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Vibrational spectrum of the periodates $M^I M^{IV} IO_6$.

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Abstract—Powder i.r. and Raman spectra of periodates $M^I M^{IV} IO_6$ ($M^I = Na, K, Rb, Cs, NH_4$; $M^{IV} = Ge, Sn, Pb$) are reported and discussed on the basis of a group theoretical analysis. The number of observed bands is smaller than the number of predicted active modes; but the results are not in contradiction with the proposed space groups ($P 312$ for the Ge, $P 6_3 22$ for the Sn and Pb compounds). Mass effects show that the 2 lowest-frequency i.r. bands are related to translational motions of the monovalent cation M^I . On the contrary, the remaining i.r., and all the observed Raman frequencies are practically insensitive to the nature of M^I , but are more or less modified by the nature of the tetravalent cation M^{IV} . The high- and medium-frequency part of the spectrum cannot be described in terms of separate IO_6 and $M^{IV} O_6$ vibrations, but is due to mixed vibrations of the lattice of $IO_6 + M^{IV} O_6$ octahedra. Finally, the i.r. spectra are briefly compared to those given by the structurally related antimonates $M^{II} Sb_2 O_6$ ($M^{II} = Ca, Sr, Ba, Pb, Cd$).

INTRODUCTION

Periodates with the general formula $M^I M^{IV} IO_6$ ($M^I = K, Rb, Cs, NH_4$; $M^{IV} = Ge, Sn, Pb$) have been synthesized by FRYDRYCH [1-3]. According to their X-ray powder diagram, all these compounds are hexagonal, but with different space groups: for the Ge compounds, all the observed reflections are compatible with either $P 3$ or $P 312$ space group [3]; for the Sn and Pb compounds, a few supplementary faint lines are observed; they can be accounted for by doubling the c axis, the proposed space group being $P 6_3 22$ [1, 2]. Vibrational data on these compounds are rather scarce and restricted to a more or less empirical assignment of the i.r. spectra of a limited number of compounds [4, 5].

We present here a more systematic investigation of the whole family, including a group theoretical analysis, together with i.r. and Raman spectra.

EXPERIMENTAL

All compounds $M^I M^{IV} IO_6$ ($M^I = K, Rb, Cs, NH_4$) were synthesized by the procedure given by FRYDRYCH [1-3]. Their purity was checked by X-ray diffractometry. In addition, we were also able to synthesize the sodium compounds $NaSnIO_6$ and $NaGeIO_6$ which, according to their X-ray powder diagram and their vibrational spectra, must have the same structure. $NaSnIO_6$ (which has also been obtained by NATARAJAN *et al.* [5]) is well crystallized, whereas $NaGeIO_6$ gives a very poor diffraction pattern, with only 4 very diffuse lines corresponding to the 001, 100, 101 and 110 reflections exhibited by the other $M^I GeIO_6$ compounds.

The i.r. spectra were registered with a Beckman

IR-12 (down to 200 cm^{-1}) and a CAMECA SI-36 ($200\text{--}50\text{ cm}^{-1}$) spectrometer.

The pressed disk technique has been used with appropriate disk materials (AgI above 200 cm^{-1} ; polythene for the low frequency region). Raman spectra were registered with a CODERG PHO double monochromator equipped with a Spectra Physics He-Ne laser.

CRYSTAL STRUCTURE AND GROUP THEORETICAL ANALYSIS

Germanium compounds $M^I GeIO_6$

Taking into account the structural analogies between $KNiIO_6$ and $M^I GeIO_6$ suggested by FRYDRYCH [3], it will be assumed here that their space group is the same, namely $P 312 - D_3^1$, with 1 molecular formula in the crystal cell. The group theoretical analysis* leads to the irreducible representation:

$$\Gamma_i = 3A_1(\text{Ra}) + 5A_2(\text{i.r.}) + 8E(\text{Ra, i.r.})$$

In addition, the correlation tables show that all atoms are allowed to move during the A_2 and E vibrations, whereas oxygen atoms only are displaced during the A_1 vibrations.

Tin and lead compounds $M^I Sn^{IV} IO_6$ and $M^I Pb^{IV} IO_6$

After FRYDRYCH [1, 2], these compounds are hexagonal, space group $P 6_3 22 - D_6^6$, $Z = 2$. The c axis is doubled with respect to the c axis of $KNiIO_6$. The atomic positions in the crystal cell have not been determined so far, and a group theoretical analysis seemed impossible.

* Details of this analysis are given in reference 6.

Table 1. Comparative atomic positions in the space groups $P 312$ and $P 6_322$.

KNiO ₆ —Space group $P 312$ KSnIO ₆ —Space group $P 6_322$					
Atoms	Positions	Site symmetry	Atoms	Positions	Site symmetry
1K	(a) 0 0 0	D_3	2K	(a) 0 0 0; 0 0 $\frac{1}{2}$	D_3
1Ni	(d) $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{2}$	D_3	2Sn	(c) $\frac{1}{3}$ $\frac{2}{3}$ $\frac{1}{4}$; $\frac{2}{3}$ $\frac{1}{3}$ $\frac{3}{4}$	D_3
1I	(f) $\frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{2}$	D_3	2I	(d) $\frac{1}{3}$ $\frac{1}{3}$ $\frac{1}{4}$; $\frac{2}{3}$ $\frac{2}{3}$ $\frac{3}{4}$	D_3
6O	(i) general	C_1	12O	(i) general	C_1

However, reasonable atomic positions may be tentatively deduced from the following considerations: (1) The periodates under discussion are very similar to the corresponding Ge compounds, not only by their chemical formula, but also by their X-ray powder diagram [1–3], and their vibrational spectrum (see below): this strongly suggests structural analogies, with a similar atomic arrangement in both types of structures; (2) indeed, there is a simple structural relationship between the space groups $P 312$ (Ge compounds) and $P 6_322$ (Sn and Pb compounds): the latter may be derived from the former by adding an helicoidal binary axis originating at point 000 and perpendicular to the 001 face. This leads to the doubling of the former c axis of the $P 312$ cell and of the number of atoms in the unit cell.

Taking these structural relationships into account, it is thus easy to propose, for the Sn and Pb compounds, atomic positions in the space group $P 6_322$ which are very similar to those already known for KNiO₆ in the space group $P 312$ (Table 1).

On the basis of these atomic positions, it is now possible to carry on the classical vibrational analysis, which leads to the following irreducible

representation:

$$\Gamma_i = 3A_1 + 5A_2 + 5B_1 + 4B_2 + 8E_1 + 9E_2$$

13 modes are i.r. active ($5A_2 + 8E_1$), whereas 20 are Raman active ($3A_1 + 8E_1 + 9E_2$). Here again, the oxygen atoms only are allowed to move during the A_1 vibrations.

RESULTS AND INTERPRETATIONS

The observed frequencies are collected in Tables 2–4*; some typical spectra are given in Fig. 1.

The essential features of these results may be summarized as follows.

Infrared spectra

(1) For a given tetravalent cation (Ge, Sn or Pb), the frequency of the 2 lowest-lying bands is very sensitive to the nature of the alkali cation, and the relationship between these frequencies and the square root of the mass of the alkali cation is roughly linear. This is not true, however, for the ammonium compounds, since the first band is observed at a frequency which is lower for the $(\text{NH}_4)^+$ than for the Na compound. This is possibly related to the larger ionic radius of the $(\text{NH}_4)^+$ ion, but this explanation is only tentative. Thus, these 2 bands correspond, at least in part, to a translational motion of the alkali cation. The situation, however, appears more complicated if we consider the influence of the tetravalent cation on the same bands. This influence is really negligible for the lowest frequency band (between 100 and 50 cm^{-1}) of the Rb and Cs compounds (Fig. 2), but is important for

* In these tables, the last column gives the labeling of the frequencies which exhibit a Raman-infrared coincidence (see below).

Table 2. i.r. and Raman frequencies of the periodates $M^1\text{GeIO}_6$

NH ₄ GeO ₆		NaGeO ₆		KGeO ₆		RbGeO ₆		CsGeO ₆		
i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra	
149 m		155 w		112 m		75 m		57 m		
246 m		220 m		188 m		140 m		123 m		
	228 m				227 m		227 m		224 m	
	310 m				313 m		310 m		305 m	
333 s	329 w	337 s	332 w	336 s	330 w	336 s	329 w	335 s	327 w	II
									364 vw	
465 m		472 m		465 m		462 m		458 m		
555 s	550 w	560 s	554 vw	556 s	549 w	557 s	549 w	553 s	545 w	IV
607 m		600 sh		605 m		606 m		607 m		
	630 w		638 vw		633 m		631 m		625 m	
	672 vw		670 vw		669 w		668 w		663 w	
	706 vs		707 vs		705 vs		707 vs		702 vs	
722 s	719 sh	730 s	724 sh	724 s	720 sh	724 s	721 sh	718 sh	715 sh	VI
738 s		740 s		735 s		736 s		732 s		

Table 3. i.r. and Raman frequencies of the periodates M^IVSnIO_6

NH_4SnIO_6		$NaSnIO_6$		$KSnIO_6$		$RbSnIO_6$		$CsSnIO_6$		
i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra	
155 m		156 m		118 m		76 m		57 m		
				175 m		126 m		108 m		
197 m	198 s	197 m		197 m	202 s	197 m	199 s	197 m	199 s	I
222 w			217 m							
287 s	282 s	292 s	290 m	289 s	290 s	288 s	284 s	287 s	278 s	II
			314 m							
351 s	349 w	352 s	353 w	351 s	350 w	351 s	350 w	349 s	348 w	III
	400 vw				410 vw		407 vw		400 vw	
470 m	469 vw	477 m		470 m	472 vw	467 m	475 vw	464 m	478 vw	
564 s	552 w	560 s	556 w	560 s	555 w	561 s	552 w	557 s	549 w	IV
	606 m				616 m		609 m		601 m	
	633 vs		628 vs		634 vs		633 vs		632 vs	
675 s	674 sh	679 s		678 s		677 s	671 sh	671 s	668 sh	V
	687 vs		686 vs	685 sh	688 vs	687 sh	687 vs	683 sh	685 vs	VI
					747 vw		750 w		744 vw	

Table 4. i.r. and Raman frequencies of the periodates M^IVPbIO_6

NH_4PbIO_6		$KPbIO_6$		$RbPbIO_6$		$CsPbIO_6$		
i.r.	Ra	i.r.	Ra	i.r.	Ra	i.r.	Ra	
78 m		90 m		76 m		57 m		
		120 m		116 m		104 m		
165 m	164 s	166 s	166 s	167 s	164 s	164 s	165 s	I
235 s	230 vw	235 s	230 w	237 s	230 w	236 s	231 vw	II
277 m	270 m		275 m		268 m		265 vw	
318 s	315 m	320 s	315 m	320 s	315 m	318 s	311 w	III
							346 vw	
							380 vw	
435 m		436 m		434 m		432 m		
520 s		516 s		516 s		513 s		
	575 vs		576 vs		575 vs		573 vs	
642 s	637 m	645 s	639 s	644 s	636 s	638 s	631 m	VI
	670 s		672 s		670 s		666 m	

the second low-frequency band ($150-100\text{ cm}^{-1}$) of these compounds, and for the 2 low-frequency bands of the potassium compounds.

In this latter case, there is no regular relationship between the frequencies and the nature of the tetravalent cation, a fact which may possibly result from a strong mixing of the translational motions of the K^+ and tetravalent cations.

(2) For all the other bands, the influence of the nature of the alkali cation is very small or even quite negligible (Tables 2-4). On the contrary, this region of the spectrum is more or less affected by the nature of the tetravalent cation: there are more bands in the spectra of the Sn and Pb compounds (in accordance with the doubling of the unit cell with respect to that of the Ge compounds), and the bands are shifted towards lower frequencies when passing from the Sn to the Pb compounds (Fig. 3) (a comparison with the corresponding Ge compounds would not be necessarily significant, since

their structure is slightly different).

The origin of these shifts is not evident (mass effect, ionic radius, type of bonding or, more probably, a combination of these factors); but since all (or nearly all) frequencies are modified by the tetravalent cation, they are assigned, not to specific vibrations of either IO_6 or M^IVIO_6 octahedral groups, but instead to vibrations of the lattice of $IO_6-M^IVIO_6$ octahedra. This assignment is also supported by the fact that, despite the structural analogies, the spectra of the corresponding $KNiIO_6$ and $KMnIO_6$ compounds are fairly different: this is easily explained by the rather different type of the $Ni^{IV}-O$ and $Mn^{IV}-O$ bonds, the spectrum corresponding to mixed $IO_6-M^IVIO_6$ vibrations.

Raman spectra

(1) *Influence of the monovalent cation.* This influence is very small to negligible for all the Raman

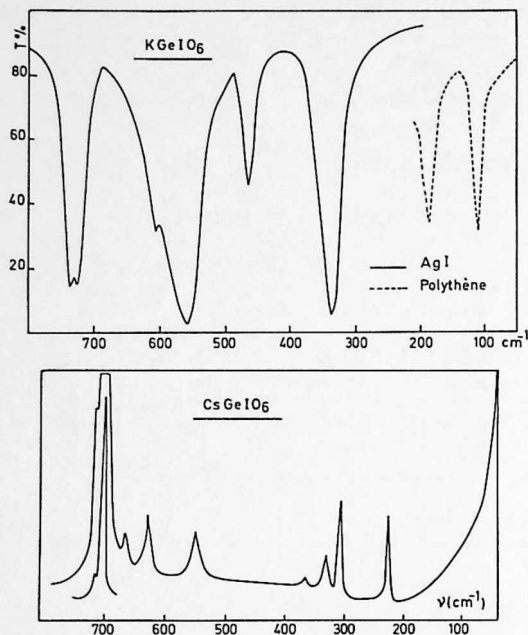


Fig. 1. Example of i.r. (KGeIO_6) and Raman (CsGeIO_6) spectrum.

peaks. It may be inferred that the alkali cations are at rest during these vibrations.

It should be pointed out that the alkali cations are allowed to move during the E vibrations (for space group $P312$) and the E_1 and E_2 vibrations (for space group $P6_322$), but this does not imply that they are really moving. On the other hand, it is quite possible that Raman bands corresponding essentially to displacements of the alkali cations are very weak and do not appear in powder spectra.

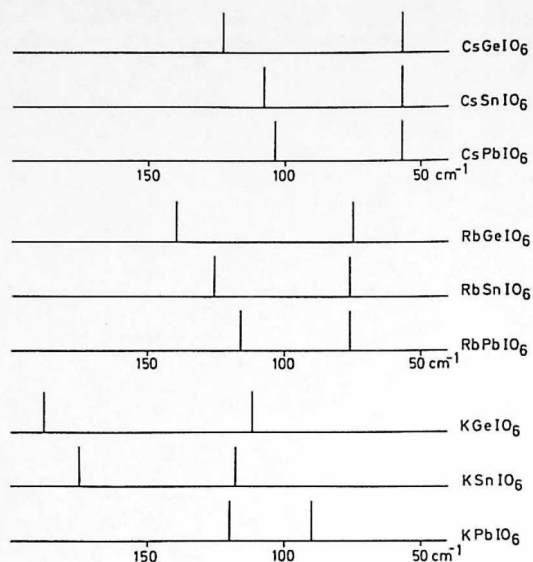


Fig. 2. Influence of the monovalent M^I and tetravalent M^{IV} cations on the position of the 2 lowest-frequency i.r. bands.

Indeed, since the i.r. spectrum of the Ge compounds exhibits the 2 bands corresponding to the translational motions of the alkali cation, one of these 2 frequencies should belong to the E class (degenerate translations along x and y axis) and thus appear also in the Raman spectrum. But a very careful search in the appropriate frequency range ($200\text{--}50\text{ cm}^{-1}$) was unsuccessful.

(2) *Influence of the tetravalent cation.* This influence is considerable and, unfortunately, rather complex. It is clearly impossible to find out a band-to-band correlation between the spectra of the corresponding Sn and Pb compounds (as it was the

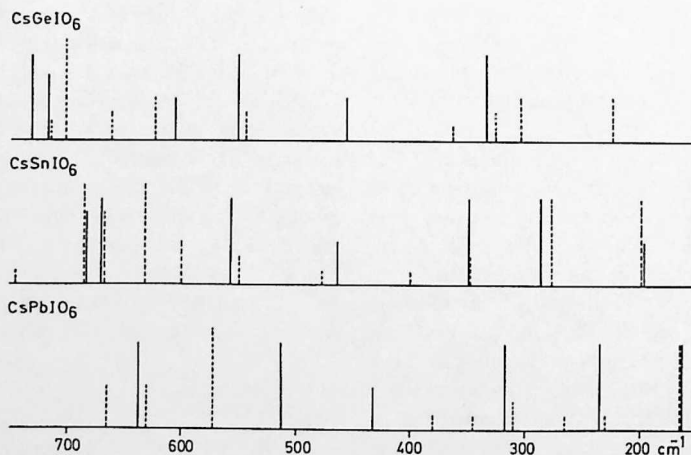


Fig. 3. Position of the bands of the $\text{CsM}^{IV}\text{IO}_6$ compounds in relation with the nature of the tetravalent cation. Full lines: i.r. frequencies; dotted lines: Raman frequencies.

case for the i.r. spectra) (Fig. 3) Some of the observed variations are possibly related to large differences in the cationic polarisabilities and thus in the intrinsic intensities of the bands. Nevertheless, even in the high-frequency region ($800\text{--}500\text{ cm}^{-1}$), which is generally considered as the most favourable one to the occurrence of internal vibrations, the differences between the Raman patterns given by the Ge, Sn and Pb compounds are such (Fig. 3) that it is excluded to assign these peaks to internal vibrations of the IO_6 octahedra. Moreover, since the spectra for a given tetravalent cation are practically independent of the nature of the alkali cation, these patterns are really characteristic of the association of IO_6 and $M^{IV}O_6$ octahedra in the considered structure. In our opinion, these Raman data definitively prove that the vibrational spectrum cannot be assigned to internal vibrations of the IO_6 or $M^{IV}O_6$ octahedra, but on the contrary is related to vibrations of the whole lattice of $IO_6 + M^{IV}O_6$ octahedra. This does not agree with previous assignments [4, 5] but there is no real contradiction, since these assignments were presented as tentative, and deduced from the investigation of a limited number of compounds.

Tentative assignment of some peculiar frequencies

A_1 modes. The group theoretical analysis predicts $3A_1$ modes, which are characterized by the fact that all cations must be at rest. An unequivocal identification of these modes is impossible since powder spectra only are available. Nevertheless, an inspection of the Raman frequency values (Tables 2–4) suggests that 2 high-frequency peaks are observed in the same spectral range ($625\text{--}640$ and $663\text{--}674\text{ cm}^{-1}$), irrespective of the nature of both monovalent and tetravalent cations. If the frequency correspondance is not fortuitous, these values reveal a complete lack of mass effect for both monovalent and tetravalent cations, and the 2 bands can be tentatively assigned to the A_1 symmetry class.

However, we obtain a completely different interpretation if we consider that the 636 cm^{-1} peak of the Pb compounds is corresponding to the 670 cm^{-1} peak of the Sn compounds. In this case, nearly each Raman band has its counterpart in the i.r. spectrum, and this coincidence suggests the assignment of these bands to degenerate E_1 modes.

This alternative interpretation will now be discussed.

Raman-i.r. coincidences. Eight E or E_1 modes (for the space group $P 312$ or $P 6_322$ respectively) are both Raman and i.r. active. In fact an unequivocal identification of these modes is not simple for the following reasons: (i) polarisation data are missing, and the symmetry properties of the bands are unknown. Thus, the coincidences are deduced from frequency values only. (ii) The comparison of the frequency values is not necessarily significant. Besides the possibility of accidental coincidences and the errors coming from the broadness and/or weakness of some bands, the most troublesome point is the fact that a conventional i.r. "absorption" spectrum is the result of both absorption and reflection phenomena, and that a maximum "absorption" frequency is in fact an average value somewhere between the LO and TO frequencies. This may lead to a significant difference between the observed i.r. and Raman frequencies corresponding to a given mode. The coincidences are the best and the most systematic for the low frequency bands labeled I, II and III (Tables 2–4); for these bands, it is very likely that the coincidences are not fortuitous, and that these bands belong, either to the E (Ge compounds) or to the E_1 (Sn and Pb compounds) symmetry class. For the higher frequency bands (IV–VI), the differences between the i.r. and Raman frequencies may be somewhat larger, and some bands are missing. Thus, their assignment to E or E_1 modes is possible, but doubtful. Since, in addition, some of these Raman frequencies may alternatively be assigned to A_1 modes, we conclude that the assignment of these bands remains an open question.

DISCUSSION

Choice of the space group of the germanium compounds

FRYDRYCH [3] has proposed 2 possible space groups, namely $P 3$ and $P 312$, for the germanium compounds.

The latter has been choosed for our group theoretical analysis because it is the true space group of the parent compound $KNiIO_6$ [7, 8]. This choice may now be briefly discussed in connection with the experimental spectra. The comparison of the theoretical predictions and the experimental results is as follows:

	Predicted $P 3$	Predicted $P 312$	Observed
Total of i.r. active modes	16(8A+8E)	13(5A ₂ +8E)	8
Total of Raman active modes	16(8A+8E)	11(3A ₁ +8E)	8–9
Number of coincidences	16	8	1 certain 2 possible

The experimental results, and particularly the fairly small number of observed coincidences, support the choice of the $P\bar{3}12$ space group, although a final choice would require the knowledge of the polarization properties of the bands.

Spectral analogies with the isomorphous antimonates $M^{II}Sb_2O_6$

These compounds ($M = Ca, Sr, Ba, Pb, Cd$) have been synthesized and investigated by MAGNELI [9]. They belong to the same space group that $KNiIO_6$ and $KGeIO_6$, namely $P\bar{3}12$ and thus, a comparison of the vibrational spectra may be interesting.

The i.r. spectra have been investigated by FRANCK *et al.* [10, 11] and interpreted on the basis of a centrosymmetric cell $P\bar{3}1m$.

The discussion of this latter point will be delayed until we have collected good Raman spectra of these compounds. Thus we shall restrict ourselves to a formal comparison, for which we use the i.r. data published by FRANCK [10, 11]. (1) The general appearance and the frequency distribution in the i.r. spectra are rather similar within the $M^{II}Sb_2O_6$ family, but very different from the patterns given by the $M^I GeIO_6$ compounds. This is not unexpected, since the distribution of the bonding forces is rather different in the periodates and in the antimonates.

(2) Remarkably enough, the number of i.r. bands is the same: eight bands are generally observed in the spectra of antimonates and $M^I GeIO_6$ periodates. (3) For both antimonates [10, 11] and periodates (this paper), the position of the 2 lowest-frequency bands is clearly related to the mass of the low-valency cation (M^{II} or M^I respectively).

(4) The influence of the low-valency cation on

the higher-frequency bands is somewhat different for the 2 families of compounds. For the $M^I GeIO_6$ family, this influence is practically negligible (Tables 2-4), but this is no longer true for the $M^{II}Sb_2O_6$ antimonates: FRANCK's i.r. data suggest that a small mass effect of the M^{II} cation is still present in the medium-frequency region. Such a different behaviour may be qualitatively explained by the fact that the bonding force is stronger for the $M^{II}-O$ than for M^I-O bonds and that, consequently, the influence on the vibrational spectrum should extend towards higher frequencies for the M^{II} cation.

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