Vibrational spectra of vanadium(V) compounds. I. Divanadates with thortveitite structure

P. SCHWENDT and V. GRAUS

Department of Inorganic Chemistry, Faculty of Natural Sciences,
Komenský University, 801 00 Bratislava

The vibrational spectra of $Cd_2V_2O_7$ and $Mn_2V_2O_7$ were measured and assigned to anion $V_2O_7^{4-}$ with respect to the D_{3d} symmetry. The calculated force constants of the modified valence force field were compared with the force constants of some analogous systems.

Compounds $M_2X_2O_7$ crystallize in one of a few structural types depending upon the ionic radii of atoms M and X. The compounds in which the ionic radius of X is greater than 0.6 A usually do not contain an isolated unit $X_2O_7^{n-}$ and the coordination of oxygen atoms around the atom X is octahedral. When the ionic radius of X is less than 0.6 A, two basic structural types are distinguishable with regard to the ionic radius of the M atom. If the radius of M is greater than *ca.* 0.97 A, the structure is of the dichromate type. The XOX bridge is then bent and the maximum point-symmetry group of the anion is C_{2v}. If the ionic radius of the atom M is less than 0.97 A, the structure is of the type of thortveitite or a type derived from it. The $X-O-X$ angle is greater than in the structures of the dichromate type, usually about 180°. For the linear group XOX, the highest possible symmetry of the anion is D_{3d} [1]. Two compounds with the thortveitite structure are known among divanadates, namely $Mn_2V_2O_7$ [2] and $Cd_2V_2O_7$ [3].

It is of great importance to establish a configuration of the bridges $V-O-V$ for the study of chaining of polyhedra VO_x in polyvanadates. Vibrational spectra of divanadates with the linear $V-O-V$ bridge are a convenient means in solving a relationship between the arrangement of the bridge $V-O-V$ and wavenumbers of the stretching vibrations $\nu_s(VOV)$ and $\nu_{as}(VOV)$.

Experimental

Preparation of $Cd_2V_2O_7$

A mixture of CdO and V_2O_5 (2 : 1) was slowly heated to 900°C and kept at this temperature for 1 hr. Then the mixture was pulverized and again heated at 900°C for 3 hrs. Chemical analysis and X-ray powder diffraction patterns confirmed that the product was identical with $Cd_2V_2O_7$ prepared by *Au* and *Calvo* [3].

Preparation of $Mn_2V_2O_7$

A mixture of MnO_2 and V_2O_5 (2 : 1) was tempered at 750°C for 2 hrs. After pulverizing, the mixture was again tempered at 750°C for 5 hrs. Chemical analysis and X-ray diffraction patterns confirmed the identity of the prepared $Mn_2V_2O_7$ with the compound prepared by *Dorm* and *Marinder* [2].

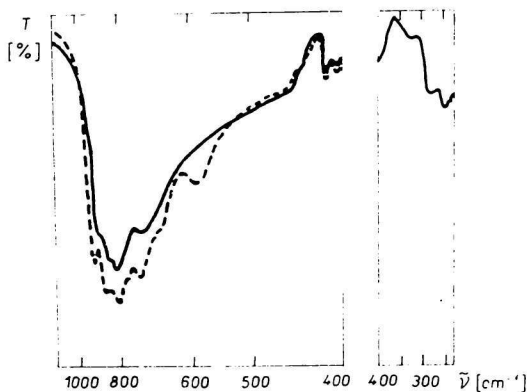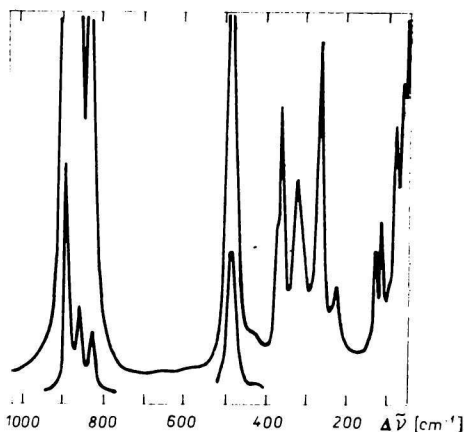Fig. 1. The i.r. spectra of $Cd_2V_2O_7$
$(-\,-\,-)$ and $Mn_2V_2O_7$ $(\underline{\qquad})$.

Fig. 2. The Raman spectrum of $Cd_2V_2O_7$.

The X-ray diffraction patterns were recorded by a Philips diffractograph with a go-niometer PW 1058, radiation CuK_α. The i.r. spectra were measured in Nujol mulls and in KBr and KI discs by instruments UR 20, IR 12 Beckman, and Perkin—Elmer 221.

The Raman spectra were measured by a Ramalog 3 instrument with the Ar^+ laser (excitation 488 nm). The Raman spectrum of $Mn_2V_2O_7$ was of poor quality (the substance was brown-black) and some changes in the spectra occurred during repeated recordings. They were probably caused by structural changes.

Infrared and Raman spectra are seen in Figs. 1 and 2. Besides the discussed bands, the i.r. spectrum of $Cd_2V_2O_7$ contains also a broad band at about 590 cm^{-1} and a shoulder at 666 cm^{-1}, probably corresponding to combination wavenumbers. A series of bands corresponding to the lattice vibrations is also seen in the Raman spectrum of $Cd_2V_2O_7$ below 200 cm^{-1}. The i.r. and Raman spectra of $Cd_2V_2O_7$ were measured by *Griffith* and *Lesniak* [10] who reported, without assignment, the following bands: I.r. 970 m, 905 s, 800 w, 375 w, 317 s, 296 vs; Raman: 877 (10), 848 (3), 820 (2), 780 (0.5), 356 (2), 317 2), 264 (2), 226 (0.5).

Results and discussion

$Cd_2V_2O_7$ and $Mn_2V_2O_7$ possess the space symmetry group $C_{2h}^3(C2/m)$ with two formula units in an elementary cell. The site symmetry group C_{2h} corresponds to this space group, thus the site symmetry group is identical with the factor group. A correlation between the groups D_{3d} and C_{2h} is $A_{1g} \rightarrow A_g$, $A_{2g} \rightarrow B_g$, $E_g \rightarrow A_g + B_g$, $A_{1u} \rightarrow A_u$, $A_{2u} \rightarrow B_u$, $E_u \rightarrow A_u + B_u$.

A model of V_2O_7 with the symmetry D_{3d} was chosen as a base for the analysis of normal vibrations. The number of vibrations in the individual types of symmetry is $3A_{1g}(R)$, $A_{1u}(-)$, $3A_{2u}(IR)$, $3E_g(R)$, $4E_u(IR)$. The following coordinates of symmetry were used in calculations:

A_{1g}
$$S_1 = 6^{-1/2} \; (r_1 + r_2 + r_3 + r_4 + r_5 + r_6),$$

744

$S_2 \quad = 2^{-1/2} \quad (d_1 + d_2),$

$S_3 \quad = 12^{-1/2} \ (\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 + \alpha_5 + \alpha_6 - \beta_1 - \beta_2 - \beta_3 - \beta_4 - \beta_5 - \beta_6).$

$\qquad A_{2u}$

$S_5 \quad = 6^{-1/2} \ (r_1 + r_2 + r_3 - r_4 - r_5 - r_6),$

$S_6 \quad = 2^{-1/2} \ (d_1 - d_2),$

$S_7 \quad = 12^{-1/2} \ (\alpha_1 + \alpha_2 + \alpha_3 - \alpha_4 - \alpha_5 - \alpha_6 - \beta_1 - \beta_2 - \beta_3 + \beta_4 + \beta_5 + \beta_6).$

$\qquad E_g$

$S_{8a} \ = 12^{-1/2} \ (2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6),$

$S_{9a} \ = 12^{-1/2} \ (2\alpha_3 - \alpha_2 - \alpha_1 + 2\alpha_6 - \alpha_5 - \alpha_4),$

$S_{10a} = 12^{-1/2} \ (2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6).$

$\qquad E_u$

$S_{11a} = 1/2 \ (r_2 - r_3 - r_5 + r_6),$

$S_{12a} = 1/2 \ (\alpha_2 - \alpha_1 + \alpha_4 - \alpha_5),$

$S_{13a} = 1/2 \ (\beta_2 - \beta_3 - \beta_5 + \beta_6).$

$S_{14a} = \varphi$

The individual internal coordinates are as follows: r_i the change of the terminal V—O bond length while r_1 and r_4, r_2 and r_5 as well as r_3 and r_6 are in *trans* position; d_i the change of the bridging V—O′ bond length; α_i the change of the angle between bonds r_j, r_k $(i, j, k = 1, 2, 3)$; β_i the change of the angle between bonds r_i and d; φ the change of the angle V—O′—V. The inactive torsion vibration of the type A_{1u} was not included

Table 1

Matrix of the force constants

A_{1g}			
$f_r + 2f_{rr} + A$			
$3^{1/2} f_{rd}$	$f_d + f_{dd}$		
0	$(3rd/2)^{1/2} f'_{d\alpha}$	$r^2/2(f_\alpha + f_\beta + 2f_{\alpha\alpha} + 2f_{\beta\beta} - 2f'_{\alpha\beta} - 4f_{\alpha\beta} + B)$	
A_{2u}			
$f_r + 2f_{rr} - A$			
$3^{1/2} f_{rd}$	$f_d - f_{dd}$		
0	$(3rd/2)^{1/2} f'_{d\alpha}$	$r^2/2(f_\alpha + f_\beta + 2f_{\alpha\alpha} + 2f_{\beta\beta} - 2f'_{\alpha\beta} - 4f_{\alpha\beta} - B)$	
E_g			
$f_r - f_{rr} + C$			
0	$r^2(f_\alpha - f_{\alpha\alpha} + D)$		
0	$rd(f'_{\alpha\beta} - f_{\alpha\beta})$	$rd(f_\beta - f_{\beta\beta} + E)$	
E_u			
$f_r - f_{rr} - C$			
0	$r^2(f_\alpha - f_{\alpha\alpha} - D)$		
0	$rd(f'_{\alpha\beta} - f_{\alpha\beta})$	$rd(f_\beta - f_{\beta\beta} - E)$	
0	0	0	$d^2 \ f_\varphi$

r and d are the bond lengths of V—O and V—O′ respectively; subscripts r and d stand for bonds of the terminal V—O groups and bridging V—O′ groups respectively, α for the angle O—V—O, β for O—V—O′; φ for V—O′—V; f_{rr}, f_{dd}, and f_{rd} are the force constants of interactions between neighbouring bonds; $f_{\alpha\alpha}, f_{\beta\beta}, f_{\alpha\beta}$ are the force constants for the case of two angles with two atoms in common, $f'_{d\alpha}$ and $f'_{\alpha\beta}$ for a bond and an angle or two angles with one common atom. A, B, C, D, and E are corresponding interactions between the internal coordinates without a common atom.

Table 2

Calculated and experimental wavenumbers of bands

Symmetry type	Assignment	Calculated wavenumbers [cm^{-1}]	Experimental wavenumbers [cm^{-1}]			
			Cd$_2$V$_2$O$_7$			Mn$_2$V$_2$O$_7$
			R	IR		IR
A_{1g}	TS	887	888			
	BS	486	486			
	TB	267	267			
A_{2u}	TS	904		905		889
	BS	730		732		725
	TB	330				330
E_g	TS	844	857			
			828			
	TB	361	360			
	TB	317	320			
E_u	TS	825		858	833	840
				805	769	811
	TB	404		413		414
				402		403
	TB	269				288
						255
	BB	200				

TS — terminal stretching; BS — bridge stretching; TB — terminal bending; BB — bridge bending.

into calculations. The following numerical values were used for calculations of the kinematic coefficients and the force constants: the V—O bond length 1.69 A, the V—O' bond length 1.76 A, the V—O'—V angle 180°, the O—V—O and O—V—O' angles 109.5°. A matrix of the force constants is listed in Table 1. An initial set of the force constants was selected by comparison with the force constants of analogous systems [5, 6] and anion VO_4^{3-} [4]. The variation was made by means of partial derivations of the wavenumbers with respect to the force constants [7]. Values of $f_{rd} = 0.35$ and $f'_{rd} = -0.21$ mdyn/A were chosen and fixed in the calculations. The resulting values of the force constants are (in mdyn/A): $f_r = 5.27$, $f_d = 4.17$, $f_{rr} = 0.79$, $f_{dd} = 1.82$, $f_\alpha + f_\beta = 0.74$, $f_{\alpha\alpha} + f_{\beta\beta} = 0.02$, $f_\alpha - f_{\alpha\alpha} = 0.45$, $f_\beta - f_{\beta\beta} = 0.27$, $f_\varphi < 0.08$, $A = -0.15$, $B = 0.12$, $D = -0.05$. Other constants were assumed to be zero.

The calculated wavenumbers together with their experimental values are summarized in Table 2. Our value of f_r is enhanced in comparison with $f_r = 4.59$ mdyn/A reported by *Müller* and co-workers for VO_4^{3-} [4]. The force constant f_d is lower than f_r in conformity with the bond lengths. The high value of f_{dd} may be a consequence of the nature of bonds in the linear arrangement of the group VO'V. In such a case, both p orbitals of the bridging oxygen can fully share in a double π system [9]. Analogously high values of the force constants of the bond interactions are characteristic of linear and planar molecules and ions XO_m^{n-} with delocalized π bonds [11]. *Mooney* and *Goldsmith* [8] reported the value 1.97 mdyn/A for ZrP_2O_7 with a linear group POP. In the mentioned molecules and ions, a negative value of the force constant of the type $f'_{d\alpha}$ is not unusual.

The negative value of f'_{dx} is unavoidable for the reproduction of the experimental value $\nu_3(A_{1g})$.

In comparison with divanadates of the dichromate type [9], the wavenumber ν_{as} (VO′V) of $Cd_2V_2O_7$ and $Mn_2V_2O_7$ is somewhat lower and the wavenumber ν_s(VO′V) is considerably lower. Thus the difference in the wavenumbers ν_{as}(VO′V) and ν_s(VO′V) increases. The decrease of wavenumbers of the stretching vibrations of the bridging group occurs in spite of the shortening of the V—O′—V bonds and the corresponding increase of the force constant f_d. The decisive factor is apparently a strong decrease of the value of the corresponding kinematic coefficient with the increase of the angle V—O′—V.

References

1. Brown, I. D. and Calvo, C., *J. Solid State Chem.* **1**, 173 (1970).
2. Dorm, E. and Marinder, B. O., *Acta Chem. Scand.* **21**, 590 (1967).
3. Au, P. K. L. and Calvo, C., *Can. J. Chem.* **45**, 2297 (1967).
4. Müller, A., Krebs, B., Rittner, W., and Stockburger, M., *Ber. Bunsenges. Phys. Chem.* **71**, 182 (1967).
5. Mattes, R., *Z. Anorg. Allg. Chem.* **382**, 163 (1971).
6. Hezel, A. and Ross, S. D., *Spectrochim. Acta* **23A**, 1583 (1967).
7. Sverdlov, L. M., Kovner, M. A., and Krainov, E. P., *Kolebatelnye spektry mnogoatomnykh molekul*, p. 86. Nauka, Moscow, 1970.
8. Mooney, R. W. and Goldsmith, R. L., *J. Inorg. Nucl. Chem. Lett.* **31**, 933 (1969).
9. Schwendt, P. and Petrovič, P., *Proc. III Conf. Coord. Chem.*, p. 307. Smolenice—Bratislava, 1971.
10. Griffith, W. P. and Lesniak, P. J. B., *J. Chem. Soc. (A)* ***1969***, 1066.
11. *Kolebatelnye spektry v neorganicheskoi khimii.* (Yu. Ya Kharitonov, Editor.) P. 25. Nauka, Moscow, 1971.

Translated by F. Kopecký