	[215] ± 15	[40] ± 10	

[a] Basis set: ECPs on thorium[28] and on bromine.[30] Experimental values from ref. 10. Values in [ ] have been extrapolated.

Table 5 ThI$_4$: equilibrium distance, harmonic frequencies (their relative intensities in parentheses), and zero-point energy[a]

	$R_{\text{Th–I}}$/Å	$v_1(a_1)$/cm^{-1}	$v_2(e)$/cm^{-1}	$v_3(t_2)$/cm^{-1}	$v_4(t_2)$/cm^{-1}	ZPE/kcal mol^{-1}
B3LYP	2.9608	147.6(0)	29.0(0)	179.6(40.7)	33.9(0.8)	1.21
BLYP	2.9795	140.6(0)	26.9(0)	172.9(35.8)	31.7(0.8)	1.16
LSDA	2.9242	150.6(0)	23.8(0)	187.4(32.8)	24.9(0.6)	1.19
HF	2.9884	151.2(0)	33.3(0)	181.5(50.2)	39.8(1.3)	1.26
MP2	2.9245	159.2(0)	32.2(0)	197.5(40.15)	33.9(0.4)	1.31
Experiment	2.91	[145] ± 10	[25] ± 5	[120] ± 15	[20] ± 10	

[a] Basis set: ECPs on thorium,[28] and iodine.[30] Experimental values from ref. 10. Values in [ ] have been extrapolated.

ThCl$_4$. In each case an error was estimated as the difference between the calculated and experimental values, divided by the total calculated value and a percentage error estimated in such a way is derived for all methods. As regards the B3LYP results for ThF$_4$ and ThCl$_4$ the values obtained by using the ECPs on the halogen have not been considered because they are very similar to the corresponding B3LYP results with the 6-311G** basis, which are considered in this statistical analysis. It can be observed that all the methods perform similarly in the equilibrium distance calculation. The percentage error varies between a minimum of 0.15% in the BLYP Th–F equilibrium distance and a maximum of 2.62% in the HF Th–I equilibrium distance. MP2 gives the lowest average error for bond length, 0.62%, followed by B3LYP, 0.75%. The errors in the frequency calculations are higher than in the bond distances, with a B3LYP lowest average error of 4.39% (the MP2 average error in the frequency calculations is 4.99%). It can thus be stated that on average B3LYP is the method that performs better, even though one has to bear in mind that this statistical analysis has been performed on a limited number of data, due to the limited amount of available experimental information.

This suggests that all methods give a better estimation of the harmonic frequencies than the empirically extrapolated values, and in future thermodynamic calculations it would be more reliable to use the B3LYP values than the empirically extrapolated values. Recommended frequencies are therefore the B3LYP values shown in Tables 2–5, although this study has highlighted the need for further experimental measurements on the vibrational fundamentals of these molecules (e.g. v_3 and v_4 by infrared spectroscopy and v_1 and v_4 by Raman spectroscopy). For example, for ThF$_4$ the B3LYP computed values of 528 and 109 cm^{-1} obtained in this work are more reliable than the empirically extrapolated values of 618 ± 10 and 121 ± 5 cm^{-1}.

The experimental results, derived from vapor phase electron diffraction measurements on a high temperature effusive beam, do not strictly correspond to the equilibrium values, since they include vibrational averaging. In order to estimate this effect, the difference between the equilibrium bond distance, R_e and the bond distance in the zeroth vibrational level, R_0, has been computed for all thorium tetrahalides. A variational numerical procedure which takes into account the anharmonic a$_1$ stretching has been followed. This procedure is described in ref. 33. The results of these computations show that this effect can be neglected for these tetrahalides, since it leads to a lengthening of the Th–X bond of 0.0008 Å at most.

4 Conclusions

This study has led to improved values of v_1, v_2, v_3 and v_4 for the ThX$_4$ molecules, compared with empirically extrapolated values from correlations observed for other tetrahalides. In ThBr$_4$ and ThI$_4$ none of the vibrational frequencies has been measured, whereas in ThCl$_4$ and ThF$_4$ only one (v_3) and two (v_3 and v_4) frequencies have been measured, respectively.

While the equilibrium geometries of the thorium tetrahalides are well established as tetrahedral, the equilibrium geometries of the uranium tetrahalides are less certain. For the uranium tetrahalides the following frequencies have been measured: UF$_4$ (v_3 and v_4) UCl$_4$ (v_3 and v_4), UBr$_4$ (v_3). As stated earlier, deduction of the structure of each molecule from the experimental entropy of sublimation depends on a knowledge of the frequencies of all the normal modes. It is proposed therefore to extend this work to compute the equilibrium structures of the UX$_4$ molecules and their vibrational frequencies, and this work is currently in progress. However, since UF$_4$ is an open shell multiconfigurational system, a theoretical approach able to handle this type of system has to be used.

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