Raman Spectrum and Factor Group Analysis of Crystalline Titanium Tetrachloride

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Summary The Raman spectrum of crystalline titanium tetrachloride has been obtained at *ca.* 77K, and a factor group analysis of the fundamentals is presented in terms of the known space group C^5_{2h}.

THE unusual isotopic structure of the a_1 band of pure liquid titanium tetrachloride, resembling as it does that of boron trichloride rather than that of carbon tetrachloride, has been interpreted to imply that in this state the molecule is dimeric,[1] a conclusion contrary to other physical evidence. Subsequent work has shown[2] that the unexpected intensity pattern persists in the solid state, at least at temperatures above 100—150K. This result is not consistent with the postulate of dimerisation, because the solid is known to crystallise in a molecular lattice of monomeric units.[3]

We now find that, by use of a specially designed liquid-nitrogen cell which minimises boil-off of coolant and thus ensures that a sample reaches a temperature very close to 77K, the pattern of the a_1 band approaches that calculated for a four-chlorine-atom vibrator. Thus the unexpected shape of the a_1 band at temperatures above 100—150K is to be attributed principally to distortion by underlying hot bands [principally $\nu_1 + v\nu_2 - v\nu_2$, $\nu_1 + v\nu_4 - v\nu_4$, and $(v + 1)\nu_1 - v\nu_1$], and not to dimerisation. Indeed this can readily be understood by a consideration of the vibrational partition functions $Q_v^{(\mathrm{harm})}$, calculated for this molecule using gas-phase values for the fundamentals,[4] $\nu_1 = 388$, $\nu_2 = 119$, $\nu_3 = 498{\cdot}5$, $\nu_4 = 139$ cm^{-1}. These are 70·44 (298·15K), 13·87 (200K), 2·32 (100K), 1·59 (77K). The influence of hot bands will obviously be more extreme in the

TABLE 1

Raman bands of crystalline titanium tetrachloride

Average of data gathered using the 5682, 5208, and 5145 Å exciting lines of Kr$^+$ and Ar$^+$

Observed bands and splitting[a] cm^{-1}			Assignments T_d nomenclature		
119·4	0·8	5·6			$\nu_2(e)$
120·2 sh					
124·1	2·5				
126·6					
132·5		3·5			$\nu_4(t_2)$
136·0		3·0			
138·4	1·2				
139·6 sh					
143·5 vw ?					
378·7	2·8		$Ti^{37}Cl_4$	0·36%[b]	$\nu_1(a_1)$
381·5	2·7		$Ti^{35}Cl^{37}Cl_3$	4·43%	
384·2	2·7		$Ti^{35}Cl_2{}^{37}Cl_2$	20·50%	
386·9	2·8		$Ti^{35}Cl_3{}^{37}Cl$	42·17%	
389·7			$Ti^{35}Cl_4$	32·54%	
477·8	9·4				$\nu_3(t_2)$[c]
487·2	9·9				
497·1	8·6				
505·7	6·5				
512·2					

[a] Spectra were calibrated against the emission lines of neon, the band maxima being considered accurate to ±0·5 cm^{-1}.

[b] Calculated abundance figures.

[c] $\nu_1 + \nu_2\,(E)$ would lie at $387 + 119 = 506$ cm^{-1} and $387 + 125 = 512$ cm^{-1}.

case of tetrabromides and tetraiodides, on account of their even lower frequency fundamentals.

It is important to note that the more intense laser lines (4880 Å, 1·0W; 5145 Å, 1·3W) induce significant local heating of the sample, despite its being held in a liquid-nitrogen cell. This is evident from the fact that by use of 1·3W at 5145 Å, the pattern of the a_1 band of titanium tetrachloride at formally 77K is abnormal, the pattern only becoming normal by attenuation of the laser power to *ca.* 130 mW.

Crystals of titanium tetrachloride at 241K are monoclinic, space group C_{2h}^5–$P2_1/c$ with $Z = 4$;[3] the site symmetry of the titanium atoms is thus C_1. There is no evidence for any phase change between 241 and 77K, and hence the factor group analysis presented in Table 2 has been carried out in terms of the above crystal data. Factor group splitting should give rise to four components to the a_1 molecular fundamental, only two of which (a_g and b_g) are Raman-active. However, the spectrum in this region provides no evidence for correlation splitting, which must therefore be $\leqslant$ 0·5 cm^{-1}. The structure of the a_1 band is thus entirely isotopic in origin, a conclusion substantiated by the fact that the observed difference between the frequencies of the a_1 modes of Ti^{35}Cl$_4$ and Ti^{37}Cl$_4$ (11·0 cm^{-1}) is in agreement with the calculated value (10·7 cm^{-1}).[5]

TABLE 2

Factor group analysis for crystalline titanium tetrachloride

Molecular group T_d	Site group C_1	Factor group C_{2h}
(ν_1) a_1	a	$a_g + a_u + b_g + b_u$
(ν_2) e	$2a$	$2a_g + 2a_u + 2b_g + 2b_u$
(ν_3, ν_4) t_2	$3a$	$3a_g + 3a_u + 3b_g + 3b_u$
Translational lattice modes		$3a_g + 2a_u + 3b_g + b_u$
Librational modes		$3a_g + 3a_u + 3b_g + 3b_u$

(a_g, b_g Raman-active, a_u, b_u i.r.-active)

The spectrum in the 120 cm^{-1} region (ν_2,e) should consist of four bands ($2a_g + 2b_g$) if chlorine isotopic splitting is negligible (the calculated shift[5] for ν_2 in going from Ti^{35}Cl$_4$ to Ti^{37}Cl$_4$ is only 3·3 cm^{-1}). Three of the expected four bands are observed, the major solid-state effect being the site splitting of the e mode by *ca.* 6 cm^{-1}. Similarly in the 136 cm^{-1} region (ν_4, t_2) six bands ($3a_g + 3b_g$) are to be expected as a consequence of site and correlation splitting. Apart from a shoulder, only site splitting (by *ca.* 3 cm^{-1}) is apparent. Again, the chlorine isotopic splitting is negligible (the calculated shift[5] for this mode on going from Ti^{35}Cl$_4$ to Ti^{37}Cl$_4$ is only 3·0 cm^{-1}).

The spectrum in the 500 cm^{-1} region consists of five bands, the separations of which are too great to be isotopic in origin; the calculated difference[5] between the t_2 modes of Ti^{35}Cl$_4$ and Ti^{37}Cl$_4$ is 6·1 cm^{-1}. The most obvious assignment of the bands is for the three of lowest frequency to arise from site splitting of the $\nu_3(t_2)$ fundamental into equally spaced components ($3a$), the average value for which (487 cm^{-1}) is close to the gas-phase value. The two components of highest frequency might arise from $\nu_1 + \nu_2$ (E in T_d, $2A$ in C_1), being enhanced in intensity by Fermi resonance with $\nu_3(t_2)$ owing to the C_1 site symmetry. However this interpretation is unlikely owing to the degree of intensity enhancement of these two components, and their lack of breadth. It seems more probable that, despite the large correlation splitting implied (6·5—9·9 cm^{-1}), the five bands in the 477–513 cm^{-1} region arise from five of the expected six Raman-active bands ($3a_g + 3b_g$).

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