

Infrared and Raman spectra of three tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$)

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Abstract. The infrared and Raman spectra of three tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$) have been recorded and analysed. A factor group model has been used to interpret the spectra of $\text{Fe}_2P_4O_{12}$ and $\text{Ni}_2P_4O_{12}$. A free ion model could explain the $\text{Zn}_2P_4O_{12}$ spectra. The frequencies have been assigned on the basis of characteristic vibrations of PO_2^{2-} and P–O–P groups. The $\text{P}_4\text{O}_{12}^{4-}$ ion is found to have C_i symmetry in $\text{Fe}_2P_4O_{12}$ and $\text{Ni}_2P_4O_{12}$ and C_{2h} in $\text{Zn}_2P_4O_{12}$. The ion in $\text{Fe}_2P_4O_{12}$ is more distorted than in the other two.

Keywords. Vibrational spectra; tetrametaphosphates; free ion symmetry; P–O–P and PO_2^{2-} groups.

1. Introduction

The infrared and Raman spectra of certain tetrametaphosphates of monovalent and divalent metals (Polataev 1968; Tokman and Polataev 1976; Steger and Simon 1958), and double metaphosphates of alkali metals and rare earths (Madii *et al* 1978; Xie *et al* 1982) have been reported. Most of their studies were in order to determine the possible symmetries of the anion ($\text{P}_4\text{O}_{12}^{4-}$) in those crystals. They explained the vibrational frequencies of the anion on the assumption that it contains the groups PO_2^{2-} and P–O–P. In these compounds the anion exists either as a chain or as a cyclic ring (Tokman and Polataev 1976; Maddi *et al* 1978; Palkina *et al* 1976). In the ring structure itself, different conformations are possible in different crystals (Polataev 1968).

Steger and Simon (1958a, b) reported a D_{2d} symmetry for the anion in $M_2P_4O_{12}$ ($M = \text{Mg, Cu}$) from IR studies. However, x-ray diffraction studies (Beucher and Gramer 1968; Bagieu-Beucher *et al* 1976) suggest a centre of symmetry for the anion in the crystals $M_2P_4O_{12}$ ($M = \text{Mg, Fe, Ni, Zn, Cu, Co, Mn}$). A detailed analysis of the vibrational spectra of these compounds is expected to give more information about the symmetry of the anion in these crystals. In the present paper the analysis of the IR and Raman spectra of the tetrametaphosphates $M_2P_4O_{12}$ ($M = \text{Fe, Ni, Zn}$) is reported.

2. Experimental

The Raman spectra (figures 1, 2 and 3) of these compounds were recorded in a SPEX 'Ramalog' using the 4880 Å line of an argon ion laser (Spectra Physics Model 165) as the excitation line. IR spectra of $\text{Ni}_2P_4O_{12}$ and $\text{Zn}_2P_4O_{12}$ were recorded in a Perkin

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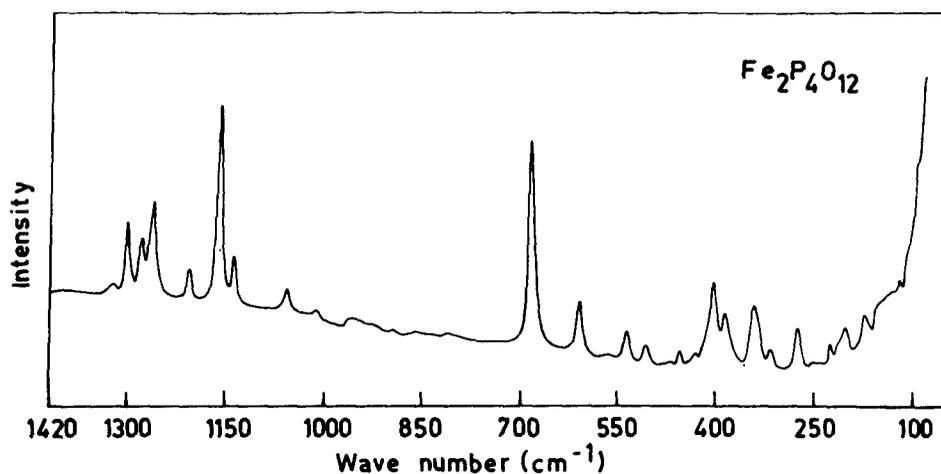


Figure 1. Raman spectrum of $\text{Fe}_2\text{P}_4\text{O}_{12}$.

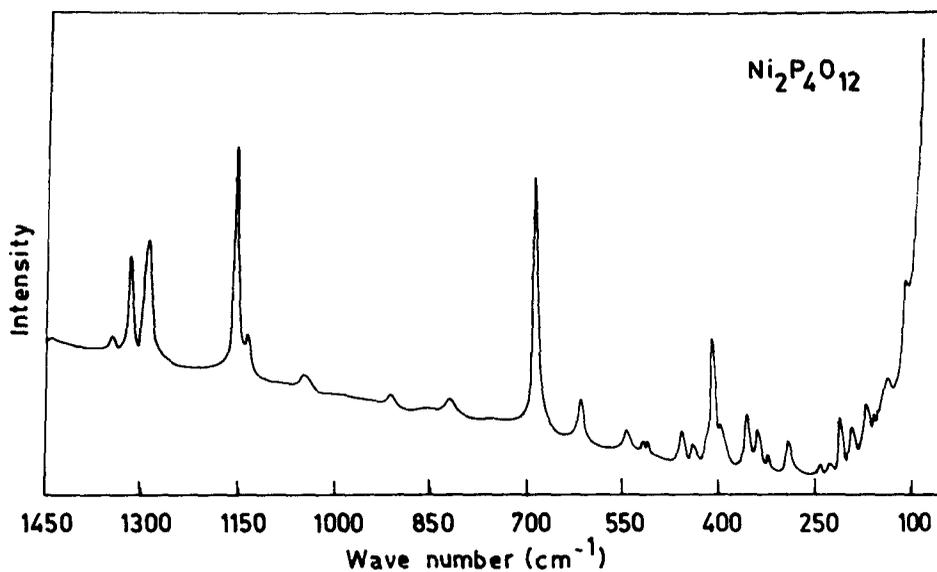


Figure 2. Raman spectrum of $\text{Ni}_2\text{P}_4\text{O}_{12}$.

Elmer 225 spectrophotometer with the samples as Nujol mulls. A Perkin Elmer 283 (spectrophotometer was used for $\text{Fe}_2\text{P}_4\text{O}_{12}$ (KBr pellet).

3. Factor group analysis

The crystal has a monoclinic structure with space group $C2/c$ (C_{2h}^6), with four formula units per crystallographic unit cell (Bagieu-Beucher *et al* 1976). The cations are located

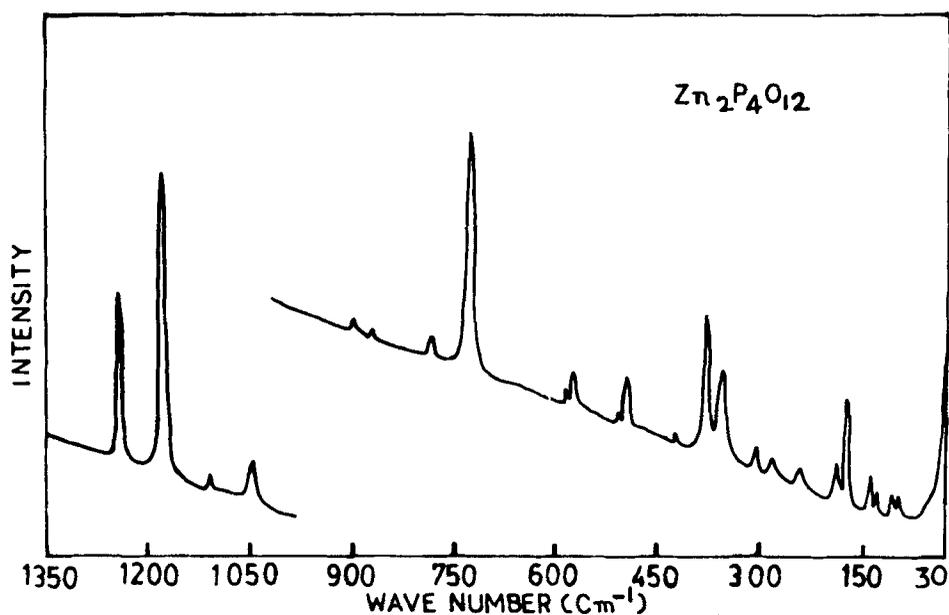


Figure 3. Raman spectrum of $Zn_2P_4O_{12}$.

at two different sites C_i and C_2 , and the phosphorus and oxygen atoms are in general positions. The environment of the phosphorus atom is tetrahedral. The $P_4O_{12}^{4-}$ ring is formed by joining the vertices of four distorted PO_4 tetrahedra. The divalent cations are octahedrally coordinated to the oxygen atoms. The distance between phosphorus and the bridging oxygen is slightly greater than that between phosphorus and terminal oxygen (sharing in the environment of the cation).

The factor group analysis with the standard correlation method (Fateley *et al* 1972), has been carried out for the Bravais unit cell. The two $M_2P_4O_{12}$ molecules in a Bravais unit cell give rise to 108 normal modes of vibrations, including the three acoustic modes. The total number of vibrations are distributed as follows:

$$\Gamma = (25A_g + 26B_g) + (27A_u + 27B_u) + (A_u + 2B_u).$$

The terms are, respectively, Raman active, IR active and acoustical vibrations. The normal vibrations of the anion with free ion symmetry C_i and C_{2h} are

$$\Gamma_{C_i} = 21 A_g + 21 A_u,$$

$$\Gamma_{C_{2h}} = 12 A_g + 9 B_g + 9 A_u + 12 B_u.$$

The correlations of the free ion symmetries C_i and C_{2h} with the factor group C_{2h}^6 are given in table 1. As the observed number of lines for $M_2P_4O_{12}$ ($M = Fe, Ni$) are more than 42, the factor group method has to be used for the interpretation of their spectra. However a free ion model seems to be sufficient for explaining $Zn_2P_4O_{12}$ spectra (only 35 bands are observed).

Table 1. Correlation of the free ion symmetry C_i and C_{2h} , with the factor group C_{2h}^6 .

Free ion symmetry group C_i	Site symmetry group C_1	Factor group C_{2h}^6
21 A_g	A	A_g 21
21 A_u		B_g 21
		A_u 21
		B_u 21
Free ion symmetry group C_{2h}	Site symmetry group C_1	Factor group C_{2h}^6
12 A_g	A	A_g 21
9 B_g		B_g 21
9 A_u		A_u 21
12 B_u		B_u 21

4. Interpretation of the spectra

$\text{Fe}_2\text{P}_4\text{O}_{12}$: The frequencies are assigned on the basis of characteristic vibrations of PO_2^{2-} and P–O–P groups. The P–O bond in the PO_2^{2-} group is stronger than that in the P–O–P bridge. Consequently, the vibrational frequencies of the PO_2^{2-} group are expected to be higher than those for P–O–P bridge. The Raman lines observed at 1323, 1300, 1277, 1259 and 1206 cm^{-1} and the IR absorption at 1263 cm^{-1} are assigned to asymmetric PO_2^{2-} stretching modes. The PO_2^{2-} symmetric vibrations are observed at 1160, 1138 and 1057 cm^{-1} in the Raman and as a very weak band at 1115 cm^{-1} in the IR spectra. The Raman bands at 1015, 960 and 895 cm^{-1} and the IR band at 1030 cm^{-1} are assigned to the asymmetric P–O–P stretching mode. The symmetric P–O–P stretching vibrations are observed at 815 and 679 cm^{-1} in the Raman and at 730 and 705 cm^{-1} in the IR spectra.

The bending modes are expected in the region $600\text{--}450\text{ cm}^{-1}$ (PO_2^{2-} group) and $420\text{--}150\text{ cm}^{-1}$ (P–O–P bridge). The Raman lines at 608, 535, 505, 454 and 430 cm^{-1} and IR bands at 635, 571, 558, 525, 497, 476, 445 and 430 cm^{-1} are due to the deformation vibrations of PO_2^{2-} group. The bending vibrations for P–O–P are 400, 386, 338, 272, 221, 199 and 170 cm^{-1} in the Raman and 386, 358, 340, 310, 298 and 280 cm^{-1} in the IR spectra. As the metal oxygen stretching vibration (around 300 cm^{-1}) occurs in the P–O–P bending region (Gonzalez Diaz and Santos 1978), it is difficult to assign this vibration unambiguously. The very weak Raman line at 315 cm^{-1} may be due to metal oxygen stretching. The details of the observed spectra and their assignments to different modes are given in table 2. $\text{Ni}_2\text{P}_4\text{O}_{12}$ and $\text{Zn}_2\text{P}_4\text{O}_{12}$: The assignments of the observed frequencies of $\text{Ni}_2\text{P}_4\text{O}_{12}$ and $\text{Zn}_2\text{P}_4\text{O}_{12}$ have been done on the same basis as for $\text{Fe}_2\text{P}_4\text{O}_{12}$ and are given in table 2. The Ni–O, Zn–O vibrations are observed at 324 cm^{-1} and 306 cm^{-1} respectively.

Table 2. The fundamentals of $P_4O_{12}^{4-}$ ion in $M_2P_4O_{12}$ ($M = Fe, Ni, Zn$).

$Fe_2P_4O_{12}$		$Ni_2P_4O_{12}$		$Zn_2P_4O_{12}$		Species	Assignment
Raman	IR	Raman	IR	Raman	IR		
1323 (2)	—	1345 (3)	—	—	1305 <i>pw</i>	A_u	$\nu_{asy} PO_2^-$
1300 (14)	—	1318 (20)	—	—	1273 <i>w</i>	B_u	
1277 (9)	—	—	1315 <i>us</i>	—	—	A_g	
—	1263 <i>m</i>	—	1288 <i>us</i>	—	—	A_u	$\nu_{asy} PO_2^-$
1259 (20)	—	1289 (24)	—	—	—	B_u	
1206 (6)	—	—	—	—	—	A_g	
1160 (39)	—	1154 (46)	—	—	—	A_g	$\nu_{sy} PO_2^-$
1138 (9)	—	1138 (8)	—	—	1140 <i>m</i>	A_u	
—	1115 <i>pw</i>	—	1112 <i>s</i>	—	—	A_g	
1057 (4)	—	—	—	—	1072 <i>s</i>	B_u	
—	—	—	—	—	1050 (7)	B_g	
1015 (2)	1030 <i>w</i>	1046 (3)	—	—	1038 <i>s</i>	B_u	$\nu_{asy} POP$
960 (2)	—	—	1022 <i>s</i>	—	—	A_g	
895 (1)	—	911 (2)	—	—	898 <i>s</i>	A_u	
—	—	—	—	—	—	A_g	
815 (1)	—	820 (3)	—	—	—	A_g	$\nu_{sy} POP$
—	730 <i>us</i>	—	739 <i>us</i>	—	—	B_g	
—	705 <i>us</i>	—	718 <i>us</i>	—	—	A_u	
679 (41)	—	686 (52)	—	—	708 <i>us</i>	B_u	
608 (9)	635 <i>w</i>	618 (8)	—	—	—	A_g	δPO_2^-
—	—	—	589 <i>m</i>	—	581 <i>s</i>	B_u	
—	571 <i>m</i>	577 (2)	—	—	—	A_g	
—	558 <i>s</i>	—	556 <i>s</i>	—	532 <i>us</i>	A_u	
535 (6)	—	542 (3)	—	—	—	B_g	
—	525 <i>s</i>	—	525 <i>s</i>	—	—	A_u	
505 (3)	—	517 (2)	—	—	459 <i>us</i>	A_g	
—	—	—	—	—	—	B_u	

Table 2. (Continued)

$\text{Fe}_2\text{P}_4\text{O}_{12}$		$\text{Ni}_2\text{P}_4\text{O}_{12}$		$\text{Zn}_2\text{P}_4\text{O}_{12}$		Species	Assignment
Raman	IR	Raman	IR	Raman	IR		
—	497 s	511 (2)	—	—	—	A_g	δPO_2^-
—	476 m	—	504 vs	—	—	A_u	
454 (3)	—	—	463 w	—	—	B_u	
—	445 m	456 (6)	—	—	—	A_g	
430 (2)	—	441 (3)	—	—	—	B_g	
—	430 m	—	—	—	—	B_u	
400 (20)	—	407 (25)	—	—	382 m	A_g	δPOP and M-O stretching
386 (10)	—	—	378 s	—	—	B_u	
—	386 m	353 (10)	—	—	—	A_g	
—	358 w	338 (6)	—	—	330 s	B_u	
—	340 w	—	338 w	—	—	A_g	
338 (10)	—	—	326 vw	—	—	B_g	
315 (3)	—	324 (3)	—	—	268 m	A_u	
—	310 w	—	312 w	—	—	A_g	
—	298 w	—	298 w	—	212 s	A_g	
—	280 vw	291 (6)	—	—	—	B_u	
272 (8)	—	—	270 s	—	—	B_g	
221 (4)	—	—	250 vs	—	—	A_u	
199 (6)	—	240 (2)	—	—	—	A_g	
170 (5)	—	—	229 m	—	—	A_g	
—	—	—	219 m	—	—	B_u	
—	—	209 (10)	—	—	—	B_u	
—	—	190 (5)	—	—	—	A_g	
—	—	169 (7)	—	—	—	A_g	
—	—	157 (2)	—	—	—	A_g	
116 (3)	—	137 (2)	—	—	—	—	Lattice modes
85 (1)	—	103 (1)	—	—	—	—	
—	—	—	—	140 (6)	—	—	
—	—	—	—	133 (3)	—	—	
—	—	—	—	105 (4)	—	—	
—	—	—	—	98 (3)	—	—	

5. Results and discussions

The noncoincidence of the observed bands in IR and Raman spectra indicates that the anion is centrosymmetric. The few coincidences observed could be accidental. Though these samples contain the same anion, there are some differences in the number and frequencies of bands observed. A comparison of the spectra of $\text{Zn}_2\text{P}_4\text{O}_{12}$ with those of $M_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$) shows that the number of lines observed in each mode in $\text{Zn}_2\text{P}_4\text{O}_{12}$ is less than those in the other two. For example, the Raman band due to the asymmetric PO_2^- stretching in $\text{Fe}_2\text{P}_4\text{O}_{12}$ splits into five lines, whereas only one is observed in $\text{Zn}_2\text{P}_4\text{O}_{12}$. Also, the IR absorption lines corresponding to the one at 708 cm^{-1} in $\text{Zn}_2\text{P}_4\text{O}_{12}$ are doublets in the other two compounds. The appearance of few vibrational bands in $\text{Zn}_2\text{P}_4\text{O}_{12}$ shows that the symmetry of the anion in this crystal is higher than that in $M_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$). Hence, it may be inferred that the anion has C_{2h} symmetry in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and C_i in $M_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$).

The splitting of the asymmetric and symmetric vibrations of the PO_2^- group into several components in $\text{Fe}_2\text{P}_4\text{O}_{12}$ suggests that the anion in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is more distorted. In $\text{Fe}_2\text{P}_4\text{O}_{12}$ the low frequency end (895 cm^{-1}) and the high frequency end (1015 cm^{-1}) of the P–O–P asymmetric stretching region are, respectively, 16 and 31 cm^{-1} lower than those in $\text{Ni}_2\text{P}_4\text{O}_{12}$. This lowering is observed in other stretching and bending regions also. This suggests that the P–O bond strength in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is slightly weaker than that in $\text{Ni}_2\text{P}_4\text{O}_{12}$. A similar comparison of the vibrational frequencies of the three compounds shows that the P–O bond strength is the highest in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and lowest in $\text{Fe}_2\text{P}_4\text{O}_{12}$.

The anion has a centrosymmetric structure in all the three samples, C_{2h} in $\text{Zn}_2\text{P}_4\text{O}_{12}$ and C_i in $M_2\text{P}_4\text{O}_{12}$ ($M = \text{Fe}, \text{Ni}$). The $\text{P}_4\text{O}_{12}^{4-}$ ion in $\text{Fe}_2\text{P}_4\text{O}_{12}$ is more distorted than in $M_2\text{P}_4\text{O}_{12}$ ($M = \text{Ni}, \text{Zn}$).

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