Single-crystal Raman and Infrared Spectra of Vanadium(v) Oxide

By **T. R. Gilson** * and (in part) **O. F. Bizri** and **N. Cheetham,** Department of Chemistry, The University, Southampton SO9 5NH

Oriented single-crystal Raman and i.r. spectra of vanadium(v) oxide are reported and absorption frequencies compared with those calculated using a simple transferred force field. It is shown that departures from previously established oxide-group frequencies are due to the relative lightness of the vanadium atom.

In a previous paper,[1] it was shown that observations on phonon spectra of metal oxides may in many cases be interpreted satisfactorily on a simple group-frequency basis. This procedure relies on the comparatively greater mass of the metal over the oxide ion in oxygen co-ordination polyhedra M_nO and, not surprisingly, is unsatisfactory for oxides of relatively light elements such as vanadium. The method is also of little help in interpreting spectra of highly cross-linked structures, *e.g.* the corundum group of metal oxides.[2] In the case of Fe_2O_3 and Cr_2O_3, the presence of a partially filled *d* shell also makes it less likely that a transferred force field would be adequate.

In all these cases it is desirable to calculate the absorption frequencies and approximate form of the normal modes in order to interpret the spectra. In this paper it is shown that a very simple transferred force field fits the observations quite closely for vanadium(v) oxide. This verifies the kinetic origin of departures from group frequencies found for many other metal oxides.[1] For metal oxides with the corundum structure, calculations are less satisfactory [3] and it is necessary to refine the force fields (and to include a large number of interaction terms) to obtain even a partially acceptable frequency fit. Nearly complete i.r. and Raman data for crystalline vanadium(v) oxide are reported in this paper, i.r.-active frequencies being obtained from normal reflectance data by Kramers–Kronig analysis.

RESULTS AND DISCUSSION

The observed reflectance spectra for vanadium(v) oxide are shown in Figure 1 and corresponding absorption frequencies are listed in Table 1. I.r. absorption spectra (obtained by Kramers–Kronig analysis of the data in Figure 1) are tabulated in Table 2 for the assumed fundamentals with approximate extinction coefficients, half-widths, and calculated frequencies. Raman data are similarly presented in Table 3 with approximate relative intensities for 632·8 nm excitation, at room temperature and 20 K. This data supercedes that of ref. 1 in that the (very weak) b_{1g} spectrum is now more clearly defined. The i.r. experiments were also repeated at liquid-nitrogen temperatures but no

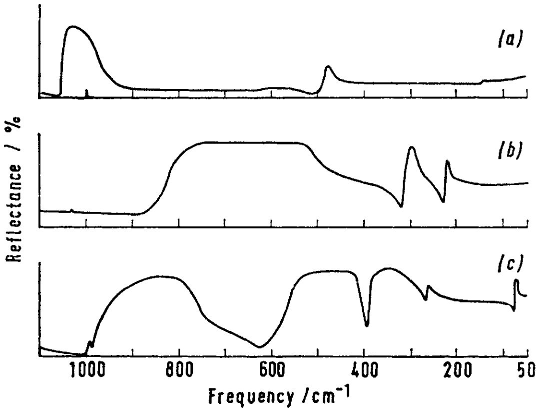

FIGURE 1 I.r. normal reflectance spectra of crystalline vanadium(v) oxide: (*a*), b_{2u}; (*b*), b_{1u}; (*c*), b_{3u}

---

[1] I. R. Beattie and T. R. Gilson, *J. Chem. Soc.* (*A*), **1969**, 2322.

[2] I. R. Beattie and T. R. Gilson, *J. Chem. Soc.* (*A*), **1970**, 980.

[3] I. R. Beattie, O. F. Bizri, and T. R. Gilson, to be published.

significant changes were found compared with the room-temperature data. In particular no sharpening of the very broad bands [with Δν(½) measured in hundreds of wavenumbers] occurred. The liquid-hydrogen temperature Raman spectra were, however, a distinct improvement on those obtained at room temperature. In particular, the b_{1g} bands at 357, 504, and 965 cm^{-1} were much more clearly defined.

TABLE 1

Reflectance data for crystalline V_2O_5

Maximum frequency/cm^{-1}	Approximate reflectance/% At maximum	At minimum
b_{1u}, μ_z		
216	85	25
293	95	20
650	100	8
1030	12	11
b_{2u}, μ_y		
140	20	16
354?	17	16
477	35	12
570	17	15
926	30	19
1027	70	5
b_{3u}, μ_x		
74	90	40
260	75	60
350	95	30
485	95	10
830	95	8
990	12	8
1040	9	8

Assignments.—Factor-group analysis for vanadium(v) oxide[1] gives equation (1). In principle, observation

$$\Gamma_{\text{cryst}} = 7a_g + 7b_{1g} + 3b_{2g} + 4b_{3g} + 3a_u + 3b_{1u} + 6b_{2u} + 6b_{3u} \quad (1)$$

of the correct number of modes with the activity required for a particular symmetry species constitutes an unambiguous assignment. In addition the adequate frequency fit obtained for a simple force field transferred from OsO_4 allows a moderately good description of

TABLE 2

I.r. absorption spectra of crystalline vanadium(v) oxide at room temperature

Frequency/cm^{-1}		Extinction † coefficient		Δν(½)/cm^{-1}	Assignment
b_{1u}		μ_z			
220		0·096		12	δOV
308		0·140		22	δOV_2 (180°)
700		0·182		275	νOV_3 (1·88)
b_{2u} *	b_{3u}	μ_y	μ_x		
	74		0·053	7	Skeletal δ
144		0·058		6	
	265		0·039	7	δOV_3
	386		0·117	35	δOV
357?		vw		5	
481		0·202		10	δOV_2
	520		0·15	170	νOV_3 (2·02)
580?		vw		35	
	880	0·20		160	νOV_2
	995		vw		νOV
1035		0·286		40	

* Weak bands in some parts of this spectrum would be obscured by slight break-through of strong b_{1u} and b_{3u} components. † Approximate value, giving a guide to relative intensities within a symmetry species only.

TABLE 3

Raman spectra of crystalline vanadium(v) oxide, 632·8 nm excitation

Room temperature							20 K					
Frequency/cm^{-1}		Peak height †					Frequency/cm^{-1}		Peak height †			
a_g	b_{1g}	*xx*	*yy*	*zz*	*xy*	Δν(½)/cm^{-1}	a_g	b_{1g}	*zz*	*xy*	Δν(½)/cm^{-1}	Assignment
104		35	160	60		4	107		60		3·5	Skeletal δ
198		70	14	20		7	200		44		4	Skeletal δ
	201				25	8		202		75	5	
306		95	17	4		10	307		20		4	δOV_3
	310				15	11		313		40	4	
	355				2	12		357		10	4	δOV
406		55	45	25		10	404		80		4	
482		95	6	15		20	484		100		7	δOV_2 (148°)
	502?				5	20		504		10	10	νOV_3 (2·02)
530		105	3	5		20	527		15		10	
	954?				2	35		965?		6	20	νOV_2
995		105	600	60		4	992		180		3·5	νOV
	995				10	4		993		45	3·5	
b_{2g}	b_{3g}	*xz*	*yz*				b_{2g}	b_{3g}	*xz*	*yz*		
144		600				6	147		1660		3·5	Skeletal δ
	147		220			7		148		570	4	
	230		4			10		231		10	4	δOV_2 (180°)
284		90				7	286		380		3·5	δOV
	287		180			5		287		600	3·5	
701		45				20	702		250		10	ν OV_3 (1·88)
	701		35			20		702		160	8	

† Arbitrary units. No correction made for variation in spectral slit width with wavelength or for fall off in sensitivity of phototube. Room-temperature and 20 K figures are only on approximately the same scale. Values were not measured for a_g components other than *zz* at 20 K.

each normal mode. However, some ambiguities arise and it is in any case instructive to analyse the results in more detail.

The structure of normal crystalline V_2O_5 is based chemically on five-co-ordinate vanadium, with a sixth oxygen atom at 2·8 Å completing a highly distorted octahedron.[4] The basic $(M_2O_2)_n$ puckered chain in the z direction (Figure 2) (common to a number of metal oxides) is in this case built up into sheets in the x direction by doubly linked bridging oxygen atoms at 1·780 Å, with ∠M–O–M = 148°. The approximate trigonal bipyramid about vanadium is completed by a terminal oxygen atom at 1·59 Å projecting alternately above and below the sheet. This latter atom also forms the closest V–O contact between sheets (2·8 Å).

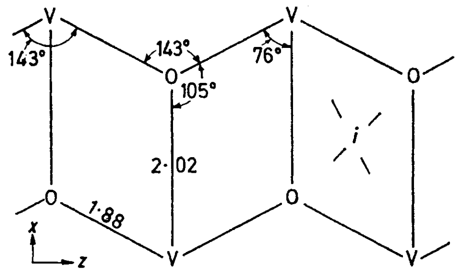

FIGURE 2 Puckered $(V_2O_2)_n$ chain

TABLE 4

Calculated potential-energy distribution

Element of co-ordination polyhedron	Classification of modes of vibration			Frequency/cm^{-1}				Calculated potential-energy distribution †											
	According to site group		According to factor group	Calc.		Obs.		ν(OV)	$\nu(OV_3)$ 1·88	$\nu(OV_3)$ 2·02	$\nu(OV_2)$	SVT_s	SVT_l	SVD	T_sOT_l	T_sOT_s	DOD	T_sVT_l	DVT_s
	C_s	C_{2h}^2	D_{2h}^{13}																
OV	$a'(\nu)$	a_g	$a_g + b_{1g}$	1066	1068	995	995	98 95											
		b_u	$b_{2u} + b_{3u}$	1067	1068	1035	995	98 95											
	$a'(\delta)$	a_g	$a_g + b_{1g}$	422	354	406	355		11 20			7	12 28	55 26		5 10	10		
		b_u	$b_{2u} + b_{3u}$	394	357	357?	386		5 9			14 29	28 39	43 9					7
	$a''(\delta)$	a_u	$a_u + b_{1u}$	249	233		220					94 59							51
		b_g	$b_{2g} + b_{3g}$	267	282	284	287					79 41						10 9	43
OV_3	$a''(\nu\ 1{\cdot}88)$	a_u	$a_u + b_{1u}$	746	747		700		90 90										
		b_g	$b_{2g} + b_{3g}$	738	739	701	701		92 92										
	$a'(\nu\ 2{\cdot}02)$	a_g	$a_g + b_{1g}$	598	568	530	502?		6	74 78	16								
		b_u	$b_{2u} + b_{3u}$	667	618	580?	520		7 9	58 66	15					5	5	5	6 6
	$a'(\delta)$	a_g	$a_g + b_{1g}$	288	275	306	310		14 5			47 44		11 14		7	5		12 24
		b_u	$b_{2u} + b_{3u}$	268	252		265		7 6	8	28	21 8		12 63					14 10
V	a'(skeletal)	a_g	$a_g + b_{1g}$	204	200	198	201		4 10	6 15			57 30	5	5 9	5	13 13	8	12
		b_u	$b_{2u} + b_{3u}$ + acoustic	118	41	144	74		7 12	5	7	5 8	25 45	19		6	50		
	a'(skeletal)	a_g b_u	$a_g + b_{1g}$	53	133	104							7 36	13 49			69		13
	a''(skeletal)	a_u	a_u + acoustic	74															97
		b_g	$b_{2g} + b_{3g}$	145	123	144	147		7			19 9			23 32			35 49	20
	C_{2v}																		
OV_2	$b_1(\nu)$		b_{1g}		971		954?				92								
			b_{3u}		974		880				91								
	$a_1(\delta$ * 148°)		a_g	492		482			5	5	56						6		12
			b_{2u}	466		481				5	48			19			13		
	$b_2(\delta$ 180°)		b_{3g}		234		230					47							52
			b_{1u}		265		308					38							58
					Force constant/mdyn Å^{-1}			f_1	f_2	f_3	f_4	f_5	f_6	f_7	f_8	f_9	f_{10}	f_{11}	f_{12}
								8·03	2·01	2·01	4·02	0·62	0·62	0·93	0·20	0·20	0·30	0·31	0·47

* This is partly a stretching frequency due to the small ∠V–O–V. † S and D represent bonds to singly and doubly linked oxygen atoms respectively, T_s and T_l to triply linked oxygen atoms at shorter and longer distances.

The observed frequencies occur for the most part as doublets[1] grouped as $(a_g + b_{1g})$, $(b_{2g} + b_{3g})$, or less obviously $(b_{2u} + b_{3u})$. (The data in Tables 2 and 3 are presented in this way.) This is apparently because the comparatively close-knit V_2O_4 chains (Figure 1, including the terminal oxygen atom) behave as self-contained units. The observed doublets may then be assigned as vibrations of these chains, the latter being coupled into pairs in the unit cell *via* the doubly linked bridging oxygen atoms. Singlets arise either from the three degrees of freedom of the bridging oxygen atom or, in the case of b_{1u} modes, because the predicted a_u component of the doublet is inactive.

The V_2O_4 chains have a site symmetry of $P2_1/m$, C_{2h}^2, with z the crystal screw axis. Within each chain the higher-frequency modes also form i.r.–Raman pairs across the centre of inversion. Thus, using the group-frequency approach,[1] we may build up a set of correlations for the vibrations. This is shown in Table 4 together with the collated i.r. and Raman data, and results of calculations using a simple force field transferred from OsO_4. The potential-energy distribution shows that many of the group-frequency assignments are only approximate.

Intensities.—Relatively little information may be obtained from a qualitative examination of the intensities. In a few cases, however, the assignments are nicely verified. Thus the terminal oxygen-atom stretching frequency is strong in the *yy* component of the Raman spectrum and also in the μ_y (b_{2u}) component of the i.r. $(b_{2u} + b_{3u})$ doublet. Similarly the symmetric deformation of this oxygen atom is strong in the $\mu_x(b_{3u})$ component of the i.r. spectrum.

Calculations.—The calculations were performed using a variant of Schachtschneider's GMATP program

---

[4] H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, *Z. Krist.*, 1961, **115**, 110.

which greatly simplifies the input for crystals and polymers. The force field was transferred from the simple valence force field for OsO_4 by scaling the force constants according to the co-ordination number of the oxygen atom. Thus the constants for singly linked- (' terminal'), doubly linked-, and triply linked-oxygen atoms were set equal to 1, $\frac{1}{2}$, and $\frac{1}{4}f_r$ respectively (f_r = force constant for OsO_4). Deformational constants were proportioned in accordance with the bonds containing the angle, in a somewhat arbitrary manner. Small arbitrary values were inserted for $\angle$V–O–V deformations. All values used are included in Table 4.

As stated in ref. 1, a simple cartesian type of symmetry co-ordinate involving the degrees of freedom of atoms, rather than of structure parameters, is often more suitable for describing the normal modes of complex polymers. In a more recent version [5] of the programs used here, such a description is provided as output. However, as this program was not available when these calculations were performed, a certain amount of care is required in interpreting the potential-energy distribution given in Table 4.

EXPERIMENTAL

Vanadium(V) oxide crystals, grown by slow cooling of a melt, gave single crystals of an adequate size (*ca.* 3 × 1 × 0·3 mm) for fairly precise Raman orientation work and several crystals were glued onto a substrate to increase the area for i.r. reflectance studies. For the crystal edge or (100) face it was possible to prepare a crystalline mass which, whilst certainly not a single crystal, was composed of individual crystals sufficiently closely aligned to one another to permit good i.r. orientation work. Only on searching for a b_{2u} band of a few percent reflectance in a region of 80—100% reflectance bands in the other orientations, was any difficulty encountered. This face was avoided in the Raman studies by using both 90 and 180° collection.

I.r. normal reflectance spectra were run on Beckmann IR11, Perkin-Elmer 225 and 337, and RIIC FS 720 spectrometers. With the latter, data points were provided as paper tape output as well as being processed by an FTC 100-7 Fourier transform computer. The paper tape was used on a digital computer with a program including both Fourier transform and Kramers–Kronig analysis facilities. The range of the RIIC FS 720 spectrometer was extended to 1250 cm^{-1} by obtaining a 4 μm signal from the existing 8 μm Moiré sampling interval device, and by using a Grubb–Parsons In/Sb filter and a toroidal mirror to replace the black Polythene lens. Some regions of the spectrum obtained in this way were too noisy to be reliable, and the authenticity of peaks therein was established by reference to the conventional spectrometers. Raman spectra were run using a Spectra Physics 125 He/Ne laser as source, on either a Cary 81 (180°) or Spex 1401 (90°) spectrometer. Spectra at 20 K were recorded by attaching a crystal to the tip of an Air Products AC-2 Joule–Thomson effect cryo-tip, mounted in the sample area of the Spex.

We thank Professor I. R. Beattie for helpful discussion and for allowing us to use his facilities, and Dr. Margaret Gardner for much help with computing.

[2/1577 *Received, 3rd July,* 1972]

---

[5] I. R. Beattie, N. Cheetham, Margaret Gardner, and D. E. Rogers, *J. Chem. Soc.* (*A*), 1971, 2240.