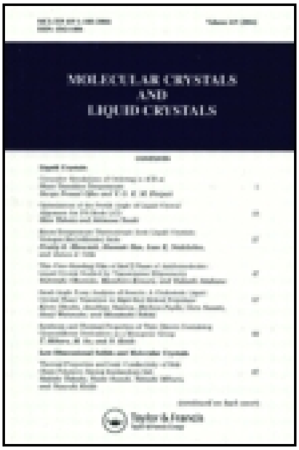

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Low Frequency Vibrations of Molecular Crystals, VIII. The Far Infrared Spectrum of Polycrystalline Hydrogen and Deuterium Cyanide

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Low Frequency Vibrations of Molecular Crystals, VIII.[‡] The Far Infrared Spectrum of Polycrystalline Hydrogen and Deuterium Cyanide

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Abstract—The infrared spectra of crystalline hydrocyanic acid, HCN, and its deuterium analog, DCN, have been recorded from 33–700 cm^{-1}. Spectral band assignments have been made on the basis of the low-temperature crystalline modification, C_{2v}^{20}. A detailed analysis of the effects of the apparently strong hydrogen bond in HCN was carried out on the basis of the dielectric properties of the system. Evidence is offered to show consistency between the $H - C^+ = N^-$ resonance structure proposed by Pauling, the high melting point, the low dielectric constant observed by Smyth and McNeight and the pyroelectric effect reported by Dulmage and Lipscomb.

Introduction

In our continuing examination of various molecular crystal sytems we have reported and interpreted the far-infrared spectrum of crystalline hydrocyanic acid, HCN, and its deuterium analog. No Raman spectra have been recorded since all vibrations group theoretically allowed in the Raman effect are permitted by the infrared selection rules. Many investigations of this molecule have been reported but we include here only a review of the litera-

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ture which has direct pertinence to our solid state investigation.

Smyth and McNeight[1] have reported dielectric constant measurements for polycrystalline HCN and they conclude that there is no evidence for molecular rotation in the solid. These workers felt that the molecule's deviation from sphericity and the large dipole moment adequately explain the behaviour of the HCN system without discussing the strength, or indeed the presence, of hydrogen bonds. Smyth and McNeight also reported a premelting phenomenon beginning approximately 13°K below the melting point at 259.1°K. They attributed this process to the presence of impurities, which is not unreasonable in view of the dielectric constant's sensitivity to the like. Giauque and Ruehrwein[2] measured the heat capacity of HCN. They reported a phase transition at 170.37°K in the solid. Furthermore, they attribute this modification to the movements of large groups of HCN molecules since the entropy change is only 0.022 e.u. These workers also found a premelting phenomenon and likewise attributed it to impurities even though, as they reported, the liquid HCN stood for over 1 year with no discoloration at room temperature. Another interesting feature which Giauque and Ruehrwein reported is that between 100° and 200°K intense flashes of bluish-white light were emitted on warming and cooling the 5 moles of crystalline HCN in their system. They further reported that the flashes were accompanied by a cracking characteristic of crystals breaking under strain. The remainder of their paper deals with the polymeric species present in the gaseous state, which they offer as the explanation for the observed high dielectric constant. The mid-infrared spectra of HCN have been reported and discussed by Hornig and Hoffman.[3] They observed a very marked change in intensity (1000X) between the gaseous and crystalline states.

Lipscomb and Dulmage[4] reported the crystal structure of both the high and low temperature modifications. They showed that only a very small change in structure occurs, involving large groups of HCN molecules, at 170°K which was consistent with the results of Giauque and Ruehrwein. This change, on going from the high temperature to the low temperature modification, was accompanied by the following structural changes: $\Delta a = -0.5$ Å, $\Delta b = +0.25$ Å, and $\Delta c = 0.0$ Å where a, b, and c are the crystallographic axes. Furthermore, the low temperature form is strongly pyroelectric, which indicates that all HCN molecules point in the same direction. The premelting phenomenon seen by Smyth and McNeight as well as by Giauque and Ruehrwein was interpreted by Dulmage and Lipscomb[4] as possibly due to a molecular reorientation at or very near the melting point rather than to impurities. The space groups reported were as follows: $T > 173°\text{K}\ \text{C}^9_{4v}$ – I4 mm, $T < 173°\text{K}\ \text{C}^{20}_{2v}$ – I mm. In both phases there are reported to be two molecules per unit cell. Both of these structures place an HCN molecule along each edge of a right parallelepiped (parallel to the c axis) and one molecule in the body-centered position (also parallel to the c axis). Their article[4] contains excellent models and discussions of the proposed structures which we will not duplicate; however, the normal modes of motion, hydrogen bonds, etc., will be discussed in terms of these models for the sake of consistency and clarity.

Pezolet and Savoie[5] have quite recently completed an examination of the Raman spectrum of crystalline HCN. Their results (in low frequency region) indicates that they were unable to observe the B_1 and B_2 modes in the low temperature phase. However they did observe the doubly degenerate E component at 161 cm^{-1} at -90°C and at 149 cm^{-1} in the heavy compound. Also, these workers recorded a band at ~ 220 cm^{-1} in both isotopes which they observed in both Phase I (high temperature modification) and Phase II (low temperature modification). They conclude that this is a reflection band and that it likely arises from piezoelectric anomalies. This effect was also seen on all the mid infrared fundamentals.

Pauling[6] has noted the unusual dipole moment dielectric constant behavior of HCN as well as HF, CH_3OH, CH_3NH_2, H_2O_2, etc. He attributes the low dielectric constant found by Smyth and McNeight to $(HCN)_x$ polymers which are unable to reorient. He further proposes that resonance structures of the kind $H-C^+=N^-$ account for the very high melting point (-13°C) of such a light substance as HCN. Pauling states, that on the basis of simple dielectric theory, in the liquid the average degree of polymerization is three. Although the hydrogen bond is weak he proposes that it is responsible for this high melting point; however, he does not mention that HF with a much stronger H bond melts at − 83°C. Nixon and King[7] recorded the matrix isolation spectra of HCN and DCN. Their results indicate HCN exists as a dimer in the matrix and they observed frequencies at 96, 137, and 144 cm^{-1} which they assigned as molecular motions arising from this species. Thus, the stability and electrical properties of the system have not been satisfactorily explained and the far infrared optical properties remain to be explored. Therefore, we have investigated the far infrared spectra of HCN and DCN to shed additional light on the effects of the crystal structure of the hydrocyanic acid on its physical properties.

Experimental

Both HCN and DCN were prepared in the same manner from concentrated H_2SO_4 and D_2SO_4, respectively. The acid was dropped into a flask which contained KCN and was surrounded by an ice water bath to retard the formation of SO_2. For increasing the effectiveness of the reaction, the KCN should be stirred to allow the acid to reach fresh reactant continually. It appeared that if this procedure was not followed, SO_2 would be formed even at the low temperature of the ice bath. A trap-to-trap distillation (dry ice–acetone and liquid nitrogen) was used to purify the product. The product was pumped on, at liquid-nitrogen temperatures, for 3–4 h and then checked in the mid-infrared spectrum for impurities. No SO_2, HNCO, or H_2O could be detected. For the DCN preparation, the entire apparatus was purged with D_2O, and then a hard vacuum of 1×10^{-4} torr was established prior to the addition of the reactants. The DCN was estimated from the infrared intensity data to be 97% deuterated.

The far infrared spectra were recorded from 33 to 500 cm^{-1} by using a Beckman IR-11 spectrophotometer. No bands were found below 100 or above 300 cm^{-1}. The atmospheric water vapor was removed by flushing the system with dry air. The instrument was calibrated by using atmospheric water vapor. The single beam energy was kept between 10–15% at all times. Various gain settings and scanning speeds were used to obtain the best presentation of the spectral data. A low temperature cell identical to the one described earlier[8] was used to examine the samples which were evaporated onto silicon support plates described elsewhere.[9] Spectra were recorded at various film thicknesses in order to confirm both the presence and the relative intensity of any given band. Whereas any individual far infrared spectrum contains some weak apparent absorptions in the generalized background, only those bands which could be reproduced at the same frequencies and relative intensities in all spectra are reported in Table I. Thus, the spectra shown in Figs. 1–3 are *original* spectra and not composite tracings. The spectra were recorded at ~100°K, and as a result all data pertain to the low temperature modification. The reported band centers are reliable only to ± 5 cm^{-1}. It was not possible to obtain data on the high temperature modification because of the limitations of our cryogenic equipment.

Results and Discussion

GROUP THEORY AND MOLECULAR SPECTRA

The lattice dimensions of the high-temperature modification are $a = 4.63 \pm 0.02$ Å and $c = 4.34 \pm 0.02$ Å and of the low-temperature modification: $a = 4.13 \pm 0.02$ Å, $b = 4.85 \pm 0.02$ Å, and $c = 4.34 \pm 0.02$ Å. As previously mentioned, the symmetry of the high-temperature modification (hereafter denoted HTM) is $C^{9}_{4v} - I_{4mm}$ and that of the low-temperature phase (LTM) is $C^{20}_{2v} - I_{mm}$. The group theory of Hornig and Halford[10] give the results shown below [$\Gamma(AT)$ designates acoustic translations, and $\Gamma(OL)$ designates optical librations] first for the HTM [(1) and (2)] and then for the LTM,

$$\Gamma(AT = A_1 + E \tag{1}$$
$$\Gamma(OL) = E \tag{2}$$
$$\Gamma(AT) = A_1 + B_1 + B_2 \tag{3}$$
$$\Gamma(OL) = B_1 + B_2 \tag{4}$$

The formation of the unique *c* axis gives rise to the LTM pyroelectricity and also to the splitting of the degenerate E mode into B_1 and B_2 components. Thus, the B_1 species and associated with motions along the *a* axis, the B_2 species with motions along the *b* axis, and the A_1 species with motions along the *c* axis.

The HCN spectrum is shown in Fig. 1 and the large arrows indicate the fundamental absorption bands arising from librational motion of the molecules. The overlay present in this figure (Curve A) is an alternate spectrum which the HCN often exhibited and we believe it to result from a different orientation of the

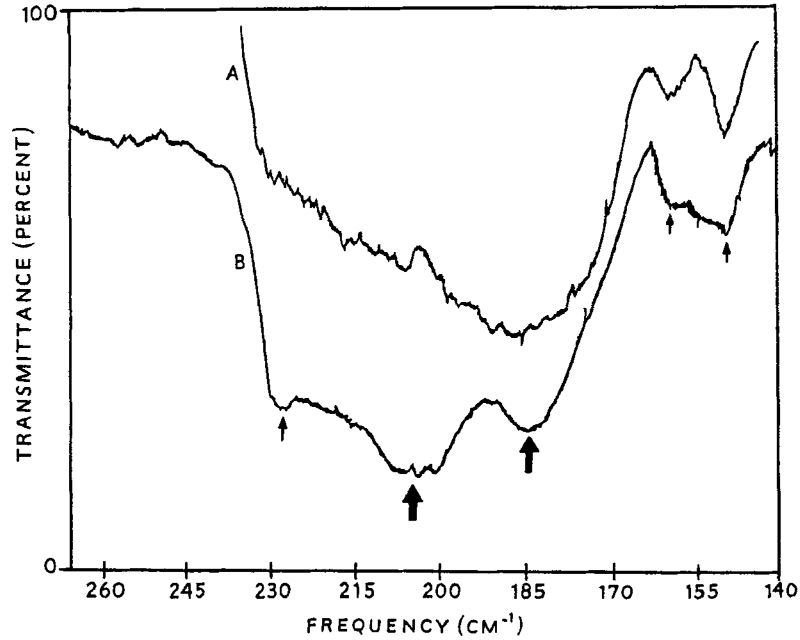

Figure 1. The far infrared spectrum of polycrystalline HCN (140–280 cm^{-1}). Top curve shows an alternate spectrum which we believe to result from a different orientation of the molecular film. The large arrows indicate the fundamental librational lattice modes.

molecular film. Whereas all samples used in recording the spectra were carefully annealed, it was not observed that these orientations interconverted. This is not to say that it is not possible, only that before the phenomenen could occur the film would resublime onto a metal portion of the cell. The orientation phenomenon seemed to be a random process.

The bands at 186 and 205 cm^{-1} in Fig. 1 are assigned as either the B_1 or B_2 components from the doubly degenerate E librations in the HTM. The overlay (A) in Fig. 1 likely represents en orientation of the crystal on the silicon plate such that the *AC* plane or *BC* planes are (see next section) parallel to the face of the sample support plate. This would account for the lack of definity in the overlay. It is possible, as pointed out by Pezolet and Savoie[5] that the effects of piezeolectric or pyroelectric may cause rather unpredictable behavior in a polycrystalline sample. The smaller

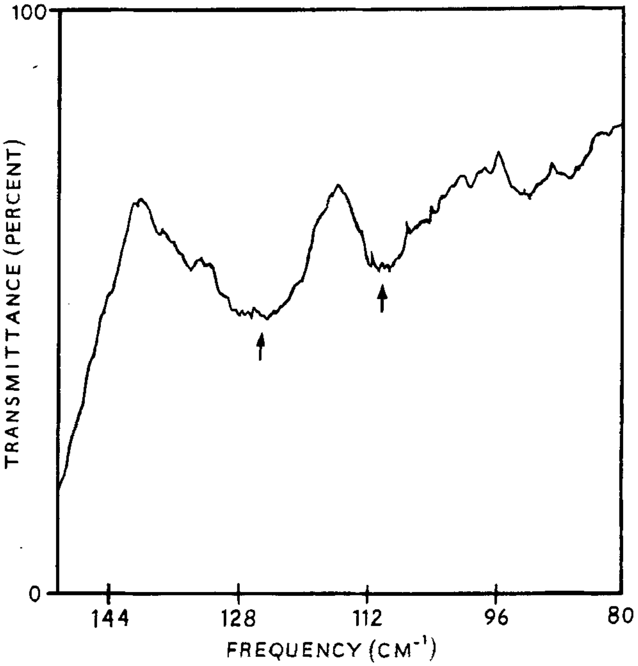

Figure 2. The far infrared spectrum of polycrystalline HCN (80–152 cm^{-1}).

arrows seen in Fig. 1 and Fig. 2 at frequencies *below* the main librational absorptions, are most probably due to either crystal disorder (including polymeric species—see for example reference 7) or anharmonic effects arising from combination or overtone frequencies of acoustic phonons. These bands were present in all spectra recorded for HCN. The shoulder, in Fig. 1, at 228 cm^{-1}, and the enhanced intensity and breadth of the 205 cm^{-1} absorption may be due to simultaneous observation of the absorption and reflection maxima of the librational modes. That is to say, the 228 cm^{-1} band could be the reflection component of the 205 cm^{-1} band and the reflection maxima of the 186 cm^{-1} band would then fall on or very near to the 205 cm^{-1} absorption band assuming the separations are equal on the basis of structural considerations. Pezolet and Savoie discuss possible origins of "anomalous features" seen in their Raman spectra; we agree with these

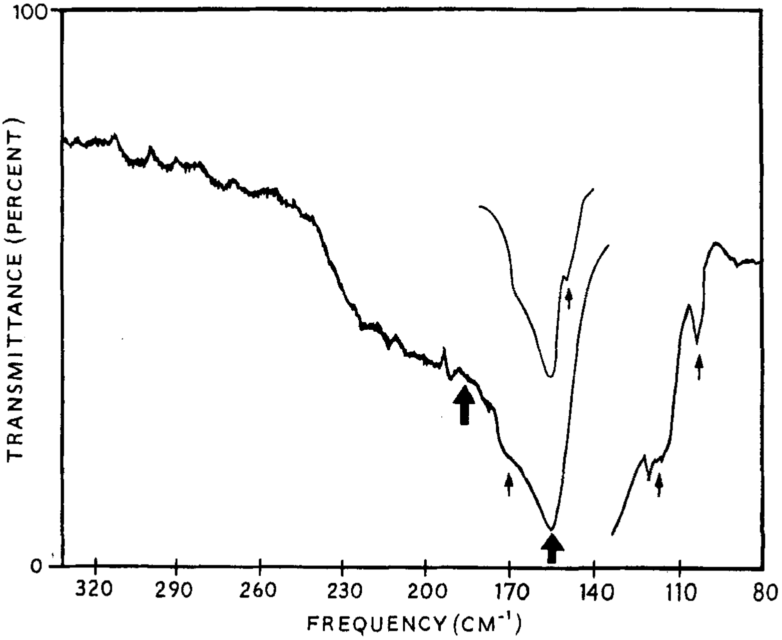

Figure 3. The far infrared spectrum of polycrystalline DCN (80–320 cm^{-1}). The large arrows indicate the fundamental librational lattice modes.

authors that the most likely explanation of these phenomena arises from the piezoelectric or pyroelectric effects. The crystal structures is almost surely correct since the NQR results[11] are also consistent with the structures proposed by Lipscomb and Dulmage.

The corresponding librational features are seen in Fig. 3 for DCN. Again the larger arrows represent the absorption bands (also the transverse components of the reflection bands) arising from librational motion of the DCN moiety in the unit cell. The absorption maxima for the two librational components are found at 160 and 180 cm^{-1} whereas their corresponding reflection maxima must lie in the broad sloping shoulder between 185 and 240 cm^{-1}. As noted above for HCN, the smaller arrows at lower frequencies in Fig. 3 may be disorder absorptions or anharmonic features We tend to favor the latter, as the weaker bands are shifted to lower frequencies by an isotopic shift parameter equal to that expected for modes of translational origin (see Table 1). It is clear that in systems where absorption and reflection bands are simultaneously observed (see for example reference 12) that the absorption frequency is very nearly equal to the transverse

TABLE 1

Observed frequencies		*Calculated* isotopic shift parameter	*Observed* isotopic shift parameter	*Calculated* DCN frequency (from Column 3)	*Assignments*
HCN	DCN				
228 (vs)[a]	224 (s)	0.982	0.982	224	R^b
205 (vs)	182	0.904	0.876	(185)[c]	B_1 or $B_2L \epsilon R$
185 (vs)	160 (s)	0.904	0.865	167	B_1 or B_2L
158 (w)	——	0.982	——	(155)[c]	T^d
149 (w)	146 (vs)	0.982	0.980	146	T^d
127 (vw)	117 (vw)	0.982	0.921	124	T^d
112 (vw)	105 (vw)	0.982	0.938	110	T^d

[a] Quantities in parenthesis are estimated intensities where v is very, s is strong, m is medium, and w is weak.

[b] T designates anharmonic translational mode; L designates librational mode; R designates a reflection component.

[c] Indicates frequencies not directly observed.

[d] See text for the possible origin of these translational modes.

component of the reflection band. Further, the high frequency cut off of this reflection or absorption-reflection band will be very nearly equal to ω_l the longitudinal component of the reflection maximum.[13] In order to lend justification to the above assignments we have used the extended Lyddane–Sacks–Teller relation and the Clausius–Mosotti equation (vide infra) to calculate the optical dielectric constant. These equations are respectively,

$$\prod_{\nu=1}^{n} \Omega_{l\nu}^2 / \Omega^2{}_{t\nu} = k_s / k_0 \tag{5}$$

where Ω_{l_ν} is the longitudinal component of the νth frequency, $\Omega_{t\nu}$ is the transverse component of the νth frequency, k_s is the static dielectric constant (recall this was measured by Smyth and McKnight[11]) and k_0 is the optical dielectric constant. The Clausius-Mosotti equation relates the optical dielectric constants to the polarizability:

$$\frac{k_0 - 1}{k_0 + 2}\left(\frac{M}{d}\right) = \frac{4\pi N}{3}\alpha_0 \tag{6}$$

where k_0 is defined above, M is the molecular weight, d is the density, N is Avogadro's number and α_0 is the molecular polarizability. This latter equation must be used with caution since the dielectric cavity in which the molecule sets is spherical and the dielectric medium is isotropic.

The k_0 values calculated via the assignments proposed and the LST relation in Eq. (5) compare favorably with that calculated by Eq. (6) i.e. 1.6 for the LST relation and 1.8 via the Clausius-Mosotti equation. It will be shown in the next section that the *single crystal* medium is not isotropic; however, our data were taken from polycrystalline samples. Whereas, the good agreement between the two k_0 values is likely fortuitous, the fact that these values are close may reflect the experimental conditions. Indeed, other workers[14,15] have reported observing unexpected optical components which have been identified in cubic crystals as p-polarized longitudinal optic phonons. Since both of these authors agree that size, shape and orientation of the sample may cause ω_l

to be observed, we feel that due to these features and the unusual optical properties of the LTM of HCN (see the following section) it is possible that ω_l optic phonons bands are present in the HCN and DCN spectra.

PYROELECTRICITY, DIELECTRIC ANISOTROPY AND OPTICAL ANOMALIES

Hydrogen cyanide blongs to a particularly unique crystal symmetry system which allows it to develop electric moments as a function of temperature. This effect is defined as pyroelectricity. For a crystal to be pyroelectric more restrictive symmetry conditions are necessary than for piezoelectricity, hence a pyroelectric crystal may also display piezoelectric effects. We have noted in the previous section that the observed bands may be understood in terms of absorption and reflection components based on the favorable agreement of the optical dielectric constant calculated by two independent methods. Wilson[16] has shown that the optical dielectric constant, k_0, may be written as follows:

$$k_0 = \tfrac{1}{3}(k_1 + k_2 + k_3) \tag{7}$$

where k_1, k_2, and k_3 represent the orthogonal components of k_0 in the crystal. If the crystal is isotropic then any individual component is equal in magnitude to k_0. However, in HCN almost the exact opposite case is true, i.e. two of the components are nearly zero while the third is approximately three times as large as k_0. If this is the situation we may rewrite Eq. (7) as

$$k_0 = \tfrac{1}{3}(k_\parallel + 2k_\perp) \tag{8}$$

Where $k_\parallel$ is parallel to the C crystallographic axis and $k_\perp$ is parallel to either the A or B crystallographic axis and very nearly isotropic in either direction. This form of the dielectric constant given by (8) is identical to that displayed by other pyroelectric systems. In particular, $k_\parallel$ for these systems completely dominates the right side of Eq. (8). This effect may be illustrated numerically be examining the dielectric constants for the tourmaline crystal which is frequently referred to as the classical example of the pyroelectric system.[17] For tourmaline, $k_{\parallel}$ equals 7.1 whereas k_0 is 2.36 so that $2k_{\perp} \approx 0$.

It should be clear from the above comments that this effect can cause two very difficult problems in further studies of HCN. First, any temperature gradient across a sample support plate or within a Raman cell will lead to inhomogeneous optical properties in the sample causing the spectra to contain ambiguous or anomalous properties. Second, the extreme dielectric anisotropy displayed by HCN crystals with $k_{\parallel}$ either parallel or perpendicular to the sample support plate. Until one is able to effect isothermal conditions within the entire sample, the first problem will remain. At this time, the likely choice of instrument to accomplish this temperature control for further reflection studies in the far infrared would be an interferometric sytem (because of the comparatively small sample area necessary) operating at liquid helium temperatures if possible.

This dielectric anisotropy also explains the very large intermolecular intensities observed in the far-infrared spectra for this substance compared to those studied previously. We estimate that, per millimeter of sample pressure, the HCN external lattice vibrations were close to 100 times more intense than any system studied earlier. In addition, since the sample may have two preferred orientations on the silicon plate, the large dielectric anisotropy may well be the explanation for the two types of observed spectra as shown in Fig. 1. The overall significance of this anisotropy is that the HCN crystal system can be well represented by a one-dimensional lattice, i.e., the principal forces holding the system together all lie along the c axis. This effect could explain the premelting phenomenon observed by earlier workers;[1,2] as the thermal energy increases, the long rods of HCN slowly begin to act more and more like chains, thus allowing increased dipole orientations and a larger and larger contribution to the dielectric constant. Finally at the melting point the chains break into pieces which, on the average, are made up of three molecules per fragment.[6,17,18]

In the introduction it was pointed out that HF, H_2O_2, CH_3OH, etc., all showed deviations in the dipole moment-dielectric constant plot but that none were as dramatic as those for HCN. The colinearity of the molecular and crystal axes and the dielectric anisotropy accompanying this coincidence appear to be the chief causes of the apparent strong hydrogen bond in crystalline HCN. Furthermore, the proposed contribution[6] of the $H - C^{+} = N^{-}$ type of resonance structures is greatly strengthened by the above proposed dielectric argument.

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