The Raman Spectra of the Vanadium Oxytrihalides in the Vapour, Dissolved, and Solid States, and of the Mixed Oxytrihalides

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The Raman spectra of vanadium oxytrichloride and vanadium oxytribromide have been recorded as solid films at *ca.* 77 K. Evidence is presented for the formation of only one solid phase by the former (a phase which is not isomorphous with that of phosphorus oxytrichloride) but of two or three phases by vanadium oxytribromide. Values for the fundamentals of these molecules in cyclohexane solutions are also given. The vapour spectrum of vanadium oxytrifluoride has been obtained, and the values for the fundamentals and the band contours are compared with the correspondingly determined i.r. values and band contours. The vapour spectrum of vanadium oxytrichloride has likewise been recorded, and the contradiction between the i.r. and Raman assignments for the lowest-lying fundamental (125 cm^{-1}) has been resolved in favour of its assignment to an *e* mode. Vanadium oxytribromide is not sufficiently stable in the vapour phase to allow its Raman spectrum to be determined. Liquid mixtures of vanadium oxytrichloride and vanadium oxytribromide are found to contain approximately statistical proportions of the mixed halogeno-species $VOCl_2Br$ and $VOClBr_2$. Assignments for the fundamentals of these mixed species are also presented. One fundamental of the molecule $VOCl_2F$ has also been located.

SEVERAL vibrational studies of the vanadium oxytrihalides have been reported. Vanadium oxytrifluoride has been studied in the vapour state (in which it is a monomer) by i.r. spectroscopy,[1] and in the solid state (in which it is polymerised) [2] by Raman spectroscopy.[3] Vanadium oxytrichloride has been studied in the vapour state (Raman, 120 °C) [3] and as a pure liquid (Raman, and in the i.r. range 300—2200 cm^{-1}); [4,5] in both states it is a monomer, the assignments of the fundamentals being made on the basis of C_{3v} molecular symmetry. For vanadium oxytribromide, the only information available is the i.r. spectrum of the pure liquid; [6] the latter is likewise a monomer with C_{3v} molecular symmetry. Previous attempts to record its Raman spectrum have failed,[6] owing to absorption of the exciting beam by the liquid (which is intensely red).

As part of a programme of study of the Raman spectra of molecular crystals at room and at liquid-nitrogen temperatures,[7-9] we have recorded the Raman spectra of vanadium oxytrichloride and vanadium oxytribromide at *ca.* 77 K, and also of cyclohexane solutions of these two molecules. The vapour-state Raman spectra of vanadium oxytrifluoride and vanadium oxytrichloride have also been recorded.

EXPERIMENTAL

Materials.—Vanadium oxytrichloride (ROC/RIC Inc.) was purified by vacuum distillation. Vanadium oxytrifluoride (Alfa Inorganics) was purified by vacuum sublimation at 50 °C; it was handled exclusively in a dry box. Vanadium oxytribromide was prepared according to reactions (1) and (2).[6,10] The dark red liquid was kept under vacuum at −40 °C. Before use, it was distilled on a vacuum line by use of breaker-arm techniques. Before sealing off a sample, the compound was pumped for several seconds to remove dissolved bromine; after having been sealed, the sample tube was centrifuged to remove any solid decomposition products, and its Raman spectrum recorded immediately.

$$V_2O_5 + 2H_2 \xrightarrow{500\,^{\circ}C} V_2O_3 + 2H_2O \qquad (1)$$

$$V_2O_3 + 3Br_2 + C \xrightarrow{200\,^{\circ}C} 2VOBr_3 + CO \qquad (2)$$

No suitable solvent could be found for vanadium oxytrifluoride. Attempts to record its vapour-phase Raman spectrum were unsuccessful when the compound was sealed into Pyrex tubes, owing to the fact that it readily

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[1] H. Selig and H. H. Classen, *J. Chem. Phys.*, 1966, **44**, 1404.

[2] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1970, 1474.

[3] I. R. Beattie, K. M. S. Livingstone, D. J. Reynolds, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1970, 1210.

[4] H. J. Eichhoff and F. Weigel, *Z. anorg. Chem.*, 1954, **275**, 267.

[5] F. A. Miller and L. R. Cousins, *J. Chem. Phys.*, 1957, **26**, 329.

[6] F. A. Miller and W. K. Baer, *Spectrochim. Acta*, 1961, **17**, 112.

[7] R. J. H. Clark, B. K. Hunter, and C. J. Willis, *Chem. Comm.*, 1971, 201.

[8] R. J. H. Clark and B. K. Hunter, *J. Chem. Soc.* (*A*), 1971, 2999.

[9] R. J. H. Clark and P. D. Mitchell, *J. Chem. Phys.*, 1972, **56**, 2225.

[10] A. G. Loomis and H. Schlundt, *J. Phys. Chem.*, 1915, **19**, 734.

attacks Pyrex. However, no difficulty was experienced in recording its spectrum in the vapour phase when it was sealed into silica tubing. Some decomposition of the compound nevertheless took place at the temperatures involved (175 °C), but the decomposition products were not volatile at this temperature. Checks indicated that they did not include such possibilities as fluorine gas or vanadium pentafluoride.

Instrumental.—Spectra were recorded with a Spex 1401 Raman spectrometer in conjunction with Coherent Radiation model 52 krypton and argon ion lasers and a cooled FW130 phototube as detector. The exciting lines used were those at 647·1 and 676·4 nm, with in addition (for vanadium oxytrichloride) that at 568·2 nm and (for vanadium oxytrifluoride) that at 514·5 nm. The maximum power available with these lines was 750, 50, 300 mW and 1·6 W respectively, although in general it was found necessary to record the spectra of the compounds at lower powers. In the case of vanadium oxytribromide in the solid state, it was found necessary to remove the focusing lens of the sample illuminator as described previously[11] in order to prevent decomposition of the sample through local heating.

Solid-state spectra were recorded by use of an evacuable cold-finger cell described elsewhere.[8] Vapour-phase spectra were recorded with samples sealed into (Pyrex or silica) ampoules, the latter then being placed inside a furnace.[12]

The spectra were calibrated by reference to the emission lines of neon, and bands should be accurate in general from ±0·5 to ±1 cm^{-1}; bands qualified by br (broad) have been less accurately located.

RESULTS AND DISCUSSION

Vapour-phase Spectra.—Vanadium oxytrifluoride. As indicated in the Experimental section, the Raman spectrum of vanadium oxytrifluoride can be successfully obtained if the sample is sealed into a silica tube and this held at 175 °C.[2] The results are in Table 1, and the spectrum in Figure 1. The three totally symmetric fundamentals, ν_1, ν_2, and ν_3 are readily distinguished by their sharp *Q* branches and by their being polarised. They lie in each case within 3 cm^{-1} of the respective *Q* branches as determined by i.r. measurements on the vapour.[1] Only ν_3 shows rotational branches. The three fundamentals of the *e* species are characterised by pronounced rotational branches and by being depolarised. The frequency of the *Q* branch of $\nu_6(e)$ as determined from its Raman spectrum is effectively identical with the value obtained[1] by i.r. measurements. The agreement is less satisfactory for the *Q* branch of the $\nu_4(e)$ fundamental (discrepancy 5 cm^{-1}). The only possible problem arises for the $\nu_5(e)$ fundamental, for which the rotational branches in the Raman spectrum are highly asymmetric although the *Q* branch differs by only 1 cm^{-1} from the reported i.r. value.[1]

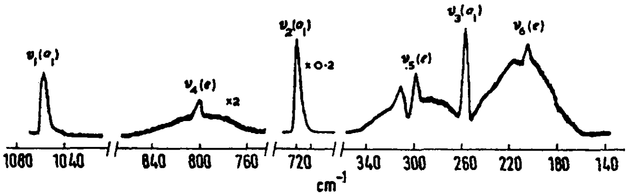

FIGURE 1 Vapour-phase Raman spectrum of vanadium oxytrifluoride at 175 °C. Instrumental settings: slit widths 80/200/80 μm, slit height 50 mm, scanning speed 10 cm^{-1} min^{-1}, time constant 0·4 s, excitation wavelength 514·5 nm at 1·6 W, range 1000 counts s^{-1} [except for $\nu_2(a_1)$ for which it was 5000 counts s^{-1}, and $\nu_4(e)$ for which it was 500 counts s^{-1}]

TABLE 1

Vibrational spectra of vanadium oxytrifluoride in the vapour state (cm^{-1})

Assignment[a] and approximate description	Raman values[b] (175 °C)		I.r. values[c] (25 °C)	
$\nu_1(a_1)$ V=O stretch			1067	(*R*)
	1055·0s,p		1057·8vs	(*Q*)
			1046	(*P*)
$\nu_2(a_1)$ VF$_3$ sym. stretch			733	(*R*)
	720·5vs,p		721·5s	(*Q*)
			712	(*P*)
$\nu_3(a_1)$ VF$_3$ sym. bend	*ca.* 279wm	(*RS*)?	268	(*R*)
	256·0s,p	(*Q*)	257·8s	(*Q*)
	ca. 236wm	(*OP*)?	248	(*P*)
$\nu_4(e)$ VF$_3$ asym. stretch	*ca.* 816vw,sh	(*RS*)		
	801·0vw	(*Q*)	806vs	
	ca. 786vw,sh	(*OP*)		
$\nu_5(e)$ F$_3$VO rock	*ca.* 322w,sh	(*RS*)?		
	309 m,dp	(*Q*)	308s	
	297·5m	(*OP*)		
$\nu_6(e)$ VF$_3$ asym. bend	215m,sh	(*RS*)	217	(*R*)
	204·0s,dp	(*Q*)	204·3s	(*Q*)
	192m,sh	(*OP*)	192	(*P*)

[a] The numbering of the fundamentals follows that used in G. Herzberg, 'Infrared and Raman Spectra of Polyatomic Molecules,' van Nostrand, Princeton, 1945, p. 312. [b] The quoted frequencies are an average of four scans with 6471 and 5145 Å excitation. An extremely weak, broad band also appears at 484 cm^{-1}. [c] H. Selig and H. H. Claassen, *J. Chem. Phys.*, 1966, **44**, 1404.

Vanadium oxytrichloride. No difficulty was experienced in obtaining a good vapour-phase Raman spectrum of vanadium oxytrichloride. The frequencies of the six fundamentals (ν_1, ν_2, ν_3 of a_1 species, ν_4, ν_5, ν_6 of *e* species, all active in both the i.r. and the Raman spectra) are within 1·5 cm^{-1} of those recently reported by Beattie *et al.*[2] However, our assignments for the two lowest fundamentals [$\nu_3(a_1)$, symmetric VCl$_3$ deformation 163 cm^{-1}, $\nu_6(e)$ asymmetric VCl$_3$ deformation 124·5 cm^{-1}] are the reverse of theirs (Table 2). The bases for our assignment, which is in agreement with the i.r. assignment,[5] are as follows: (*a*) Reversal of the present assignment puts two fundamentals of the same (*e*) symmetry close together in frequency. This argument has already been used against such a reversal of assignment in the case of vanadium oxytrifluoride;[1] moreover, the present Raman results (see above) on vanadium oxytrifluoride[7] have confirmed the i.r. assignments of the fundamentals of this molecule. (*b*) The depolarisation ratio of the 163 cm^{-1} band (0·65) is significantly below that expected and found for depolarised bands using laser excitation (0·75). (*c*) The band contours of the fundamentals ν_1, ν_2, and ν_3 (1042·5,

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[11] R. J. H. Clark, B. K. Hunter, and P. D. Mitchell, *J.C.S. Faraday II*, 1972, 476.

[12] R. J. H. Clark, B. K. Hunter, and D. M. Rippon, *Inorg. Chem.*, 1972, **11**, 56.

409·5, and 163 cm^{-1} respectively) are all sharp and, with the exception of ν_3, have no obvious rotational structure, in agreement with the selection rules for totally symmetric bands of symmetric top molecules (strong *Q* branch, weak *O*, *P*, *R*, and *S* branches).[13] On the other hand the three fundamentals assigned to *e* modes, ν_4, ν_5, and ν_6 (503, 248, and 124·5 cm^{-1} respectively) are all broad, and for ν_5 the *OP* branch is observed clearly, while for ν_6 both the *OP* and the *RS* branches are apparent (Figure 2).[14] Underlying hot bands blur out the inherent isotopic structure to the $\nu_2(a_1)$ fundamental.

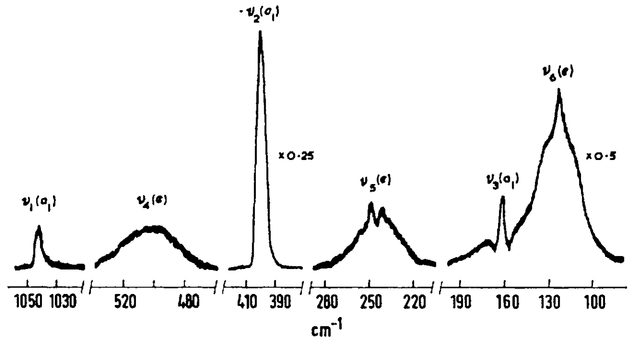

FIGURE 2 Vapour-phase Raman spectrum of vanadium oxytrichloride at 206 °C. Instrumental settings: slit widths 90/250/90 μm, slit height 50 mm, scanning speed 10 cm^{-1} min^{-1}, time constant 1 s, excitation wavelength 647·1 nm at 750 mW, range 500 counts s^{-1} [except for $\nu_2(a_1)$ for which it was 2000 counts s^{-1}, and $\nu_3(a_1)$ and $\nu_6(e)$ for which it was 1000 counts s^{-1}]

Spectra in Cyclohexane Solution.—Vanadium oxytrichloride. The values for the fundamentals of vanadium oxytrichloride in cyclohexane solution as found in the present study lie within 2 cm^{-1} of those originally reported by Miller and Cousins[5] on the basis of i.r. measurements on the pure liquid. Our Raman values for the fundamentals of the pure liquid are within 2 cm^{-1} of the solution values, and are accordingly not reported separately. The assignments follow from the discussion in the previous section (Table 2).

Chlorine isotopic structure is observable only for $\nu_2(a_1)$, the symmetric VCl_3 stretching fundamental. The average value of the isotopic splitting (3·0 cm^{-1}) is similar to that found for the a_1 fundamental of molecular tetrachlorides,[8] *e.g.*, CCl_4, 3·15 cm^{-1}; $SiCl_4$, 2·87 cm^{-1}; $TiCl_4$, 2·75 cm^{-1}; $GeCl_4$, 2·72 cm^{-1}; $SnCl_4$, 2·60 cm^{-1}; and $PbCl_4$, 2·15 cm^{-1}.

TABLE 2

Raman spectra of vanadium oxytrichloride (cm^{-1})

Assignment [a] and approximate description		Vapour (200 °C)		C_6H_{12} solution [b]	Solid	$\nu_{vap} - \nu_{soln}$
ν_1 (a_1)	V=O stretch	1042·5m		1037·5m	1022·0m	5·0
ν_2 (a_1)	$V^{35}Cl_3$ sym. stretch			410·7vs	410·5ms	
	$V^{35}Cl_2{}^{37}Cl$ sym. stretch	409·5vs		407·4vs	407·3s	2
	$V^{35}Cl^{37}Cl_2$ sym. stretch			404·5s,sh	404·6m	
	$V^{37}Cl_3$ sym. stretch				401·6w	
ν_3 (a_1)	VCl_3 sym. bend	173	(*RS*)			
		163·0w		163·5w	170·5	−0·5
		152	(*OP*)			
ν_4 (*e*)	VCl_3 asym. stretch				523·5w	
		503vw,br		505w,br	504·5w	*ca.* 0
		±2		±2	500·0m	
ν_5 (*e*)	Cl_3–V–O rock	248w	(*Q*)	247w	249·5ms	1
		241w	(*OP*)?			
ν_6 (*e*)	VCl_3 asym. bend	133m	(*RS*)		133·5s	
		124·5ms	(*Q*)	128·5m	130·0m	−4·0
		ca. 117m	(*OP*)		125·0s	

[a] See footnote *a* to Table 1. [b] Depolarisation ratios for vanadium oxytrichloride in cyclohexane are as follows: 0·07, 0·02, 0·65, 0·72, 0·71, 0·71 for ν_1 to ν_6 respectively.

The frequency shifts of the fundamentals on change of state from vapour to cyclohexane solution are such that the stretching modes occur at lower frequencies in the condensed state (with the possible exception of ν_4, for which the shift was indeterminate owing to the weakness and breadth of the band), but that the bending modes are either not significantly shifted (ν_3 and ν_5) or else occur at higher frequency (ν_6). These shifts are of the same order and in the same direction as those both calculated and found for certain molecular tetrahalides.[15] The V=O stretching mode (ν_1) also shows a large further shift (15·5 cm^{-1}) to lower frequency, and the VCl_3 symmetric bend shows a shift (7 cm^{-1}) to higher frequency on solidification.

Vanadium oxytribromide. The assignments of the Raman fundamentals of vanadium oxytribromide (Table 3) have been made by analogy with those for vanadium oxytrichloride, and by consideration of the depolarisation ratios of the bands. The assignments are in complete agreement with those made by Miller and Baer[6] on the basis of i.r. measurements on the pure liquid. Indeed our values for five of the six fundamentals lie within 1·5 cm^{-1} of the i.r. values; ν_1 (a_1) differs by 4 cm^{-1} from the i.r. value. However, this fundamental is the most sensitive one to change of state and the Raman value refers to cyclohexane solutions of the molecule whereas the i.r. value refers to the

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[13] E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.

[14] The assignment given in ref. 3 has been changed in G. A. Ozin, *Progr. Inorg. Chem.*, 1971, **14**, 173, but without comment.

[15] J. Heicklen, *Spectrochim. Acta*, 1961, **17**, 82.

pure liquid; the difference is thus accountable on a solvent shift basis.

The $\nu_1(a_1)$ fundamental suffers a large shift of 19·5 cm^{-1} to lower frequency on condensation to solid A (see below), *cf.* the same situation with vanadium oxytrichloride. It is significant (*cf.* the dipole coupling model) that this fundamental also gives rise to the most intense i.r. band.

TABLE 3

Raman spectra of vanadium oxytribromide (cm^{-1})

Assignment [a] and approximate description		C_6H_{12} solution [b,c]	Solid A [d]	Solid B
$\nu_1(a_1)$	V=O stretch	1029·0w	1009·5wm	1027·0w
				1013·0w
$\nu_2(a_1)$	VBr_3 sym. stretch	272·0vs	285·5vw	276·0vs
			266·0s	266·5vs
$\nu_3(a_1)$	VBr_3 sym. bend	118·5w	133·0m	131·5m
				124·5w
				119·5w
$\nu_4(e)$	VBr_3 asym. stretch	401·0wm	415·0w	
			403·5m	403·5wm
			397·0ms	397·5wm
			387·0w	393·5w
				388·0w
$\nu_5(e)$	Br_3–V–O rock	213·0w	223·5m	222·5w
				215·5w
				209·0w
$\nu_6(e)$	VBr_3 asym. bend	82·0wm	82·5s	84·0s
			78·5s	79·5s
				76·0s

[a] See footnote *a* to Table 1. [b] Depolarisation ratios for ν_1, ν_2, and ν_3 in solution are approximately 0·41, 0·04, and 0·46 respectively; ν_4, ν_5, and ν_6 are depolarised. [c] Very weak additional bands appearing at 315, 479, and 543 cm^{-1} have been assigned as $\nu_4 - \nu_6$, $\nu_4 + \nu_6$, and/or $\nu_2 + \nu_5$, and $2\nu_2$ respectively. [d] Possible lattice modes occur at 57·5, 56·0, 54·5, 46·0, 42·5, 39·5, 36, and 25 cm^{-1}.

Vanadium oxytrihalide mixtures. Previous work has shown that mixed chlorobromides of germanium, titanium, and tin are readily obtained simply by mixing the appropriate tetrahalides.[16] We now report that mixtures of vanadium oxytrichloride and vanadium oxytribromide redistribute their halogen atoms virtually instantaneously at room temperature. Note, by contrast, that mixtures of the corresponding phosphorus oxytrihalides do not redistribute their halogen atoms at room temperature.[17] Although no quantitative measurement has been carried out, qualitative measurements indicate that the resulting distribution of halogen atoms is approximately statistical. The basis for these conclusions is the appearance in the mixtures of two new bands between the band corresponding to a given fundamental of the oxytrichloride and the band corresponding to the same fundamental of the oxytribromide. This situation is most clearly illustrated for the $\nu_2(a_1)$ region (Figure 3), in which clear evidence for the molecules $VOCl_2Br$ and $VOClBr_2$ is apparent. The frequencies of all the bands, and their suggested assignments, are in Table 4. The assignments for the mixed halides are given for simplicity in C_{3v} nomenclature, although of course these molecules have a lower symmetry (C_s) in which the degeneracies of the *e* modes are strictly removed. This effect is, however, not apparent in the spectra.

Mixtures of vanadium oxytrifluoride and vanadium oxytrichloride have also been studied. The oxytrifluoride is only very slightly soluble in the oxytrichloride and the only convincing evidence for the formation of any mixed species is the appearance of a polarised band of medium strength at 446 cm^{-1} which can logically be assigned as $\nu_2(a_1)$ of the molecule $VOCl_2F$. The same band has also been observed in the vapour phase at 446 cm^{-1}. Vanadium oxytrifluoride is insoluble in vanadium oxytribromide, and no exchange takes place at room temperature in this case.

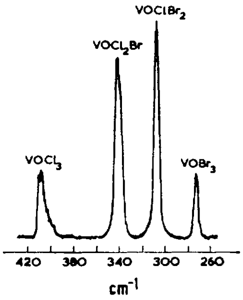

FIGURE 3 Raman spectrum of a cyclohexane solution of a 2 : 1 mixture of vanadium oxytrichloride and vanadium oxytribromide in the region of the $\nu_2(a_1)$ fundamental of each molecule. The intensities of the a_1 bands of the bromine-containing species are greater than the abundance of such species (calculated statistically) would suggest owing to the fact that metal–bromine bond polarisability derivatives are greater than metal-chlorine bond polarisability derivatives (*cf.* ref. 15)

TABLE 4

Band positions for an approximately 2 : 1 mixture of vanadium oxytrichloride and vanadium oxytribromide in cyclohexane solution and the appropriate assignments (cm^{-1})

Frequencies and assignments		
1033m,br	ν_1	$VOCl_3$ $VOCl_2Br$ $VOClBr_2$ $VOBr_3$
501w	ν_4	$VOCl_3$
479w	ν_4	$VOCl_2Br$
459m	ν_4	$VOClBr_2$
424vw,br		C_6H_{12}
409s	ν_2	$VOCl_3$
400w,sh	ν_4	$VOBr_3$
341vs	ν_2	$VOCl_2Br$
307vs	ν_2	$VOClBr_2$
272s	ν_2	$VOBr_3$
246m	ν_5	$VOCl_3$
227m	ν_5	$VOCl_2Br$
221m	ν_5	$VOClBr_2$
215w,sh	ν_5	$VOBr_3$
163w	ν_3	$VOCl_3$
150m	ν_3	$VOCl_2Br$
134m,sh	ν_3	$VOClBr_2$
127ms	ν_6	$VOCl_3$
117s	ν_3	$VOBr_3$
108s	ν_6	$VOCl_2Br$
88m,br	ν_6	$VOBr_3$, $VOClBr_2$

Solid-state Spectra.—Vanadium oxytrifluoride. The

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[16] R. J. H. Clark and C. J. Willis, *Inorg. Chem.*, 1971, **10**, 1118.

[17] M.-L. Delwaulle and F. François, *Compt. rend.*, 1945, **220**, 817.

Raman spectrum of vanadium oxytrifluoride has been reported,[3] and has not been restudied in this investigation. The compound does not crystallize as a molecular solid, but as a fluorine-bridged polymer.[2] It is therefore, in the solid state, not analogous to vanadium oxytrichloride or vanadium oxytribromide.

Vanadium oxytrichloride. There appears to be only one solid form of vanadium oxytrichloride down to *ca.* 77 K. Annealing the sublimate by raising it to the m.p. and recooling several times removes from the spectrum two weak broad bands at 163·5 and 1032 cm^{-1} which appear to correspond to bands of the liquid.

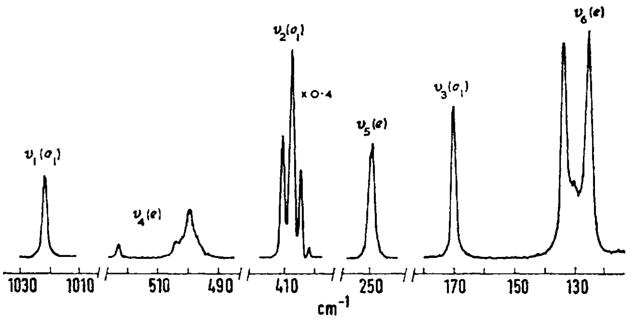

FIGURE 4 Raman spectrum of crystalline vanadium oxytrichloride. Instrumental settings: slit widths 20/200/40 µm, slit height 50 mm, scanning speed 10 cm^{-1} min^{-1}, time constant 1 s, excitation wavelength 647·1 nm at 400 mW, range 2000 counts s^{-1} [except for the region of $\nu_2(a_1)$ for which the range was 5000 counts s^{-1}]. Symmetry designations are given in C_{3v} nomenclature

The chlorine isotopic splitting of $\nu_2(a_1)$ is clearly resolved into the expected four components corresponding to ν_2 for the molecules $VO^{35}Cl_3$, $VO^{35}Cl_2{}^{37}Cl$, $VO^{35}Cl^{37}Cl_2$, and $VO^{37}Cl_3$, with an average isotopic splitting of 3·0 cm^{-1} (in agreement with the solution values). However, as found for the metal tetrahalides[8] and for boron trichloride in the solid state,[9] the relative intensities of the four bands do not correspond exactly to the relative abundances of the different molecules present (Figure 4). Presumably the relative intensities of the bands are slightly affected by the lowered symmetry of the mixed isotopic species; *cf.* the similar behaviour of the corresponding band of phosphorus oxytrichloride.[18,19]

No factor-group splitting of the molecular fundamentals of a_1 symmetry is observed, but the degeneracies of two of the three molecular fundamentals of e symmetry are removed in the solid state. Apart from weak bands at *ca.* 130 and 523·5 cm^{-1}, no factor-group splitting is apparent; this suggests that the molecule may crystallise in a unit cell of relatively high symmetry and, in any case, in a unit cell of higher symmetry than that deduced for phosphorus oxytrichloride (D_{2h}).[18,19]

Vanadium oxytribromide. Vanadium oxytribromide appears to exist at *ca.* 77 K in at least two forms. If the compound is allowed to sublime on to the cold finger it forms a yellow (sometimes yellow-orange) film. Where the laser beam strikes this film, an orange spot is formed (this colour change can to some extent be eliminated by removal of the focusing lens from the illuminator assembly). Most of the scans of this film yielded poorly defined spectra which varied in band intensity with time; the results are listed in Table 3 under the heading Solid B. This solid is clearly a mixture of a metastable form and solid A (see below). Evidence for this arises from observation of the two bands at *ca.* 270 cm^{-1} assigned as ν_2 for solids A and B. With time the lower-frequency band (266·5 cm^{-1}) increases in intensity and the higher-frequency band (276·0 cm^{-1}) decreases. The lower-frequency band corresponds to the single band at 266 cm^{-1} observed in solid A. Solid B could never be isolated without some solid A being present.

If solid B is annealed a brown-orange transparent solid is formed. This solid (solid A) gives very reproducible, well-defined spectra, and appears to be the stable form at *ca.* 77 K. None of the a_1 fundamentals of solid A is split in the solid state, but two of the e fundamentals show solid-state splittings (ν_4 and ν_6) (Figure 5). This behaviour is closely similar to that displayed by solid vanadium oxytrichloride, but completely different from that displayed by solid phosphorus oxytrichloride[19] and by solid phosphorus oxytribromide.[20] However, insufficient information is available on which to deduce the factor group into which the molecule has crystallised.

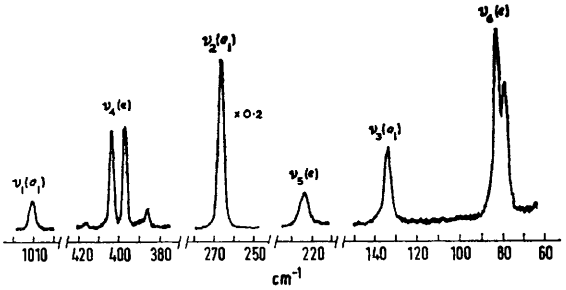

FIGURE 5 Raman spectrum of crystalline vanadium oxytribromide (stable form A). Instrumental settings: slit widths 100/200/100 µm, slit height 50 mm, scanning speed 25 cm^{-1} min^{-1}, time constant 1 s, excitation wavelength 647·1 nm at 50 mW (unfocused beam), range 1000 counts s^{-1} [except for $\nu_2(a_1)$ for which the range was 5000 counts s^{-1}]. Symmetry designations are given in C_{3v} nomenclature

We thank the S.R.C. and the N.A.T.O. for financial support.

[2/1150 *Received, 22nd May,* 1972]

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