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The Vibrational Spectra of Some Antimony Phosphates

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Six antimony phosphates, $K_3Sb_3P_2O_{14}$, xH_2O, KSb_2PO_8, $KSbP_2O_8$, $SbOPO_4$, K_2SbPO_6, and $K_5Sb_5P_2O_{20}$, have been studied by vibrational spectroscopies: infrared absorption and Raman diffusion. An assignment of the observed frequencies is given, more particularly for the stretching P–O and Sb–O domains. The number of bridging and unshared oxygen atoms in the PO_4 groups has been related to the highest ν_{as} (P–O) frequency of the spectra. For the three types of Sb–O bonds the frequency ranges have been specified.

Introduction

Within a research program devoted to compounds likely to exhibit fast alkali-ion mobility the K_2O–Sb_2O_5–P_2O_5 system was recently investigated. Several phases were identified and their crystal structures determined: $K_3Sb_3P_2O_{14}$, xH_2O (*1, 2*), KSb_2PO_8 (*3*), $KSbP_2O_8$ (*4*), $SbOPO_4$ (*5*), K_2SbPO_6 (*6*), and $K_5Sb_5P_2O_{20}$ (*7*). In some of these compounds the potassium ions can be easily exchanged in acidic medium thus leading to phosphatoantimonic acids which are very good ion exchangers (*8*) and protonic conductors. These acids and related compounds prepared from an ion-exchange process are, generally, poorly crystallized. Vibrational spectroscopies, infrared absorption and Raman diffusion, are well adapted to the characterization of such materials and especially to infer valuable information about protonic species. It is, however, essential to identify first the various vibrations corresponding to the atoms of the covalent frameworks. This paper reports on the vibrational spectra of the above-mentioned antimony phosphates. An assignment of the observed frequencies is given, more particularly for the stretching P–O and Sb–O domains. It is supported by

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a complete vibrational study of the layered compound $K_3Sb_3P_2O_{14}, xH_2O$ for which Raman polarized spectra have been recorded from single crystals, thereby allowing a normal coordinate analysis reported previously (*9*).

Experimental

In the K_2O–Sb_2O_5–P_2O_5 system, six phases corresponding to K_2SbPO_6, $K_3Sb_3P_2O_{14}, xH_2O$, $KSbP_2O_8$, $K_5Sb_5P_2O_{20}$, KSb_2PO_8, and $SbOPO_4$ were synthesized according to a procedure previously described (*2–7*) and characterized by their X-ray powder diffraction pattern. The infrared and Raman spectra of the powder samples have been recorded under conditions described earlier (*9*).

Previous Structural Data

The crystal structures of the phosphates have already been accurately determined by X-ray diffraction (*1–7*). They are built up from PO_4 and SbO_6 polyhedra linked together according to different arrangements as shown in Fig. 1. $SbOPO_4$ (Fig. 1a), KSb_2PO_8 (Fig. 1b), and $K_5Sb_5P_2O_{20}$ (Fig. 1e) exhibit a three-dimensional framework. The crystal structure of $SbOPO_4$ may be described as consisting of chains of corner-shared octahedra running parallel to the **c** axis and linked together by PO_4 tetrahedra. Then, there are two types of Sb–O bonds: Sb–O···Sb and Sb–O···P. In KSb_2PO_8 and $K_5Sb_5P_2O_{20}$ the octahedra share both corners and edges and are linked to the tetrahedra via corners. There is then a new type of Sb–O bond, hereafter called $Sb–O_{cyc}$, which corresponds to oxygen atoms of shared edges. In both $SbOPO_4$ and KSb_2PO_8 the phosphate groups share all their corners with octahedra and there is one type of P–O bond: P–O···Sb. On the other hand, in $K_5Sb_5P_2O_{20}$ there are three types of PO_4 groups linked by two, three, or four vertices to the octahedra and having, respectively, two, one, or no unshared oxygen atoms (i.e., not bonded to antimony). Hereafter, a bond between a phosphorus atom and a so-called unshared oxygen atom will be named a terminal bond.

$KSbP_2O_8$ (Fig. 1c) and $K_3Sb_3P_2O_{14}, xH_2O$ (Fig. 1d) have layered structures. The $(SbP_2O_8^-)_n$ infinite layers are built up from SbO_6 octahedra and PO_4 tetrahedra sharing corners so that each octahedron is connected to six tetrahedra and each tetrahedron to three octahedra. The fourth vertex of each phosphate group is unshared and points into the interlayer space. All of the Sb–O bonds are of Sb–O···P type. Within the $(Sb_3P_2O_{14}^{3-})_n$ layers of $K_3Sb_3P_2O_{14}, xH_2O$, each SbO_6 octahedron is connected via corner sharing to four SbO_6 octahedra and two PO_4 groups. Thus, there are two types of Sb–O bonds: Sb–O···Sb and Sb–O···P. In K_2SbPO_6 (Fig. 1f) the SbO_6 octahedra and PO_4 tetrahedra are arranged in infinite chains running parallel to the **b** axis. The SbO_6 octahedra are linked together by sharing edges. The PO_4 groups are linked to these rutile-like strings of octahedra via two vertices and have two unshared oxygen atoms. There are two types of Sb–O bonds: $Sb–O_{cyc}$ and Sb–O···P.

In the potassium phosphatoantimonates the K^+ ions are located in the interchain or interlayer spaces, respectively, for the one- and two-dimensional compounds and in the channels or channel-like cavities for the three-dimensional ones. The K–O bonds exhibit a very ionic character.

In Table I are listed the different types of bonds existing in each compound and their lengths.

Results and Discussion

The theoretical group analysis by the Bhagavantam method (*10*) has been carried out to number the vibrations and determine the IR and Raman-active modes for each

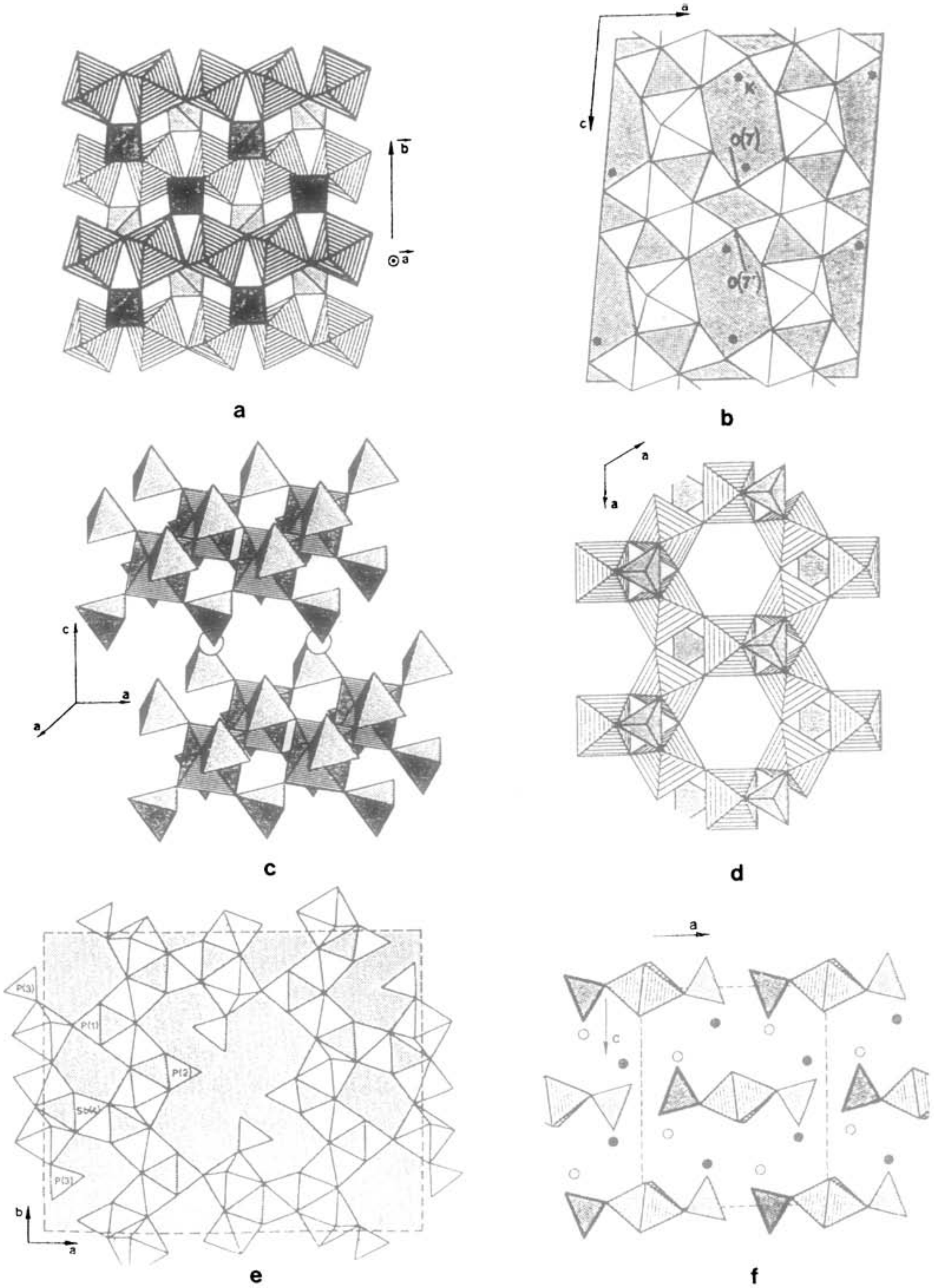

FIG. 1. Crystal structure of the antimony phosphates. (a) SbOPO$_4$; (b) KSb$_2$PO$_8$; (c) KSbP$_2$O$_8$; (d) K$_3$Sb$_3$P$_3$O$_{14}$, xH$_2$O; (e) K$_5$Sb$_5$P$_2$O$_{20}$; (f) K$_2$SbPO$_6$.

TABLE I

Description of the Chemical Bonds in the Antimony Phosphates

Compounds	P–O bonds			Sb–O bonds		
	Type[a]	Length (Å)	K–O[b] (Å)	Type	Length (Å)	K–O[b] (Å)
K_2SbPO_6	2 P–O_{ter}	1.50	2.65–2.94	Sb–O_{cyc}	1.98	2.70–2.90
	2 P–O_b	1.58	2.76	Sb–O···P	2.02	2.76
$K_3Sb_3P_2O_{14}$, $x H_2O$	1 P–O_{ter}	1.49	>3.0	Sb–O···Sb	1.94	2.75
	3 P–O_b	1.56	2.95	Sb–O···P	2.02	2.95
$KSbP_2O_8$	1 P–O_{ter}	1.47	2.93	Sb–O···P	1.95	>3.0
	3 P–O_b	1.56	>3.0			
$K_5Sb_5P_2O_{20}$	2 P–O_{ter}	1.53	2.61–3.06	Sb–O_{cyc}	1.95_5	2.90
	2 P–O_b	1.54	2.93	Sb–O···Sb	1.92–1.99	>3.0
	1 P–O_{ter}	1.49	2.74–2.90	Sb–O···P	1.97–2.17	2.72–3.0
	3 P–O_b	1.56	2.72–2.91			
	4 P–O_b	1.51–1.59	2.90–2.96			
KSb_2PO_8	4 P–O_b	1.53_5	>2.99	Sb–O_{cyc}	1.97	2.87
				Sb–O···Sb	1.94	2.80
				Sb–O···P	2.03	≥2.99
$SbOPO_4$	4 P–O_b	1.53	*X*	Sb–O···Sb	1.90	*X*
				Sb–O···P	1.99	*X*

[a] ter, terminal P–O bond; b, bridging P–O bond.

[b] Lengths of the K–O bonds sharing the concerned oxygen atom.

unit cell at **k** = 0. The results are given in Table II. An approximation has been made for the two layered compounds $K_3Sb_3P_2O_{14}$, $x H_2O$ and $KSbP_2O_8$ containing three layers in their unit cell. If one considers that interactions between two layers are negligible, it is possible to simplify the elementary unit and to consider only one covalent layer instead of three (*9*). For the two compounds $K_3Sb_3P_2O_{14}$, $x H_2O$ and $K_5Sb_5P_2O_{20}$ where the potassium sites are not fully occupied, it is necessary here to account for the symmetry and then to consider them as fully occupied.

Figures 2 and 3 present the Raman and IR spectra of the compounds. Due to overlapping of bands and to weak intensities, the number of bands observed in the spectra is smaller than that predicted by the group theory, except for $K_3Sb_3P_2O_{14}$, $x H_2O$ and $KSbP_2O_8$ which justifies the simplification of their elementary unit.

P–O Bonds

The tetrahedral PO_4^{3-} ion with T_d symmetry has four internal modes of vibration (*11*), i.e., symmetric and antisymmetric stretching modes (ν_1 = 938 cm^{-1}, ν_3 = 1017 cm^{-1}) and bending modes (ν_2 = 420 cm^{-1} and ν_4 = 567 cm^{-1}). Table III gives the correlation scheme for the stretching modes of the PO_4 groups through their site symmetry in the different crystalline cells except for KSb_2PO_8 where the symmetry is very low. An assignment of the observed frequencies is also presented. The antisymmetric stretching modes are found between 1290 and 1050 cm^{-1} and the symmetric stretching modes between 1050 and 900 cm^{-1}. In addition, the highest frequency ob-

TABLE II

THEORETICAL NUMBERING OF VIBRATIONS IN THE CRYSTAL CELLS

K_2SbPO_6 D_{2h}^{16} $Z = 4$ (Ref. (6))

$\Gamma_{op} =$	$17\ A_g$	$+\ 10\ B_{1g}$	$+\ 17\ B_{2g}$	$+\ 10\ B_{3g}$	$+\ 13\ A_u$	$+\ 19\ B_{1u}$	$+\ 12\ B_{2u}$	$+\ 19\ B_{3u}$
	(R)[a]	(R)	(R)	(R)	(i)	(IR)	(IR)	(IR)

$\Gamma_{ac} = B_{1u} + B_{2u} + B_{3u}$

$KSbP_2O_8$ C_{3i}^2 $Z = 3 \rightarrow 1$[b] (Ref. (4))

$\Gamma_{op} =$	$5\ A_g$	$+\ 5\ E_g$	$+\ 6\ A_u$	$+\ 6\ E_u$
	(R)	(R)	(IR)	(IR)

$\Gamma_{ac} = A_u + E_u$

$K_3Sb_3P_2O_{14}, xH_2O$ D_{3d}^5 $Z = 3 \rightarrow 1$[b] (Refs. (1, 2))[c]

$\Gamma_{op} =$	$8\ A_{1g}$	$+\ 2\ A_{2g}$	$+\ 10\ E_g$	$+\ 3\ A_{1u}$	$+\ 9\ A_{2u}$	$+\ 12\ E_u$
	(R)	(i)	(R)	(i)	(IR)	(IR)

$\Gamma_{ac} = A_{2u} + E_u$

$K_5Sb_5P_2O_{20}$ D_{2h}^{12} $Z = 6$ (Ref. (7))[c]

$\Gamma_{op} =$	$87\ A_g$	$+\ 87\ B_{1g}$	$+\ 63\ B_{2g}$	$+\ 63\ B_{3g}$	$+\ 63\ A_u$	$+\ 62\ B_{1u}$	$+\ 89\ B_{2u}$	$+\ 89\ B_{3u}$
	(R)	(R)	(R)	(R)	(i)	(IR)	(IR)	(IR)

$\Gamma_{ac} = B_{1u} + B_{2u} + B_{3u}$

KSb_2PO_8 C_s^4 $Z = 8$ (Ref. (3))

$\Gamma_{op} =$	$142\ A'$	$+\ 143\ A''$
	(R, IR)	(R, IR)

$\Gamma_{ac} = 2\ A' + A''$

$SbOPO_4$ C_{2h}^6 $Z = 4$ (Ref. (5))

$\Gamma_{op} =$	$16\ A_g$	$+\ 20\ B_g$	$+\ 21\ A_u$	$+\ 24\ B_u$
	(R)	(R)	(IR)	(IR)

$\Gamma_{ac} = A_u + 2\ B_u$

[a] R, Raman active; IR, infrared active; i, inactive.

[b] Simplified unit cells (see text).

[c] K^+ sites considered as fully occupied (see text).

served both in the Raman and IR spectra is due to an antisymmetric stretching involving the terminal bond(s) or the shortest bond. These frequencies are at about 1280 cm^{-1} in the compounds presenting PO_4 groups with one terminal bond; they are shifted to about 1200 cm^{-1} for K_2SbPO_6 which possesses two terminal P–O bonds and to about 1100 cm^{-1} for the compounds without terminal P–O bonds. This could be explained in terms of a decreasing of π bonding electron density (*12, 13*). These results must be related to the recent high-resolution solid-state ^{31}P NMR study of these compounds which shows the correlation between the isotropic chemical shift of the ^{31}P resonance line and the connectivity of the PO_4 groups (*14*).

We have not found in the literature any vibrational study about antimony phosphates. However our P–O stretching assignment is in good agreement with that of Stranford and Condrate (*15, 16*) on $VOPO_4$, $NbOPO_4$, and $MoOPO_4$ phosphates exhibiting a structure close to that of $SbOPO_4$ and the same type of P–O bonds. Such P–O bonds are also found in the compound $KTiOPO_4$ studied by Jacco (*17*).

Sb–O Bonds

For the SbO_6 groups it is not possible to establish correlation schemes as for the PO_4 groups because, except in $KSbP_2O_8$, the SbO_6 octahedra are very distorted and (or) exhibit a low symmetry. Three types of Sb–

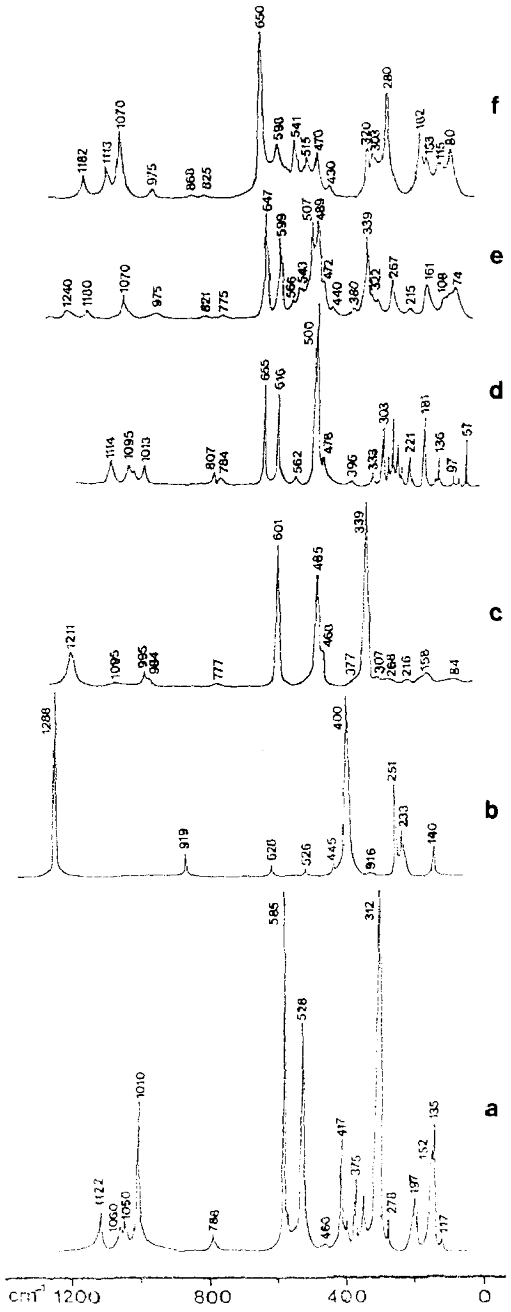

FIG. 2. Raman spectra of the antimony phosphates. (a) SbOPO$_4$; (b) KSbP$_2$O$_8$; (c) K$_3$Sb$_3$P$_3$O$_{14}$, xH$_2$O; (d) KSbP$_2$O$_8$; (e) K$_5$Sb$_5$P$_2$O$_{20}$; (f) K$_2$SbPO$_6$.

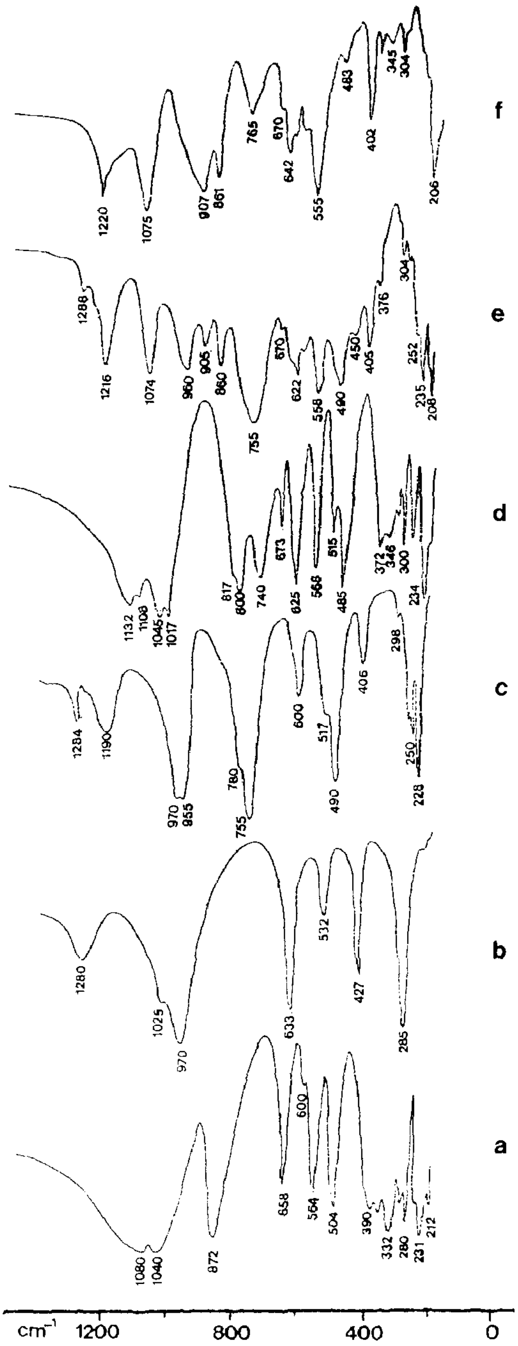

FIG. 3. Infrared spectra of the antimony phosphates. (a) SbOPO$_4$; (b) KSbP$_2$O$_8$; (c) K$_3$Sb$_3$P$_2$O$_{14}$, xH$_2$O; (d) KSb$_2$PO$_8$; (e) K$_5$Sb$_5$P$_2$O$_{20}$; (f) K$_2$SbPO$_6$.

O bonds are found in these compounds:

—The Sb–O_{cyc} bonds created by edge-shared linkage of the octahedra have an average length of 1.97 Å and their frequency stretching range is between 880 and 750 cm^{-1}.

—The Sb–O···Sb bonds created by corner-shared linkage of the octahedra have an average length of 1.95 Å except in $SbOPO_4$ where they have a length of 1.90 Å. Their stretching frequencies are found in the range 790–670 cm^{-1}, in good agreement with those found for the same type of Sb–O bonds in antimonates of pyrochlore structure (*18*). In $SbOPO_4$, the IR band at 872 cm^{-1} is particularly high and can be explained by the short length of the Sb–O···Sb bonds and by the fact that the oxygen atom concerned is not bonded to a K^+ cation, which strengthens the rigidity of the bonds. On the other hand, the existence of chains of octahedra, which allows the couplings of the Sb–O vibrations in these chains, can also explain the high value of this frequency.

—The Sb–O···P bonds existing in all the compounds have an average length of 2.02 Å. Their stretching vibrations are probably coupled with the O–P–O bending ν_4 mode as it was seen in $K_3Sb_3P_2O_{14}$, $x H_2O$ (*9*). These frequencies are found between 680 and 470 cm^{-1}.

The three ranges of Sb–O stretching frequencies are related to the difference in the nature of the Sb–O bonds: the Sb–O_{cyc} bonds are more rigid than the Sb–O···Sb ones due to the mode of linkage, respectively, edge and corner sharing of the SbO_6 octahedra. The Sb–O···P bonds are weakened by the strong P–O bonds sharing the same oxygen atom.

TABLE III

CORRELATION SCHEME AND ASSIGNMENT OF STRETCHING FREQUENCIES FOR PO_4 GROUPS

Compounds	Ideal sym.	Real sym.	Site sym.	Factor group	Assignment
K_2SbPO_6	T_d	C_s	C_s	D_{2h}	
	$\nu_s\ A_1$	A'	A'	$A_g + B_{2g}$	975
				$B_{1u} + B_{3u}$	935, 907
	$\nu_{as}\ F_2$	$2A' + A''$	$2A' + A''$	$2A_g + B_{1g} + 2B_{2g} + B_{3g}$	1182, 1113, 1070
				$A_u + 2B_{1u} + B_{2u} + 2B_{3u}$	1220, 1200, 1175
$KSbP_2O_8$	T_d	C_{3v}	C_3	C_{3i}	
	$\nu_s\ A_1$	A_1	A	A_g	919
				A_u	1025–970
	$\nu_{as}\ F_2$	$A_1 + E$	$A + E$	$A_g + E_g$	1288
				$A_u + E_u$	1280, 1240
$K_3Sb_3P_2PO_{14}$, $x H_2O$	T_d	C_{3v}	C_{3v}	D_{3d}	
	$\nu_s\ A_1$	A_1	A_1	A_{1g}	995–984
				A_{2u}	970–955
	$\nu_{as}\ F_2$	$A_1 + E$	$A_1 + E$	$A_{1g} + E_g$	1211, 1095
				$A_{2u} + E_u$	1284, 1190
$K_5Sb_5P_2O_{20}$	T_d	C_s	C_s	D_{2h}	
	$\nu_s\ A_1$	A'	A'	$A_g + B_{1g}$	975
				$B_{2u} + B_{3u}$	995–960, 905
	$\nu_{as}\ F_2$	$2A' + A''$	$2A' + A''$	$2A_g + 2B_{1g} + B_{2g} + B_{3g}$	1240–1230, 1180, 1070
				$A_u + B_{1u} + 2B_{2u} + 2B_{3u}$	1288–1245–1216, 1074
$SbOPO_4$	T_d	C_{2v}	C_2	C_{2h}	
	$\nu_s\ A_1$	A_1	A	A_g	1010
				A_u	1040
	$\nu_{as}\ F_2$	$A_1 + B_1 + B_2$	$A + 2B$	$A_g + 2B_g$	1122, 1060–1050
				$A_u + 2B_u$	1080

Other Modes

—Below 450 cm^{-1}, the observed frequencies involve strong couplings between the different bending vibrations: O–P–O, O–Sb–O, Sb–O–P, Sb–O–Sb as in $K_3Sb_3P_2O_{14}$, $x H_2O$ and correspond to deformations of the polyhedra or of the whole covalent network.

—The bands due to the K–O bonds are supposed to appear at very low frequencies, below 150 cm^{-1}, in agreement with their strong ionic character and their length.

Conclusion

This study allowed us to:

—characterize the different compounds by their IR and Raman spectra;

—propose an assignment of the observed frequencies, more particularly for the stretching P–O and Sb–O domains, taking into account the chemical environment of the oxygen atoms:

· the number of bridging and unshared oxygen surrounding the phosphorus atoms has been related to the highest frequency of the spectra (ν_{as} P–O);

· the frequency ranges of the three types of Sb–O bonds encountered have been specified.

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