

Vibrational spectra of vanadium(V) compounds. II. Vibrational spectra of divanadates with nonlinear bridge VOV

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The vibrational spectra of α -Zn₂V₂O₇, Mg₂V₂O₇, and Pb₂V₂O₇ were measured and assigned. Difference between wavenumbers of stretching vibrations of bridge bonds decreases monotonously with the angle V—O—V. The value of the difference can be used in order to estimate the configuration of bridge in divanadates, M₂V₂O₇.

Были измерены и интерпретированы колебательные спектры α -Zn₂V₂O₇, Mg₂V₂O₇ и Pb₂V₂O₇. Разница волновых чисел валентных колебаний мостиковых связей монотонно понижается с углом V—O—V и ее величина может быть использована для оценки конфигурации мостика в двухванадатах M₂V₂O₇.

Structures of divanadates, M₂V₂O₇, can be divided into two basic structural types: dichromate type and thortveitite type, differing in the position of the end VO₃ groups and arrangement of the VOV bridge in V₂O₇⁴⁻ anion. The type of the structure is determined mainly by the size of cation M²⁺. Larger cations usually give rise to a dichromate type structure, while smaller cations to a thortveitite type structure [1, 2].

Recently, the number of papers dealing with the crystallochemistry of divanadates has considerably increased. Following structures were solved and refined: α -Zn₂V₂O₇ [3], Mg₂V₂O₇ [4], Co₂V₂O₇, Ni₂V₂O₇ [5], Pb₂V₂O₇ [6], β -Sr₂V₂O₇ [7], α -Cu₂V₂O₇ [8], β -Cu₂V₂O₇ [16], Hg₂V₂O₇ [17]. Vibrational spectra of following compounds were measured: Ca₂V₂O₇, Sr₂V₂O₇, Ba₂V₂O₇ [9—11]. Mn₂V₂O₇, Cd₂V₂O₇ [1, 12], Cu₂V₂O₇, α -Zn₂V₂O₇, Ni₂V₂O₇, Co₂V₂O₇, Mg₂V₂O₇ [12].

This paper presents thus far not published vibrational spectra of Mg₂V₂O₇(R), α -Zn₂V₂O₇(R), Pb₂V₂O₇(IR, R) and deals with the relation between the bridge configuration and wavenumbers of stretching vibrations $\nu_s(\text{VOV})$ and $\nu_{as}(\text{VOV})$.

Experimental

Mg₂V₂O₇, α -Zn₂V₂O₇, and Pb₂V₂O₇ were prepared by a reaction in solid state from V₂O₅ and appropriate oxide [6, 13]. The composition and the structure of product was checked by chemical analysis and X-ray powder diffraction patterns.

The X-ray diffraction patterns were recorded by a Philips diffractograph with PW 1058

Table 1

Correlation diagram for α -Zn₂V₂O₇

Site symmetry group C_2	Factor group C_{2h}	Activity
A (11)	A_g (11)	R
	A_u (11)	IR
B (10)	B_g (10)	R
	B_u (10)	IR

Table 2

Infrared and Raman spectra of α -Zn₂V₂O₇ and Mg₂V₂O₇

α -Zn ₂ V ₂ O ₇		Mg ₂ V ₂ O ₇		Assignment
IR, cm ⁻¹	R, cm ⁻¹	IR, cm ⁻¹	R, cm ⁻¹	
936 s	964 w 912 vs	992 s 925 sh	1012 s	$\nu_s(\text{VO}_3)$
845 vs	863 s 858 m	878 s 856 sh	897 w 881 vs	$\nu_{as}(\text{VO}_3)$
807 s, b	812 w 786 s	815 vs	861 m 846 s	
772 s	719 s	715 s	784 m	$\nu_{as}(\text{VOV})$
540 m	514 m	535 m	526 m	$\nu_s(\text{VOV})$
475 m		472 m		$\nu(\text{M}-\text{O})?$
398 s	431 s	440 m	411 w	$\delta(\text{VO}_3)$
380 w		400 sh	400 w	
345 sh	352 s	390 sh	382 w	
330 w	325 w	381 s		
320 s	303 m	334 s	341 w	
305 s	296 m	305 w	308 w	
265 w	269 m	281 s	284 m	$\delta(\text{O}-\text{VO}_3)$
240 m	245 m 221 s	260 w 246 w 225 w	248 m 244 m	
	188 w		201 w	$\delta(\text{VOV})$
	166 m 148 m 72 m		161 w 148 w 117 m 50 sh	Torsional vibrations and lattice vibrations

Table 3

Vibrational spectra of $\text{Pb}_2\text{V}_2\text{O}_7$

IR, cm^{-1}	R, cm^{-1}	Assignment
880 sh 872 s	876 vs	$\nu_s(\text{VO}_3)$
835 s 820 s 750 sh	817 s 751 w	$\nu_{as}(\text{VO}_3)$
700 s 680 sh	673 w	$\nu_{as}(\text{VOV})$
577 m	582 m	$\nu_s(\text{VOV})$
376 m 354 m 305 w	371 m 351 s 324 m	$\delta(\text{VO}_3)$
248 m 240 w 227 m	258 w 232 m	$\delta(\text{O}-\text{VO}_3)$
	196 w 181 w	$\delta(\text{VOV})$
	140 w 124 m 112 w 89 m 74 m	Torsional vibrations and lattice vibrations

Table 4

Geometrical data on configuration of V—O—V bridge and average wavenumbers of bridge vibrations

Compound	Angle V—O—V in degrees	Mean length of bridge bonds in Å	$\tilde{\nu}_{as}(\text{VOV})^*$ cm^{-1}	$\tilde{\nu}_s(\text{VOV})^*$ cm^{-1}	$\Delta\nu_b$ cm^{-1}	Ref.
$\text{Cd}_2\text{V}_2\text{O}_7$	180	1.764	732	486	246	[15, 1]
$\alpha\text{-Zn}_2\text{V}_2\text{O}_7$	149.3	1.775	746	527	219	[3]
$\text{Mg}_2\text{V}_2\text{O}_7$	140	1.80	749	531	218	[3, 4]
$\beta\text{-Sr}_2\text{V}_2\text{O}_7$	123	1.81	740	586	154	[7, 10]
$\text{Pb}_2\text{V}_2\text{O}_7$	122	1.817	684	580	104	[6]
$\text{Co}_2\text{V}_2\text{O}_7$	117.5	1.846	647	565	82	[3, 12]

* Average value from infrared and Raman spectra.

goniometer, radiation $\text{CuK}\alpha$. Infrared spectra were measured in nujol suspension and in KBr and KI tablets on Perkin—Elmer 225 and UR 20 spectrophotometers. Raman spectra were measured using Ramalog 3 spectrophotometer with Ar^+ laser (excitation 488 nm).

Infrared spectrum of $\text{Mg}_2\text{V}_2\text{O}_7$ is analogous to the already published one, while infrared spectrum of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ is partly different [12]. This is mainly due to the fact that the good quality spectrum of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ has not yet been obtained.

Results and discussion

$\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ [3] crystallizes in monoclinic system, the space group is $C2/c$ (C_{2h}^6), $Z = 4$, the site symmetry of anion being C_2 . From the correlation diagram (Table 1) it follows that in both infrared and Raman spectra should be 21 active internal vibrations. Representation of lattice vibrations is $L_1 = 5A_g + 4A_u + 7B_g + 5B_u$. Representation of translations of elementary cell is $L_a = A_u + 2B_u$. $\text{Mg}_2\text{V}_2\text{O}_7$ belongs to the space group $P\bar{1}$ (C_i^1), $Z = 2$, site symmetry of anion being C_1 [4]. In infrared and Raman spectra should appear 21 active internal vibrations of $\text{V}_2\text{O}_7^{4-}$.

Wavenumbers and assignment of bands in infrared and Raman spectra of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ and $\text{Mg}_2\text{V}_2\text{O}_7$ are presented in Table 2. The assignment of bands 472(IR) in $\text{Mg}_2\text{V}_2\text{O}_7$ spectrum and 475(IR) in $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ spectrum appears to be somewhat problematic. In comparison with spectra of many other vanadates these values seem to be a little to high for $\delta\text{-VO}_3$. However, in these divanadates anion $\text{V}_2\text{O}_7^{4-}$ is not fully independent and a partial covalent interaction Zn—O or Mg—O is to be considered. For example distances Zn—O in $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ (the shortest being 1.97 Å) are comparable with distances Zn—O in zinc oxide (the shortest being 1.94 Å) and in the infrared spectrum of ZnO appears a broad band at 450 cm^{-1} [14]. From

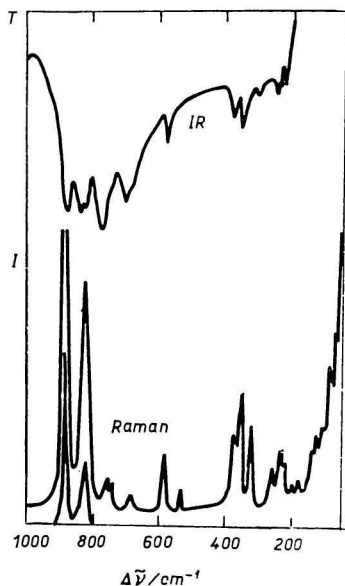


Fig. 1. Infrared and Raman spectra of $\text{Pb}_2\text{V}_2\text{O}_7$.

this point of view the division into internal vibrations and lattice vibrations must be considered to be only approximate and most of the deformation vibrations of $V_2O_7^{4-}$ are probably coupled with Mg—O and Zn—O vibrations, respectively.

$Pb_2V_2O_7$ belongs to the space group $P2_1/a$ (C_{2h}^3), $Z = 4$, site symmetry of anion is C_1 . Number of vibrations determined by the factor group analysis is as follows: internal vibrations $21A_g + 21B_g + 21A_u + 21B_u$; lattice vibrations $12A_g + 12B_g + 11A_u + 10B_u$; acoustical vibrations $A_u + 2B_u$. However, number of bands appearing in the vibrational spectra of $Pb_2V_2O_7$ (Fig. 1, Table 3) is lower than predicted, and practically no correlation splitting was observed. Besides the bands presented in Table 3 also some lines of argon plasma can be seen in Fig. 1 (506.2, 500.9, and 496.5 nm).

Some previously published data on the configuration of the VOV bridge in different divanadates together with wavenumbers $\nu_s(\text{VOV})$ and $\nu_{as}(\text{VOV})$ are presented in Table 4. It is obvious that there is no a simple relation between the angle V—O—V, bond lengths, and wavenumbers of stretching vibrations of bridge group. Generally, there is a tendency to an increasing bond length [10] with decreasing angle V—O—V; simultaneously for studied divanadates $\nu_s(\text{VOV})$ mostly increases, while $\nu_{as}(\text{VOV})$ decreases. The quantity the most sensitive towards changes of V—O—V angle is the wavenumber difference $\Delta\nu_b = \nu_{as}(\text{VOV}) - \nu_s(\text{VOV})$, which increases monotonously with increasing V—O—V angle. The value of $\Delta\nu_b$, however, depends also on electronegativity of cation which can be demonstrated *e.g.* by comparing $Pb_2V_2O_7$ and $\beta\text{-Sr}_2V_2O_7$. The Pb^{2+} and Sr^{2+} cations have nearly equal ionic radii and configuration of the V_2O_7 group in both divanadates is similar [6], but $\Delta\nu_b$'s are distinctly different.

Thus the difference of wavenumbers of bridge vibrations $\Delta\nu_b = \nu_{as}(\text{VOV}) - \nu_s(\text{VOV})$ can be considered to be a good qualitative criterion for estimate of the VOV bridge configuration in divanadates of bivalent cations.

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