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The Vibrational Spectra of α-$MoPO_5$ and α-$NbPO_5$[1]

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Infrared and Raman spectra were measured and analyzed for α-$MoPO_5$ and α-$NbPO_5$. Band assignments made for these phases using normal coordinate analysis were consistent with those made earlier for α-VPO_5. Trends in related force constants from their modified valence force fields can be interpreted on the basis of differences in their chemical parameters.

Introduction

α-ABO_5-type materials possess layered structures that are useful for catalytic, electronic, or ion exchange applications. Recently, Stranford and Condrate have analyzed the infrared and Raman spectra of α-VPO_5, α-VSO_5, and α-$VMoO_5$ by force constant studies to obtain structural information (*1*). While McConnell *et al.* reported the Raman spectrum of α-$NbPO_5$ (*2*), Deulin *et al.* reported its infrared spectrum (*3*). In this study, both the infrared and Raman spectra of α-$MoPO_5$ and α-$NbPO_5$ have been analyzed using normal coordinate analysis. The results of the analyses are compared to those recently obtained for α-VPO_5 (*1*). Trends in the resulting force constants are discussed in terms of differences in chemical parameters.

Experimental

α-$MoPO_5$ was prepared using a method described by Kierkegaard and Westerlund (*4*). A mixture of 13.1 g of ammonium paramolybdate and 6 ml of 14.8 *M* H_3PO_4 was placed in a platinum crucible, heated over a burner to remove water and placed in a furnace at 950°C (±10°C) for 20 min. At this temperature, the mixture melted. After cooling, crystalline α-$MoPO_5$ could be retrieved by washing away the water-soluble glass matrix with large quantities of boiling water. α-$NbPO_5$ was prepared using a method described by Hahn (*5*). Two grams of Nb_2O_5 was fused with 10 g of potassium pyrosulfate. After cooling, the fused mass was leached with boiling distilled water, dried, dissolved in a 4% oxalic acid solution with the aid of heat, and filtered to remove the insoluble matter. This solution was placed on a steam bath, and a mixture of distilled water, 10 ml of 15.8 *M* HNO_3, and 10 ml of 14.8 *M* H_3PO_4 was added. After a few minutes, 1 g of $KBrO_3$ was added, and the resulting precipitate was digested on the steam bath for 1 hr, filtered, washed with large amounts of water, and finally dried in air. The resulting precipitate was a crystalline hydrate of $NbPO_5$. This precipitate was heated to 1000°C and formed α-$NbPO_5$.

Raman spectra were measured using a

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Spex Model 1401 monochromator and a CRL Model CR3 argon ion laser. The spectra were obtained in the Stokes region of the 4880-Å and/or 5145-Å line. The spectra were recorded by sealing the sample in a capillary tube or pressing the powder into a pellet and using 90° optics. The pellets were arranged at 60° to the incident beam. For samples which rapidly absorbed water in air, a pellet was pressed, heated to drive off water, and then sealed in an evacuable cell. The spectrometer was calibrated using vacuum-distilled indene.

Infrared spectra were measured on a Perkin–Elmer Model 621 spectrophotometer using KBr pellets. The instrument was calibrated using polystyrene.

Results and Discussion

Crystallographic data have been obtained for α-$MoPO_5$ and α-$NbPO_5$ by Kierkegaard *et al.* (*4, 6*), and by Longo and Kierkegaard (*7*), respectively. The space group for these phases is $P4/n$-C_{4h}^3 with two molecular units/unit cell. The lattice of an α-APO_5-type material contains highly distorted AO_6 groups sharing four equatorial oxygen atoms with four different PO_4 groups (*6, 7*). These groups are arranged to form layers. A distortion of the AO_6 octahedra occurs along the *c* axis, generating a short and an elongated A–O bond. The selection rules and symmetry species of the first-order modes which are predicted by factor group analysis are as follows:

$$5A_g(\mathrm{R}) + 4B_g(\mathrm{R}) + 6E_g(\mathrm{R}) + 5A_u(\mathrm{ir}) + 3B_u(\mathrm{ia}) + 5E_u(\mathrm{ir}).$$

No predicted coincidences occur between first-order infrared and Raman modes because of the center of symmetry present in the unit cells. A total of 15 fundamental bands are expected in the Raman spectrum while 10 fundamental bands are expected in the infrared spectrum. Three fundamental modes would be optically inactive.

The vibrational spectra of each phase were analyzed by normal coordinate analysis using an earlier described program (*1*) which incorporated a Born von Karman correction. A modified valence force field was used which was described previously for α-VPO_5, α-VSO_5, and α-$VMoO_5$ (*1, 8*). The symmetry coordinates for α-APO_5 which simplify the calculation were also described (*1*).

While the Raman spectra of α-$MoPO_5$ and α-$NbPO_5$ are illustrated in Fig. 1, their infrared spectra are illustrated in Fig. 2. The observed and calculated wavenumbers for the first-order modes of α-$MoPO_5$ and α-$NbPO_5$ along with those of α-VPO_5 are collected in Table I. First-order modes that are not observed are either too weak to be observed, overlapped with other bands, or below the observed spectral ranges.

The bands between 450 and 900 cm^{-1} for α-$NbPO_5$ are associated with coupled modes involving mainly the stretching of the various Nb–O bonds present in the

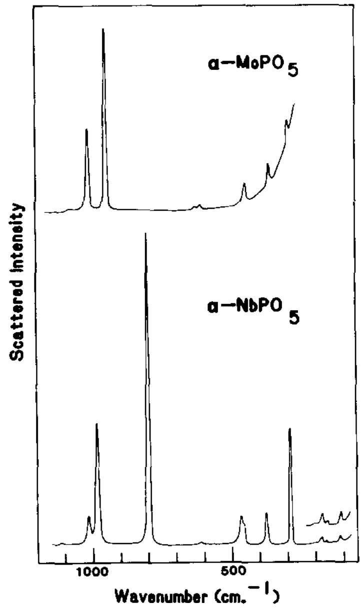

FIG. 1. Raman spectra of α-$MoPO_5$ and α-$NbPO_5$.

TABLE I

THE OBSERVED AND CALCULATED WAVENUMBERS (cm^{-1}) FOR α-$NbPO_5$, α-$MoPO_5$, AND α-VPO_5

Symmetric species	α-$NbPO_5$		α-$MoPO_5$		α-VPO_5(1)	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
A_g	984	1003	1013	1012	994	1001
	800	857	947	927	944	915
	458	470	447	460	468	439
	160	160		249	264	261
		94		141	133	139
B_g	1113	1111	1079	1095	1090	1078
	612	570	607	584		533
	(376)	376		431	435	431
	177	184		206		201
E_g	1014	1090		1092	980	1072
	467	469	621	579	590	586
	376	374	361	369	401	369
	288	284	292	298	302	318
	200	204		237		225
	111	103		108	102	118
A_u	1211	1167	1193	1132	1211	1125
	891	858		931	910	928
	629	630	631	615	602	586
		278		300	(313)	331
	260[a]	260		275		274
B_u (inactive)		901		946		906
		452		471		422
		270		371		369
E_u	1040	1090	998	1093	990	1073
	583	455	585	561	(602)	573
	380[a]	381		384	379	380
	284[a]	287		310	313	313
	216[a]	241		259		270
Least-squares deviation		4.02%		3.57%		4.28%

Note. Bands in parentheses are overlapped.

[a] Deulin *et al.* (*3*).

structure with different magnitudes of bond order. The potential energy distribution for α-$NbPO_5$ (*8*) indicates strong vibrational coupling for most of the bands. The bands at 800 cm^{-1} (A_g) in the Raman spectrum and 891 cm^{-1} (A_u) in the infrared spectrum correspond to the terminal stretching vibration of the short Nb–O_I bond. The asymmetric Nb–O_{II} stretching modes are found at 612 cm^{-1} (B_g), 467 cm^{-1} (E_g), and 583 cm^{-1} (E_u), while the symmetric Nb–O_{II} stretching mode is found at 629 cm^{-1} (A_u). The elongated Nb–O_I bond does not have a specific vibrational mode associated with it. The potential energy distribution (*8*) indicates that this coordinate makes a small contribution to the vibrational bands associated with the short Nb–O_I bond.

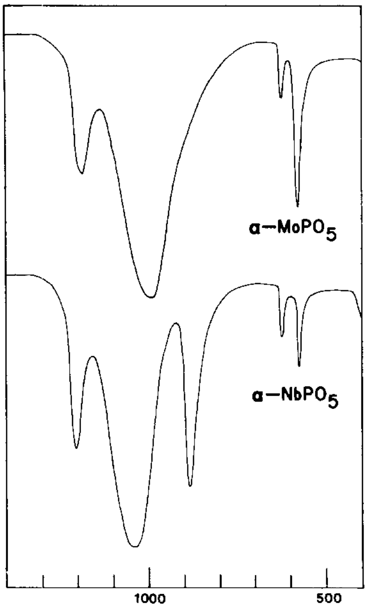

FIG. 2. Infrared spectra of α-$MoPO_5$ and α-$NbPO_5$.

The band at 984 cm^{-1} (A_g) in the Raman spectrum can be assigned mainly to the symmetric P–O_{II} stretching mode. This type of symmetric stretching mode is not observed in the infrared spectrum because the related mode belongs to the B_u symmetry species which is both infrared and Raman inactive. The band involving mainly the triply degenerate asymmetric stretching vibrations of the isolated PO_4 tetrahedrons is split into one doubly degenerate and one nondegenerate band for the α-$NbPO_5$ crystal. The bands occur at 1113 cm^{-1} (B_g), 1014 cm^{-1} (E_g), 1211 cm^{-1} (A_u), and 1040 cm^{-1} (E_u). The bands at 458 cm^{-1} (A_g), 376 cm^{-1} (E_g), 111 cm^{-1} (E_g), and 380 cm^{-1} (E_u) correspond to mainly the O–P–O bending modes. The remaining bands are associated with various O–Nb–O bending modes. The potential energy distribution indicates that none of these bands can be assigned to pure skeletal modes involving Nb–O_{II}–P or Nb–O_I–Nb bending coordinates. However, such coordinates do make a contribution to several of the bending modes.

Normal coordinate analysis also leads to a consistent set of band assignments for α-$MoPO_5$. The band at 947 cm^{-1} (A_g) in the Raman spectrum of α-$MoPO_5$ involves mainly the symmetric stretching vibration of the short Mo–O_I bond. The corresponding stretching mode probably is not seen in the infrared spectrum because it is either too weak to be distinguished from the spectral background or overlapped by the strong broad band at 998 cm^{-1}. The modes involving mainly the asymmetric stretching vibrations of the Mo–O_{II} bonds are found at 607 cm^{-1} (B_g), 621 cm^{-1} (E_g), and 585 cm^{-1} (E_u) while the mode involving the symmetric Mo–O_{II} stretching vibration is found at 632 cm^{-1} (A_u). Normal coordinate analysis indicates that the mode involving the symmetric stretching motion of the P–O bond for α-$MoPO_5$ is observed at 1013 cm^{-1} (A_g) while the bands at 1079 cm^{-1} (B_g), 1193 cm^{-1} (A_u), and 998 cm^{-1} (E_u) involve mainly symmetric P–O stretching vibrations. The Raman-active doubly degenerate P–O stretching mode was not distinguished from background for this material. Normal coordinate analysis indicates that the bands observed at 447 cm^{-1} (A_g), 361 cm^{-1} (E_g), and 632 cm^{-1} (A_u) involve couplings among O–P–O, P–O–Mo, and O–Mo–O bending or Mo–O_{II} stretching motions. The remaining band at 292 cm^{-1} (E_g) corresponds to mainly the O_I–Mo–O_{II} bending vibrations.

A comparison of the vibrational spectra for α-$NbPO_5$, α-VPO_5, and α-$MoPO_5$ shows that although these compounds are isostructural, significant differences exist between their spectra. Many of the bands shift significantly from compound to compound. The large number of shifting bands for this phosphate series is due to the high degree of coupling between modes involving PO_4 groups and those of the AO_6 octahedra. Shifts for the P–O stretching vibrations can be related not only to changes in

TABLE II

THE FORCE CONSTANTS AND STRUCTURAL PARAMETERS FOR α-NbPO$_5$, α-MoPO$_5$, AND α-VPO$_5$

	Units	α-NbPO$_5$	α-MoPO$_5$	α-VPO$_5$
Force constant				
f_r	mdyn/Å	5.51	5.41	5.36
f_{d_a}	mdyn/Å	3.10	3.76	3.11
f_{d_b}	mdyn/Å	1.04	1.10	0.67
f_{d_c}	mdyn/Å	4.84	5.85	5.37
f_α	mdyn Å/rad^2	0.54	0.49	0.54
f_{β_a}	mdyn Å/rad^2	0.70	1.33	1.16
f_{β_b}	mdyn Å/rad^2	0.61	0.48	0.53
f_{β_c}	mdyn Å/rad^2	0.62	1.28	1.05
f_γ	mdyn Å/rad^2	0.45	0.34	0.11
f_δ	mdyn Å/rad^2	0.07	0.05	0.21
f_{d1d2}	mdyn/Å	0.47	0.32	0.39
f_{rr}	mdyn/Å	−0.24	−0.01	−0.05
f_{d1d3}	mdyn/Å	1.09	0.55	0.68
Coordinate[a]				
P–O	Å	1.528	1.528	1.541
$A-\mathrm{O}_{\mathrm{II}}$	Å	1.969	1.974	1.865
$A-\mathrm{O}_{\mathrm{I}}$ elongated	Å	2.321	2.630	2.857
$A-\mathrm{O}_{\mathrm{I}}$ short	Å	1.783	1.663	1.580
O–P–O		109.5	109.5	109.1
$\mathrm{O}_{\mathrm{I}}-A-\mathrm{O}_{\mathrm{II}}$		81.3	77	78.4
$\mathrm{O}_{\mathrm{II}}-A-\mathrm{O}_{\mathrm{I}}$		98.7	103	101.6
$\mathrm{O}_{\mathrm{II}}-A-\mathrm{O}_{\mathrm{II}}$		88.7	87	87.7

[a] Related parameters for α-VSO$_5$ and α-VMoO$_5$ may be found in Ref. (*1*).

bond lengths, bond angles, and bond strengths for the PO$_4$ groups but also to changes for the same parameters and the mass of the A atom in AO$_6$ groups. The potential energy distributions indicate that many of the P–O stretching modes are strongly coupled with $A-\mathrm{O}_{\mathrm{II}}$ stretching modes. For instance, approximately 30% of the band assigned to the symmetric P–O stretching vibration for α-NbPO$_5$ involves the displacements of the $A-\mathrm{O}_{\mathrm{II}}$ coordinates.

The trend in force constants for this series of α-APO$_5$-type phases can be related to differences in structural parameters. Table II lists the calculated force constants for this series along with related bond distances and bond angles. Since the P–O bond distances are very close, their force constants should also be very close. The calculated P–O stretching force constants are 5.36, 5.51, and 5.41 mdyn/Å for α-VPO$_5$, α-NbPO$_5$, and α-MoPO$_5$, respectively. These force constants are lower than the P–O stretching force constant calculated for PO$_4^{3-}$ ions (*9*). This difference is expected because the free ions do not involve oxygen atoms bonded to other atoms. The trend in calculated force constants for the A–O bonds for each α phase follows the trend predicted by Badger's rule with respect to bond distances:

$$f_d \text{ (short } A\text{–O)} > f_d \text{ (equatorial } A\text{–O)} > f_d \text{ (elongated } A\text{–O).}$$

The force constant for the equatorial A–O single bond in α-NbPO$_5$ is 3.10 mdyn/Å. This value is consistent with values of 3.325 and 3.345 mdyn/Å for the Nb–O single bonds in LiNbO$_3$ and Ba$_2$NaNb$_5$O$_{15}$ (*10*). The force constant for the short Nb–O bond in α-NbPO$_5$ is 4.84 mdyn/Å. Force constants ranging from 4.95 to 5.62 mdyn/Å were obtained for the Nb–O terminal bonds in MNbO$_6$ compounds (*11*). The similarity in the values of force constants suggests that the short Nb–O bond in α-NbPO$_5$ is also a double bond. The extremely low values for the force constants of the elongated A–O bonds suggest that the interaction forces between their atoms are weak, possibly involving the Van der Waals type of forces.

The force constants for the Mo–O bonds in the MoO$_6$ octahedra of α-MoPO$_5$ are comparable in terms of trends and approximate magnitudes to those observed for two related structures, PMo$_9$O$_{34}$ units and crystalline MoO$_3$ (*12, 13*). A decrease in force constant was noted for the latter structures as one proceeded from a short Mo–O bond either involving a terminal oxygen atom or sharing a bridging oxygen atom with an elongated Mo–O bond to an intermediate-sized Mo–O bond sharing a bridging oxygen atom with a similar type of bond to an elongated Mo–O bond. However, exact magnitudes cannot be correlated because the normal coordinate analysis treatment of α-$MoPO_5$ involves a modified valence force field containing stretching interaction terms while those of the latter structures involve a simple valence force field.

The interaction force constants between A–O bonds *trans* to each other on AO_6 octahedra are larger than those for A–O bonds *cis* to each other. A similar trend was noted for perovskite compounds containing NbO_6 and TiO_6 octahedra (*14*). The ratio of the *cis* interaction force constant to the *trans* interaction force constant in this study was comparable to those obtained in the latter study.

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