

Infrared and Raman Study of Amorphous V_2O_5

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Amorphous V_2O_5 can be obtained by cooling from the melt. This amorphous oxide is very sensitive to water vapour and can even be dissolved in water to give a vanadium pentoxide gel. The hydration process has been followed by infrared and Raman spectroscopy between 20 and 4000 cm^{-1} . Short-range order in the amorphous oxide appears to be almost the same as in orthorhombic V_2O_5 . The amorphous phase could even be described as made of small crystallites about 100 \AA in diameter. The structure of amorphous V_2O_5 does not seem to be modified by water adsorption, at least during the first stages of the hydration process. However, a drastic modification occurs when enough water is added to give a gel. A general shift to lower frequencies is observed, indicating a weakening of the V—O bonds, presumably associated with the formation of new V—OH₂ bonds. Two different water species have been identified, one of which seems to be almost free of hydrogen bonding. Short-range order in the gels seems to be quite well defined and the spectra could be interpreted either in terms of crystallites, as in amorphous V_2O_5 , or in terms of molecular (or macromolecular) species containing V_2O_5 , $(H_2O)_x$ groups.

INTRODUCTION

It has been shown that amorphous V_2O_5 readily dissolves in water, whereas crystalline V_2O_5 does not.¹ A viscous gel or a colloidal solution may be obtained, depending on the amount of water added.² This property appears to be related to the fibrous texture of the amorphous oxide³ and the action of water can be described as the swelling process⁴ of an inorganic polymer.

Detailed studies of the action of water on amorphous V_2O_5 have been undertaken. They show that the amorphous oxide consists of entangled polymeric V—O chains, the structure of which presumably corresponds to the double chains running along the *c* axis of orthorhombic V_2O_5 .⁴ Upon hydration, water molecules are adsorbed at the surface of the fibres, destroying their entanglement and giving a more or less viscous gel.² ESR experiments show a drastic modification of the coordination around V^{4+} ions as soon as water molecules are adsorbed, together with the appearance of a Brownian motion of the polymeric chains.⁵ Thermal analysis shows that a new hydrated amorphous phase is obtained in which some water appears to be irreversibly linked to the vanadium oxide.⁶

This paper presents an IR and Raman study of amorphous V_2O_5 at different stages of hydration, from the anhydrous oxide to the colloidal solution. This preliminary study was undertaken in order to obtain more information about vanadium coordination modifications during the hydration process, to characterize the new hydrated species and to study the dynamics of adsorbed water molecules.

The discussion has been based on the orthorhombic structure of V_2O_5 .⁵ The basic V_2O_5 unit (Fig. 1) contains one short V≡O bond (1.58 \AA) and four, longer V—O bonds (around 1.8 \AA). Many IR and Raman studies of crystalline V_2O_5 can be found in the literature,^{8–11} but

only one IR study of amorphous V_2O_5 has been published¹ and no Raman data can be found.

EXPERIMENTAL

Polycrystalline V_2O_5 was obtained commercially from Johnson–Matthey, whereas amorphous V_2O_5 was made by cooling from the molten oxide either with the Roller technique or the Gun method previously described.¹² Amorphous samples obtained by these techniques which have identical spectral features will not be differentiated in the following discussion. Hydration was achieved by keeping the amorphous oxide under a controlled pressure of water ($P_{H_2O} = 19\text{ mmHg}$) at room temperature. An equilibrium is obtained after a few hours, corresponding to the composition $V_2O_5 \cdot 2.8\text{ H}_2O$. Gels and colloidal solutions were obtained by

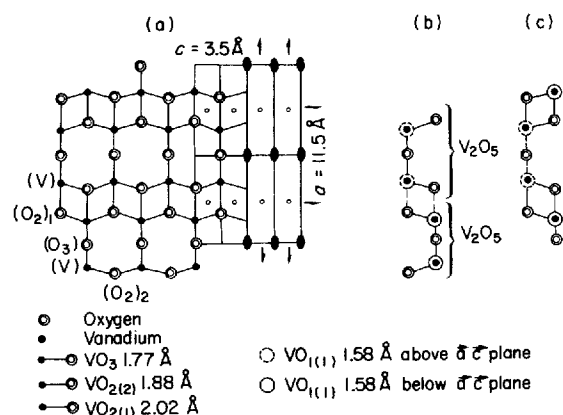


Figure 1. Structure of crystalline V_2O_5 : (a) projection on 010 plane; (b) V_2O_5 chemical units bonded through long V—O bonds (2.02 \AA); (c) V_2O_5 chemical units belonging to two different chains bonded through O—V—O bridge.

grinding the amorphous oxide with a known amount of water. The following samples have been studied.

Sample I: Amorphous V₂O₅

Sample II: Hydrated amorphous V₂O₅·2.8H₂O

Sample III: Vanadium pentoxide gel: V₂O₅·112H₂O

Sample IV: Vanadium pentoxide colloidal solution: V₂O₅·1120H₂O

IR spectra were recorded using a Perkin Elmer 580 spectrometer. Samples were prepared as nujol mulls. KBr pellets were not used because some reduction¹³ of the vanadium pentoxide occurs when the amorphous oxide is mixed with KBr; gel-sprays were deposited on CaF₂ and KBr windows.

Raman spectra were recorded with a CODERG T 800 triple monochromator spectrometer using the 488.0 nm (Ar⁺) and the 514.5 and 647.1 nm (Kr⁺) laser lines. All samples were kept in sealed tubes in order to keep a constant water content and rotated during experiments, so avoiding local heating. No significant polarization changes were observed for gels and colloidal solutions.

RESULTS AND DISCUSSION

(a) Amorphous phases

Raman and IR spectra of polycrystalline and amorphous V₂O₅ are shown in Figs. 2 and 3. The corresponding vibration frequencies are reported in Table 1. The Raman bands observed around 820 cm⁻¹ correspond to those reported in the literature around 880 cm⁻¹ for crystalline V₂O₅.⁹ A detailed assignment of these bands will be given in a forthcoming paper.

The Raman spectra of amorphous and crystalline V₂O₅ are almost identical, and only a slight broadening is observed. The low frequency vibration bands around

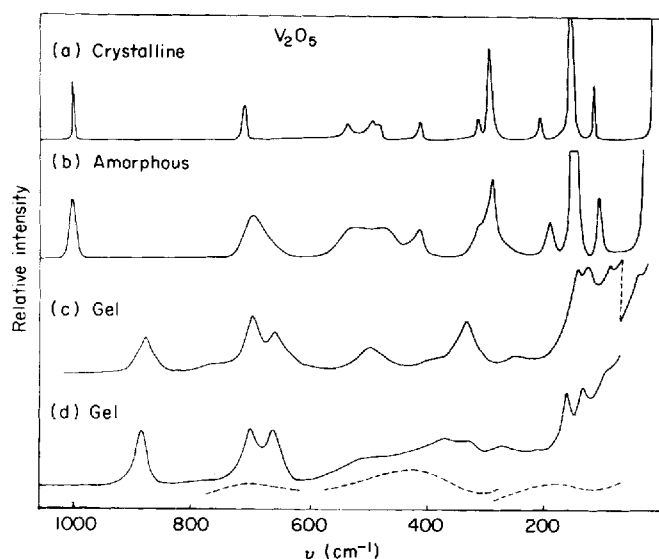


Figure 2. Raman spectra of different phases of vanadium pentoxide: (a) polycrystalline V₂O₅; (b) amorphous V₂O₅; (c) H₂O gel 1M (one mole V₂O₅ per litre of H₂O); (d) H₂O gel 0.1M (0.1 V₂O₅ mole per 1); dashed line: pure water spectrum from ref. 13.

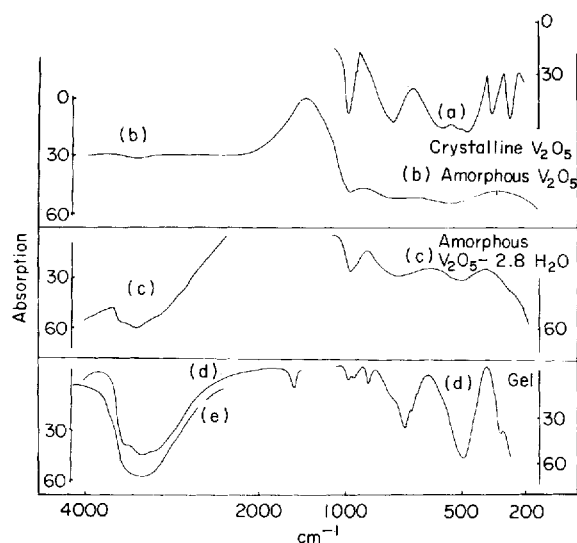


Figure 3. IR Spectra of different phases of vanadium pentoxide: (a) polycrystalline sample (KBr disc); (b) amorphous V₂O₅ (KBr disc and Nujol mull); (c) amorphous V₂O₅·2.8 H₂O (Nujol mull) (d) H₂O gel of V₂O₅; (e) liquid H₂O (from ref. 00).

150 cm⁻¹ appear to be remarkably narrow in the amorphous compound. They are probably due to delocalized modes and therefore their sharpness suggests that a three-dimensional, long-range order still exists in the amorphous oxide. The broadening of most of the Raman bands is more obvious between 700 and 500 cm⁻¹. The half-width of the observed bands increases from 18 cm⁻¹ in crystalline V₂O₅ up to 59 cm⁻¹ in the amorphous oxide. It suggests random potential fluctuations arising from the amorphous state. In our case, however, such fluctuations cannot be attributed to large distortions arising from surface effects. The number of atoms in the bulk material appears to be much larger than the number of atoms lying at the borderline between different domains. Assuming a sensitivity of about 5% for our Raman measurements, the observed linewidth could be fitted with domains containing 20 unit cells along their smallest dimension, i.e. about 100 Å.

The broad and poorly resolved IR spectrum of amorphous V₂O₅ (Fig. 3(b)) appears to be the envelope of the IR bands observed with polycrystalline V₂O₅, the broadening factor being about 5 times, as for the Raman bands. The main difference between the spectra of amorphous and crystalline V₂O₅ is the narrow components around 300–380 cm⁻¹, which are not observed in the spectrum of amorphous V₂O₅.

Hydration of amorphous V₂O₅ does not appear to modify the Raman or IR spectra of the oxide. The Raman spectrum of amorphous V₂O₅·2.8H₂O (sample II) is similar to that of amorphous V₂O₅ (sample I). The only modification observed concerns the band at 700 cm⁻¹ in crystalline V₂O₅, which is shifted toward 689 cm⁻¹ in sample I and 697 cm⁻¹ in sample II. This insensitivity of the Raman frequencies indicates that short-range order, and especially vanadium coordination, is not modified by water adsorption on the powder. The IR bands are not shifted either, but their width decreases and the IR spectrum of sample II appears to be better resolved than for anhydrous amorphous V₂O₅.

Table 1. V₂O₅ spectra

Crystalline V ₂ O ₅		Amorphous V ₂ O ₅		Gel V ₂ O ₅ (1 M)		Gel V ₂ O ₅ (0.1 M)
IR ν (cm ⁻¹)	Raman ν (cm ⁻¹)	IR ν (cm ⁻¹)	Raman ν (cm ⁻¹)	IR ν (cm ⁻¹)	Raman ν (cm ⁻¹)	Raman ν (cm ⁻¹)
1018 s		1018 s		1015 w		
983	993		995	980	887	890
				915		
				920		
820		820 br		760	710	711
	703		689	720 sh	670	
600	528.5		(697 H ₂ O)	680 sh		
520			523	500	514	514
480	483	br	473			
	476					
380	405		407	370	404	
300	285, 305		300	330	344	354
	198		280		264	328
	147		194		151	260
	105		142		136	205
			100		98	154
					50	130
						89

Frequencies of OH(OD) IR bands of Fig. 4:

A (3610, 3550) this band can be deconvoluted into a narrow component at 3610 cm⁻¹ and a broad one at 3550 cm⁻¹.

B (3770), C (3200), D (3040), E (2900)

A' (2650), B' (2480), C' (2400), D' (2250), E' (2150)

1628, 1450, 1210 assignments discussed in the text.

This could be related to a decrease of crystallite size (see Conclusion).

Finally, the well-resolved band at 1000 cm⁻¹ and its shoulder at 980 cm⁻¹, together with the ν_{OH} stretching absorption band around 3500 cm⁻¹, could be used to characterize the degree of hydration of the amorphous oxide.

(b) Gels and colloidal solutions

A drastic modification of the Raman spectrum is observed when water is added to amorphous V₂O₅ in order to make a gel (Fig. 2(c)). The V≡O stretching Raman frequency is shifted from 995 cm⁻¹ down to 890 cm⁻¹, while a new band appears at 711 cm⁻¹. This could indicate a solvation of vanadium by water molecules. The first band could be assigned to a V=O double bond and the second one to a V—OH₂ stretching mode. Occurrence of well-resolved bands suggests the existence of a short-range order to some extent similar to the one observed in molecular compounds.

This conclusion is in agreement with that of IR experiments (Fig. 3(d)). The strong absorption band at 1018 cm⁻¹ corresponding to the V≡O stretching frequency in the crystalline or amorphous oxide has almost disappeared showing that almost all vanadium sites have been solvated.

The presence of low frequency Raman modes down to 50 cm⁻¹ indicates that the 'molecular' entities contain several V₂O₅ units giving rise to low energy torsional and translational motions. The diffuse Rayleigh background extending up to 150 cm⁻¹ indicates that long-range order has been destroyed and that the three-dimensional network still observed in the amorphous oxide no longer exists in the gel.

The Raman spectrum of the gel is not greatly modified when more water is added in order to obtain a colloidal solution (sample IV) (Fig. 2(d)). A better resolution is observed. The half-width of the bands at 890, 711, 154 and 130 cm⁻¹ decreases. The intensity of the 670 cm⁻¹ band increases, while the one at 344 cm⁻¹ decreases.

These observations suggest that water molecules contribute to an increase in the molecular character of the colloidal particles, and presumably modify their conformation. The existence of a broad and diffuse background around 350 cm⁻¹ ($\Delta\nu_{\frac{1}{2}} \sim 150$ cm⁻¹) could correspond to librational motions of water molecules. Such motions are observed around 435 cm⁻¹ in pure water.¹⁴ Their shift toward lower frequencies could suggest that water molecules have more freedom to rotate in the gel than in pure water, i.e. they are less hydrogen bonded. These molecules being bonded to a vanadium V—OH₂, their oxygen is no longer available for O...H bonding.

Because of their low Raman intensity, the H₂O stretching and bending modes are only observed in the IR spectra. The frequency of the stretching OH band of sample IV (Fig. 3(d)) is nearly the same as for pure water (Fig. 3(e)), while that for the same sample evaporated on CaF₂ exhibits several well-resolved components (Fig. 4(a)). Such components are also observed for the corresponding D₂O compound (Fig. 4(f)). The A components centred at 3610 cm⁻¹ and 3550 cm⁻¹, respectively, can be attributed to relatively free water molecules. Their intensity is larger in the concentrated gel (sample III) than in the colloidal solution (sample IV). This indicates that the proportion of free (i.e. non-hydrogen bonded) water is larger in the gel than in the colloidal solution. It presumably corresponds to H₂O molecules directly bonded to vanadium through their oxygen atom.

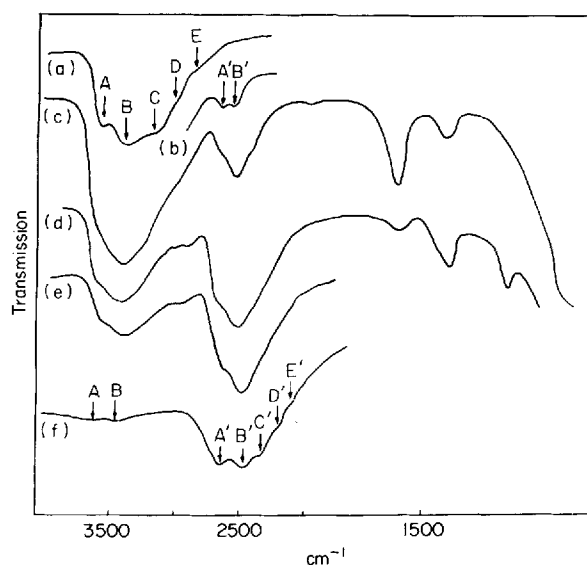


Figure 4. Stretching OH and OD region of IR spectra of gels: (a) concentrated gel in H_2O ; (b–e) isotopically enriched in D_2O ; (f) concentrated gel in D_2O containing H_2O .

The B component, around 3370 cm^{-1} , could be attributed to water molecules associated through hydrogen bonds either with oxygen atoms of the V_2O_5 skeleton or with other H_2O molecules.

The C, D and E components, which have disappeared in the isotopically diluted sample (H_2O in D_2O) (Fig. 4(d)), probably arise from Fermi resonances between fundamental stretching modes and the first overtones of the bending modes.¹³ All these components (A–E) are shifted under deuteration (Fig. 4(f)) and their isotopic frequency ratio is 1.35:1. The asymmetric and symmetric stretching modes cannot be separated. The δOH_2 bending mode can easily be assigned to the 1628 cm^{-1} band which is shifted towards 1450 cm^{-1} for δOHD and 1210 cm^{-1} for δOD_2 .

CONCLUSION

It is usually admitted that short-range order is conserved in glasses, while long range order might be more or less destroyed. The high frequency vibrational spectrum of amorphous compounds then generally corresponds to the envelope of the corresponding bands in the crystalline phase. Well-resolved bands can, however, be observed when short-range forces dominate, as in molecular compounds. These bands correspond to characteristic frequencies of groups of atoms (localized modes). The low frequency spectra of amorphous compounds are usually diffuse. A strong density of states is observed below 150 cm^{-1} corresponding to dispersive, acoustic modes. IR absorption bands always appear to be broader than the corresponding Raman bands. This is mainly due to the reststrahlen region lying between TO–LO components of each polar mode of the IR spectrum. The TO frequency is more representative of the force constant associated with the chemical bond, while the LO frequency is partly determined by the macroscopic electric field associated with the in-phase vibration of the dipoles. Such an effect is expected to decrease with the size of the ordered

domains: the local electric field originating from randomly distributed dipoles moments is thus expected to be averaged out.

Raman and IR spectra of amorphous and crystalline V_2O_5 shows that short range order is almost the same in both phases, i.e. a VO_5 pyramid with a short $V\equiv O$ triple bond between vanadium and the apical oxygen.⁷ The relatively small broadening factor for both Raman and IR spectra indicates that the random distribution of local fields is remarkably narrow. Moreover, instead of the low frequency density of states usually revealed by the Raman spectra of amorphous compounds, one observes well-defined bands below 200 cm^{-1} . As already stated, this suggests that the corresponding low frequency modes, involving inter-chain motions, can still be considered as normal modes with $k=0$, the correlation length being at least 100 \AA . Moreover, the observed bands are slightly broadened (two or three times). This proves that we do not have a phase mixture, since, for a crystalline and glass phase mixture, one should observe narrow bands of the crystal superimposed on a broad background.

These spectra are not modified when some water is adsorbed at the surface of the powder, showing that coordination around vanadium ions is not affected by water molecules. This result is inconsistent with previous ESR experiments⁶ which indicated a drastic change of vanadium coordination in the amorphous oxide as soon as some water is adsorbed. This may be due to the fact that ESR is only sensitive to V^{4+} paramagnetic ions (about 1% in the non-stoichiometric oxide), while Raman and IR experiments are mainly concerned with the V^{5+} ions (99%).

A comparison of both techniques seems to suggest that water molecules are first adsorbed on V^{4+} sites which could act as 'active sites' in the catalytic properties of V_2O_5 . The insensitivity of amorphous V_2O_5 spectra towards H_2O can be related to the non-existence of V_2O_5 crystalline hydrates.¹⁵

Vibrational spectra of amorphous V_2O_5 are drastically modified when enough water is added to obtain a gel. Some water molecules should participate in the vanadium coordination. The low frequency shift of the $V=O$ stretching mode indicates a weakening of the vanadium–oxygen double bond which could be due to the fixation of a water molecule hydrogen bonded to the apical oxygen. The appearance of a new band at 711 cm^{-1} , attributed to a $V-OH_2$ stretching mode, suggests that the sixth coordination site of vanadium, opposite to the vanadyl group, has been solvated by a water molecule. This water molecule appears to have a great degree of freedom for rotation and to be less hydrogen bonded than in pure water. It is presumably bonded to vanadium through its oxygen atom.

Moreover, addition of water to the amorphous oxide progressively breaks the three-dimensional network, leading to molecular or macromolecular species. This result agrees with previous work showing that water molecules are able to destroy the entangling of the fibres leading to a swollen gel. The question of the correlation of these fibres with the structure of orthorhombic V_2O_5 in the a–c plane still remains. The V_2O_5 crystal can be described by the primitive D_{2h} space group,⁷ with two V_2O_5 groups per unit cell (Fig. 1(a)). We may assume that the polymeric fibres in the amorphous oxide are

related to the V_2O_5 chains along the \tilde{c} axis, but it is not yet possible to say which bonds are broken. Two possibilities may be examined. Either the longest V—O bonds ($VO_{2(1)} = 2.02 \text{ \AA}$) are broken, leading to a basic

unit shown in Fig. 1(b), or the V—O—V bridges leading to the basic unit shown in Fig. 1(c). This question is being investigated, in particular by studying the Raman spectra of Molten V_2O_5 .

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