

FT-IR and Polarized Raman Spectra of $N(\text{CH}_3)_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

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FT-IR and polarized Raman spectra of $N(\text{CH}_3)_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ have been recorded and analyzed. From the spectra, the vibrations due to the H_2PO_4^- ion, the complex $N(\text{CH}_3)_4^+$, and the water molecules have been identified. The splitting of the triply degenerate ν_3 and the doubly degenerate ν_2 modes of the PO_4^{3-} ion confirm the lowering of the symmetry of the orthophosphate ion from T_d to C_{2v} . The observation of totally symmetric CN and CH stretching modes of A species in the IR spectra indicates that the $(\text{CH}_3)_4\text{N}^+$ groups are distorted in the crystalline lattice. Bands due to hydroxyl OH stretching, P–O–H in plane and out of plane bendings, and ABC bands have been observed. The assignments of these bands are confirmed by the isotopic shift on deuteration. © 1995 Academic Press, Inc.

INTRODUCTION

The monobasic orthophosphate ion, H_2PO_4^- , is found to have different conformations (1–3) and peculiar bonding features depending on the environment and the nature of cations. Though such orthophosphates have been subjected to detailed vibrational analysis (1–13) orthophosphates of tetramethyl ammonium cations have not been reported so far. Tetramethyl ammonium ion is of spectroscopic interest due to its high symmetry. Accordingly, several authors have investigated its vibrational spectrum (14–18). Edsall (17) was the first to examine the Raman spectra of an aqueous solution of $(\text{CH}_3)_4\text{N}^+$ and later Von Der Ohe (18) did the same. Vibrational spectra of the tetramethyl ammonium ion incorporated into solid salts have widely been reported (19–24). Solid state IR spectra of the $(\text{CH}_3)_4\text{N}^+$ cation in different crystalline environments demonstrated the presence of hydrogen bonding between the cation C–H bond and the anions such as halides, halates, and borates (25). In the present investigation, IR and polarized Raman spectroscopic studies of $N(\text{CH}_3)_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (TMAP) have been performed and analyzed in order to understand the nature of the vibrations of the H_2PO_4^- ion,

the $(\text{CH}_3)_4\text{N}^+$ complex, and to elucidate the distribution of vibrational energy levels in their crystal lattice.

EXPERIMENTAL

For the preparation of the crystal, the method of Ohama and Machida (26) was followed. Orthophosphoric acid was added to a solution of tetramethyl ammonium hydroxide and the pH was adjusted to 4.5. The concentrated solution yielded polycrystals of TMAP. Single crystals were grown in a refrigerator by slow evaporation of the aqueous solutions of the polycrystals. Deuteration of the compound was carried out by repeatedly dissolving the samples in heavy water of isotopic purity 99.5%.

The sample, cut in the form of a rectangular prism with the faces polished, was used for the Raman investigation. A spex Ramalog 1401 double monochromator (514.5 nm 60 mW) was used to record single crystal Raman spectra (Figs. 1–3), whereas a DILOR Z24 was used for polycrystalline samples (Fig. 4). The IR spectra (Fig. 5) were obtained using Bruker IFS-85 (4000–500 cm^{-1}) and Bio-rad FTS-7 (500–200 cm^{-1}) FT-IR spectrometers with the sample in KBr.

FACTOR GROUP ANALYSIS

TMAP crystallizes in the monoclinic system with the space group $P2_1/c$ (C_{2h}) having four molecules in the unit cell (26). The factor group analysis (Table 1) using the standard correlation method (27) has been carried out with H_2PO_4^- , $(\text{CH}_3)_4\text{N}^+$, and H_2O occupying general positions. Excluding the acoustical modes 321 normal modes are predicted. These are distributed as follows.

$$\Gamma_{\text{TMAP}} = 81A_g + 81B_g + 80A_u + 79B_u$$

Here the g modes are Raman active and the u modes are IR active.

In this compound, the phosphate tetrahedron deviates significantly from tetrahedral symmetry. The distances of 1.499 and 1.497 Å correspond to the terminal P–O bonds, while the other two 1.565 and 1.561 Å correspond to the

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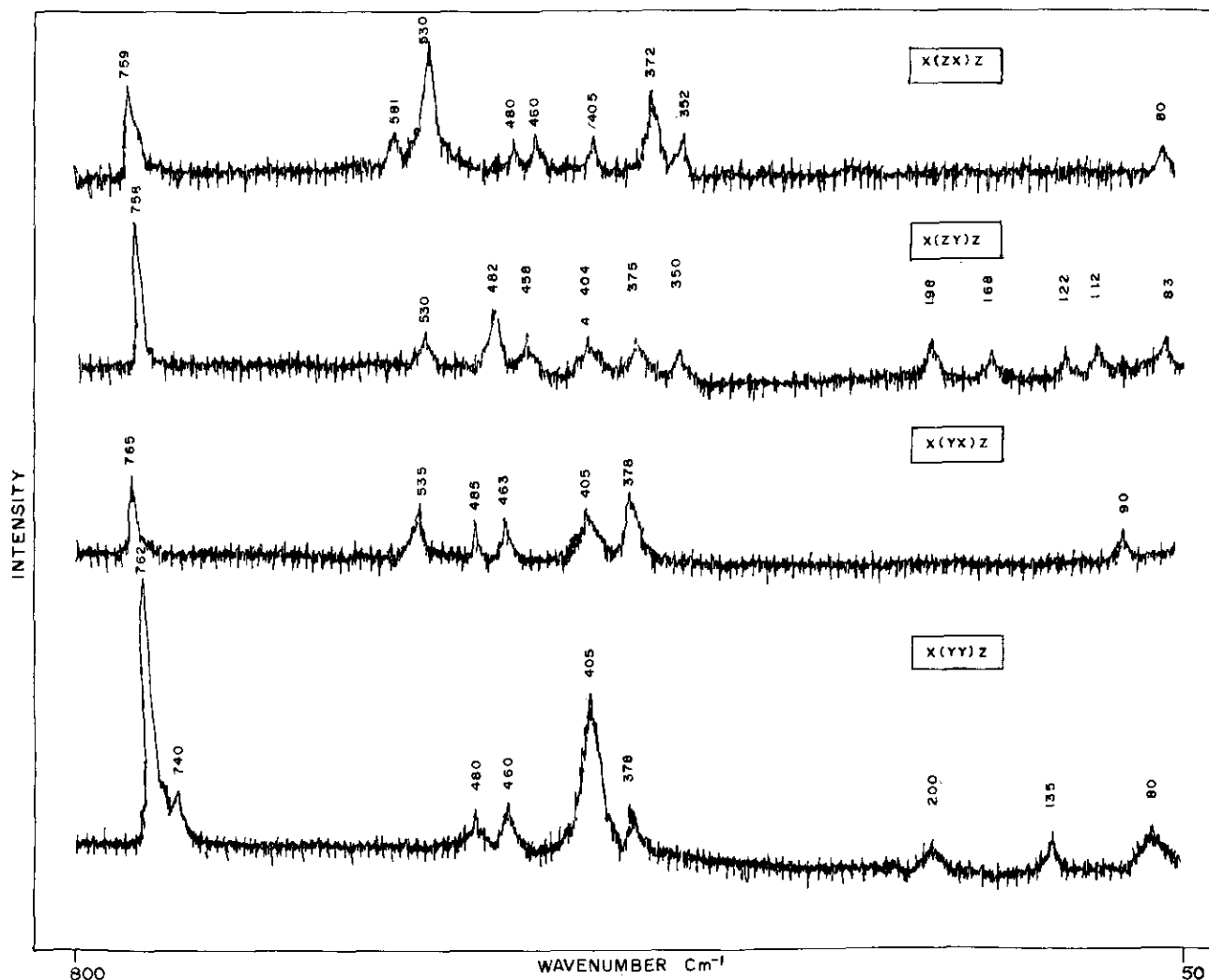


FIG. 1. Raman spectra of $N(CH_3)_4H_2PO_4 \cdot H_2O$ in the $50\text{--}800\text{ cm}^{-1}$ region.

P–O(H) bonds. The correlation schemes for the internal modes of $(CH_3)_4N^+$, $H_2PO_4^-$, and H_2O are given in Tables 2a, 2b, 3, and 4.

INTERPRETATION OF THE SPECTRA

Vibrations of $H_2(D_2)PO_4^-$ Ions

A “free” PO_4 tetrahedral group (point group T_d) has four vibrational frequencies: a Raman active totally symmetric vibration of frequency $\nu_1(A_1)$, a doubly degenerate Raman active vibration $\nu_2(E)$, and two triply degenerate Raman and IR active vibrations $\nu_3(F_2)$ and $\nu_4(F_2)$. Their frequencies are approximately $\nu_1 = 936$, $\nu_2 = 420$, $\nu_3 = 1004$, and $\nu_4 = 573\text{ cm}^{-1}$ (3). These are likely to be modified in the crystalline environment.

The $H_2PO_4^-$ ion can have the symmetries S_4 , C_{2v} , and C_s in different compounds. Consequently, the vibrational

spectra is expected to differ in frequency values and intensities depending upon the symmetry. Correlation schemes showing the variation in frequencies and splittings due to changes in symmetry are given in Table 5. The observed IR and Raman bands are tabulated in Table 6. As per the correlation scheme, the asymmetric stretching mode $\nu_3(F_2)$ of PO_4 splits into two modes E and B for S_4 symmetry, whereas into three each for C_{2v} (A_1 , B_1 , B_2) and C_s ($2A^1$, A^{11}). For S_4 symmetry the modes of H_2PO_4 derived from $\nu_2(E)$ of PO_4 should appear as doublets with wave numbers around 395 and 437 cm^{-1} , while for C_{2v} symmetry the corresponding bands must be around 360 and 393 cm^{-1} (3). In the observed IR spectrum three bands (1104 , 1045 , and 949 cm^{-1}) have been observed for $\nu_3(F_2)$ and two at 369 and 407 cm^{-1} for $\nu_2(E)$ modes. This rules out the possibility of S_4 for the $H_2PO_4^-$ ion in the crystal which leaves C_s and C_{2v} as the alternate possible symmetries.

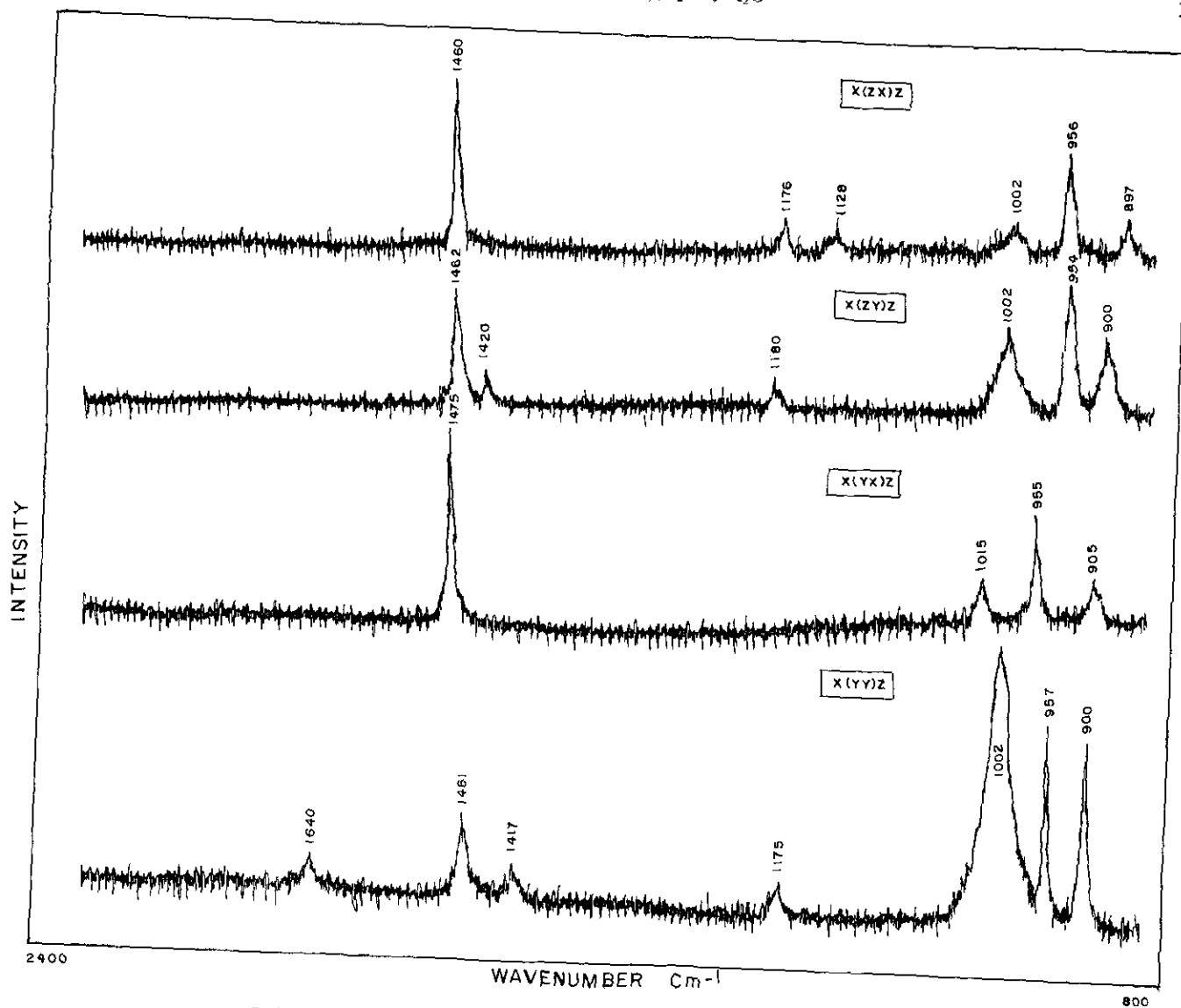


FIG. 2. Raman spectra of $N(CH_3)_4H_2PO_4 \cdot H_2O$ in the 800–2400 cm^{-1} region.

From group theoretical predictions, six polarized lines are expected in the Raman spectra for C_s symmetry while only four may appear for C_{2v} . The observation of four polarized bands around 1002, 900, 535, and 405 indicate that C_{2v} is the probable symmetry for the $H_2PO_4^-$ ion. Moreover, the observed frequencies agree well with those of $H_2PO_4^-$ in crystals with C_{2v} symmetry (1–3).

The internal vibrations of the $H_2PO_4^-$ ion can be divided into vibrations of the two groups PO_2 and $P(OH)_2$. The stretching modes of PO_2 and $P(OH)_2$ will be in the following sequence $\nu_{as}PO_2 > \nu_sPO_2 > \nu_{as}P(OH)_2 > \nu_sP(OH)_2$ (1). The intense band at 1104 cm^{-1} in IR and the weak band at 1128 cm^{-1} in Raman are assigned to the asymmetric stretching mode of PO_2 . The symmetric stretching mode $\nu_1(A_1)$ of PO_2 is expected to be the most intense and polarized band in the Raman spectrum. The observed polarized

band at 1002 cm^{-1} is easily assigned to this mode. Its counterpart in IR is observed at 1045 cm^{-1} . The strong IR band at 949 cm^{-1} and the unpolarized intense Raman band at 957 cm^{-1} are unambiguously assigned to the asymmetric stretching mode of $P-O(H)$, as the asymmetric stretching mode is expected to be intense (IR and Raman) and unpolarized in Raman. The symmetric stretching mode of $P-O(H)$ is expected around 860 cm^{-1} (2) which is observed at 900 cm^{-1} (Raman) and 869 cm^{-1} (IR). In IR, two bands at 647 and 667 cm^{-1} are observed for the bending modes of PO_2 . The splitting of the PO_2 mode in IR is indicative of correlation field effect.

As in other phosphates (1), the observed shoulder at 1270 cm^{-1} and the weak band at 826 cm^{-1} are assigned to δ_{P-O-H} in-plane bending and γ_{P-O-H} out-of-plane bending modes, respectively. The bands corresponding to δ_{P-O-D}

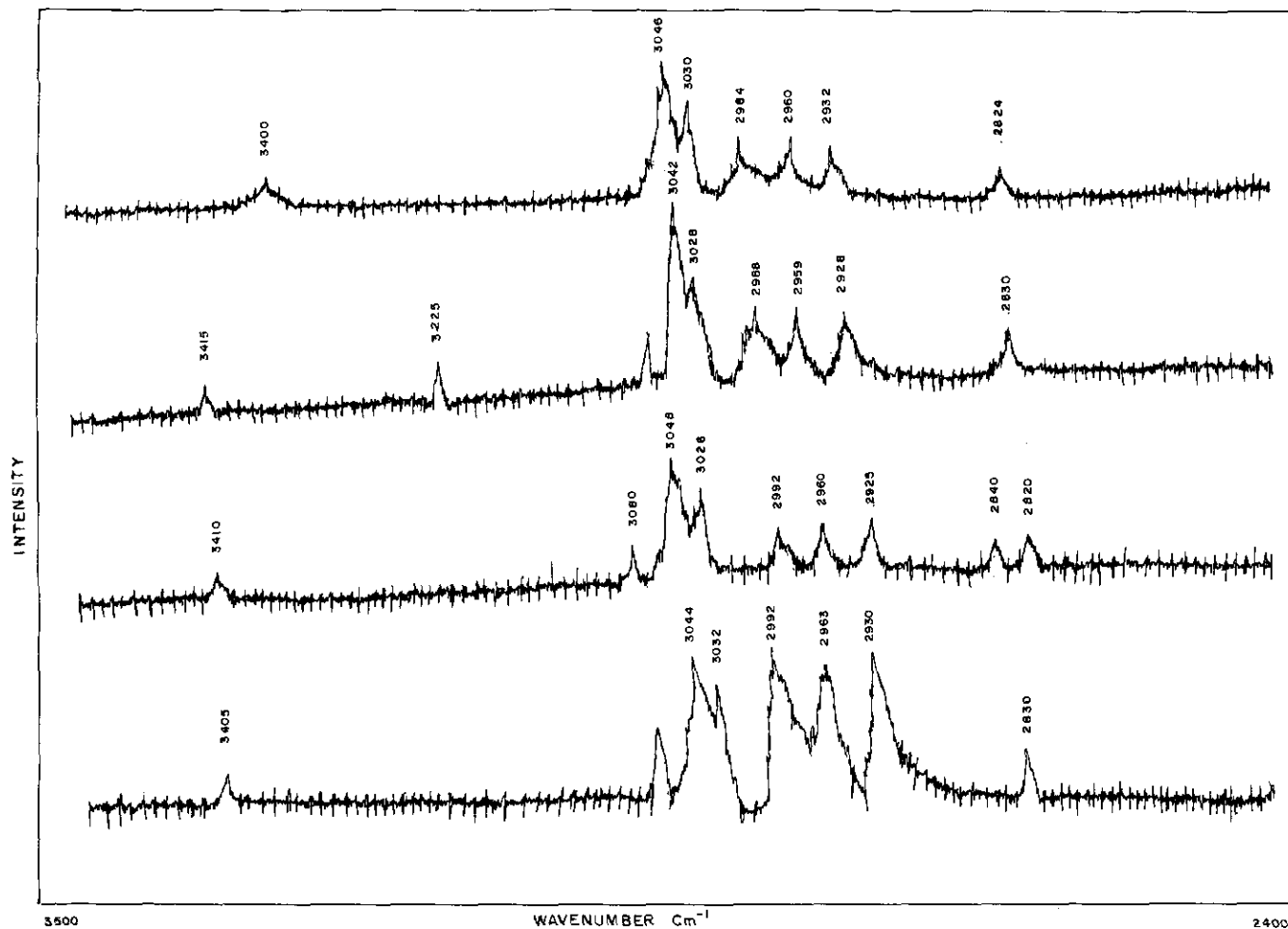


FIG. 3. Raman spectra of $N(\text{CH}_3)_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in the $2400\text{--}3500\text{ cm}^{-1}$ region.

TABLE 1
Vibrational Analysis of the Tetramethyl Ammonium Dihydrogen Phosphate Monohydrate
(Space Group $P2_1/C = C_{2h}^5$, $Z = 4$)

Unit cell group symmetry	Lattice vibrations				Internal vibrations											Raman	IR	
	C_{2h}	N	A	T	R	$(\text{CH}_3)_4\text{N}^+$	PO_4				$\text{O-H} \cdots \text{O}$			H_2O				
							ν_s	δ_s	ν_{as}	δ_{as}	ν	δ	γ	ν_s	δ			ν_{as}
A_g		81	0	9	9	45	1	2	3	3	2	2	2	1	1	1	$(\alpha_{xx}, \alpha_{yy}, \alpha_{xz}, \alpha_{xy})$	f
B_g		81	0	9	9	45	1	2	3	3	2	2	2	1	1	1	$(\alpha_{xz}, \alpha_{yz})$	f
A_u		80	-1	9	9	45	1	2	3	3	2	2	2	1	1	1	f	a
B_u		79	-2	9	9	45	1	2	3	3	2	2	2	1	1	1	f	a

Note. N , number of degrees of freedom; A , number of acoustic vibrations; T , number of translational vibrations; R , number of rotational vibrations; ν , stretching; δ , bending; γ , out-of-plane bending; S , symmetric; as , asymmetric; a , active; f , forbidden.

TABLE 2a
Correlation Scheme for the Numbers and Types of Vibrations Related to CH_3 Stretching (or Deformation) Modes of $N(CH_3)_4^+$

f^g Isolated CH_3 (C_{3v}) CH vibrations (stretching or deformations)	TMA (T_d) species	
32 $2A_1$ Sym	A_1	8
	F_2	8
64 $2E$ asym	E	8
	F_1	8
	F_2	8

TABLE 2b
Correlation Scheme for the Internal Vibrations of the TMA Ion in $N(CH_3)_4H_2PO_4 \cdot H_2O$

f^g Free ion symmetry T_d	Site symmetry C_1	Factor group symmetry C_{2h}
12 $3A_1$	A	A_g 45
4 A_2		B_g 45
32 $4E$		A_u 45
48 $4F_1$		B_u 45
84 $7F_2$		

and ν_{P-O-D} modes in the deuterated crystal appear around 876 and 576 cm^{-1} , respectively, with the isotopic ratio around 1.4.

The frequencies of the symmetric stretching mode of P-O(H) and the asymmetric stretching and bending modes of PO_2 decreased by about 30 cm^{-1} on deuteration. These

shifts could mainly be due to the mass effect and coupling with other vibrations (5). For ν_3PO_2 and $\nu_{as}P-O-H$ an unusually high frequency shift is noticed. This may be due to the different geometries of the H_2PO_4 and $D_2PO_4^-$ ions (5).

The high frequency OH bonds of the strong hydrogen bonded crystals such as KDP, $PbHPO_4$, NaH_2PO_4 , $CsHSO_4$, and CsH_2PO_4 (5, 11, 28-30) are characterized by three broad bands of the ABC type which appear in both IR and Raman spectra. Two bands each are observed at 2788 and 2736 cm^{-1} and at 2458 and 2417 cm^{-1} for the A and B bands, respectively. These bands also shift under deuteration to 2092 and 2039 cm^{-1} and to 1772 and 1740 cm^{-1} in IR (see Fig. 6). This must be due to the OH bonds of different hydrogen bond strengths. The C band appears at 1695 cm^{-1} in IR, which on deuteration shifts to 1200

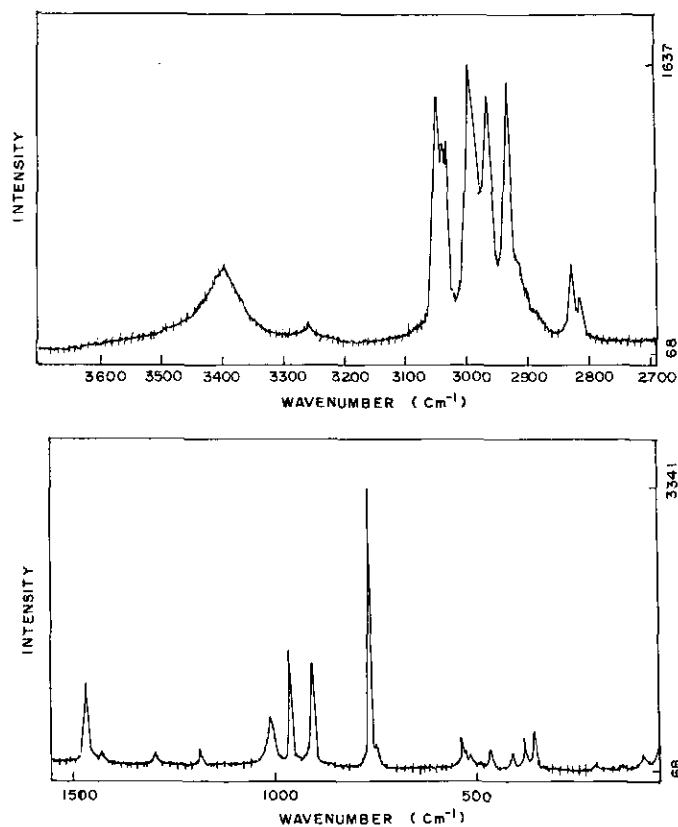


FIG. 4. Raman spectra (powder spectra) of $N(CH_3)_4H_2PO_4 \cdot H_2O$ in the 50-4000 cm^{-1} region.

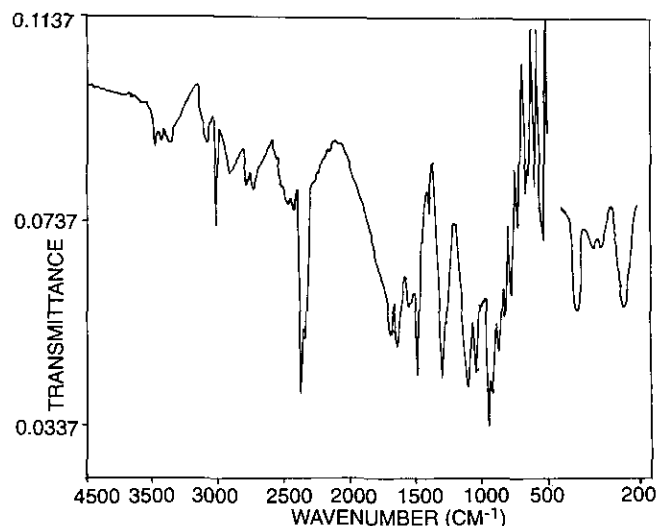


FIG. 5. IR spectra of $N(CH_3)_4H_2PO_4 \cdot H_2O$ in the 200-4000 cm^{-1} region.

TABLE 3
Correlation Scheme for the Internal Vibrations of the PO₄ Ion in N(CH₃)₄H₂PO₄ · H₂O

PO ₄ ion symmetry <i>T_d</i>	H ₂ PO ₄ ion symmetry <i>C_{2v}</i>	Site symmetry <i>C₁</i>	Factor group symmetry <i>C_{2h}</i>
(ν ₁)A ₁	A ₁	A	A _g + B _g (R) A _u + B _u (IR)
	ν _s P(OH) ₂		
(ν ₂)E	A ₁	A	A _g + B _g (R) A _u + B _u (IR)
	δ _s P(OH) ₂		
	A ₂	A	A _g + B _g (R) A _u + B _u (IR)
	tPO ₂		
(ν ₃)F ₂	A ₁	A	A _g + B _g (R) A _u + B _u (IR)
	ν _s PO ₂		
	B ₁	A	A _g + B _g (R) A _u + B _u (IR)
	ν _{as} PO ₂		
	B ₂	A	A _g + B _g (R) A _u + B _u (IR)
	ν _{as} P(OH) ₂		
	A ₁	A	A _g + B _g (R) A _u + B _u (IR)
	δ _s PO ₂		
(ν ₄)F ₂	B ₁	A	A _g + B _g (R) A _u + B _u (IR)
	γPO ₂ /ωP(OH) ₂		
	B ₂	A	A _g + B _g (R) A _u + B _u (IR)
	ωPO ₂ /γP(OH) ₂		

cm⁻¹. The resulting isotopic shift ratio for this band is then 1.412.

Vibrations of (CH₃)₄N⁺

The tetramethyl ammonium (TMA) group with *T_d* has 45 internal modes. The 45 degrees of vibrational freedom of the TMA ion are distributed as 3A₁ + A₂ +

4E + 4F₂ + 7F₂. In the crystal, all the modes are expected to be active in both IR and Raman as it occupies a symmetry C₁. Assignments of the observed bands are done on the basis of vibrations due to CH₃, CN, and skeletal modes. For an isolated CH₃ group having C_{3v} symmetry according to group theoretical calculation the stretching/deformation modes produce two vibrations each of species A₁ and E.

TABLE 4
Correlation Scheme for the Vibrational
Modes of the H_2O in $N(CH_3)_4H_2PO_4 \cdot H_2O$

f^g	Free ion symmetry H_2O C_{2v}	Site symmetry C_1	Factor group symmetry C_{2h}
Internal vibrations			
4	$A_1 \nu_s$	A	$A_g(\nu_s + \delta_s + \nu_{as})$
4	$A_1 \delta_s$		$B_g(\nu_s + \delta_s + \nu_{as})$
4	$B_1 \nu_{as}$		$A_u(\nu_s + \delta_s + \nu_{as})$
			$B_u(\nu_s + \delta_s + \nu_{as})$
Librational motions			
4	$B_1 \rho_r$	A	$A_g(\rho_r + \rho_t + \rho_w)$
4	$B_1 \rho_t$		$B_g(\rho_r + \rho_t + \rho_w)$
4	$A_2 \rho_w$		$A_u(\rho_r + \rho_t + \rho_w)$
			$B_u(\rho_r + \rho_t + \rho_w)$

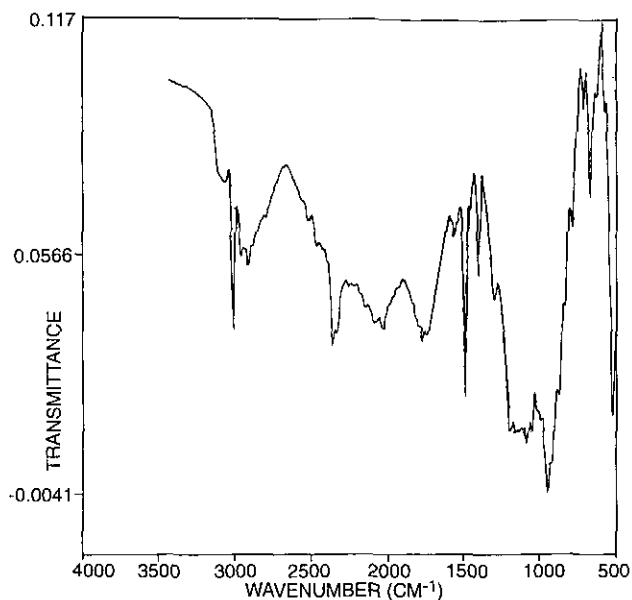


FIG. 6. Deuterated IR spectra of $N(CH_3)_4H_2PO_4 \cdot H_2O$ in the 500–4000 cm^{-1} region.

TABLE 5
Possible Symmetries of the H_2PO_4 Ion and Correlation of Their Vibrations to PO_4

T_d	S_4	C_{2v}	C_s
$\nu_1(A_1)$ 936 [R]	934(A) [R]	878(A_1) [R, IR]	878 (A') [R, IR]
ν_2 420 (E) [R]	395(A) [R]	360(A_1) [R, IR]	379(A') [R, IR]
	[R, IR] 437(B)	[R] 393(A_2)	379(A'') [R, IR]
ν_3 1004 (F_2) [R, IR]	1060(B) [R, IR]	1072(A_1) [R, IR]	1072(A') [R, IR]
	[R, IR] 978(E)	947(B_1) [R, IR]	947(A') [R, IR]
		1150(B_2) [R, IR]	1150(A'') [R, IR]
ν_4 573 (F_2) [R, IR]	528(B) [R, IR]	510(A_1) [R, IR]	514(A') [R, IR]
		527(B_1) [R, IR]	514(A') [R, IR]
	554(E) [R, IR]		567(B_2) [R, IR]
			514(A'') [R, IR]

TABLE 6
Vibrational Spectral Data (cm^{-1}) and Band Assignment^a of Tetramethyl Ammonium
Dihydrogen Orthophosphate Monohydrate

Powder	X[YY]Z	X[YX]Z	X[ZYZ]	X[ZX]Z	IR/H ₂ O	IR/D ₂ O	Assignments
3394 m, br 3260 vw, br	3405 vw, br 3232 w	3410 vw, br	3415 vw, br 3225 w	3400 vw, br	3482 w 3382 w 3371 w	2514 w 2462 w	ν OH/OD
3047 s 3040 s 3033 s 2998 vs 2965 s 2932 vs 2829 m 2817 vw	3080 w 3044 s 3032 s 2992 s 2963 s 2930 s 2830 w	3080 w 3048 m 3026 m 2992 w 2960 w 2025 w 2840 vw 2820 vw	3080 w 3042 s 3028 m 2988 w 2959 w 2928 w 2830 w	3046 s 3030 m 2984 w 2960 w 2932 w 2824 vw	3092 w 3018 s 2920 vw 2788 w 2736 w 2458 w 2417 w 1695 m 1648 m 1562 w 1490 s 1403 w 1300 vs 1270 sh	3072 w 3016 s 2960 w 2911 w 2092 w 2039 w 1772 w 1740 w 1200 m 1161 m 1561 vw 1488 s 1401 m 1299 m 876 w	ν_{as} CH ₃ ν_s CH ₃ A } B } ν OH/OD C } δ H ₂ O; D ₂ O δ CH ₃ γ CH ₃ δ P-OH (D) γ CH ₃ ν_{as} PO ₂ (B ₁) ν_s PO ₂ (A ₁) ν_{as} P-OH (D) (B ₂) ν_{as} C ₄ N ν_s P-OH (D) (A ₁) γ P-OH (D)/ ρ_s H ₂ O ν_s C ₄ N ρ t H ₂ O/tD ₂ O δ PO ₂ (A ₁) 600 s 534 s 526 s 466 w 407 w 369 w 250 m 647 w 628 vvw
1468 s 1430 vw 1295 vw 1183 vw 962 vs 905 s 767 vvs 750 sh 539 w 467 w 401 vw 384 w 358 m 209 vvw	1649 vw, br 1461 m 1417 w 1002 vvs 957 s 900 s 762 vvs 740 w 480 vw 460 vw 405 m 378 vw 200 w 135 vvw 80 vw	1475 s 1015 w 965 m 905 w 765 w 535 vw 485 vw 463 w 405 w 378 w 198 vw 168 vw 122 vvw 112 vvw 90 vvw	1462 s 1420 vw 1002 m 954 s 900 w 758 m 530 vvw 482 w 458 w 404 w, br 375 w 350 vw 198 vw 168 vw 122 vvw 112 vvw 83 vw	1460 s 1176 vw 1128 vw, br 1002 vw 956 m 897 w 759 m 581 vw, br 530 m 480 vw 460 w 405 vvw 372 w 352 vw 80 vw	1490 s 1403 w 1300 vs 1270 sh 1104 s 1045 m 949 vs 922 m 869 w 826 w 788 w 729 w 667 m 647 w 600 s 534 s 466 w 407 w 369 w 250 m 647 w 628 vvw	1488 s 1401 m 1299 m 876 w 1084 m 1056 m 953 vs 922 sh 838 w 576 w 785 w 709 w 666 w 628 vvw 526 s 466 w 407 w 369 w 250 m 647 w 628 vvw	δ CH ₃ γ CH ₃ δ P-OH (D) γ CH ₃ ν_{as} PO ₂ (B ₁) ν_s PO ₂ (A ₁) ν_{as} P-OH (D) (B ₂) ν_{as} C ₄ N ν_s P-OH (D) (A ₁) γ P-OH (D)/ ρ_s H ₂ O ν_s C ₄ N ρ t H ₂ O/tD ₂ O δ PO ₂ (A ₁) $\rho\omega$ H ₂ O (γ , ω) P(OH) ₂ , (γ , ω) PO ₂ δ_{as} C ₄ N δ_s P(OH) ₂ , (A ₁), tPO ₂ (A ₂) δ_s C ₄ N t CH ₃ R PO ₄ T PO ₄

^a Relative intensities: vvs - very very strong, vs - very strong, s - strong, m - medium, w - weak, vw - very weak, sh - shoulder, br - broad, T - translation, R - libration, t - twisting, ω - wagging, r - rocking.

Under T_d symmetry the four symmetric stretchings or deformations of species A_1 and asymmetric stretchings or deformations of species E , of the four CH₃ groups in the TMA ion, are distributed as $A_1 + F_2$ and $E + F_1 + F_2$, respectively.

The region of symmetric stretching vibrations of CH₃ shows complex band shape with three intense polarized bands. Though the presence of three bands in this region

may be attributed to the possibility of linear distortion of CH₃ groups with different C-H bond lengths or to coupling between different vibrating groups, vibrational studies on TMA compounds reported by different authors (14, 16, 18, 31) suggest that these bands arise from the Fermi resonance between methyl stretching fundamentals and overtone or combination modes of methyl deformation modes. Two depolarized Raman bands at 3032 and 3044 cm^{-1}

and the one at 3080 cm^{-1} are assigned to the asymmetric stretching mode of CH_3 . The splitting of this mode may be due to the correlation field effect. The corresponding IR band is observed at 3018 and 3092 cm^{-1} . In the bending mode of CH_3 two bands each are observed in the two polarization geometries $X(\text{YY})Z$ and $X(\text{ZY})Z$ and one band each in the other two $X(\text{YX})Z$ and $X(\text{ZX})Z$. The corresponding IR bands are observed at 1403 , 1490 , and 1562 cm^{-1} . The strong polarization Raman band at 762 cm^{-1} and the one at 788 cm^{-1} in IR are assigned to the symmetric stretching mode of C_4N . The observation of totally symmetric CN and CH stretching modes of the A species which are inactive in IR under T_d symmetry clearly indicates that the $(\text{CH}_3)_4\text{N}^+$ group is distorted in the lattice (32).

Internal Vibrations of Water Molecules

The site symmetry of the water molecules in the crystal is C_1 and they are involved in hydrogen bonding. Consequently, the ν_1 and ν_3 frequencies are lowered by around 300 cm^{-1} from corresponding to the frequencies of the free molecule. In the bending mode region, a medium intense band at 1648 cm^{-1} in IR (1640 cm^{-1} in Raman) has been observed. This band shifts under deuteration to 1161 cm^{-1} in IR with the isotopic ratio 1.419.

Libration Modes of H_2O

The three librational modes of H_2O are the wagging, twisting, and rocking modes. Lutz *et al.* (33) tried to assign these bands in the sequence: $\nu_{\text{wag}} > \nu_{\text{twist}} > \nu_{\text{rock}}$ within the region $300\text{--}775\text{ cm}^{-1}$. Singh *et al.* (34) assigned these bands in the region $500\text{--}900\text{ cm}^{-1}$ in the order $\nu_{\text{rock}} > \nu_{\text{wag}} > \nu_{\text{twist}}$. However, we have assigned the frequency observed in the region $600\text{--}850\text{ cm}^{-1}$ on the basis of the well-known Miyazawa intensity criteria (35): $I_{\text{wag}} > I_{\text{rock}} \gg I_{\text{twist}}$. In IR, the weak band at 729 cm^{-1} is assigned to the twisting mode. The intense band at 600 cm^{-1} in IR and the weak band at 581 cm^{-1} in Raman is assigned to the wagging mode. The fact that these modes have shifted on deuteration confirm the assignments of these modes to the librational modes of H_2O .

Other External Modes

The region below 300 cm^{-1} is complicated with the translational and librational modes of PO_4 and CH_3 and the translational modes of water. A clear assignment between the translational and vibrational modes of the PO_4 is very difficult, as there can be considerable overlapping between the two modes. However, a tentative assignment is made by considering the fact that the rotational modes appear at higher frequencies than the translational modes (36–38). The complete vibrational assignment is given in Table 6.

RESULTS

(i) The use of polarized Raman spectra has allowed the determination of the symmetries of the various molecular vibrations. The symmetry of the orthophosphate ion is found to be C_{2v} .

(ii) Site symmetry and correlation field effects are strong in the compound.

(iii) The $(\text{CH}_3)_4\text{N}^+$ group is found to be distorted in the crystal lattice.

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