The Vibrational Spectra of some Tetrachlorides in Rare Gas Matrices with particular Reference to the Molecular Shapes of $ThCl_4$ and UCl_4

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Infrared spectra of tin, lead, hafnium, thorium, and uranium tetrachlorides isolated in inert gas matrices are reported. The results obtained for the tin, lead, and hafnium compounds follow the expected isotope patterns for a tetrahedral molecule except for the observation of additional weak features to high frequency of the all-^{35}Cl isotopomers. By contrast for thorium tetrachloride the observed spectrum is not characteristic of a T_d molecule but can be fitted to a species with C_{2v} symmetry. Similar results (although less detailed) were obtained for uranium tetrachloride.

The molecular shapes of many metal halides as discrete monomers (MX_4) is in doubt. For the (non-transition) elements of the first two rows of the Periodic Table, or where there is a closed d^{10} shell, the molecular structures of the halides appear to follow the simple Sidgwick and Powell rules.† By contrast for d^n and f^n systems the picture is much less clear. The experimental data available on MX_2 and MX_3 species (X = Cl or F) have been summarised by Drake and Rosenblatt.[1] However, the techniques used to study structures (electric dipole deflection in a molecular beam; i.r. and Raman spectra of matrix isolated species; electron spin resonance of matrix isolated species; electron diffraction of gases) are all open to criticism. We are interested in rotational analysis of spectra obtained from such species in a seeded molecular beam. Matrix isolation spectroscopy is a useful preamble to such detailed experiments. One of the most well documented (and spectacular) results of such experiments to date is the proposed T-shaped structure for uranium trioxide in an argon matrix.[2] It is also interesting to note that geometries predicted from calculation appear to show increasing reliability for the heavier elements.[3] Matrix isolation spectroscopy has been used extensively to study oxide species using ^{16}O–^{18}O partial substitution to assign the point group. Much less use has been made of the naturally occurring isotopes of chlorine (or sulphur) for studying equivalence or inequivalence of ligands or matrix site effects. We have recently examined a variety of heavy-metal chlorides using i.r. spectroscopy of the matrix isolated species. The purpose of this paper is to present our results on the tetrachlorides.

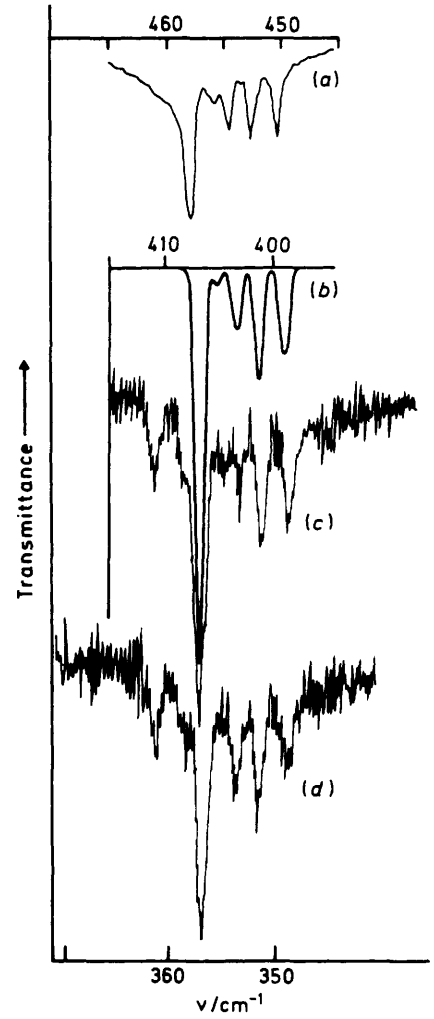

Figure 1. The i.r. spectra of some d^{10} tetrachlorides isolated in argon matrices: (*a*) $^{74}GeCl_4$ (from Königer *et al.*[4]), (*b*) calculated spectrum for $^{124}SnCl_4$, (*c*) $^{124}SnCl_4$, and (*d*) $PbCl_4$

Results and Discussion

Regular Tetrahedral Tetrachlorides.—Figure 1 shows the i.r. spectra of the d^{10} tetrachlorides of germanium, tin, and lead in an argon matrix. (In all cases chlorine was present in natural abundance, but to improve the quality of the spectra monoisotopic germanium and tin were used.) The spectrum of germanium tetrachloride is taken from the work of Königer *et. al.*[4]

These spectra can all be interpreted on the basis of a monomeric tetrachloride with tetrahedral symmetry. The only anomaly observed is that for the tetrachlorides of tin[5] and lead, where, one, or occasionally two, weak bands are found in the i.r. spectrum to higher frequency of the ' all-^{35}Cl ' isotopomer (Table 1). It is of interest to describe briefly the principal features of these spectra as this will aid in the discussion of the more complex spectra. A Raman spectrum of lead tetrachloride isolated in a nitrogen matrix gave the frequency difference $\nu_3 - \nu_1$ equal to 19.5 cm^{-1}. This is similar to the value found by Clark and Hunter[6] for solid lead tetrachloride at 80 K (24.1 cm^{-1}). In the following account as a first approximation any perturbation of components of ν_3 by components of ν_1 is ignored. The ' all-^{35}Cl ' and ' all-^{37}Cl ' isotopomers retain T_d symmetry. The $^{35}Cl^{37}Cl_3$ and $^{35}Cl_3{}^{37}Cl$ species are lowered in symmetry to C_{3v}, while the single species $^{35}Cl_2{}^{37}Cl_2$ is of C_{2v} symmetry. Note that for the C_{3v}

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† The case of XeF_6 is exceptional.

Table 1. Observed i.r. spectra and calculated (T_d) frequencies (cm^{-1}) for the tetrachlorides of tin, lead, and hafnium isolated in argon or nitrogen matrices

$^{124}SnCl_4$		$PbCl_4$		$HfCl_4$				$HfCl_4$		
Obs. (argon)	Calc.[a]	Obs. (argon)	Calc.[b]	Obs. (nitrogen)	Obs. (argon)	Calc.[c]	Assignment[d] ν_3 components	Obs. (argon)	Calc.[c]	Assignment[d] ν_1 components
411.0		361.6		356.1	402.2		Unassigned		389.0	(a_1) $HfCl_4$
		359.0								
406.5	406.4	357.0	356.9	354.5	399.4	399.4	(t_2) $M^{35}Cl_4$, (e) $M^{35}Cl_3{}^{37}Cl$ (b_1) $M^{35}Cl_2{}^{37}Cl_2$	384.7	384.3[e]	(a_1) $Hf^{35}Cl_3{}^{37}Cl$
404.4	404.7		355.4			398.2	(a_1) $M^{35}Cl^{37}Cl_3$	381.6	381.9[e]	(a_1) $Hf^{35}Cl_2{}^{37}Cl_2$
402.9	402.9	353.7	353.7	352.0	397.0	396.8	(a_1) $M^{35}Cl_2{}^{37}Cl_2$		380.0[e]	(a_1) $Hf^{35}Cl^{37}Cl_3$
400.8	400.8	351.6	351.6	349.6	395.1	394.9	(a_1) $M^{35}Cl_3{}^{37}Cl$		378.4	(a_1) $Hf^{37}Cl_4$
398.3	398.4	349.0	349.0	346.6	390.8	390.8	(t_2) $M^{37}Cl_4$, (e) $M^{35}Cl^{37}Cl_3$ (b_2) $M^{35}Cl_2{}^{37}Cl_2$			

[a] $f_r = 2.60$, $f_{rr} = 0.087$ mdyn Å^{-1}; $\nu_1 = 369.9$ cm^{-1} (assumed). [b] $f_r = 2.18$, $f_{rr} = 0.039$ mdyn Å^{-1}; ν_1 (obs.) = 335.5 cm^{-1} for $Pb^{35}Cl_4$. [c] $f_r = 2.73$, $f_{rr} = 0.129$ mdyn Å^{-1}; $\nu_1 = 389.0$ cm^{-1} (assumed). [d] See also Figure 3. [e] ν_1 Components which are formally i.r. active.

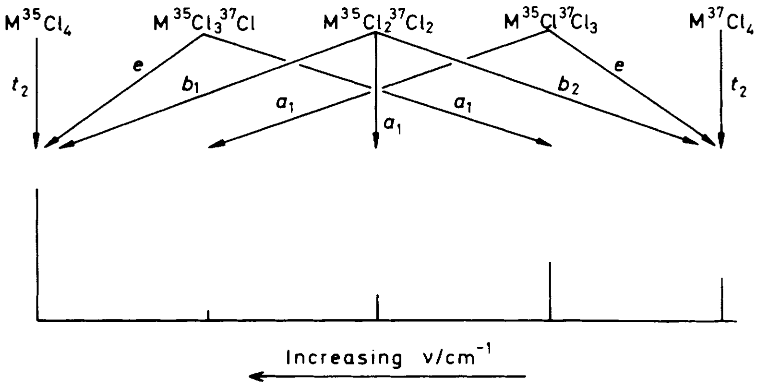

Figure 2. Diagram to illustrate the production of a five-line isotope pattern for a tetrahedral MCl_4 molecule. (Heights of lines represent peak heights based on natural abundance ^{35}Cl : ^{37}Cl)

species the unique chlorine lies on the C_3 axis, while for the C_{2v} isotopomer the C_2 axis bisects both the $^{35}ClM^{35}Cl$ and the $^{37}ClM^{37}Cl$ angle. Thus the e components of the C_{3v} isotopomers involve motion of only the $M^{35}Cl_3$ or $M^{37}Cl_3$ moiety, resulting in a coincidence of these modes with those of the $^{35}Cl_4$ or $^{37}Cl_4$ T_d species. Similarly the b_1 and b_2 components of the C_{2v} molecule coincide with those of the T_d species because they involve only $M^{35}Cl_2$ or $M^{37}Cl_2$ residues. The a_1 modes deriving from the C_{3v} isotopomers occur in the reverse order to that intuitively expected because they involve stretching of the unique bond (coincident with the C_3 axis) as the principal component. This is further clarified by reference to the correlation diagram shown in Figure 2. Thus in the spectra shown in Figure 1 the isotopomers occur in the following *decreasing* frequency sequence: $^{35}Cl_4$ (coincident with e from $^{35}Cl_3{}^{37}Cl$ and b_1 from $^{35}Cl_2{}^{37}Cl_2$); $^{35}Cl^{37}Cl_3$; $^{35}Cl_2{}^{37}Cl_2$; $^{35}Cl_3$-^{37}Cl; and $^{37}Cl_4$ (coincident with e from $^{35}Cl^{37}Cl_3$ and b_2 from $^{35}Cl_2{}^{37}Cl_2$). This accounts for the intensity pattern of the three central isotopomers. Using a simple two parameter (stretch only) force field the vibrational frequencies of the isotopomers were calculated. Intensities were estimated on the basis of statistical weight of the isotopomers, coupled with the assumption that the intensity of any component is proportional to the degeneracy of that mode. The result for tin tetrachloride is shown in Figure 1 where a Gaussian profile has been added to assist the comparison of theory with experiment. The results are summarised in Table 1.

Figure 3 shows the i.r. spectrum of the d^0 tetrachlorides of silicon, titanium, and hafnium (see also Table 1). The spectra for silicon [7] and titanium [4] are again taken from the work of Königer *et al.* As the interpretation for silicon and titanium tetrachloride is straightforward we shall concentrate on hafnium tetrachloride. Apart from the weak band to higher frequency of the all-^{35}Cl isotopomer, the pattern is clearly appreciably different from those of the other d^{10} and d^0 tetrachlorides shown in Figures 1 and 3. The central three bands appear to have been pushed up in frequency towards the all-^{35}Cl species and additional bands are observed to low frequency. The reason for this is the proximity of ν_3 to ν_1. From gas phase studies Clark and Rippon [8] give $\nu_3 - \nu_1$ as only 8 cm^{-1}. The minor perturbation of ν_3 by ν_1 found by a detailed study of lead tetrachloride becomes of major significance for hafnium tetrachloride. Although for a T_d molecule ν_1 and ν_3 are of different symmetries (a_1 and t_2), for the partially substituted ^{35}Cl–^{37}Cl species this is no longer true. Thus a_1 in T_d symmetry clearly remains a_1 in either C_{3v} or C_{2v} symmetry. However the important point to note is that the components responsible for the central three bands of an (unperturbed) isotope pattern of ν_3 are also all of a_1 symmetry. Thus the a_1 components of ν_3 will interact with the appropriate a_1 molecular components of ν_1. The central three bands of ν_3 will thus be pushed ' away ' from ν_1, in this case to higher frequency as ν_1 lies below ν_3. Further, the three components of ν_1 arising from the (two) C_{3v} molecules and the (one) C_{2v} molecule can now exhibit i.r. activity because of this coupling.

To interpret this spectrum a two parameter force field was

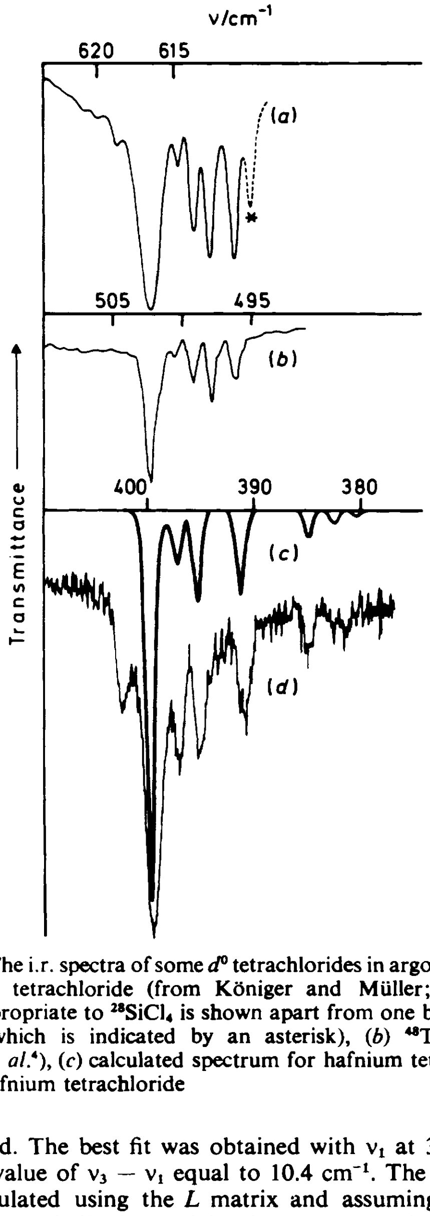

Figure 3. The i.r. spectra of some d^0 tetrachlorides in argon matrices: (*a*) silicon tetrachloride (from Königer and Müller;[7] only the region appropriate to $^{28}SiCl_4$ is shown apart from one band due to $^{29}Si^{35}Cl_4$ which is indicated by an asterisk), (*b*) $^{48}TiCl_4$ (from Königer *et al.*[4]), (*c*) calculated spectrum for hafnium tetrachloride, and (*d*) hafnium tetrachloride

again used. The best fit was obtained with ν_1 at 389.0 cm⁻¹ giving a value of $\nu_3 - \nu_1$ equal to 10.4 cm⁻¹. The intensities were calculated using the *L* matrix and assuming the conventional bond dipole model. The agreement between the observed spectrum and the calculated spectrum (Figure 3) is satisfactory for the T_d model adopted (see also Table 1).

Thorium and Uranium Tetrachlorides.—Figure 4(*a*) shows an i.r. spectrum of the stretching region for uranium tetrachloride isolated in a krypton matrix. The ^{35}Cl–^{37}Cl isotope pattern is not that expected for a monomeric tetrahedral molecule. Figure 4(*b*) shows the corresponding spectrum for thorium tetrachloride and it is apparent that there are considerable similarities between the two spectra (see also Table 2). Because thorium tetrachloride is a d^0 system we decided to concentrate our studies on this molecule, in the anticipation that the spectra might be easier to understand than those from a system with a partially filled *d* or *f* shell.

Experimentally the greatest differences between hafnium and thorium tetrachlorides lie in their vapour pressure *versus* temperature curves. In the matrix isolation experiments hafnium tetrachloride was vaporised at temperatures of the order of 270 °C, while thorium tetrachloride required temperatures close to 500 °C. This is reflected in the different crystal structures (hafnium is six-co-ordinated in the crystal[9] and thorium eight-co-ordinated[10]) and correspondingly lower vapour pressure curve of thorium tetrachloride.[11] Thus hafnium tetrachloride[12] sublimes at 317 °C, whereas thorium tetrachloride boils at above 900 °C. There is no evidence for the presence of appreciable quantities of polymer in the vapour for either tetrachloride under the conditions of our experiments.[13] Further, in the photoelectron spectroscopy of thorium tetrachloride vapour it has been estimated that less than one part in one thousand is polymer.[14] In our experiments the spectrum of thorium tetrachloride isolated in a matrix was independent of the nature of the sample from which vaporisation occurred. [Samples included thorium metal plus silver chloride; thorium tetrachloride synthesised from the elements and also obtained commercially; potassium hexachlorothorate(IV).] However, the possibility remains that radiation from the sample and susceptor caused (unwanted) annealing of the matrix and/or higher surface mobility during deposition. This could again lead to the formation of polymers. Against this the i.r. spectrum showed no evidence for bridging Th–Cl–Th modes in the region clear of the (assumed) terminal stretching region. Annealing did not cause (polymer) bands in the stretching region to grow at the expense of other (monomer) species. To attempt to simulate for hafnium tetrachloride the higher temperature deposition conditions required for thorium tetrachloride the compound potassium hexachlorohafnate(IV) was prepared. This has a vapour pressure[13,15] of approximately 0.01 Torr (~1.3 Pa) at 500 °C. The complex was heated to just below 500 °C to record a matrix spectrum of hafnium tetrachloride identical to that obtained previously. We conclude from this experiment that the unusual spectrum observed for thorium tetrachloride is not due to matrix effects arising from the higher deposition temperature, but is a feature of this molecule. It is possible that co-ordination of impurities such as water or hydrogen chloride could affect the spectra. However, as spectra were obtained from many different samples using three separate instruments involving two different matrix isolation units, with no evidence for systematic changes, we consider that impurities are unlikely to account for our results. Similarly

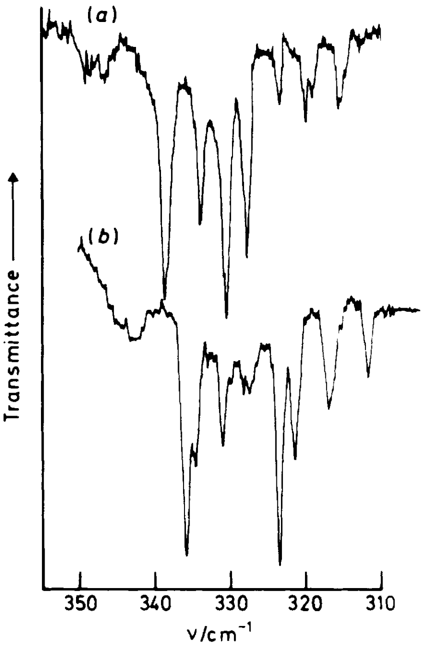

Figure 4. The i.r. spectrum of (*a*) uranium tetrachloride and (*b*) thorium tetrachloride isolated in a krypton matrix

Table 2. Observed i.r. spectra (cm^{-1}) for thorium and uranium tetrachlorides isolated in matrices

$ThCl_4$				UCl_4			
Ar	Kr	N_2	Xe	Ar	Kr	N_2	CO
351	345		~337	355	350		
349	343			353	347		
342.7	335.8		328.0	346.2	339.3		
340.4	334.3	314.8		344.8		317.7	
337.3	330.9	310.9	323.0	341.4	334.6	315.2	308
		307.8					
	328.4	304.3	320.3	337.6	331.2	311.4	
						308.4	
331.1	323.1		316.8	334.9	328.4		
329.2	321.0		314.8	330.4	324.0		
325.4	316.6		310.0	328	320.6		
319.8	311.8		305.0	327	319.6		
				322.8	316.0		

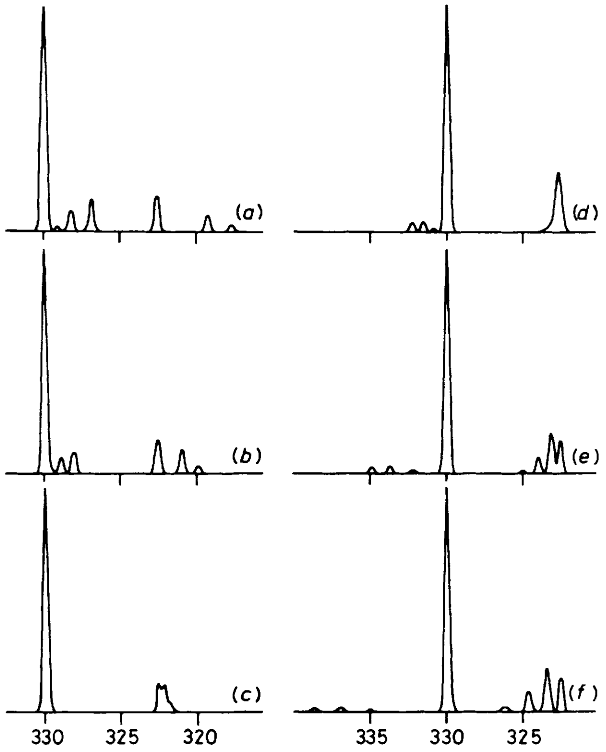

Figure 5. Calculated i.r. spectra of thorium tetrachloride with ν_3 of $Th^{35}Cl_4$ assumed constant at 330 cm^{-1}, ν_1 taken as: (*a*) 324, (*b*) 327, (*c*) 328.5, (*d*) 333, (*e*) 336, and (*f*) 340 cm^{-1}. (ν_3 of $Th^{37}Cl_4$ is constant at 322.5 cm^{-1}; ordinate is absorbance)

the presence of lower chlorides may be ruled out as the material deposited on the apparatus was colourless.

An obvious alternative is the ubiquitous ' matrix site effect '. A gas-phase electron diffraction study of hafnium tetrachloride [16] gave the Hf–Cl distance as 2.33 Å. In the case of thorium tetrachloride [17] a slightly greater distance of 2.58 Å was found. If we now consider ***substitution*** of an MCl_4 tetrahedron into a close packing of inert gas atoms (*i.e.* replacing four inert gas atoms) there are two principal possibilities. An inert gas atom is present on one face of the tetrahedron or a ' hole ' is present on this face. These correspond respectively to hexagonal- and cubic-close packing. (The fact that the inert gases under study pack in the cubic form is somewhat irrelevant when considering a matrix) [18]. This gives two possible sites (at least), one being somewhat similar to the van der Waals compounds formed in molecular beams.

It is possible that the change in size from hafnium tetrachloride to thorium tetrachloride could cause site changes. However spectra of thorium tetrachloride in argon, krypton, and xenon are almost identical. Further, if the spectra were due to site effects each site should exhibit isotope patterns for a molecule containing four atoms of chlorine. We do not believe that these spectra can be explained on the basis of site effects.

Another possibility is that the results arise from the proximity of ν_1 to ν_3. In the case of hafnium tetrachloride $\nu_3 - \nu_1$ was of the order of 10 cm^{-1}. For thorium tetrachloride the value is not known, but is expected to be even less. Figure 5 shows computed frequency and intensity patterns for the isotopomers of ν_3 and ν_1, allowing for various values of $\nu_3 - \nu_1$. In inspecting this Figure it is important to remember that for ν_1 the frequency sequence for the partially substituted species is $^{35}Cl_3{}^{37}Cl > {}^{35}Cl_2{}^{37}Cl_2 > {}^{35}Cl^{37}Cl_3$ whereas for ν_3 (for the reasons outlined previously) it is $^{35}Cl^{37}Cl_3 > {}^{35}Cl_2{}^{37}Cl_2 > {}^{35}Cl_3{}^{37}Cl$. None of the patterns shown accounts for the observations.

The effects of isotope enrichment are shown in Figure 6 and Table 3. The positions of the bands for $Th^{37}Cl_4$ can formally be calculated from the known frequencies of the $Th^{35}Cl_4$ molecule. However, in view of the complexity of the spectra of the partially substituted species it was felt to be worthwhile preparing the $Th^{37}Cl_4$ species to obtain accurate frequencies for subsequent use in identification of bands. The spectra of the essentially pure $Th^{35}Cl_4$ or $Th^{37}Cl_4$ molecules [Figure 6(*a*) and (*d*)] show four main bands. This four-line pattern * cannot occur for a T_d molecule unless there are at least four sites. As we have indicated above (*i*) the sharp break between the spectrum of hafnium tetrachloride and that of thorium tetrachloride, (*ii*) the independence of matrix gas, and (*iii*) the similarity of the spectra of thorium tetrachloride and uranium tetrachloride lead us to eliminate site effects as the solution to this problem. The only aspect not discussed is a deviation from tetrahedral geometry.

Lau and Hildenbrand,[19] on the basis of entropy data, prefer

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* The band at 335.8 cm^{-1} shows a shoulder at 334.3 cm^{-1} for $Th^{35}Cl_4$. Annealing increased the intensity of the main band at the expense of the shoulder. This shoulder, and shoulders on equivalent bands for other isotopomers, are thus assigned to matrix site effects (see Table 4).

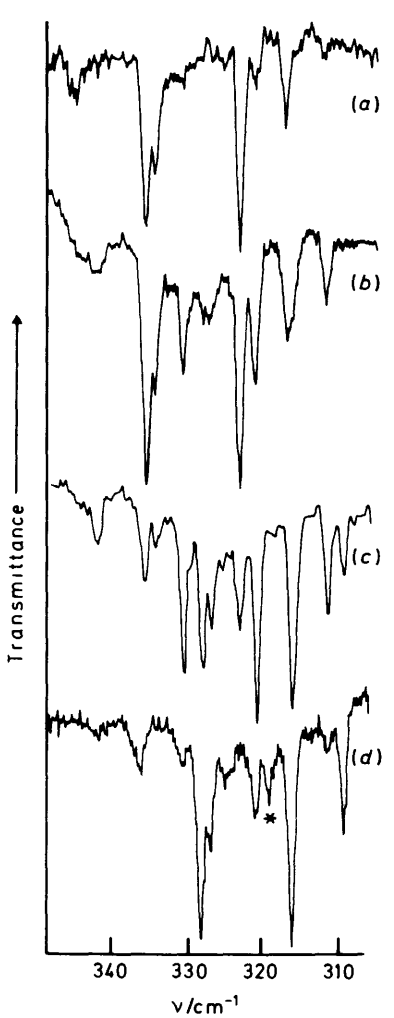


Figure 6. The i.r. spectrum of thorium tetrachloride in krypton matrices at various ^{35}Cl : ^{37}Cl ratios: (a) 45 : 1, (b) 3 : 1, (c) 1 : 2, (d) 1 : 9 (* = impurity)

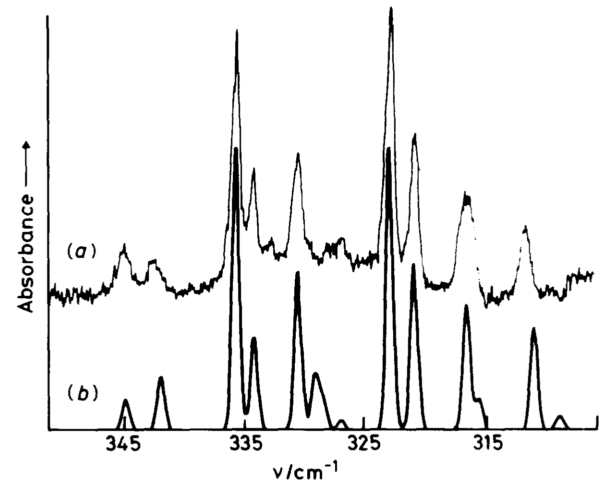
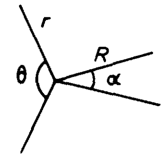


Figure 7. (a) Observed i.r. spectrum of thorium tetrachloride in a krypton matrix, and (b) calculated spectrum using a C_{2v} model

a distorted C_{2v} structure for uranium tetrafluoride. They also refer to work on uranium tetrachloride [20] suggesting a C_{2v} distortion. We note that the bonding in thorium tetrachloride is likely to exhibit considerable ionic character.[21] Remembering the high polarisability of the thorium *atom* (71.9 Å^3; compared to hafnium, 27.7 Å^3) we may use a polarisation model [22] to discuss possible distortions. It could be argued that maximum polarisation of the thorium would occur when the four chlorines occupy the minimum space on the ' surface ' of the thorium. Taking the ionic radius of Th^{4+} as 2.58 Å and that of Cl$^-$ as 1.81 Å leads to a C_{2v} structure with bond angles of 90° (' equatorial ') and 180° (' axial '), analogous to that proposed for tellurium tetrachloride. This model ignores repulsive interactions between the four Cl$^-$ ions close packed on the surface of Th^{4+}.

The bond angle in *molecular* barium dichloride is of the order of 100°.[1] If this is (arbitrarily) taken to be the ' equatorial ' angle in thorium tetrachloride, then using the reasoning above the ' axial ' angle becomes approximately 140°. For our calculations we adopted this type of model. We assume that the observed spectra of Th^{35}Cl$_4$ and Th^{37}Cl$_4$ are representative of the isolated molecule [with no matrix effects apart from that on the 335.8 cm^{-1} band (at 334.3 cm^{-1}) and related isotopomers]. For Th^{35}Cl$_4$ we adopted a four parameter force field (f_r, f_R, f_{rr}, f_{RR} with f_{Rr} set at zero), shown below, with θ in the xz plane, and z defining the C_2 axis. Initially the angle θ was set at 180° and α varied between 130 and 100°.



The best fit for frequencies of the all-^{35}Cl species occurred at α = 110°. Optimisation of the axial angle θ occurred at 160°. Using this geometry three possible frequency assignments were acceptable, without invoking negative force constants. Two of these were unacceptable when applied to the ^{35}Cl–^{37}Cl isotopomers. The resultant force field and assignments are as follows: 345 (a_1 ax), 335.8 (b_1 ax), 323.1 (b_2 eq), and 317.0 (a_1 eq); $f_r = 2.097$, $f_R = 1.830$, $f_{rr} = 0.309$, $f_{RR} = 0.052$, and $f_{Rr} = 0.0$ mdyn Å^{-1} (dyn = 10^{-5} N).

The force-field calculation is not sensitive to the angles due to: (*i*) the small mass difference of ^{35}Cl to ^{37}Cl; (*ii*) the mass of the thorium relative to chlorine; and (*iii*) the low frequency at which the Th–Cl stretching vibrations occur. Further, the force field adopted cannot be considered satisfactory when f_{Rr} is equated to zero. However we note that for an undistorted (T_d) molecule, ν_1 (involving an $f_r + 3f_{rr}$ type of term) and ν_3 (involving an $f_r - f_{rr}$ type of term) would be similar in frequency. On the basis of the usual valence force field assumptions, for a heavy metal atom using no stretch–bend interaction this would lead to a small value for f_{rr}. (The use of a stretch only solution is acceptable as we scanned the i.r. spectrum to 90 cm^{-1} with no evidence for the deformations.) Finally it should be noted that the change of approximately 50 cm^{-1} between ν_3 of hafnium tetrachloride and ν_3 of thorium tetrachloride is exceptional when compared with the calculated value (on a mass only basis) of 10 cm^{-1}.

Table 4 summarises our calculations and assignments for C_{2v} thorium tetrachloride. Figure 7 shows the excellent agreement between the calculated spectrum and the observed spectrum. However in view of our comments above *this agreement must not be taken to mean that we have the correct model.* A matrix Raman spectrum would be valuable, but we have not yet been successful in obtaining this.

Table 3. Frequencies (cm^{-1}) observed for ThCl$_4$ of various isotopic enrichment isolated in krypton matrices

^{35}Cl : ^{37}Cl ratio				
45 : 1	8 : 1	3 : 1	1 : 2	1 : 9
345.0 ± 0.4		345.0 ± 0.4		
		342.6 ± 0.4		
				336.2 ± 0.4
335.6 ± 0.2	335.6 ± 0.2	335.8 ± 0.2	335.8 ± 0.2	
334.4 ± 0.2	334.5 ± 0.2	334.3 ± 0.2	334.4 ± 0.2	
	330.8 ± 0.2	330.6 ± 0.2	330.6 ± 0.2	(330.8 ± 0.4)
			329.6 ± 0.4	
	(327.9 ± 0.4)	328.0 ± 0.4	328.4 ± 0.2	328.4 ± 0.2
		327.0 ± 0.4	326.9 ± 0.2	327.0 ± 0.2
323.1 ± 0.2	323.2 ± 0.2	323.1 ± 0.2	323.2 ± 0.2	
	321.2 ± 0.2	321.0 ± 0.2	320.9 ± 0.2	321.0 ± 0.2
				319.2 *
			316.4 ± 0.2	316.2 ± 0.2
317.0 ± 0.2	317.0 ± 0.2	316.6 ± 0.2		
	311.7 ± 0.2	311.8 ± 0.2	311.6 ± 0.2	
			309.6 ± 0.2	309.4 ± 0.2

* This weak feature remains unassigned.

Table 4. Calculated and observed frequencies (cm^{-1}) for ThCl$_4$ isolated in krypton matrices

Observed frequency [a]	Calculated frequency [b] (intensity)	Assignment [b]
345.0 ± 0.4	344.9 (11.0)	a_1 Th^{35}Cl$_4$(C_{2v}), a' Th^{35}Cl$_3$^{37}Cl($C_s[yz]$), a_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v})
342.6 ± 0.4	342.0 (19.6)	a' Th^{35}Cl$_3$^{37}Cl($C_s[xz]$), a Th^{35}Cl$_2$^{37}Cl$_2$(C_1), a' Th^{35}Cl^{37}Cl$_3$($C_s[xz]$)
336.2 ± 0.4	335.9 (1.6)	a_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v}), a' Th^{35}Cl^{37}Cl$_3$($C_s[yz]$), a_1 Th^{37}Cl$_4$(C_{2v})
335.8 ± 0.2	335.8 [c] (100)	b_1 Th^{35}Cl$_4$(C_{2v}), a'' Th^{35}Cl$_3$^{37}Cl($C_s[yz]$), b_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v})
334.3 ± 0.2	334.3 [c] (33.3)	
330.6 ± 0.2	330.7 [c] (56.5)	a' Th^{35}Cl$_3$^{37}Cl($C_s[xz]$), a Th^{35}Cl$_2$^{37}Cl$_2$(C_1), a' Th^{35}Cl^{37}Cl$_3$($C_s[xz]$)
329.6 ± 0.2	329.2 [c] (18.8)	
328.4 ± 0.2	328.7 [c] (10.8)	b_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v}), a'' Th^{35}Cl^{37}Cl$_3$($C_s[yz]$), b_1 Th^{37}Cl$_4$(C_{2v})
327.0 ± 0.2	327.2 [c] (3.6)	
323.1 ± 0.2	323.1 (99.2)	b_2 Th^{35}Cl$_4$(C_{2v}), a'' Th^{35}Cl$_3$^{37}Cl($C_s[xz]$), b_2 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v})
321.0 ± 0.2	321.0 (59.1)	a' Th^{35}Cl$_3$^{37}Cl($C_s[yz]$), a Th^{35}Cl$_2$^{37}Cl$_2$(C_1), a' Th^{35}Cl^{37}Cl$_3$($C_s[yz]$)
316.2 ± 0.2	315.8 (10.8)	b_2 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v}), a'' Th^{35}Cl^{37}Cl$_3$($C_s[xz]$), b_2 Th^{37}Cl$_4$(C_{2v})
317.0 ± 0.2	316.8 (44.1)	a_1 Th^{35}Cl$_4$(C_{2v}), a' Th^{35}Cl$_3$^{37}Cl($C_s[xz]$), a_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v})
311.6 ± 0.2	311.3 (36.0)	a' Th^{35}Cl$_3$^{37}Cl($C_s[yz]$), a Th^{35}Cl$_2$^{37}Cl$_2$(C_1), a' Th^{35}Cl^{37}Cl$_3$($C_s[yz]$)
309.6 ± 0.2	309.1 (5.1)	a_1 Th^{35}Cl$_2$^{37}Cl$_2$(C_{2v}), a' Th^{35}Cl^{37}Cl$_3$($C_s[xz]$), a_1 Th^{37}Cl$_4$(C_{2v})

[a] See Table 3; force constants as in text. [b] Planes for the symmetry elements are given in square brackets. [c] To reproduce the matrix site effects the total intensity for this mode has in each case been divided in a 3 : 1 ratio, using the *observed* frequency differences.

Conclusions

We conclude that of the tetrachlorides of Si, Ti, Hf, Th, Ge, Sn, and Pb only that of thorium shows evidence of departure from tetrahedral symmetry. The i.r. spectra of Th^{35}Cl$_4$ and of Th^{37}Cl$_4$ isolated in krypton matrices exhibit four bands in the stretching region. In the absence of matrix site effects or polymers (which are both discussed in detail in the preceding sections) this implies C_{2v} symmetry or lower. This behaviour can be rationalised, in a very elementary way, on the basis of a polarisation model.

There is no shortage of theoretical studies on the shapes of molecules of the heavier elements. Both Th^{IV} and U^{VI} have the electronic configuration of radon. Uranium trioxide from matrix studies has a T-shaped structure.[2] The polarisation model applied to UO$_3$ would give a pyramidal structure akin to the Group 5 trichlorides MCl$_3$ (M = N, P, As, Sb, or Bi). The authors of the uranium trioxide paper suggest the shape may be rationalised on the basis of a $[UO_2]^{2+}O^{2-}$ interaction. This illustrates the dilemma. The theoretical models are not able to suggest which molecules are of major interest. The experimental work is so fragmentary that the models cannot be tested adequately.

As an aid to selection of molecules which may show distortions the Drake and Rosenblatt approach [1] is useful. However, even at this level the lack of consideration of 'directed valence,' and in particular the limitations of the polarizability data and the restriction to consideration of a single parameter (the polarizability of the central atom), make the approach interesting but possibly of limited value. The high polarizability of the barium *atom* (67.7 Å^3) drops to 1.56—2.5 Å^3 for the doubly charged ion.[23] This change is due to the loss of the (outer) 6s^2 electrons to give an ion with the electronic structure of xenon. Contrast this with mercury. The mercury atom has a polarizability of only 12.1 Å^3 but that of the doubly charged ion is comparable to that of the barium ion (Ba^{2+} 1.56—2.5 Å^3; Hg^{2+} 0.5—3.18 Å^3). Thus, as Drake and Rosenblatt [1] point out, an attempt to utilize the ionic model based upon the polarizability of the central-metal doubly charged ion leads one to expect BaCl$_2$ and HgCl$_2$ to have the same structure. The fact that they do not (on the experimental evidence available) can be explained by the directed (co)valency in the case of mercury. Drake and Rosenblatt avoid this dilemma, empirically, by basing their correlation upon the polarizability of the neutral central-metal atom. In this way they predict

$BaCl_2$ to be bent and $HgCl_2$ to be linear. The approach may be rationalized[24] by recognizing that, even in these ionic molecules, charge transfer is far from complete. The polarizability of an electronically distorted or partially charged central atom may be (depending upon the degree of charge separation) equal to, greater, or less than that of the unperturbed atom. Because Drake and Rosenblatt sought a simple one-parameter correlation which agreed with available experimental results, they assumed that trends in polarizability for the perturbed metal atoms in these ionic molecules could be approximated by trends for the neutral atoms.

An extension to the polarizability theory is thus to consider the degree of ionic character in the bond. Distortion from the ' normal ' structures would occur for species having a high degree of ionic character (or for more covalent compounds where directed valency predicts a distortion). Thus more ionic species would show distortions in the order $F > Cl > Br > I$ (which would also be the order based on ligand repulsion). Lower oxidation states would favour distortion as would ' central ions ' having the electronic configuration of an inert gas. The situation with partially filled *d* shells would be more difficult to rationalize on this approach. However even here the limited experimental observations appear to follow the ionic ⟶ covalent change across the first transition series for example.

Experimental

$^{124}SnCl_4$ was prepared from the reaction of ^{124}Sn (>98%) metal with dry chlorine gas at room temperature. Lead tetrachloride was obtained[25] by the action of concentrated sulphuric acid on bis(pyridinium) hexachloroplumbate(IV). Hafnium tetrachloride was (*a*) obtained from Alpha Chemicals or (*b*) prepared by the *in situ* decomposition of $K_2[HfCl_6]$[13,15] at just below 500 °C. (The compound $K_2[HfCl_6]$ was prepared by reacting the components in stoicheiometric quantities.) Uranium tetrachloride was (*a*) provided by A.E.R.E. Harwell, (*b*) obtained from the disproportionation of UCl_3 (UCl_3 was prepared[26] by chlorination of uranium hydride with dry hydrogen chloride at 250 °C. Uranium hydride was obtained from the reaction of uranium with hydrogen at 225 °C), or (*c*) prepared from the decomposition of $Cs_2[UCl_6]$ in the matrix apparatus at 625 °C (the compound $Cs_2[UCl_6]$ was prepared[27] by mixing stoicheiometric quantities of UCl_4 and CsCl in concentrated hydrochloric acid, followed by passage of hydrogen chloride gas to increase the amount of precipitation). Thorium tetrachloride was (*a*) obtained from Alpha Chemicals, (*b*) prepared from the direct reaction of thorium metal and chlorine at 700 °C in a silica tube, (*c*) prepared by the reaction of silver chloride with thorium metal *in situ* on the matrix trolley (this method was also used to obtain ^{35}Cl- or ^{37}Cl-enriched $ThCl_4$), or (*d*) obtained by *in situ* decomposition of $K_2[ThCl_6]$[13] at 650 °C (the $K_2[ThCl_6]$ was obtained by heating stoicheiometric quantities of the components).

$^{124}SnCl_4$ was premixed with argon for the matrix isolation experiments. In the case of lead tetrachloride the vapour from a sample at −20 °C was admitted *via* a Teflon needle valve and cocondensed with argon. Hafnium tetrachloride was vaporised from a borosilicate glass spray-on dome at 230 °C. Alternatively the matrix isolated species was obtained by *in situ* decomposition of $K_2[HfCl_6]$ at just below 500 °C in a silica apparatus. Uranium tetrachloride matrices were produced (*a*) by heating UCl_4 at 480 °C, (*b*) decomposing UCl_3 above 700 °C, or (*c*) decomposing $Cs_2[UCl_6]$ at 625 °C. Thorium tetrachloride was studied in a matrix (*a*) by vaporisation of the tetrachloride from a silica tube at 510 °C, (*b*) from decomposition of $K_2[ThCl_6]$ in silica at 650 °C, or (*c*) by heating AgCl and thorium metal to *ca.* 500 °C in silica.

The general procedures for the matrix isolation i.r. experiments have been given elsewhere.[28] Most spectra were run on a Perkin-Elmer 580 or Perkin-Elmer 225 i.r. spectrometer, with a resolution of the order of 0.5 cm^{-1} for frequencies in the region of 350 cm^{-1}. In the case of thorium tetrachloride spectra were also studied using a Nicolet FTIR instrument, which gave frequency coverage to 90 cm^{-1}.

Calculations.—For $^{124}SnCl_4$ and $PbCl_4$ a simple two parameter force field was used on the SOTONVIB program.[29] The results are summarised in Table 1, where the force constants are also given. For the intensities (Figure 1) a statistical weighting was applied to allow for the abundance of the isotopomers and the degeneracy of the modes.

In the case of hafnium tetrachloride ν_1 of $Hf^{35}Cl_4$ was varied in 2 cm^{-1} steps from 379 cm^{-1} to 393 cm^{-1} (with ν_3 constant for the all-^{35}Cl species at 399.4 cm^{-1}). The best fit was obtained at $\nu_1 = 389$ cm^{-1}. The data are summarised in Table 1 which also includes the force constants applicable to this case. The *L* vector output from SOTONVIB was used to calculate relative intensities assuming the usual bond-dipole approximation.

Similar, but more extensive calculations on the effect of the proximity of ν_1 to ν_3 on the isotope patterns observed were made for T_d thorium tetrachloride. The results are summarised in Figure 5.

In the case of the C_{2v} thorium tetrachloride molecule the intensity patterns were calculated from the *L* vectors using the bond-dipole approximation as indicated previously.

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