Vibrational Spectroscopy and Structural Phase Transitions in Molecular Crystals

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Vibrational spectroscopy can give useful information, both structural and dynamical, about phase transitions in molecular crystals. In particular, the data concerning the mechanism of the transformation at molecular level can be obtained. This is illustrated by examples of pure van der Waals crystals such as 3,5-di-chloropyridine and 4-methylpyridine, hydrogen bonded malonic acid, inorganic ferroelectrics cesium dihydrogen phosphate and triammonium hydrogen disulphate, a superionic protonic conductor cesium hydrogen sulphate and a coordination compound: propylene diammonium manganese tetrachloride.

INTRODUCTION

Vibrational spectroscopy has been widely used in the study of structural phase transitions of a number of crystals and can give useful information about phases and their transformation, i.e. about the structural and dynamic aspects, respectively. As far as crystalline structures are concerned, X-ray and/or neutron diffraction methods and vibrational spectroscopy are complementary. The latter is particularly useful in determining the position of the proton in strong hydrogen bonds, the symmetry of disordered crystals and the nature and degree of disorder, for example. If there are no X-ray data, which frequently happens for low temperature phases, the vibrational spectroscopy may help to find out the space group and the number of molecules in the unit cell. It can also identify non-equivalent molecules and in the case of hydrogen bonded crystals the type of molecular association. The spectroscopic data are used in studying the dynamics of phase transitions and this area was developed particularly fast after the theoretical investigations of Cochran who worked out the dynamical concept of phase transitions implying soft mode and are helpful in determining the order—first or second—of the transformation, whether its nature is of displacive order-disorder (or mixed) or reconstructive type and the mechanism at the molecular level. Such information can be obtained by studying the frequency, intensity and half-width of infrared and Raman bands as a function of temperature and pressure. The low-frequency bands associated with lattice modes generally appear more phase transition sensitive than high-frequency bands due to intramolecular vibrations.
We were interested in the relationship which may exist between the mechanism of a given phase transition and the nature of intermolecular forces responsible for the cohesion of the crystal. We have thus examined a number of different types of compounds: (a) pure van der Waals crystals such as tetrahalobenzenes, pyrazine, 3,5-dichloropyridine, 1-picoline and malononitrile and malonic acid and squaric acid, (b) hydrogen-bonded organic crystals like oxalic, malonic and squaric acid, (c) inorganic ferroelectrics cesium dihydrogen phosphate CsH2PO4, rubidium dideuterium phosphate RbD2PO4, trimmonium hydrogen disulphate (NH4)3H(SO4)2, (d) superionic protonic conductors, hydrated uranyl phosphate (HUP) H3O+UO2-P-O3-3H2O, cesium hydrogen sulphate CsHSO4 and selenate CsHSeO4, (e) organometallic and coordination compounds such as MgBr2·2(C2H5OH), propylene diammonium manganese tetrachloride (NH3(CH2)NH3)MnCl4, ferrocene and nickelocene.

In this paper, we are reviewing some recent examples of various types of crystals investigated in our laboratory in order to show typical structural and dynamical information that vibrational spectroscopy can give about different phase transitions in molecular crystals.

1. 3,5-DICHLOROPYRIDINE, C5H3NCI

3,5-Dichloropyridine (DCP) (Figure 1) undergoes two phase transitions at 287.5 and 167.5 K with the corresponding enthalpies of 1200 and 0.4 J mole⁻¹, respectively, as shown by calorimetric measurements. There are thus three crystalline phases: I above 287.5 K, II between 287.5 and 167.5 K and III below 167.5 K. The I→II transition has been confirmed by nuclear quadrupole resonance of both 35Cl and 14N nuclei. The II→III transition is difficult to determine with accuracy by 35Cl NQR while 14N NQR does not give any indication of this transition.

Infrared and Raman spectra of DCP have been recorded at various temperatures between 15 and 300 K in the regions of both intramolecular and lattice vibrations. The latter are much more temperature sensitive than the former and are shown in Figures 2 and 3. General pattern of both Raman and infrared spectra is different for the three phases, the largest change being observed for the I→II phase transition. The temperature dependence of frequencies and Raman intensities of lattice bands shows clearly the II→III phase transition in the 150—170 K region (Figure 4).
Figure 2. Low-frequency Raman spectra of 3,5-dichloropyridine crystal at various temperatures. After reference²³.

Crystalline Structures

Phase I of DCP has been investigated by X-ray diffraction: the crystal belongs to the monoclinic system with the space group either $P2_1/m$ or $P2_1$ and $Z = 2$. The NQR of $^{35}$Cl shows only one frequency, implying that all Cl atoms are equivalent: the site symmetry of DCP molecules is thus $C_2$. 
Figure 3. Far-infrared spectra of 3,5 dichloropyridine crystal at various temperatures. After reference\textsuperscript{12}.

or $C_v$. The vibrational spectra indicate the existence of symmetry centers since several internal frequencies show a significant $g-u$ splitting and help to choose the $P2_1/m$ space group. The corresponding factor group analysis predicts nine external modes represented by: $3A_g(R'y, 2T') + 3B_g(R'x, R'y, T') + 2A_u(R'x, R'z) + 1B_u(R'y)$ where $R'$ and $T'$ are are rotational and translational vibrations. Librations designated by $R'x$ correspond to rotational motions about the $x$-axis perpendicular to the molecular plane, $R'z$ about
Figure 4. Temperature dependence of far-infrared frequencies (above) and Raman intensities (below) of some lattice bands of 3,5 dichloropyridine crystal. After reference 10.

z-axis which coincides with the two-fold molecular axis (C2) and R'y about the y-axis perpendicular to the x and z axes (Figure 1). Different geometries of Raman scattering on a single crystal of DCP helped to assign five lattice fundamentals out of the six expected: 3Ag at 34(T'), 46(T') and 85(R'y) cm\(^{-1}\) and 2Bg at 20.5(R'x,R'z) and 46(R'z,R'x) cm\(^{-1}\) (Figure 2). All the three infrared bands were identified at 39(Au,R'x,R'z), 60(Au,R'x,R'z)
and 85(Bu, R'y) cm$^{-1}$ (Figure 3). The external modes are thus also consistent with the $P_2/m$ symmetry and $Z = 2$.

No X-ray data are available for low temperature phases II and III. The NQR results show that the molecules of DCP are crystallographically equivalent in all three phases since only one $^{14}$N line is observed for each $v_+$ and $v_-$ resonance. The $^{35}$Cl line, on the other hand, splits into two components in phases II and III which implies a change of crystal symmetry and a lowering of the $C_s$ site symmetry to general position below 275 K. Vibrational spectra of phases II and III are similar but different from those of phase I. The splitting of numerous infrared and Raman bands due to internal modes of phase II suggests a doubling of the unit cell while the non-coincidence of their frequencies indicates the presence of symmetry centers. The number of external bands is consistent with the $C_{2h}$ factor group and $Z = 4$. The same conclusions apply to phase III.

Nature and Dynamics of Phase Transitions

The I$\rightarrow$II transition is characterized by a discontinuity of the Raman and infrared lattice frequencies in the frequency versus temperature plot. These results indicate that the I$\rightarrow$II transition is of first order and is likely to be of a reconstructive type (single DCP crystals shatter during the transition) with a doubling of the unit cell, in spite of two strongly damped modes in Raman near 30 cm$^{-1}$ and in infrared near 60 cm$^{-1}$ (Figure 4).

As far as the transition mechanism is concerned it should be pointed out that the lowest Raman frequency at 20 cm$^{-1}$ of phase II goes over to that at 20 cm$^{-1}$ in the spectrum of phase I (Figure 2). This high phase transition sensitivity implies that the corresponding lattice mode, assigned to a mixed $R'x, R'z$ libration must play an important role in the mechanism of the transformation. Its infrared counterpart has been identified near 60 cm$^{-1}$ in phase II and softens to 39 cm$^{-1}$ in phase I. These librational motions about $x$ and $z$ molecular axes (Figure 1) induce molecular rotation which destroys or creates the $C_{2h}$ site symmetry of the DCP molecule.

The II$\rightarrow$III transition, on the other hand, does not manifest itself by any discontinuity of lattice frequencies but can be detected from a relative variation of Raman intensities of several lattice bands (Figure 4) which implies a molecular reorientation. The infrared frequency at 67 cm$^{-1}$ also sharply decreases in the 100–170 K region (Figure 4). The vibrational spectra of phases II and III being very similar, it is likely that the crystal symmetry is not broken during the transition which is believed to be of a displacive type. The motion responsible for this transformation must be sought in the behaviour of the 67 cm$^{-1}$ infrared frequency which drops to 59 cm$^{-1}$ in phase II: it corresponds to a predominantly $R'z$ libration, i.e. a rotation about the $C_2$ molecular axis since there is no anomaly in the $^{14}$N NQR spectra at this temperature.

2. 4-METHYLPYRIDINE ($\gamma$-PICOLINE), CH$_3$-C$_5$H$_4$N

4-methylpyridine (4MP) crystal is interesting since, besides the low frequency lattice modes, the rotational — or torsional motion of methyl group plays an important role in the mechanism of phase transitions. The first transition at 254 K has been evidenced by calorimetry and $^{14}$N nuclear
quadrupole resonance. The results of the vibrational spectroscopy, i.e. band splitting and slope discontinuities in the Raman lattice frequencies versus temperature plot as well as internal band splitting, confirm this transition and show a new one at 100 K. There are thus three different phases in 4MP between 5 K and the melting point 276.8 K: phase I (254—276.8 K), phase II (100—254 K) and phase III (5—100 K).

Symmetry and structure

**Phase II**

The only crystalline structure which has been determined by X-ray diffraction is that of phase II (Figure 5). At 120 K, 4MP crystal is tetragonal I41/a (C16h) with four molecules in the primitive unit cell and the C2 site symmetry implying a disordered methyl group. The corresponding factor group analysis predicts twelve lattice modes, eight Raman (2Ag + 2Bg + 4Eg) and four infrared (Au + 2Eu) active. Three infrared absorption bands have been observed at 96, 63 and 38 cm⁻¹ and assigned to mixed R' and T' motions. Five Raman bands at 108, 83, 74, 67.5 and 59 cm⁻¹ are

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**Figure 5.** (left) Crystal structure of γ-picoline in phase II. After reference 30.

**Figure 6.** (right) Low-frequency Raman spectra of 4-ethylpyridine crystal at various temperatures (a) phase I, (b) phase II, (c) phase III. After reference 31.
also assigned to mixed rotational-translational modes, except for the 108 cm\(^{-1}\) band which is due to a predominant R'z libration, i.e. libration about the binary axis\(^{13}\) (Figure 6).

Phase III

X-ray powder diffraction data at 93 K suggest a \(P2_1/c = C_{2h}^5\) space group with four molecules in the unit cell.\(^{31}\) Symmetry lowering is manifested spectroscopically by the splitting of several internal modes which were degenerate (\(E_g, E_u\)) in phase II. \(Ag-Bg\) splitting gives rise to Raman components, of different intensities indicating a \(C_1\) site symmetry of the 4MP molecule since equal intensity of \(Ag-Bg\) components is expected for \(C_s\) site symmetry. The methyl groups are thus frozen in a non-symmetric conformation with respect to the aromatic molecular plane. Seven infrared and eight Raman external bands out of the nine and twelve, respectively, expected for the \(C_{2h}\) symmetry and \(Z = 4\), have been observed (Figure 6).

Phase I

The Raman as well as the infrared spectra of phases II and I are rather similar and the molecular organization is likely to be almost the same in both phases. The \(^{14}N\) NQR frequency splitting\(^{32}\) observed in phase II decreases rapidly with increasing temperature and reaches a constant value at 254 K. This indicates that the site symmetry of the molecules is higher, in phase I. Among all possible non-centrosymmetric sites only the \(C_{2v}\) point group symmetry appears consistent with the molecular symmetry implying a dynamically disordered \(CH_3\) group. The vibrational spectra, on the other hand, suggest that the factor group symmetry of phase I can be either \(C_{2v}\) with \(Z = 2\) or \(D_{4h}\) with \(Z = 4\). The latter has been chosen since the \(C_{2v}\) point group is a subgroup of \(D_{4h}\) and not of \(C_{2v}\) factor group.

Phase Transitions

The \(I \rightarrow II\) phase transition is characterized by a small (60 J mol\(^{-1}\)) enthalpy variation\(^{39}\) and continuity of Raman frequencies\(^{44}\) and NQR lines\(^{45}\) in the 160–270 K temperature range. The \(v_\alpha - v_\beta\) splitting follows Landau's law: \(a + b(T - T_c)^{1/2}\) near the critical temperature \(T_c\). The transition is thus of a displacive type, probably of second order, and may be induced by a rotation of the molecule around the binary molecular axis (Z).

The \(II \rightarrow III\) transition appears to be mainly of the order-disorder type where both librational motions of 4PM molecule and torsional vibrations of methyl groups play an important role as shown below.

Dynamics of Methyl Torsion

Comparison of Raman (Figure 7) and inelastic neutron scattering\(^{25}\) spectra of 4MP at 5 K shows at least five frequencies due to methyl torsion at 4.2, 11.5, 15.4, 31.7 and 42 cm\(^{-1}\). This unusual amount of data gives accurate information concerning the corresponding potential function. As a matter of fact, three models describing this motion can be considered: (i) free top with a fixed axis, (ii) periodic and (iii) non periodic potential function.

The above frequencies as well as those of the totally deuterated derivative, 4MP-\(d_7\), do not fit the first two models but are in agreement with
the assumption that in the low-temperature phase III the torsional motion of \( \text{CH}_3 \) group loses its periodic character and may be approximated by a Taylor series expansion about the equilibrium position. The non-periodic potential implies that the \( \text{CH}_3 \) torsion induces some deformation of the crystal which cannot be suppressed after \( 2\pi/3, 4\pi/3 \) or \( 2\pi \) rotation. This happens if methyl groups are correlated along infinite chains and if their rotations are coupled much in the same way as gear wheels, as shown in Figure 8. The non periodic potential corresponds thus to out-of-phase rotations and reflects the imperfection of methyl-methyl correlation and/or some dephasing along the chains, which prevents the recovery of the initial state after \( \text{CH}_3 \) rotation.\(^{12}\)

In phase \( II \) near \( 100 \) K, the Raman \( \gamma\text{CH}_3 \) bands at 32 and 42 cm\(^{-1} \) (at \( 5 \) K) converge to 50 cm\(^{-1} \) band which has been assigned to the \( 3\pi\to0 \) transition.
of a freely rotating methyl group while the 1\textbeta-0 transition is observed at 5 cm\(^{-1}\). The correspondence of energy levels of models (I) and (III) shows that aperiodic function goes over continuously to freely rotating methyl group and the molecular site symmetry increases from C\(_1\) to C\(_z\). The III\textleftarrowII phase transition is monitored by the coupling of the methyl torsion with an external mode near 61 cm\(^{-1}\) which is interpreted as a mainly rotational vibration R' around an axis perpendicular to the binary axis of the molecule: the methy-methyl correlation along the chains is thus destroyed when the temperature increases and the free rotation appears. In phase I, above 254 K, large amplitude motions appear for the librational vibration about the binary (z) molecular axis and the site symmetry increases to C\(_{3v}\).

Thus, the vibrational spectra of 4MP at various temperatures show three different phases characterized by different degrees of order (disorder) along two vibrational coordinates: the methyl torsion and the molecular libration around the binary axis z. The mean molecular organization is rather similar in all three phases. At very low temperature (5 K) the depopulation of the excited librational states cancels most of the random fluctuations of the

Figure 9. (left) Crystal structure of the room temperature \(\beta\) phase of malonic acid after reference\(^{20}\). B is the direction which becomes the two fold axis in the \(\alpha\) phase. Figure 10. (right) High frequency Raman spectra of malonic acid at 50 K (\(\beta\) phase and 7 K (\(\gamma\) phase). After reference\(^{20}\).
crystal field due to phonons and weak methyl-methyl interactions become dominant providing a new ordered crystalline state with a singular methyl dynamics.

**3. MALONIC ACID, CH₂(COOH)₂**

Two structural phase transitions at 360 and 48 K have been observed for the malonic acid crystal using calorimetric and spectroscopic measurements. There are thus three crystalline phases, designated α (above 360 K), β (360-48 K) and γ (below 48 K).

**β-Phase**

The structure of the β phase alone has been determined by X-ray diffraction: the crystal is triclinic with the \( \text{P}1 \) space group and two molecules per unit cell; the molecules are linked through hydrogen-bonded dimer rings into infinite chains. There are two crystallographically non-equivalent dimer rings, nearly orthogonal to each other, with different C=O, C-O, C-C and O···O distances. The existence of centrosymmetric dimers is shown spectroscopically following the mutual exclusion rule, i.e. the infrared and Raman frequencies generally do not coincide; in the case of the characteristic \( \nu \text{C}=\text{O} \) vibration, for instance, the average infrared frequency at 1765 cm\(^{-1}\) is considerably different from the Raman value at 1650 cm\(^{-1}\). The presence of non-equivalent dimers, on the other hand, may be sought in the appearance of doublets of the \( \nu \text{C}=\text{O} \) mode at 1630-1670 cm\(^{-1}\) in Raman (Figure 10) and at 1690-1740 cm\(^{-1}\) in infrared, as well as of other characteristic bands such as \( \delta \text{OH}, \nu \text{C}--\text{C}, \delta \text{COO}, \ldots \) (Figure 10).

When the crystal is cooled below 48 K, the corresponding Raman spectra are modified in the region of internal and external vibrations. In the high frequency region (Figure 10) doublets of characteristic bands split into quadruplets: for \( \nu \text{C}=\text{O} \) mode, for instance, four Raman components at 1622, 1629, 1676 and 1683 cm\(^{-1}\), are observed. The infrared-Raman exclusion, on the other hand, persists. These spectroscopic data indicate a doubling of the unit cell with the symmetry centres preserved. A \( \text{P}1 \) space group with the unit cell containing four non-equivalent dimer rings can thus be suggested, in agreement with the ENDOR study showing four magnetically non-equivalent protons of this compound at liquid helium temperature.

**γ-Phase**

The low frequency Raman spectra of the γ phase (Figure 11) show an increase of the number of bands. However, the most interesting appears to be a very strong new band with the lowest frequency of 30 cm\(^{-1}\) at 7 K which shifts to 16 cm\(^{-1}\), just below \( T_c \), while its halfwidth increases from 1.5 to 8 cm\(^{-1}\). This band has the characteristics of a soft mode and it has been assigned to antitranslational vibration of neighbouring chains. It has no equivalent in β phase at 50 K containing only one chain in the unit cell (Figure 9). From the behaviour of this soft mode, it can be concluded that the β→γ transition is of first order, of mainly displacive type and that the
transformation mechanism must be sought in an out-of-phase gliding of infinite chains which creates new non-equivalent dimers resulting in the doubling of the unit cell.19

α-Phase

When the crystal is heated above 360 K, the most significant changes are observed for carboxylic dimer bands (Figure 12). The v C=O doublet, for instance, merges into a single band at 1665 cm⁻¹ and the same happens to v C—O, δ OH and γ CCO doublets.17 A comparison of the infrared and Raman spectra of the α phase shows a considerable gerade-ungerade splitting for the v C=O (1655—1730 cm⁻¹), δ OH + v C—O (1455—1413 cm⁻¹), δ COO (855—630 cm⁻¹) and δ CCO (420—448 cm⁻¹). The molecules are thus still associated in centrosymmetric dimers forming infinite chains. The spectroscopic results of α phase, therefore, show two equivalent centrosymmetric dimer rings which implies the appearance of a glide plane the existence of which
makes ring I a mirror image of ring II (Figure 9). The space group \( C2/c \equiv C_{3h}^6 \) satisfies this condition: it contains four molecules in the monoclinic \( C \)-base centred cell or two molecules in the corresponding primitive cell.\(^{17}\)

\( \beta \rightarrow \alpha \) Transition

It has been shown that the malonic acid crystal undergoes a reversible first order phase transition at \( 360 \) K with an enthalpy change of 1.47 kJ mol\(^{-1}\).\(^{23}\) The behaviour of Raman lines for a number of modes is consistent with this conclusion since discontinuities are observed for a number of frequencies at the transition temperature. The largest discontinuities are found for carboxylic bands due to \( \nu C=O, \delta OH, \nu C-O \) and skeletal bending motions while \( CH_2 \) scissoring frequency does not change at all.\(^{17}\) The most characteristic changes, however, appear in the low-frequency region (Figure 13). Two strong Raman bands due to external modes drop suddenly at \( T_c \) from 86 and 52 cm\(^{-1}\) to 73 and 32 cm\(^{-1}\), respectively. A detailed investigation of these bands as a function of temperature shows a hysteresis effect, as expected for a first order transition.\(^{17}\)

![Figure 13. Low-frequency Raman spectra of malonic acid at 300 K (\( \beta \) phase) and 370 K (\( \alpha \) phase). After reference\(^{11}\).](image)

These two bands can be assigned to librational motions on the ground of their isotopic shifts of \( CD_2(COOH) \) derivative. They consists mainly of a twisting motion of the dimer ring \( (\gamma OH \cdot \cdot \cdot O) \rightarrow R' \) and a libration about the long molecular (dimer) axis \( R' \). Softening of these two frequencies suggests that the \( \alpha \rightarrow \beta \) structural transformation would principally result from an overall rotation of the chain of dimers about its long axis parallel to \( c \) (Figure 9). This would be accompanied by a twisting of the \( COOH \) groups, setting them along the chain with the rings roughly perpendicular to each other and associated with a shear of the whole cell along the normal to centred-base \( C \). All these deformations have \( B_g \) symmetry in the \( C_{3h} \) group. As a result, when the molecules settle to their new equilibrium positions at the transition, the two-fold axis and the glide plane are destroyed and only the centre of symmetry is preserved. It is probable that during
the transition the reorientation of the molecule about the c-axis is strongly coupled with the $R'_1$ and $R'_2$ modes. This mechanism is also consistent with a relatively small increase of the $\alpha \rightarrow \beta$ transition temperature of about 6 K of the Cd$_2$(COOD) crystal.$^{17}$

4. CESIUM DIHYDROGEN PHOSPHATE, CsH$_2$PO$_4$

CsH$_2$PO$_4$ is interesting as a pseudo-onedimensional ferroelectric crystal. Its phase diagram shows a paraelectric-ferroelectric phase transition at 153 K at normal pressure$^{48}$ while an antiferroelectric phase becomes stable at high pressure of a few kilobars and at low temperature.$^{41}$

The crystal structures of the paraelectric phase (Figure 14) consist of layers of hydrogen-bonded phosphate groups.$^{42}$ Unlike in KDP, there are two non equivalent OH···O hydrogen bonds: the shorter hydrogen bond (248 pm) links phosphate tetrahedra into chains along b axis while the longer hydrogen bond (254 pm) crosslinks the chains into layers. The paraelectric phase is disordered and the disorder is due to the short hydrogen bond, which can be described in terms of a statistical distribution of the proton in two off-centre equivalent sites above $T_C = 153$ K and ordered asymmetric configuration below, i.e. in ferroelectric phase. In this proton ordering process the crystallographic centre of inversion is lost and the $P_{21}/m$ space group transforms to $P2_1$ while the number of molecules per unit cell, $Z = 2$, remains the same. The long hydrogen bond is ordered in both phases.$^{42}$

Paraelectric Phase

The selection rules of the $C_{3h}$ factor group of the paraelectric phase predict 15 optically active lattice modes, 5Ag + 4Bg + 3Au + 3Bu, i.e. nine Raman and six infrared active. All these lattice bands have been observed at 234, 219, 118, 110, 75, 61, 49, 45 and 43 cm$^{-1}$ in Raman (Figure 15) and at 220, 146, 106, 100, 76 and 38 cm$^{-1}$ in infrared.$^{19}$ The bands have been
assigned to their symmetry species using polarized radiation on single crystals, as well as to translational motions of Cs\(^+\) cations and H\(_2\)PO\(_4^-\) anions and librations of anions employing isotopic derivatives CsD\(_2\)PO\(_4\) and CsH\(_2\)P\(^{18}\)O\(_4\) and a normal coordinate calculation. Among these modes the Raman frequencies at 220 cm\(^{-1}\) and 75 cm\(^{-1}\) are particularly interesting: the former corresponds to a mainly short hydrogen bond stretching (v\(\text{OH} \cdots \text{O}\)) vibration (R"b) and the latter to a mainly translational motion of Cs\(^+\) ions.

The internal vibrations, on the other hand, do not obey the same selection rules and do not see centres of symmetry. It turns out that in CsH\(_2\)PO\(_4\), like in several other disordered crystals,\(^{18,21,23}\) the external vibrations see the (average) symmetry of the crystal in the same way as X-ray (or neutron) diffraction while the internal vibrations see only the given symmetry of a molecule or ion and not the statistical one.

**Ferroelectric Phase**

The symmetry lowering gives rise to new external bands in the spectra of the ferroelectric phase of CsH\(_2\)PO\(_4\), two infrared at 111 and 125 cm\(^{-1}\) and a Raman at 74 cm\(^{-1}\) which were forbidden in the paraelectric phase. A new kind of bands also appears in the region of both external and internal modes: this is due to the transverse optical (TO) and longitudinal optical (LO) splitting of Raman modes as a modification of selection rules of the polar ferroelectric phase. Backward scattering (180\(^\circ\)) geometry must be used for a correct assignment of pure LO and TO components, which has been done for A modes. Significant TO—LO splitting has been observed for two external bands at 122—130 cm\(^{-1}\) and 205—249 cm\(^{-1}\), the latter, due to short
Figure 16. High-frequency backward Raman scattering of CsH$_2$PO$_4$ single crystal at 80 K showing $A_{TO}$ and $A_{LO}$ modes. After reference$^{19}$.

Figure 17. Low-frequency Raman spectra of CsD$_2$PO$_4$ single crystal under various pressures. After reference$^{19}$.

hydrogen bond stretching vibration, yields the highest relative splitting of about 25% and corresponds to a very strong far infrared absorption band. Several internal bands are also split and the largest splitting is found for a P—O stretching vibration at 993(TO)—1051(LO) cm$^{-1}$ (Figure 16)$^{19}$.

**Antiferroelectric Phase**

Raman spectra of the antiferroelectric phase (AFE) of a CsD$_2$PO$_4$ single crystal were recorded at 80 K and under 8 kbar pressure.$^{44}$ Different scattering geometries showed no angular dispersion, i.e. no TO—LO splitting occurred to indicate that this phase was centrosymmetric. Previous neutron studies showed a doubling of the unit cell and the existence of a glide plane along $a$. This is confirmed by the fact that new external Raman bands at 23 and 88 cm$^{-1}$ for Ag species (Figure 17) and 68 cm$^{-1}$ for Bg species are observed when crossing the PE-AFE transition line. The spectroscopic results suggest the $P2_1/a$ space group with $Z = 4$ for AFE phase.$^{44}$
Para-ferroelectric Transition

Pseudo-one-dimensional character of CsH_2PO_4 makes the order parameter anisotropic. Zumer and Blinc et al. have shown that this anisotropy implies that the soft mode of CsH_2PO_4 has a very low frequency compared to that of KH_2PO_4. Para-ferroelectric transition is thus expected to be governed by a relaxational rather than a resonant type of motion.

This is confirmed by the infrared reflection spectrum of a single crystal of CsH_2PO_4 which shows a wing of the central mode type in the low fre-
frequency region (Figure 18). The reflectivity increase in this region can be explained by a relaxational type of motion of dipoles. The observed spectrum is in good agreement with the calculated one following the relation of Merten and Borstel which supposes a relaxational motion in the crystal. A number of Raman bands shows critical behaviour: Raman intensity varies as the square of the order parameter (spontaneous polarization) as a function of temperature. The first type of bands corresponds to longitudinal modes (LO) and the experimental curve can be compared to the theoretical one calculated on the basis of the Ising model developed by Blinc and Barret. The second type of bands is due to (silent) lattice modes which are forbidden in the paraelectric phase. It is significant that the Raman band at 74 cm\(^{-1}\) also behaves critically (Figure 19): this band has been assigned to a mainly translational motion of Cs\(^+\) ions, which implies that there is a non-negligible displacive contribution of heavy atoms to the essentially order-disorder PE-FE phase transition.

The ferroelectric→paraelectric transition is accompanied by an unusual shortening of the short hydrogen bond. The O...O distance decreases from 248.8 to 247.6 pm in the paraelectric phase and the corresponding OH stretching frequency is lowered from 2200 to 2100 cm\(^{-1}\). The hydrogen bond stretching frequency ν\(\text{OH}...\text{O}\) at 205 cm\(^{-1}\) (TO) is remarkably constant in the ferroelectric phase in the 80 to 153 K range and increases rapidly in the 153 to 300 K range to 220 cm\(^{-1}\) indicating that there is a continuous shortening of the O...O distance with temperature increase in the paraelectric phase.

**Antiferroelectric Fluctuations**

A detailed investigation of single crystals of CsH\(_2\)PO\(_4\) and CsD\(_2\)PO\(_4\) at ordinary pressure shows that the same bands appear in the vicinity of the paraelectric-ferroelectric phase transition (Figure 20) and that their intensity reaches a maximum just at the Curie temperature. The appearance of these bands shows clearly that antiferroelectric ordering exists partially at atmospheric pressure. Such antiferroelectric fluctuations have been predicted by the model of Blinc and Barret and a quantitative interpretation of the corresponding spectroscopic manifestation was given using the above model (Figure 20).

**Para-antiferroelectric Transition**

The PE-AFE transition point at 80 K has been determined by measuring the intensity ratio of the 83 and 88 cm\(^{-1}\) Raman bands of a single crystal of CsD\(_2\)PO\(_4\) as a function of pressure. A large hysteresis of about 800 bars was observed showing the first order character of this transition.

**Isotope Effect**

There is considerable isotope effect of the hydrogen substitution by deuterium on the phase diagram of CsH\(_2\)PO\(_4\): the PE-FE transition temperature increases from 153 K to 267 K and a substantial increase of pressure is necessary to reach AFE phase. The deuterium also changes the O...O distances of both short and long hydrogen bonds. However, the short
hydrogen bond expands much more, from 247.6 pm to 249.8 pm, than the long one, 253.7 to 254.0 pm. This positive isotope effect is manifested spectroscopically by the lowering of the $\nu_{OH}/\nu_{OD}$ isotopic frequency ratio: 1.27 and 1.13 for the short and long bonds, respectively; in both cases, the ratio is much lower than 1.37, the harmonic oscillator value; another manifestation of the isotope effect is the behaviour of the $\nu_{OH}\cdots O$ vibration of the short hydrogen bond: the temperature dependence of the half width $\Delta \nu_{1/2}$ of the corresponding $\nu_{OH}\cdots O$ and $\nu_{OD}\cdots O$ Raman bands is very different: the $\Delta \nu_{1/2}$ of the $\nu_{OH}\cdots O$ band varies from 5 to 45 cm$^{-1}$ when the temperature $T - T_e$ increases from $-80$ to $+140$ °C while there is hardly any variation of the $\Delta \nu_{1/2} = 15$ cm$^{-1}$ of the $\nu_{OD}\cdots O$ band under the same conditions. This difference may be related to proton jumps along hydrogen (deuterium) bonds and to different vibrational anharmonicity.

It may be argued qualitatively that the activation energy which is roughly the height of the potential barrier of the double well potential must be considerably higher for OD$\cdots O$ than for OH$\cdots O$ bond, the former being longer. The corresponding correlation time, or tunnelling probability, and halfwidth are thus expected to be smaller for OD$\cdots O$ than for OH$\cdots O$ stretching band.

5. TRIAMMONIUM HYDROGEN DISULPHATE. (NH$_4$H(SO$_4$)$_3$)

At atmospheric pressure, the crystal of triammonium hydrogen disulphate (NHS) undergoes five phase transitions and the six corresponding phases are represented as follows:

<table>
<thead>
<tr>
<th>VII</th>
<th>V</th>
<th>IV</th>
<th>III</th>
<th>II</th>
<th>I</th>
<th>T/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>133</td>
<td>137</td>
<td>265</td>
<td>413</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The room temperature phase II belongs to the monoclinic system with $A2/a$ space group and two formula entities in the unit cell. The NH$_4^+$ ions
form complex NH···O hydrogen bonds and occupy two sites of non-equivalent positions, one of which is presumed ordered. The \( \text{SO}_4^{2-} \) ions form centrosymmetric one proton dimers via strong OH···O hydrogen bonds 254 pm long. \(^{25}\) Phase III also appears to be monoclinic with \( P2_1/b \) space group\(^{26}\) while phase VII is ferroelectric and thus non-centrosymmetric.\(^{27}\)

Raman and infrared spectra of each of the investigated phases II, III, V and VII are different and allow characterizing the given phase unambiguously (Figures 21 and 22). The largest spectral differences are observed in the low frequency region below 500 cm\(^{-1}\) (Figure 21) and in the high frequency NH stretching region (Figure 22). The bands of the room temperature phase, particularly the low frequency bands due to external vibrations, are quite broad indicating that phase II is strongly disordered. In fact, there are two kinds of disorder in NHS crystal: the first is due to a statistical or dynamical distribution of proton in a crystallographically centrosymmetric hydrogen bond\(^{34}\) similar to that in paraelectric phase of CsH\(_3\)PO\(_4\),\(^{45}\) and the second to an orien-
Figure 22. Raman spectra of (NH₄)₄H(SO₄)₂ in NH stretching region at 300 K (phase II), 150 K (phase III), 120 K (phase V) and 50 K (phase VII). After reference 21.

An internal disorder of ammonium ions. A relative ordering is observed when the temperature is lowered and ammonium ions appear to be involved in all phase transitions. Only the polar phase VII presents narrow bands or fine structure and its Raman spectrum is characteristic of a fully ordered molecular crystal.

**Room Temperature Phase II**

If the (SO₄HSO₄)₃⁻ dimers are truly centrosymmetric, the OH group vibrations are forbidden in Raman and only one totally symmetric stretching ν₁SO₄ mode (Ag) is expected for a dimer. The fact that two strong Ag bands
appear at 966 and 1078 cm\(^{-1}\) in the Raman spectrum of NHS (Figure 23) may be considered as a spectroscopic evidence of a non centrosymmetric dimer.\(^{25}\) The splitting of 112 cm\(^{-1}\) is much too large to be due to a correlation field. By analogy with MHSO\(_4\) (M = K, Na) type of compounds,\(^{27}\) the 966 and 1070 cm\(^{-1}\) bands can be assigned to the proton donor (HSO\(_4^\cdot\)) and acceptor (SO\(_4^{2\cdot}\)) groups, respectively. The crystallographic symmetry is thus of a statistical nature. The OH stretching vibration has been observed as a very strong and broad absorption (Au) in the polarized infrared spectrum of a single crystal of NHS.\(^{55}\) This absorption extends from 2000 to 300 cm\(^{-1}\), with characteristic Evans holes at 1030, 888 and 446 cm\(^{-1}\). The vOH centre of gravity frequency is found near 1200 cm\(^{-1}\), in agreement with the O···O distance of 254 pm.

### Low Temperature Phases III, V and VII

The low frequency Raman spectrum of NHS appears to be the most temperature sensitive (Figure 21). In the spectrum of phase II only three broad bands are observed near 440, 185 and 80 cm\(^{-1}\); the first has been assigned to the vSO\(_4^{2\cdot}\) bending modes and the last two to the external vibrations. Comparison of the spectra of NHS with those of the isomorphous crystal, KJH(SO\(_4\))\(_2\) (KHS) at various temperatures, shows that the latter exhibits narrow bands already at room temperature while the former are changed gradually and become narrow and structured only in phase VII below 78 K. This indicates that the OH···O hydrogen bond disorder in dimers does not affect much the band breadth in KHS and thus neither in NHS. The main responsible factor of the band broadening is thus the disorder of ammonium ions which must be responsible for phase transitions. No phase transition has been reported for KHS.

In phase III, there is some structure in the low frequency (Figure 21) and NH stretching region (Figure 22) but on the whole the spectral pattern is similar to that of phase II. The II ↔ III transition involves a unit cell doubling and a rearrangement of NH···O hydrogen bonds but not a significant ordering of ammonium ions. The spectral data are consistent with the P2/b space group and \(Z = 4\) given by X-ray diffraction.\(^{56}\) This space group implies...
the disappearance of one of the two centres of inversion: the \((\text{SO}_4\text{HSO}_4)^{2-}\) dimers may, therefore, be on general positions and the OH\(\cdot\cdot\cdot\)O hydrogen bonds become ordered but remain asymmetric. However, this does not change much the splitting of the \(v_3\text{SO}_4\) bonds; the dimer structure and its O\(\cdot\cdot\cdot\)O length are believed to be very similar to those of phase II.\(^{21}\)

Phase V at 120 K is characterized by a strong enhancement of the NH stretching absorption and by considerable narrowing of lattice bands. New bands assigned to NH\(_4^+\) librations appear in the 300 to 230 cm\(^{-1}\) region, showing that a serious ordering of ammonium ions occurs.

Finally, phase VII at 50 K appears fully ordered at least as far as NH\(_4^+\) ions are concerned. The low frequency Raman spectra consist of numerous narrow bands and the distinction between NH\(_4^+\) and HSO\(^{-}\) librations becomes possible. The \(V \leftrightarrow VII\) phase transitions are a first order transition since there are discontinuities in the Raman frequency vs. temperature plot. It is of order–disorder type and the main mechanism appears to be the orientational ordering of ammonium ions. The latter contributes mostly to the ferroelectricity of phase VII, in any case much more than the ordering of protons in sulphate dimers.\(^{21}\)

6. CESIUM HYDROGEN SULPHATE, CsHSO\(_4\)

Cesium hydrogen sulphate aroused a considerable interest since its high temperature phase above 417 K exhibits unusually high conductivity\(^{26}\) of the order of \(10^{-6}\) \(\Omega^{-1}\) cm\(^{-1}\). It belongs, thus, to superionic protonic conductors and these materials may be used potentially in various conversion systems such as fuel cells, capacitors, sensors or electrochromic displays.\(^{26}\)

![Diagrammatic representation of temperature and enthalpy changes of phase transitions in CsHSO\(_4\). After reference\(^{21}\).](image)

Calorimetric and spectroscopic measurements\(^{21,60}\) show that the phase transformations of CsHSO\(_4\) depend considerably on the thermal history of the sample and on pressure. On heating a freshly prepared crystal the room temperature phase I goes to phase II at 318 K and to phase III at 417 K while on cooling phase II' at 408 K and phase I' at 353 K were obtained instead of phases II and I (Figure 24). The infrared and Raman spectra of all these phases are different.

**Phase I**

Crystalline structure of CsHSO\(_4\) at room temperature has been determined by X-ray diffraction.\(^{41}\) The monoclinic crystal belongs to \(P2_1/m\) (\(C\text{\(\cap\)s}\)) space group with two formula units per unit cell. There are infinite hydrogen
bonded chains of $SO_4$ tetranedra with the $O\cdots O$ distance of 257.2 pm and
the proton appears to be disordered between two equilibrium sites creating
a statistically symmetric hydrogen bond. On the whole, the structure of
CsHSO$_4$ is very similar to that of the paraelectric phase of CsH$_2$PO$_4$ apart for
the extra hydrogen (long hydrogen bond) in the latter (Figure 14). There is
also a similarity with the structure of ionic conductors such as Li$_2$SO$_4$,
LiNaSO$_4$ or even NASICON.$^{62,63}$

Vibrational spectra are consistent with the X-ray diffraction results. The
selection rules derived from the $C_{2h}$ symmetry are obeyed by external vibra-
tions: the single crystal Raman spectra show $3A_g$ and $4B_g$ bands out of
$5A_g + 4B_g$ predicted and polarized infrared reflection spectra $3A_u$ and $1B_u$
out of $3A_u + 3B_u$. The low frequency bands at 40, 50 and 80 cm$^{-1}$ have been
assigned to mainly Cs$^+$ translational and the high frequency bands at 215,
190 and 115 cm$^{-1}$ to mainly librational motions of $HSO_4^-$ ions by analogy with
the spectra of CsH$_2$PO$_4$. Internal vibrations, on the other hand, see neither
centres nor planes of symmetry and, in particular, the Raman bands due to
$\nu S-(OH)$ (donor) and $\nu S-O$ (acceptor) vibrations identified at 865 and 995
cm$^{-1}$, respectively, show that each given $OH\cdots O$ hydrogen bond is asym-
metrical and that the crystallographic symmetry is statistical.

The structure of phase I appears to be the same down to liquid helium
temperature and no spectroscopic evidence of a ferroelectric ordered phase,
a possibility suggested by Itoh et al.$^{61}$, has been found.

Phase II

Heating of CsHSO$_4$ crystal to 350 K brings about significant changes
both in internal and lattice regions (Figure 25). The $\nu S-O$ (acceptor) Raman
frequency at 998 cm$^{-1}$ which was remarkably constant from 18 to 300 K
rises to 1024 cm$^{-1}$ and its infrared counterpart even more, from 1000 to 1050
cm$^{-1}$ and broadens. The skeletal bending bands are also significantly modified.
These changes reflect a more substantial rearrangement of $SO_4$ tetrahedra
and a conversion of chains to cyclic dimers has been suggested.$^{64}$ A mutual
exclusion rule is expected for centrosymmetrical dimers and this has been
observed, in particular for the $\nu S-O$ mode, for which the largest ungerade-
grade splitting 1050—1024 cm$^{-1}$ has been found. This conversion of chains
des into dimers is accompanied by a weakening of the hydrogen bond: the dif-
ference between the $\nu S-O$ and $\nu S-OH$ frequencies increases and the OH
stretching band shifts by about 100 cm$^{-1}$ towards higher wave-numbers. It
should be pointed out that on some other alkali hydrogen sulphates $HSO_4^-$
anions pass easily from chains to ring dimers, $\alpha$ and $\beta$ phases of NaHSO$_4$,$^{65}$
for instance, contain chains and dimers, respectively while in KHSO$_4$ crystal
both forms coexist.$^{66}$

In the low frequency region the Raman bands due to mainly librational
motions of $HSO_4^-$ anions disappear or broaden while those corresponding to
mainly translational modes of Cs$^+$ cations are less affected.

On the whole, the spectral data show that the I $\leftrightarrow$ II transition is of first
order (discontinuity in the S—O stretching frequency versus temperature
plot) and of reconstructive type with a structural transformation of infinite
chains into ring dimers, an increased orientational disorder of anions and
weakening of OH$\cdots O$ hydrogen bonds.
Phase III

The spectroscopic changes of phase III (Figure 25) consist of broadening of the skeletal stretching and bending Raman bands and further diminishing of their number. This indicates a higher (average) symmetry of this phase and certainly a highly disordered structure. The most dramatic changes, however, are observed for external modes where all the bands collapse into a broad wing near the Rayleigh line.

This behaviour is characteristic of a plastic phase of molecular crystals and implies a «free» rotation of \( \text{HSO}_4^- \) ions on given sites. Moreover, the Cs\(^+\) sublattice becomes also disordered. The Raman spectrum of phase III can thus be considered a spectroscopic manifestation of a quasi-liquid state of the superionic conductor phase. Phase III is thus both a protonic and ionic conductor while in phase II and I the conductivity is essentially protonic and this may explain the drastic increase in conductivity for almost five orders of magnitude in going from phase II to phase III.

The above conclusions agree with a recent work of Haynovskiy et al.\(^{17}\) who found out that there is almost no difference in conductivity of phase III of \( \text{CsHSO}_4 \) and \( \text{CsDSO}_4 \) while at lower temperatures (phases II and I) the conductivity of the deuterated crystal decreases by about two orders of magnitude.
The propylene diammonium manganese tetrachloride layer compounds having a general formula \((\text{NH}_3\text{(CH}_2\text{nNH}_3)\text{MnCl}_4}\) with \(n = 2, 3, 4, 5\) and \(M = \text{Cu, Mn, Fe, Cd, ...}\) belong to the perovskite structural family and are interesting because of their magnetic properties and structural phase transitions. These compounds crystallize in a two-dimensional structure consisting of nearly isolated layers of corner sharing \(\text{MCl}_6\) octahedra parallel to the \((a, c)\) planes. The interlayer bonding in the \(b\) direction is achieved by the alkylene diammonium cations through \(\text{N-H} \cdots \text{Cl}\) hydrogen bonds.

For the propylene diammonium manganese tetrachloride (abbr. PDA) the calorimetric measurements show phase transitions at 336 and 306 K while Raman spectroscopy indicates another one at about 110 K. There are thus four solid phases of PDA designated \(I (> 336 \text{ K}), II (336 \text{ K} – 306 \text{ K}), III (306 - 110 \text{ K})\) and \(IV (< 110 \text{ K})\). The room temperature phase \(III\) is disordered according to neutron diffraction results and it can be concluded from proton magnetic resonance that this disorder is of a dynamical nature, the PDA ions undergoing rotational motions around their long \(b\)-axis. Kind et al. on the other hand, have suggested, from nuclear quadrupole resonance and nuclear magnetic resonance measurements, that in phase \(III\) chains are almost ordered and that a dynamical disorder can be observed only above 306 K. Besides, they do not see any phase transition at 110 K.

Raman spectra of PDA in the low-frequency region 350—10 cm\(^{-1}\) (Figure 26) characterize phases \(I, II, III\) and \(IV\). The broadness of bands indicates a

![Figure 26. Low-frequency Raman spectra of \(\text{NH}_3\text{(CH}_2\text{nNH}_3)\text{MnCl}_4\) single crystal at various temperatures. After reference.](image-url)
large amount of disorder in high temperature phases while only the spectrum of phase IV is that of a fully ordered crystal. Discontinuities are observed in frequency variation with temperature for I ↔ II ↔ III transitions the two lowest Raman frequencies near 60 and 70 cm⁻¹ assigned to chlorine atom motions being the most sensitive. The above results confirm the first order character of the I ↔ II ↔ III transitions.²⁹,³¹ The frequency and half-width variation of Raman bands of PDA are continuous between 10 and 300 K but the corresponding curves present an inflection point at about 110 K. The infrared spectra of four different phases are also different, in particular, in the NH₃ bending (1620—1400 cm⁻¹) and MnCl stretching (480—200 cm⁻¹) regions.³⁸

There is some controversy about the structure of phase III. A neutron diffraction study³⁹ gives Ima-D₂h⁻² space group with Z = 2 while NQR dielectric and optical results appear to be consistent with Pnma-D₂h²⁸ symmetry and Z = 4. Raman and infrared spectra of single crystals of PDA agree better with the structure proposed by neutron diffraction³⁹ on the ground of the number of observed external bands.³⁸ The spectra of phase IV can also be interpreted in terms of D₂h factor group with Z = 2.

As far as the III ↔ IV phase transition is concerned, the most sensitive Raman bands are those assigned to the torsion of NH₃⁺ group at 325 cm⁻¹, stretching Mn—Cl vibrations near 320 and 200 cm⁻¹ and the libration of the cation ‘NH₃(CH₂)₃NH₃⁺’ around its long axis (R’y) near 190 cm⁻¹. The curves in the frequency versus temperature plot present an inflection point at about 100 K. From the variation of the torsional NH₃ frequency, the thermal expansion coefficient could be determined, γ = —0.25 × 10⁻³ and —0.40 × 10⁻³ K⁻¹ below 120 and above 150 K, respectively. The most dramatic change, however, is observed for the integrated intensity of NH₃ torsional band (Figure 26).

This is the strongest Raman band in phase IV at 10 K but its intensity decreases very rapidly above 100 K and the band is hardly observed in the room temperature phase. It also presents an inflection point at 110 K. The corresponding curve I = f(T) reflects a thermally activated process governed by Boltzmann’s law: when the temperature is raised, an increasing proportion of NH₃ groups start to jump and escape to the Raman observation while the Rayleigh line broadens. Finally, from the half-width variation of the τ NH₃

Figure 27. Infrared spectra (NH stretching region) of an isotopically diluted crystal of ND₃(CH₂)₃ND₃MnCl containing about 9% of hydrogenated compound at 300 and 100 K. After reference³⁸.
band with temperature it can be concluded that the life-time of the torsional 
mode is limited, at high temperature, mainly by the rotational jumps of NH3+ 
groups. The experimental curve for NH3 torsion has been fitted to the equation\(^1\) 
\[ \Gamma_{1/2} = (a + bT) + (c' \text{exp} - E_0/kT) \]
where \( \Gamma_{1/2} \) is the half width of the phonon, \( a, b \) and \( c' \) constants and \( E_0 \) the activation energy corresponding approximately 
to the potential barrier \( V_0 \) governing the disorder mechanism. The obtained 
value \( E_0 = 4.2 \text{ kJ mol}^{-1} \) can be compared with the six-fold potential barrier, 
derived from the torsional frequency, \( V_0 = 5.0 \text{ kJ mol}^{-1} \). The correlation time 
\( \tau_c = \tau_\text{exp} E_0/kT \) is then \( 1.5 \times 10^{-11} \text{ s} \) at 100 K and \( 5.6 \times 10^{-13} \text{ s} \) at 300 K. At 
room temperature the correlation time is of the same order of magnitude as 
the observation time and this could explain the fact that at 300 K the 
infrared spectrum of an isotopically diluted sample of PDA shows only a broad 
diffuse absorption in the NH stretching region (Figure 27). At 100 K, 
on the other hand, the residence time would be long enough to distinguish 
three non-equivalent protons, i.e. three NH stretching bands at 3120, 3087 
and 3036 cm\(^{-1} \) (Figure 27). The broadening of the R'Y librational band of PDA 
cation can be partly explained by the same type of process: above 250 K it 
seems that a certain proportion of cations is already jumping; both NH3 tor-
sion and R'Y libration can get coupled and induce the next III \( \leftrightarrow \) II transition. 

A recent neutron scattering study\(^2\) of PDA confirms that the reorientatio-
nal motions of protons of NH groups take place in phases III and IV. However, 
the dynamics of NH3 groups at room temperature is governed by a correlation 
time \( \tau = 1 \times 10^{-11} \text{ s} \) and by an activation energy of 26.6 kJ mol\(^{-1} \). The value 
of 4.24 J mol\(^{-1} \) observed from Raman line broadening is thus considerably 
underestimated.

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Vibracijska spektroskopija in strukturalni fazni prehodi molekulskih kristalov

Vibracijska spektroskopija lahko preškerbi koristne strukturne in dinamične podatke o faznih prehodih v molekulskih kristalih, posebno tiste o mehanizmu strukturne transformacije na molekulski ravni. Pričujoči članek pokaže to s primeri različnih tipov kristalov — od čisto vanderwaalsovskih (3,5-diklorpiridin in 4-metilpiridin) preko vodikovo vezanih organskih kristalov (malonska kislina) in anorganskih feroelektrikov (CSH2P04 in (NH4)3H(80412) do superionskega protonskega prevodnika CsHSO4 in koordinacijske spojine (NH3(CH2)6NH3)MnCl4.