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# BRIEF COMMUNICATIONS

## IR and Polarized Raman Spectra of $(NH_3)_2(CH_2)_2HPO_4$

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The IR and polarized Raman spectra of $(NH_3)_2(CH_2)_2HPO_4$ have been recorded and analyzed. In the crystal, symmetry of the $HPO_4$ ion is found to be reduced from $C_{3v}$ to $C_1$. The observed splittings indicate that the site symmetry and the correlation field effects are appreciable in the crystal. Strong vibrational coupling between the P–O(H) stretching and POH out-of-plane bending modes is observed. Ethylene diammonium groups are crystallographically different in the unit cell. © 1989 Academic Press, Inc.

### Introduction

Ethylenediamine forms crystals of the very stable ethylenediammonium phosphate, $(NH_3)_2(CH_2)_2HPO_4$, when mixed with orthophosphoric acid in the stoichiometric ratio and evaporated slowly at room temperature. The compound crystallizes in the monoclinic system $P2_1/a$ with four formula units per unit cell (*1*). A detailed vibrational analysis of its IR and Raman spectra has not been done so far. In the present investigation, the IR and single-crystal Raman spectroscopy studies have been taken up in order to understand the nature of the $HPO_4$ ion and to elucidate the distribution of vibrational energy levels in the crystal lattice.

### Experimental

Raman spectra (Fig. 1) of the single crystal were recorded for the $A_g$ and $B_g$ species in the Stokes region of the 5145-Å line using a SPEX RAMALOG 1401 double monochromator equipped with a Spectra Physics Model 165 $Ar^+$ laser. A Polytec FIR 30 interferometer was used to record the far-infrared spectrum in the region 50–500 $cm^{-1}$ with the sample in polyethylene. The IR spectrum in the region 200–4000 $cm^{-1}$ was obtained on a Perkin–Elmer 983 spectrophotometer with the sample in KBr and nujol. The spectrum in the 50–4000 $cm^{-1}$ is shown in Fig. 2.

### Discussion

In the crystal, the $HPO_4$ ions occupy site $C_1$ of lower symmetry than the free ion symmetry $C_{3v}$. This may lead to the activation of inactive modes along with shifting and splitting of the internal modes. The factor group analysis predicts 237 normal modes and they are distributed as

$$\Gamma_{237} = 60\,A_g + 60\,B_g + 59\,A_u + 58\,B_u.$$

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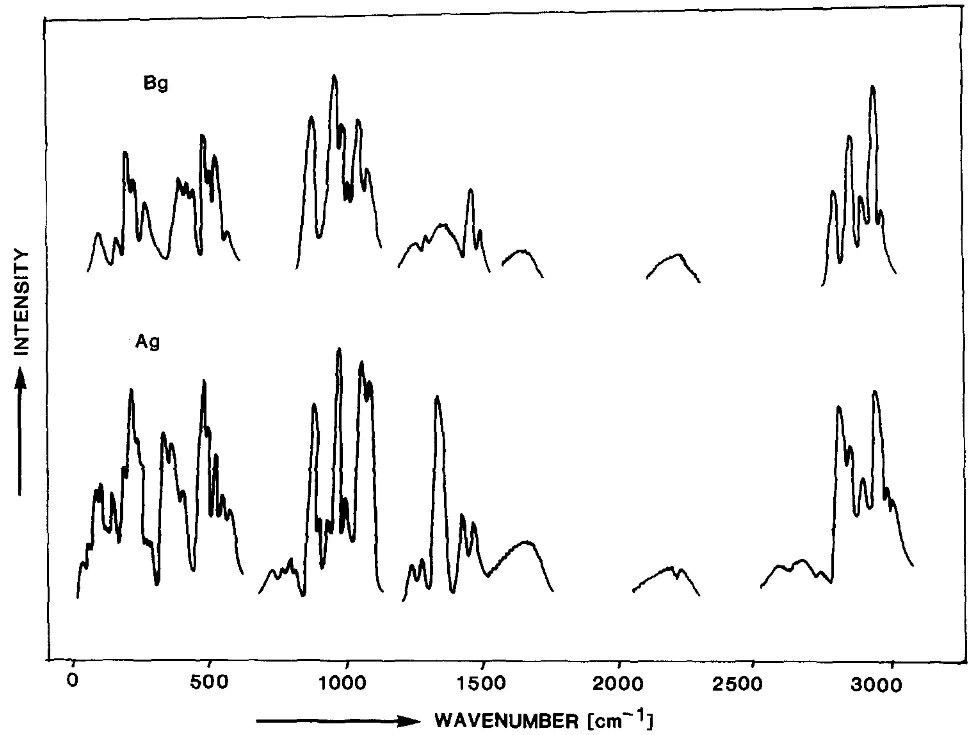

FIG. 1. Raman spectrum of $(NH_3)_2(CH_2)_2HPO_4$.

The free ion approach predicts three bands each for the stretching ($2A_1 + E$) and bending ($A_1 + 2E$) modes of the $PO_4$ part of the $HPO_4$ ion in both Raman and IR spectra. However, the site symmetry approach leads to four and five bands, respectively,

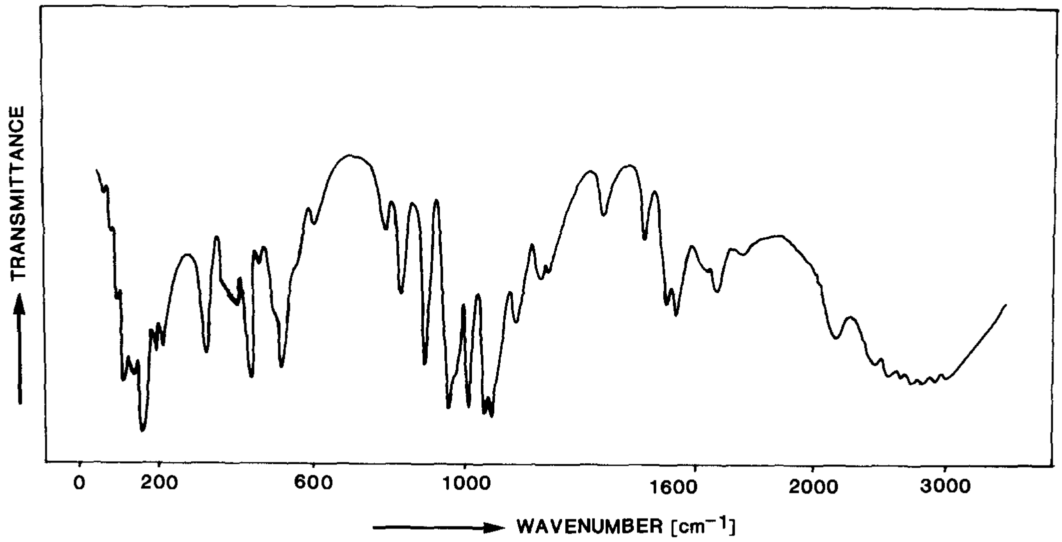

FIG. 2. IR spectrum of $(NH_3)_2(CH_2)_2HPO_4$.

TABLE I

VIBRATIONAL SPECTRAL DATA AND BAND ASSIGNMENTS (cm$^{-1}$) OF $(NH_3)_2(CH_2)_2HPO_4$

| Raman | | | |
|---|---|---|---|
| $A_g$ | $B_g$ | IR | Assignments |
| 3016(m)<br>2983(m) | 2983(m) | 3018(w,br) | $\nu_s$ and $\nu_{as}$ $NH_3^+$ |
| 2966(vs)<br>2902(s) | 2968(vs)<br>2921(m) | 2940(w) | $\nu_{as}$ $CH_2$ |
| 2862(s)<br>2821(vs) | 2876(s)<br>2818(m) | 2850(w) | $\nu_s$ $CH_2$ |
| 2740(w,br)<br>2676(w,br)<br>2600(w,br)<br>2200(w,br)<br>2180(w,br) | 2224(w,br) | 2741(w,br)<br>2665(w)<br>2590(w)<br>2490(w)<br>2200(s,br)<br>1750(vw,br) | OH vibrations, overtones, and combinations |
| 1635(m,br) | 1645(w,br) | 1665(m)<br>1640(w) | $\delta_{as}$ $NH_3^+$ |
| | | 1565(s)<br>1540(s) | $\delta_s$ $NH_3^+$ |
| 1470(m)<br>1445(m) | 1478(w)<br>1455(m) | 1473(m) | $\delta$ $CH_2$ |
| 1335(vs)<br>1282(w) | 1338(m,br)<br>1280(w,br) | 1365(m) | Twist and wag of $CH_2$ |
| 1249(w) | 1252(w,br) | 1224(w)<br>1200(m) | POH in-plane bend ($A_2$) |
| | | 1140(m) | $\rho$ $NH_3^+$ |
| 1071(vs)<br>1053(vs) | 1066(m)<br>1056(s) | 1080(vs)<br>1060(vs) | $\nu_{as}$ $PO_3$ ($E$) |
| | | 1028(vs) | $\nu$ C–N |
| 992(m)<br>963(vvs) | 995(w)<br>972(m)<br>965(vs) | 977(sh)<br>966(vs) | $\nu_s$ $PO_3$ ($A_1$) |
| 926(m) | | | $\rho$ $NH_3^+$ and $\rho$ $CH_2$ |
| 887(w)<br>879(vs) | 879(s) | 901(vs) | P–O(H) stretch ($A_1$) |
| 816(w) | | 829(s)<br>792(m) | POH out-of-plane bend ($A_2$) |
| 778(w)<br>762(w)<br>745(w) | | 600(w) | Combinations |
| 570(w)<br>550(m) | 558(w)<br>530(s) | 555(w)<br>522(vs) | $\delta_{as}$ $PO_3$ ($E$) |
| 519(s) | | 502(m) | $\delta_s$ $PO_3$ ($A_1$) |
| 479(w) | 482(m) | | t $NH_3^+$ |
| 466(vs)<br>462(w) | 473(s) | 451(w) | $\delta$ C–CN |
| 407(m)<br>384(s)<br>375(s) | 424(m)<br>413(m)<br>395(m) | 430(s)<br>410(s)<br>330(s) | OPO(H) $\delta_s$ ($E$) |
| 260(w,br)<br>237(m)<br>212(m) | 250(m)<br>202(m) | 256(m)<br>230(m) | t $NH_3^+$ |
| 200(vs) | 198(s) | | R ? |
| 187(m)<br>144(s) | 154(w) | 182(vs)<br>150(s,br)<br>130(s) | T |
| 116(m,br) | | | $\nu$ O–H · · · O |
| 83(s)<br>72(s) | 88(w) | 95(m)<br>75(w) | T ? |
| 58(m)<br>55(w) | | 65(vw) | $\delta$ O–H · · · O |

*Note.* (vvs) Very very strong; (vs) very strong; (s) strong; (m) medium; (w) weak; (vw) very weak; (sh) shoulder; (s,br) strong broad; (m-br) medium broad; (w,br) weak broad; (δ) bending; (ν) stretching; (t) twisting; (ρ) rocking. Subscripts "as" and "s" refer to asymmetric and symmetric, respectively. R and T refer to the rotation and translation of the $HPO_4$ ion, respectively.

for these modes. The observation of more bands than this predicted number shows that both site symmetry and correlation field effects are appreciable in the crystal.

The $PO_3$ symmetric stretching mode ($A_1$) is expected to be the most intense and polarized in Raman spectrum. It splits into two components in $A_g$ (963 and 992 cm$^{-1}$) and into three in $B_g$ (965, 972, and 995 cm$^{-1}$) due to correlation field effect. In the IR spectrum it is also observed as two bands (966 and 977 cm$^{-1}$). Site symmetry effect is probably responsible for the observation of the $PO_3$ asymmetric stretch ($E$) as a doublet in both Raman and IR. In compounds with $HPO_4$ ions, the polarized P–O(H) stretch ($A_1$) is expected around 860 cm$^{-1}$ (*2*). Here, it is observed at 879 cm$^{-1}$ in the Raman spectrum. However, in IR it is shifted to 901 cm$^{-1}$. The splitting of the $F_2$ stretching mode of the $PO_4$ ion into three very strong components in IR [1080 ($E$), 1060 ($E$) and 901 cm$^{-1}$ ($A_1$)] confirms (*3*) the lowering of the symmetry of the $HPO_4$ ion from $C_{3v}$ to $C_1$ in the crystal. The deformation vibrations are also identified (Table I).

Strong vibrational coupling between P–O(H) stretching and POH out-of-plane bending (829 $cm^{-1}$) is evident (*3*) from the large intensity of the latter. The shift observed in IR for the P–O(H) stretching frequency also supports this. This vibrational coupling and correlation field effect are probably responsible for the splitting observed for these modes. The observation of triobands (*4*) for the $HPO_4$ ion in the regions 2800–2400, 2350–1900, and 1720–1600 $cm^{-1}$ and the lowering of the $NH_3^+$ stretching frequency suggest that the system is strongly hydrogen bonded.

Doubling is observed for all the internal vibrations of the $CH_2$ group in Raman and also for the bending modes of $NH_3^+$ in IR with splittings of more than 20 $cm^{-1}$. This indicates the presence of crystallographically different ethylenediammonium groups in the unit cell which is in agreement with the structural data (*1*).

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