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The vibrational frequencies, molecular geometry and thermodynamic properties of the actinide tetrahalides

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Abstract

The molecular structure of a number of actinide tetrahalides is deduced from a thermochemical analysis of vapour pressure measurements. For this analysis a set of consistent spectroscopic data and molecular constants is presented based on recent results of infrared spectroscopic measurements for UCl_4, UF_4 and ThF_4, that are discussed briefly, and empirical correlations for MX_4 molecules. The results offer no evidence for deviations from a tetrahedral symmetry. © 1998 Elsevier Science S.A.

Keywords: Actinide tetrahalides; Vibrational frequencies; Molecular geometry

1. Introduction

During more than 40 years the molecular structure of the actinide tetrahalides has been the subject of discussion. The first experimental electron diffraction studies for the thorium as well as the uranium tetrahalides date from 1958 and were interpreted as regular tetrahedral geometries [1]. Since that time, a large number of experimental and theoretical studies have been performed. These indicated a tetrahedral geometry for the thorium tetrahalides but in many cases suggested a distorted tetrahedral geometry for the uranium tetrahalides, which is generally explained by Jahn–Teller distortion as a result of the f^2 electronic configuration of U^{4+}.

A distorted tetrahedral geometry was also deduced from thermochemical analyses of torsion–effusion vapour pressure studies [2]: the difference between the total entropy evaluated from the second-law entropy of sublimation and the condensed phase entropy, and the entropy calculated from the molecular parameters for the T_d geometry (symmetry number $\sigma=12$) could be removed by lowering the molecular symmetry to C_{2v} ($\sigma=2$). These thermochemical analyses were made using entropies of the gases calculated from estimated frequencies that were generally accepted at that time. However, recent infrared spectroscopic [3–6] studies of UCl_4, UF_4, and ThF_4 in the gas phase revealed that the bending modes of these molecules occur at much lower wavenumbers than the estimates have suggested, as we will discuss in this paper. This difference justifies a re-analysis of the calculated and experimental entropies of the uranium tetrahalides in particular and the actinide tetrahalides in general, which is the goal of the present paper.

2. The tetrahalides of uranium

The infrared spectroscopic measurements of UF_4 and UCl_4 in the gas phase that were performed at ECN [3–5] yielded for the asymmetric bending frequencies $\nu_4=114$ cm^{-1} and $\nu_4=71.7$ cm^{-1}, respectively. These values are considerably lower than the estimated ones which have been generally used in literature, 160 cm^{-1} for UF_4 [7] and ~115 cm^{-1} for UCl_4 [8].

In addition to the ν_4 asymmetric bending bands, the ν_3 asymmetric stretching bands were observed in the infrared spectra of UF_4 and UCl_4 [3–5]. Based on the infrared selection rules, this would imply a tetrahedral structure. However, at the temperatures of the measurements the absorption bands are broad so overlap of two close-lying bands cannot be excluded. Therefore the results of the infrared spectroscopy do not present sufficient proof for the tetrahedral geometry of these molecules. Gas-phase electron diffraction (GED) is a more adequate technique.

The results of the first GED studies for the uranium

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tetrahalides were interpreted as a regular tetrahedral structure (T_d) [1,9], but subsequent studies by the same technique suggested a distorted tetrahedral structure for UF_4, UCl_4 as well as UBr_4 [10–12]. This information is, however, obtained by comparing the results of least-squares refinements on different symmetry models and the 'best fit' does not necessarily represent the equilibrium geometry. This was discussed by Haaland et al. [3,4] who argued that the better fit of the C_{2v} model for UCl_4 is not statistically significant because a C_{2v} model has more adjustable parameters than a T_d model. Similar conclusions were drawn from the latest GED study on UF_4 by Girichev et al. reported in [5].

The recommended values for the molecular parameters of UF_4 and UCl_4 listed in Table 1 have been used to calculate the entropies using a rigid-rotor/harmonic oscillator approximation. When the calculated entropies are compared to the experimental entropies derived from thermochemical measurements, it is clear that the discrepancy between experimental and calculated entropies noted before [2] is removed, as is shown in Table 2. The experimental values were evaluated from second-law entropies of sublimation from torsion–effusion vapour pressure measurements performed at SRI, combined with the condensed phase entropies evaluated by Fuger et al. [15] from calorimetric measurements. The experimental values for the bending frequencies lead to a change in the calculated entropy ($1R$–$2R$) which is of the same magnitude as the lowering of the symmetry from T_d to C_{2v} ($R \ln (12/2) = 1.8R$).

Table 2
Comparison of calculated entropies and experimental ones for the actinide tetrahalides

Compound	T/K	$S°(T)$/J K^{-1} mol^{-1}		Reference
		Exp.	Calc.^{a}	
UF_4	1100	504±3	498±4	[19]
UCl_4	700	500±3	502±3	[20]
UBr_4	700	547±8	546±10	[20]
ThF_4	1100	478±3	484±3	[21]
$ThCl_4$	700	489±8	490±4	[22]
$ThBr_4$	700	535±8	538±10	[23]
ThI_4	700	571±12	596±18	[20]
NpF_4	900	465±10	477±4	[27]
$NpCl_4$	700	513±10	504±4	[28]
$PuCl_4$	850	523±10	529±6	[29]

[a] $p^0 = 10^5$ Pa.

Based on empirical correlations (Fig. 1) we have estimated a new set of molecular parameters for UBr_4 and UI_4, listed in Table 1. The comparison of calculated and experimental entropies of UBr_4 is included in Table 2. The

Table 1
The molecular parameters for the gaseous uranium tetrahalides

Molecule	r(U–X)^{a}/pm	$I_A I_B I_C$/g^3 cm^6	ν_i (degeneracy)^{b}/cm^{-1}	ϵ_i (degeneracy)/cm^{-1}
UF_4	205.9^{c}	4.537×10^{-113}	*625, 123(2),* 539(3)^{c}, 114(3)^{c}	0(3), *500(2), 2000(3), 3000(1), 4000(5)*
UCl_4	250.6^{c}	9.583×10^{-112}	327^{d}, 62(2)^{d}, 337(3)^{d}, 72(3)^{d}	0(3), 710(2), 1700(3), 2500(1), 4200(5)^{e}
UBr_4	269.3^{f}	1.690×10^{-110}	*220, 50(2),* 233(3)^{g}, *45(3)*	0(3), *710(2), 1700(3), 2500(1), 4200(5)*
UI_4^{h}	*285*	9.509×10^{-110}	*150, 30(2), 150(3), 25(3)*	0(3), *710(2), 1700(3), 2500(1), 4200(5)*
ThF_4	214^{i}	5.718×10^{-113}	*618, 121(2),* 520(3),^{j} 116(3)^{k}	0(1)
$ThCl_4$	256.7^{l}	1.107×10^{-111}	*325, 60(2),* 335(3),^{j} *70(3)*	0(1)
$ThBr_4$	*273*	1.834×10^{-110}	*220, 50(2), 215(3), 40(3)*	0(1)
ThI_4	*291*	1.078×10^{-109}	*145, 25(2), 120(3), 20(3)*	0(1)
NpF_4	*204*	4.291×10^{-113}	*635, 125(2), 560(3), 120(3)*	0(6), *400(4)*
$NpCl_4$	*249*	9.221×10^{-112}	*340, 80(2), 330(3), 70(3)*	0(6), *400(4)*
PuF_4	*203*	4.167×10^{-113}	*635, 125(2), 565(3), 120(3)*	0(5), *500(6), 2000(25)*
$PuCl_4$	*248*	9.001×10^{-112}	*340, 80(2), 335(3), 70(3)*	0(5), *500(6), 2000(25)*
AmF_4	*202*	4.045×10^{-113}	*640, 125(2), 570(3), 120(3)*	0(8), *800(6), 3000(12)*

(T_d symmetry, $\sigma = 12$); internuclear distance r, product of moments of inertia, vibrational frequency ν, and electronic energy level ϵ; estimated values in italics.

[a] For the calculation of $I_A I_B I_C$ the r_g distance is used, which is obtained from the approximation $r_g = r_a + l^2/r_a$, where r_a is the effective internuclear distance from GED and l is the mean vibrational amplitude [13].

[b] For the experimental values the uncertainty is ±3 cm^{-1}; for the estimated values the uncertainty is ±15 cm^{-1} for ν_3, ±10 cm^{-1} for ν_1 and ν_4, and ±5 cm^{-1} for ν_2.

[c] [5], GED measurements ($r_a = 205.6$ pm, $l = 7.6$ pm) and gas-phase infrared spectroscopy.

[d] [3], GED measurements ($r_a = 250.3$ pm, $l = 8.9$ pm), density functional calculations (ν_1 and ν_2) and gas-phase infrared spectroscopy (ν_3 and ν_4).

[e] Electronic levels for UCl_4 are from [8] and are a simplification of the results in [14].

[f] [16], GED measurements ($r_a = 268.1$ pm, $l = 18.1$ pm). Although these values were obtained for a C_{2v} structure we adopt this value and because only one U–Br distance was adjusted.

[g] [17], gas-phase infrared spectroscopy.

[h] The value reported in [18], 297.5 pm, does not fit the general trend in MX_4 molecules. It was obtained for a C_{2v} structure, but it should be close to that of a T_d structure since only one U–I distance was adjusted (as is the case for UBr_4).

[i] [10], GED measurements ($r_a = 214$ pm, $l = 9$ pm).

[j] [26], gas-phase infrared spectroscopy.

[k] [6], gas-phase infrared spectroscopy.

[l] [24], GED measurements.

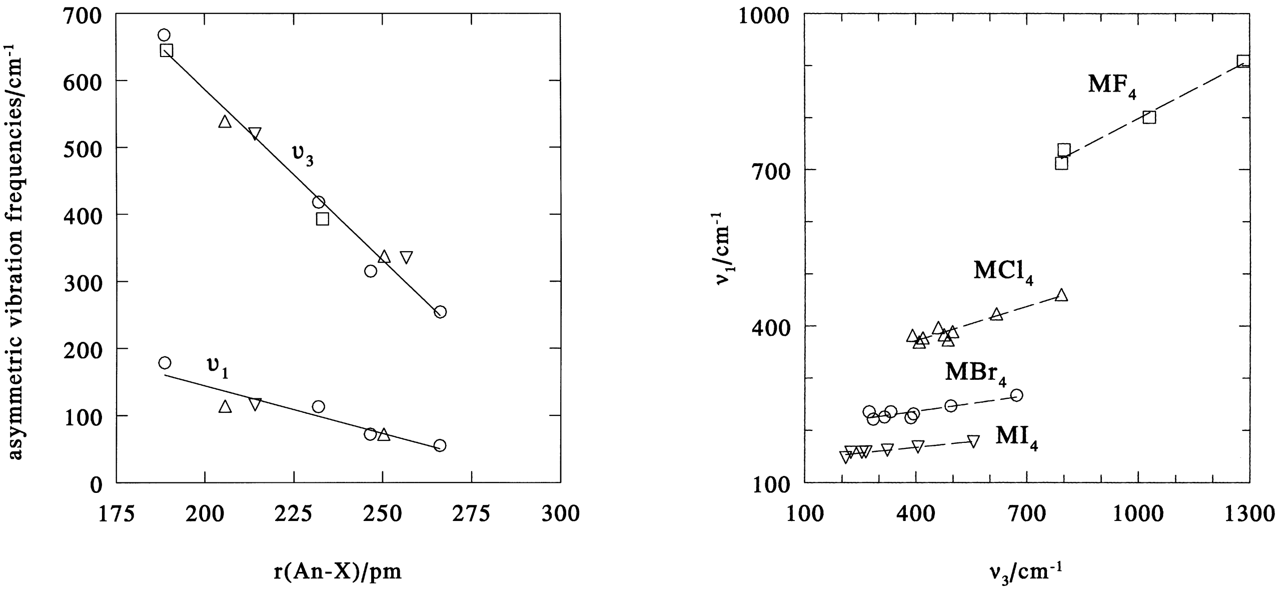

Fig. 1. Empirical correlations used for the estimation of the vibrational frequencies of the tetrahedral AnX_4 molecules. The relation between the internuclear distance M–X and the asymmetric vibration bands (left); the relation between the symmetric and asymmetric stretching fundamentals (right); M=C, Si, Ti, Zr, Hf, U.

results are consistent with a tetrahedral geometry for this molecule also, but it should be noted that the experimental entropy of UBr_4 is considerably more uncertain because only an estimate of the condensed phase entropy is available [15]. No experimental entropy data are given for UI_4 because of uncertainties about the nature of the sublimation/decomposition process.

3. The tetrahalides of thorium

The situation for the thorium tetrahalides is much clearer. Experimental information from electron-diffraction measurements [10,24] and thermochemical studies [21,22] confirm the tetrahedral geometry for these molecules deduced in the first experimental investigations [9]. However, the values for the vibrational frequencies of the thorium tetrahalides that were used in the thermochemical analyses [2,19,20] were estimates by Rand [25], which seem to be in error in view of the experimental results for the uranium compounds.

Using infrared spectroscopy the ν_4 fundamental of the ThF_4 molecule was found as a low intensity band at 116 cm^{-1} [6], which is very close to the value (520 cm^{-1}) reported for UF_4. In combination with the ν_3 value reported by Büchler et al. [26] we estimate $\nu_1=618$ cm^{-1} and $\nu_2=121$ cm^{-1} for ThF_4, using the empirical correlation shown in Fig. 1. These values differ significantly from the estimates by Rand [25] who suggested $\nu_1=555$ cm^{-1}, $\nu_2=145$ cm^{-1} and $\nu_4=155$ cm^{-1}.

The resulting entropy comparisons in Table 2 show that the new frequency assignment for ThF_4 remains compatible with tetrahedral symmetry, as are the newly estimated frequencies of the chloride and the bromide (Table 1). Again, the experimental entropy of ThF_4 is known more accurately because the condensed phase entropy is derived from calorimetric measurements, while the others are based on estimates [15]. For ThI_4, however, a significant discrepancy between the experimental and calculated entropy is observed, which most likely originates from the fact that the bending bands were estimated in a relatively low wavenumber range in which small changes in the frequencies introduce relatively large changes in the calculated entropy. However, to match the experimental entropy the values $\nu_4=50$ cm^{-1} and $\nu_2=40$ cm^{-1} are required for the bending frequencies, which is not consistent with the general trend (see Fig. 1).

4. The tetrahalides of the transuranium elements

Experimental data for the molecular parameters for the tetrahalides of other actinide elements are lacking. Based on the results for the tetrahalides of uranium and thorium and the empirical correlations discussed above, we have estimated the molecular properties of NpF_4, $NpCl_4$, PuF_4, $PuCl_4$ and AmF_4, assuming a tetrahedral geometry. These are presented in Table 1.

Vapour pressure studies indicate that the NpF_4 and $NpCl_4$ molecules are stable in the gas-phase above the condensed phase and experimental entropies derived from second-law treatment of the vapour pressure data are given in Table 2. The data for the compounds in the solid state are, however, much less well-known than those of the tetrahalides of thorium and uranium [15], leading to much larger uncertainties in the experimental entropies that can be derived from the results. Anyway, the experimental and calculated entropies agree within the limits of uncertainty, giving no indications for Jahn–Teller distortion of the tetrahedral geometry for the neptunium tetrahalides.

The vapour pressure studies show that PuF_4, $PuCl_4$ and AmF_4 partly disproportionate, possibly due to the interaction with traces of oxygen and/or water and no reliable second-law entropies can be derived. For $PuCl_4$ additional information can be obtained from the study by Benz [29] who measured the equilibrium constant of the reaction

$$PuCl_3(s) + \tfrac{1}{2}Cl_2(g) = PuCl_4(g)$$

for which he obtained $\Delta_r S°(850\ K) = 118\ J\,K^{-1}\,mol^{-1}$. This value leads to $S°(850\ K) = 522\ J\,K^{-1}\,mol^{-1}$, in acceptable agreement with the calculated value $S°(850\ K) = 533\ J\,K^{-1}\,mol^{-1}$.

5. Conclusions and summary

After more than 40 years the uncertainty about the geometry of the uranium tetrahalides seems to be resolved. The determination of the vibration frequencies of UF_4 and UCl_4 by high-temperature infrared spectroscopy has been an important achievement in this respect and has helped in obtaining more reliable estimates for unobserved vibration bands. When applied in the thermochemical analysis of vapour pressure measurements, the new spectroscopic data and assigned molecular constants for the uranium tetrahalides offer no evidence for deviations from tetrahedral symmetry.

Analysis of the vapour pressure data also confirm the tetrahedral symmetry of the thorium tetrahalides, though the results of spectroscopic measurements for ThF_4 made a significant adjustment of the molecular parameters necessary. For the transuranium elements a comparison of experimental and calculated entropies can only be made for NpF_4, $NpCl_4$ and $PuCl_4$. Again the data are consistent with a tetrahedral structure.

All told, only the entropy comparisons for UF_4, UCl_4, and ThF_4 (where experimental entropies of the solids are available) can be considered as fully definitive; there the evidence is undeniable. Final conclusions on the other tetrahalides, where uncertainties may be larger than the stated 8 $JK^{-1}\,mol^{-1}$, must await experimental entropy data on the solid tetrahalide phases, for which there is no satisfactory substitute.

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