The Infrared Spectra of Matrix Isolated Thorium and Uranium Tetrachlorides. Change of Shape with Matrix Gas

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When thorium or uranium tetrachlorides are isolated in neon matrices, the spectra can be interpreted in terms of a T_d molecule with a small site effect. Spectra obtained using sputtering techniques to generate $ThCl_4$ in argon matrices agreed with those obtained previously using conventional vaporisation techniques. Detailed calculations of the i.r. spectra of isotopically enriched and natural abundance $Th^{35/37}Cl_4$ show that in krypton $ThCl_4$ is not tetrahedral.

It is usually assumed that the geometry of molecules or fragments isolated in matrices of the inert gases or nitrogen, for example, is close to that of the gaseous molecule.[1] However it is also accepted that species in crystals are affected by their environment. The term 'interallogon' was coined to describe an extreme case where both square-planar and tetrahedral forms of a nickel(II) complex occurred in the same unit cell of a single crystal.[2] Species isolated in matrices, if they could be examined in terms of their detailed geometry, represent unique systems for studying atom–molecule interactions at low temperatures. Guests likely to be strongly affected by the host matrix would be those where the central atom is co-ordinatively unsaturated and where bonding forces are not highly directional in character. Such molecules would have fewer ligands than those normally present in stable compounds of the central element, a high degree of ionic character, or many possible combinations of bonding orbitals. These are precisely the types of molecules which exhibit 'anomalous geometries' in matrices. Examples include non-linear SrF_2,[3] ThO_2,[4] pyramidal LaF_3,[5] and T-shaped UO_3.[6] This raises the problem that some of the geometries reported could arise from the presence of the matrix. Put in an alternative way, if the sequence from the inert gas Xe through N_2 and CO to the conventional ligand MeNC is considered, for many acceptors it is not clear that there is an *abrupt* change at any point.

In a recent paper[7] following on from earlier work on $CsUF_6$[8] it has been suggested that the *molecule* $CsNbF_6$ changes shape as a function of matrix gas. Thus in weakly interacting matrices such as neon or argon $CsNbF_6$ adopts C_{3v} symmetry, while in carbon monoxide or nitrogen C_{2v} symmetry is adopted. In this case the matrices were 'calibrated' by use of the molecule $CsClO_4$ which shows a bidentate interaction between the caesium ion and the perchlorate anion.[9]

It is also well established that the stretching frequencies of alkali metal–halide molecules show large shifts between the gas phase and even a neon matrix.[10] This behaviour has been reasonably well explained on the basis of dipole-induced dipole interactions.[11] Matrix shifts for diatomic molecules tend to increase in the order:[10] $Ne < Ar < Kr < Xe < N_2$.

The determination of bond angles and bond lengths in matrix isolated species is difficult. At present the principal approach is the use of isotopic data obtained from i.r. spectroscopy. For compounds of the heavier elements such data are normally not sensitive to bond angles. However, distortions of a T_d AB_4 molecule away from tetrahedral symmetry, or of a D_{3h} (or C_{3v}) AB_3 molecule so that the C_3 axis is removed, leads to significant changes in the characteristic intensity and frequency patterns for partial isotopic substitution at the ligand atom. We are only aware of two examples of such behaviour: UO_3[6] and $ThCl_4$.[12] Both warrant further consideration. The data on UO_3 are more extensive and compelling because of the larger isotopic shifts ($^{16}O/^{18}O$) and the more favourable frequency region for oxides. It is noteworthy that both Th^{IV} and U^{VI} are d^0f^0 systems, and both central elements occur in the same region of the Periodic Table. The main objective of this work was to extend the previous studies on $ThCl_4$. In particular, because both $ThCl_4$ and UCl_4 show large matrix shifts between argon and carbon monoxide for example, we felt that significant perturbation could be brought about by the host matrix.

Results and Discussion

(a) *The Inert Gases.*—For T_d MCl_4 where $\nu_3(t_2)$ is of appreciably higher frequency than $\nu_3(a_1)$ the chlorine isotopes give a characteristic regularly spaced five-line pattern for ν_3 in the i.r. spectrum.[12a] Each of the three central components of this pattern corresponds to the vibration of one isotopomer. These vibrations have the same symmetry as those of each of the three central components of ν_1 which derive from the same isotopomers (but in reverse frequency order to those of ν_3). Thus as ν_3 and ν_1 approach one another the three central components of ν_3 are pushed towards the all-^{35}Cl position (for ν_3). At the same time the central components of ν_1 gain in i.r. intensity from this interaction. Such behaviour can be seen in the spectrum of $HfCl_4$[12] where $\nu_3 - \nu_1$ is less than 10 cm^{-1}. Because of such interaction no totally symmetric vibration of the mixed isotopomer is pure ν_3 or pure ν_1 in origin. In the case where $\nu_1 \approx \nu_3$ *all* of the components lie under the all-^{35}Cl or all-^{37}Cl positions, leading to a two-line spectrum. This is essentially what is observed in our spectra of $ThCl_4$ isolated in a neon matrix (Figure 1).

$ThCl_4$ is a d^0f^0 system and as such is expected to be regular tetrahedral. The spectra in Figure 1 can reasonably be interpreted in terms of a T_d molecule with satellite bands due to some occupancy of a second site showing a shift of approximately 7 cm^{-1} to lower frequency. This result is at variance with spectra observed in argon, krypton, and xenon. In particular Arthers and Beattie[12a] interpreted their i.r. spectra of $ThCl_4$ in krypton in terms of a C_{2v} molecule. In view of the result for neon it appeared important to consider the results in the other matrix gases in more detail.

Possible sources of error in such work include: that the $ThCl_4$ is not monomeric in certain matrices, that some chloride other than $ThCl_4$ has been isolated, that several matrix 'sites' can account for the observed spectra, and that an impurity is present in Ar, Kr, and Xe but not in Ne.

We find that sputtering thorium foil in an argon carrier gas doped with a small amount of chlorine gives an identical i.r. spectrum to that obtained by vapourising $ThCl_4$ into an argon matrix, emphasising the monomeric nature of the isolated molecule (Figure 2). Further, in all our $ThCl_4$ vapourisation experiments the inevitable deposits on cooler parts of the

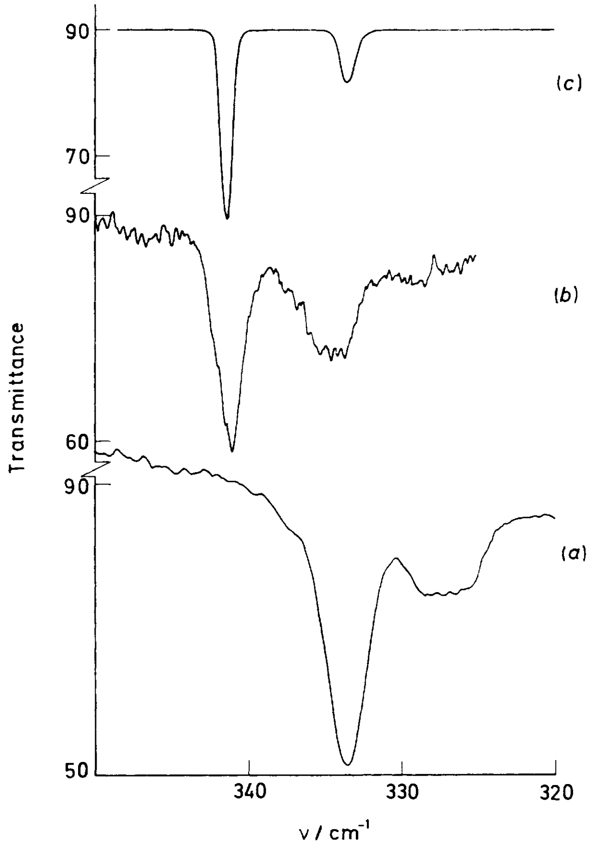


Figure 1. The i.r. spectrum of thorium tetrachloride isolated in neon matrices at several ^{35}Cl:^{37}Cl ratios: (*a*) 1:20, (*b*) natural abundance, and (*c*) calculated natural abundance spectrum with ν_1 and ν_3 coincident

apparatus were always colourless, in agreement with a +4 oxidation state for the thorium. We thus conclude that our spectra refer to monomeric $ThCl_4$.

Returning now to the results of Arthers and Beattie[12a] for krypton matrices, the spectra of the 'all-^{37}Cl' or 'all-^{35}Cl' molecules each show four main bands. Four additional bands occur in molecules containing both ^{35}Cl and ^{37}Cl. These do not lie in the central positions between the appropriate 'all-^{35}Cl and all-^{37}Cl' isotopomers. Their frequencies are: 342.6 (+2.0), 330.6 (−1.5), 321.0 (+1.3), and 311.6 (−1.7) cm^{-1} [values in parentheses indicate by how much the bands have been pushed up (+) to higher frequencies or pushed down (−) to lower frequencies relative to the central position].

Several deductions can be made from the krypton spectra. (*a*) They cannot arise from (four) T_d molecules in four different sites. On the basis of frequency and intensity calculations it is not possible to predict spectra with only one ^{35}Cl/^{37}Cl band between each of the all-^{35}Cl and all-^{37}Cl pairs. Further, the fact that two bands are pushed up in frequency while two are pushed down suggests that at most two parent molecules of non-T_d symmetry are present. (*b*) They cannot arise from one D_{2d} molecule, which would give rise to only two all-^{35}Cl or all-^{37}Cl bands. In no case can we match the spectra using two D_{2d} molecules in different sites using realistic values for ν_1. (*c*) Finally all of the spectra for different ^{35}Cl:^{37}Cl ratios can be satisfactorily calculated using a C_{2v} molecule with opposite angles of 110 and 160°. The results of our frequency and intensity calculations are summarised in Figure 3. We have not allowed for the previously proposed site effect on the band at 335.8 cm^{-1}. However, the agreement is clearly excellent.

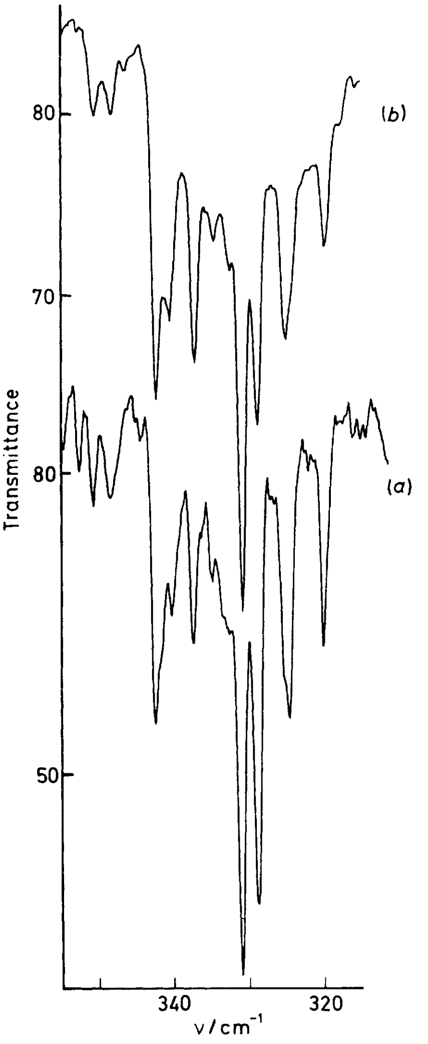


Figure 2. The i.r. spectrum of (*a*) thorium tetrachloride in an argon matrix and (*b*) thorium foil sputtered using argon containing 0.1 mol% chlorine

Our *independent* spectra on natural abundance $ThCl_4$ in krypton or argon agreed closely with those of Arthers and Beattie[12a] (maximum difference 0.2 cm^{-1}). However, we note that in Table 3 of their paper under ^{35}Cl:^{37}Cl of 1:2 ratio the band at 342.6 cm^{-1} should be included.

We are once again forced to the conclusion that in certain matrix gases $ThCl_4$ does not adopt a T_d conformation. The complexity of the vibrational problem and the assumptions inherent in the bond–dipole method for calculating intensities means that both the proposed force field and geometry should be treated with caution.

We also carried out very careful annealing experiments on $ThCl_4$ isolated in a krypton matrix. We could not obtain any data which showed unambiguously that the bands concerned did not all originate from the same molecular species. However after annealing at the very high temperature of 55 K for 10 min a band was observed to grow in at 327.6 cm^{-1}, although the strongest bands in the original spectrum were now only about a quarter of their original intensity. Similarly codepositing $ThCl_4$ with argon at 25 K did not affect the general spectral features although some broadening of the bands was observed.

(b) *Nitrogen and Carbon Monoxide.*—Between neon and carbon monoxide there is a shift of approximately 40 cm^{-1} for

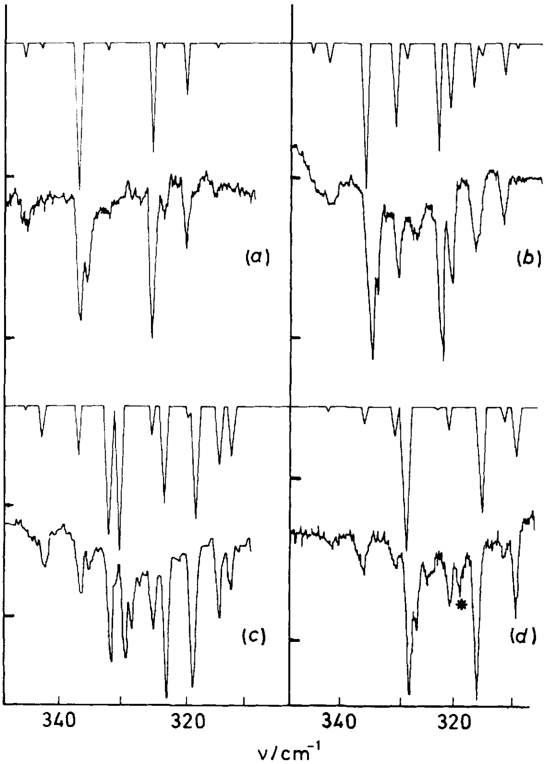


Figure 3. Calculated (upper trace) and observed (lower trace) i.r. spectra of thorium tetrachloride in krypton at various $^{35}Cl:^{35}Cl$ ratios: (*a*) 45:1, (*b*) natural abundance, (*c*) 1:2, (*d*) 1:9 (* = impurity). The range of transmittance values for the calculated spectra is in all cases 95—45%. Marked points on axes refer to 90% or 60% transmittance for experimental spectra

both $ThCl_4$ and UCl_4. This represents a decrease in the antisymmetric stretching frequency by some 12%. It is *roughly equivalent to the addition of one chloride ion.* The spectrum of $ThCl_4$ in nitrogen can be modelled by assuming two matrix sites for a T_d molecule, separated by *ca.* 7 cm^{-1}. The spectra in carbon monoxide were of poor quality.

Conclusions

Our observations are summarised in the Table and in Figures 1 and 2. In neon matrices the i.r. spectra of $ThCl_4$ and UCl_4 can be explained on the basis of tetrahedral molecules assuming: (*a*) there is partial occupancy of a second site in the matrix and (*b*) ν_1 and ν_3 are coincident or nearly coincident. Figure 4 shows the effect of carrying out a D_{2d} distortion on the T_d $ThCl_4$ molecule. Clearly the initial steps of such a distortion would be a broadening of the bands. (A similar broadening could also occur if ν_1 and ν_3 are not exactly coincident.) For $ThCl_4$ and UCl_4 the full width at half peak height for the main ^{35}Cl i.r. band in a neon matrix is *ca.* 2 cm^{-1}. This may be compared with that of *ca.* 1 cm^{-1} found in spectroscopy on related compounds. Modelling spectra for small D_{2d} distortions suggested that the maximum deviation from tetrahedral (for the angles enclosing the S_4 axis) would be 1°. In nitrogen (and probably carbon monoxide, where the bands are too broad to give isotopic data) the spectra can also be modelled on a T_d MCl_4 unit.

This set of conclusions, apart from the fact that $ThCl_4$ and UCl_4 are tetrahedral in the gas phase and neon, may seem unlikely. However our detailed interpretation of $ThCl_4$ in krypton gives quite excellent agreement with the experimental

Table. The i.r. spectra of thorium and uranium tetrachlorides in various matrix gases

Compound	Matrix	$^{35}Cl:^{37}Cl$	Frequencies (cm^{-1})
$ThCl_4$	Neon	Natural	341.0, 334.0
$ThCl_4$	Neon	9:1	341.0, 334.0
$ThCl_4$	Neon	1:20	333.5, 325.8
$ThCl_4$	CO	9:1	302
$ThCl_4$	CO	1:20	297
UCl_4	Neon	Natural	347.2, 339.6

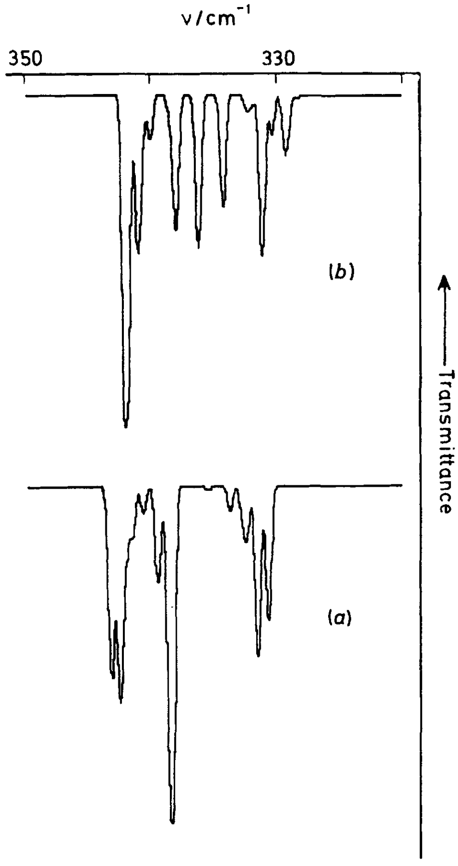


Figure 4. Calculated i.r. spectrum of $ThCl_4$ for a D_{2d} distortion. Bond angle bisected by S_4: (*a*) 105 and (*b*) 115° (ν_1 fixed at 340 cm^{-1})

data. There is very strong evidence that $CsNbF_6$ changes shape between neon and nitrogen for example. Further, within the inert gases the greatest change in physical properties occurs between neon and argon. Finally is should be recalled that the spectrum of $HfCl_4$ in argon and in nitrogen can be fully explained on the basis of a tetrahedral molecule. It is interesting to note that if we place four Cl^- ions on the surface of a Th^{4+} sphere, using reasonable ionic radii and assuming all spheres are nearly in contact, this leads to a structure very close to that proposed by Arthers and Beattie.[12a] It is possible that two krypton atoms complete a highly distorted octahedron around the central thorium.

Clearly if these results are correct, they throw doubt on structures derived from studies of 'co-ordinatively unsaturated' molecules in inert matrices, notably where these molecules have a high degree of ionic character and many bonding orbitals are available.

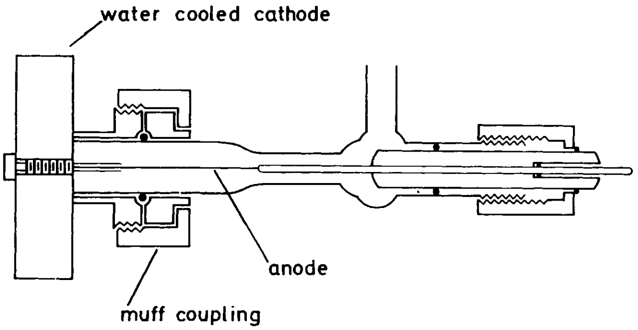
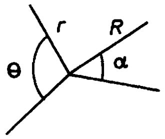


Figure 5. The sputtering device

Experimental

The conditions used to matrix isolate $ThCl_4$ and UCl_4 were the same as those used previously[12a] except that a modified cryopump (Air Products DE204SL) was used which was (just) capable of isolating samples in neon (tip temperature 8—9 K). For spectra in neon we also used a liquid-helium cryostat. The results obtained (Figure 1) were identical to those found using the DE204SL except that the bands were narrower. Infrared spectra were recorded (4 000—180 cm^{-1}) on a Perkin-Elmer 983G i.r. spectrometer calibrated using residual water vapour in the instrument. The sputtering device was similar to that described by Green and Reedy[13] (Figure 5). The glass vacuum jacket was attached to the water cooled metal flange carrying the hollow cathode *via* an Edwards SC10 muff coupling. The platinum anode was held in the centre of the poly(tetrafluoroethylene) barrel of a modified greaseless tap, thus allowing the position of the anode to be varied. A thin silica tube was used to hold the anode centrally in the hollow cathode. The high voltage power supply was designed to operate in the 300—600 V, 0—50 mA range.

Calculations.—The spectra were calculated using the SOTONVIB program.[14] Intensity patterns were obtained *via* the *L*-vectors using the bond–dipole approximation. The diagram below defines the geometry and force constants adopted (dyn = 10^{-5} N).



$\alpha = 110°$, $\theta = 160°$, $f_r = 2.0_{97}$, $f_R = 1.8_{30}$, $f_{rr} = 0.3_{09}$, $f_{RR} = 0.0_{52}$, $f_{Rr} = 0.0$ mdyn $Å^{-1}$

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