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Infrared Intensities of Crystalline HCN and DCN

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The absolute infrared intensities of crystalline HCN and DCN were measured at the temperature of liquid N_2. In comparison with the gaseous values, both stretching fundamentals (ν_1, ν_3) exhibited a striking increase in the integrated absorption, while the bending (ν_2) was almost unchanged. From the observed intensity change, the change in the dipole-moment derivatives with respect to the molecular internal coordinates was calculated to be $\partial \Delta \boldsymbol{M}/\partial r_{\mathrm{C\equiv N}}=1.43$ D/Å and $\partial \Delta \boldsymbol{M}/\partial r_{\mathrm{C-H}}=2.01$ D/Å, those values were chosen from two alternative possibilities as the more probable set. The significance of these values, however, is somewhat peculiar to the optically-active crystalline vibrations, so they were then resolved into derivatives with respect to purely intramolecular and intermolecular coordinates: $[\partial \Delta \boldsymbol{M}/\partial r_{\mathrm{C-H}}]=0.58$ D/Å and $[\partial \Delta \boldsymbol{M}/\partial r_{\mathrm{H\cdots N}}]=-1.43$ D/Å. The general intensity features were reasonably interpreted by considering the contribution of a charge-transfer structure to the H–N hydrogen bonding.

The study of the infrared intensity in condensed phases is supposed to be a potential source of information about the nature of interactions between molecules. It is quite common knowledge that the formation of a hydrogen bond, X–H···Y, gives rise to a striking increase in the integrated absorption of the X–H stretching vibration, as well as to a large frequency shift and a broadening of the band. This intensity behavior has thus far been qualitatively interpreted as being mainly due to the vibronic contribution of the charge-transfer effect.[1–3] In the present investigation, a somewhat detailed study of the intensity was attempted so as to obtain a closer understanding of the electronic features in the hydrogen-bonding interactions. Then, crystalline hydrogen cyanide was chosen as a particularly favorable system for an analytical study of the intensity change, because, besides its simple molecular structure, it forms strictly linear hydrogen-bonded chains, as has been shown by Dulmage and Lipscomb's X-ray data.[4]

Actually, the crystal has two modifications bounded at 170°K, that is, the high-temperature tetragonal phase described by the space group C_{4v}^{9}-*I4mm* and the low-temperature orthorhombic phase described by C_{2v}^{20}–*Imm*. In either phase, HCN (DCN) molecules are linked in a straight chain with a C–H···N distance of 3.18 Å, and such chains are assembled parallel with each other (Fig. 1). So far as the hydrogen bonding is concerned, the difference between these two phases seems to be of little significance; therefore the low-temperature phase crystal, which is experimentally more tractable, has been dealt with exclusively in the present work.

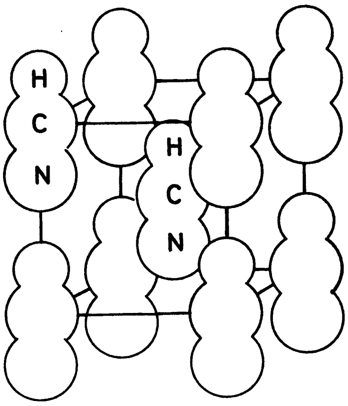

Fig. 1. Crystal structure of hydrogen cyanide (low temperature phase).

The infrared spectrum of crystalline (low-temperature-phase) HCN has been obtained by Hoffmann and Hornig,[5] and the Raman spectra of HCN and DCN crystals were investigated by Pézolet and Savoie[6] recently. In general these observations accord with the above crystal structure and indicate the formation of fairly strong hydrogen bonds. Pézolet and Savoie also observed high-frequency shoulders for each band in their spectra; they ascribed them to longitudinal vibrations, which will be discussed later in relation to the infrared intensities. Now, Hoffmann and Hornig[5] observed a remarkable change in the relative intensities from gaseous to crystalline HCN, and afterwards the absolute intensity was determined exactly for gaseous HCN and DCN by Hyde and Hornig.[7] In comparing the gaseous and crystalline relative intensities described above, it is noticeable that a striking change, certainly an intensification, has occurred not only in the usual C–H stretching vibration, ν_3, but also in the C≡N stretching, ν_1. A possible cause of the latter may be looked for in an increased mixing of the C–H stretching coordinate into the normal coordinate, Q_1, whose effect is further enhanced by the magnified value of the dipole-moment derivative, $\partial\mu/\partial r_{\mathrm{C-H}}$. However, a brief consideration suggests that the $\partial\mu/\partial r_{\mathrm{CN}}$ may also be influenced by the hydrogen bonding in the crystal. The intensity change in the acceptor-group vibration has been established for some carboxylic acid dimers by Wenograd and Spurr,[8] but

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[1] G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).

[2] H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).

[3] K. Szczepaniak and A. Tramer, *J. Phys. Chem.*, **71**, 3035 (1967).

[4] W. J. Dulmage and W. N. Lipscomb, *Acta Crystallogr.*, **4**, 330 (1951).

[5] R. E. Hoffmann and D. F. Hornig, *J. Chem. Phys.*, **17**, 1163 (1949).

[6] M. Pézolet and R. Savoie, *Can. J. Chem.*, **47**, 3041 (1969).

[7] G. E. Hyde and D. F. Hornig, *J. Chem. Phys.*, **20**, 647 (1952).

[8] J. Wenograd and R. A. Spurr, *J. Amer. Chem. Soc.*, **79**, 5844 (1957).

the change in hydrogen cyanide is far more conspicuous and may be adequate for the attainment of an unambiguous interpretation.

Experimental

HCN and DCN were obtained by adding aqueous H_2SO_4 or D_2SO_4 to potassium cyanide. The evolved gas was dried over calcium chloride and magnesium perchlorate, and was purified by repeated distillation within a vacuum line. The infrared spectra did not show any indication of impurities except for a minor amount of HCN mixed in the DCN sample, whose deuterium concentration was estimated at 85% from the intensity of the HCN bands.

The infrared spectra of the low-temperature-phase crystals were recorded on a Perkin-Elmer model 125 spectrophotometer. Thin solid films of the samples were obtained by spraying the gas onto a window cooled with liquid nitrogen in a conventional vacuum cell. The thickness of the deposited films was measured by monitoring the interference fringes at a fixed wavelength of one micron during the formation of films on a KRS-5 window.[9] The density at 77°K was calculated based on the X-ray data,[4] and the refractive index for the wavelength of one micron was obtained by extrapolating Anderson *et al.*'s[9a] dispersion data and by adjusting it for 77°K using Lorentz-Lorenz formula. The rate of film growth was about 3 to 4 microns per hour. The slit width was so chosen that it was always less than one-third of the half-width of the measured band.

The experimental quantity,

$$B' = \int_{\text{band}} \ln (T_0/T)\mathrm{d}\nu$$

where T/T_0 is the observed transmittance, was calculated by the use of Lagrange's polynomial of the third order fitted to four successive points among 13 to 20 experimental points. The integrations were carried out over such frequency ranges as cover more than 12 times the half-windth.

Results and Discussion

The Beer's law plots for the fundamental bands are illustrated in Figs. 2 and 3, where n is the concentration in mol/cm^3 and where l is the thickness in cm. The integrated absorption coefficient,

$$A = \int \alpha \mathrm{d}\nu$$

was obtained from the limiting slope of the curves, it is given in Table 1, and compared with the gaseous value by Hyde and Hornig.[7] If the Lorentz curve is assumed for the band shape, the errors caused by the finite slit width and the finite integration range are estimated to be about 3% and 6% at most,[10] but the composite error in the experiment may be roughly estimated at 20% at the maximum, considering other sources of error, such as in drawing the base-line and in the film-thickness determination. It may be seen that both stretching absorptions are intensified very much, whereas the bending intensity is almost unchanged, despite its considerable shift in frequency.

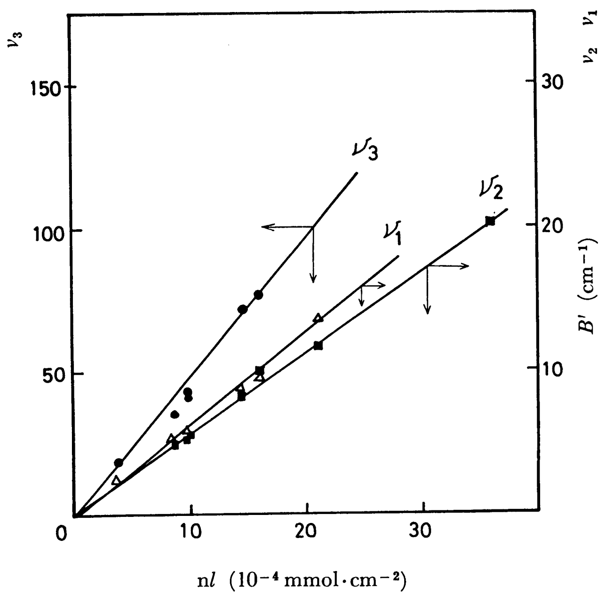

Fig. 2. The Beer's law plots of fundamental bands of crystalline HCN.

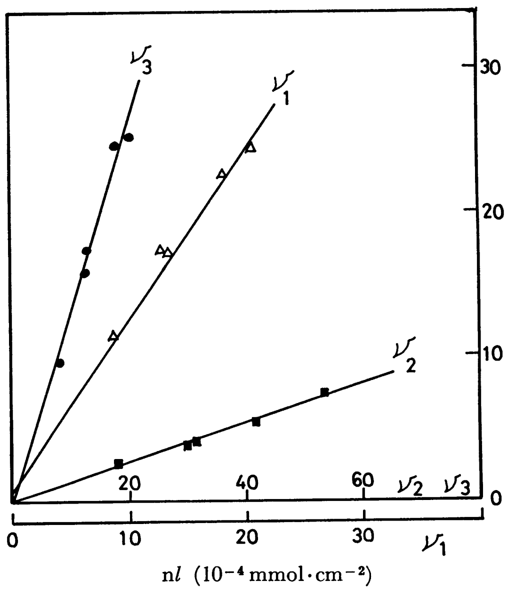

Fig. 3. The Beer's law plots of fundamental bands of crystalline DCN.

In Table 1 are also included the relative intensity values predicted by Pézolet and Savoie[6] based on their Raman observation, as well as those measured by Hoffmann and Horig.[5] The correspondence between the predicted values and the present observations is surprisingly good, supporting the conclusion of Pezolet and Savoie about the longitudinal and transverse frequencies.[11] The observed intensity, A, is related to the dipole-moment derivative by:

$$A_i = (N\pi/3c^2)\,|\partial \boldsymbol{M}/\partial q_i|^2, \tag{1}$$

where $\boldsymbol{M}$ is the dipole moment of the crystal and where q_i is a molecular vibrational coordinate which partici-

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[9] J. L. Hollenberg and D. A. Dows, *J. Chem. Phys.*, **34**, 1061 (1961); *ibid.*, **37**, 1300 (1962).

[9a] J. L. Lowry and S. T. Anderson, *Proc. Roy. Soc.* (London), **A136**, 474 (1932).

[10] D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).

[11] In that case, however, there remains a question about the interpretation of the splitting of the ν_2 band also observed in the infrared spectra.

Table 1.

	Solid					Gas		
	freq. (cm^{-1})	A[a] (10^4 cm/mM)	rel. intensity H.H.[b]	rel. intensity P.S.[c]	$\partial M/\partial q$ (10^2 esu)	freq. (cm^{-1})	A (10^4 cm/mM)	$\partial \mu/\partial q$[e] (10^2 e.s.u.)
HCN								
ν_1	2099	0.518	1.0	1.0	0.81	2096.9	0.00143	0.045
ν_2	828, ~840	0.462	1.4	1.2	0.57	712	0.457	0.57
ν_3	3130	3.94	5.7	7.2	2.36	3311.4	0.540	0.88
DCN								
ν_1	1885	0.99		1	1.18	1925.3	0.0269	0.20
ν_2	649	0.141		1/6	0.32	569	0.137	0.31
ν_3	2545	1.07		1	1.23	2630.3	0.305	0.66

a) Corrected value for the field effect by multiplying 1/1.22 given from Polo-Wilson's equation (Ref. 17).
b) Measured by Hoffmann and Hornig (Ref. 5).
c) Predicted by Pézolet and Savoie (Ref. 6).
d) Measured by Hyde and Hornig (Ref. 7).
e) Calculated based on the Hyde and Hornig's intensity (see text).

pates in an optically-active ($\boldsymbol{k}=0$) normal coordinate, Q_i, of the crystal. In the oriented gas model, q_i is equivalent to the corresponding molecular normal coordinate; this, however, may be unsatisfactory in the present system of strong interactions.

Since the unit cell contains only a single molecules,[4] Q_i is given by the normalized total sum of q_i:

$$Q_i = n\sum_j (q_i)_j, \tag{2}$$

where n is a normalization constants and where $\sum_j$ implies a summation over all the molecules in the crystal. q_i may be expressed in terms of molecular internal coordinates as:

$$q_i = \sum_k L^{-1}_{ki} r_k, \tag{3}$$

so that the dipole-moment derivative with respect to r_k is given by:

$$\frac{\partial M}{\partial r_i} = \sum_j L^{-1}_{ji} \frac{\partial M}{\partial q_j}. \tag{4}$$

Now, let us consider the quantity

$$\Delta \boldsymbol{M} = \boldsymbol{M} - \sum_i \boldsymbol{\mu}_i. \tag{5}$$

which represents the contribution from the intermolecular interaction, where $\boldsymbol{\mu}_i$ is the dipole-moment of an isolated molecule, i, and, $\sum_i \boldsymbol{\mu}_i$ is equivalent to the $\boldsymbol{M}$ for the oriented gas model. Eq. (4) is also valid for $\Delta \boldsymbol{M}$; that is,

$$\frac{\partial \Delta M}{\partial r_i} = \sum_j L^{-1}_{ji} \frac{\partial \Delta M}{\partial q_j}, \tag{6}$$

(Bending vibration, ν_2)

As may be seen in Table 1, the gaseous and solid intensities of ν_2 coincide well within the limits of experimental error for both HCN and DCN. This may suggest that the charge distribution in a molecule was changed little as a result of hydrogen bonding. However, this mode of vibration necessarily involves a compensating rotation (or a libration in solids) of the molecule, so that the observed intensity includes the contribution from the accompanying rotation of the molecular dipole moment. It has been shown[12] from the gaseous data that the physically unambiguous quantity, $\boldsymbol{P}_R$,[13] which is obtained by subtracting such a rotational contribution from the observed $\partial\mu/\partial q$, is in closer agreement between HCN and DCN, resulting in an average value of 1.08 D/rad, with the polarity shown in Fig. 4. As the molecular dipole moment in solids is not known (although it could be estimated from the intensity of a librational mode), the corresponding quantity in solids can not now be determined. The values tentatively given in Table 2 were calculated assuming that the dipole moment was equal to the gaseous value, 3.00 D.[14] At all events, such a close agreement between gaseous and solid data suggests no remarkable change in the dipole moment due to the hydrogen bonding in this case.

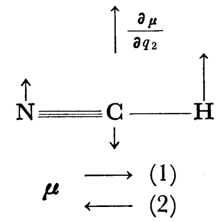

Fig. 4. Relative polarity of $\boldsymbol{\mu}$ and $\partial\boldsymbol{\mu}/\partial q_2$ in hydrogen cyanide.

(Stretching vibrations ν_1 and ν_3)

If the stretching coordinates of the C≡N and C–H (C–D) bonds are expressed by r_1 and r_2, Eq. (4) for these parallel modes may be solved to give $\partial\boldsymbol{M}/\partial r_1$ and $\partial\boldsymbol{M}/\partial r_2$ from the observed $\partial\boldsymbol{M}/\partial q$. The $\boldsymbol{L}^{-1}$ matrix was obtained on the basis of the force constants, which were chosen so as to minimize the standard deviation of the frequency for both HCN and DCN. For the sake of consistency, the $\boldsymbol{L}^{-1}$ was also calculated for

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[12] J. Overend, "Infrared Spectroscopy and Moelcular Structure," ed. by M. Davies, Elsevier Publ. Comp., Amsterdam (1963), p. 374.

[13] B. Crawford, Jr., *J. Chem. Phys.*, **20**, 977 (1952); A. D. Dickson, I. M. Mills, and B. Crawford, Jr., *ibid.*, **27**, 445 (1957).

[14] C. H. Towns and A. L. Shawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955).

Table 2.

	rel. sign $\partial M/\partial q_2$, μ[a]	$p_R(\nu_2)$ HCN (D/rad)	$p_R(\nu_2)$ DCN (D/rad)	rel. sign $\partial M/\partial q_1$, $\partial M/\partial q_3$	$\partial M/\partial r_1$ HCN (D/Å)	$\partial M/\partial r_1$ DCN (D/Å)	$\partial M/\partial r_2$ HCN (D/Å)	$\partial M/\partial r_2$ DCN (D/Å)
Gas	(1)	1.06	1.11	++	−0.33	−0.47	1.06	1.08
	(2)	−0.20	0.25	+−	−0.62	−1.67	1.02	0.58
Solid	(1)	1.10	1.14	++	1.19	0.86	3.18	2.98
	(2)	−0.24	0.21	+−	−4.43	−5.72	2.31	−0.28
average								
Gas	(1)	1.08		++	−0.40		1.07	
Solid	(1)	1.12		++	1.03		3.08	

a) (1) and (2) in this column correspond to those in Fig. 4.

Table 3.

relative sign $\partial\mu/\partial r_1$ (gas), $\partial M/\partial r_1$ (solid)	$\partial\Delta M/\partial r_1$ (D/Å)	$\partial\Delta M/\partial r_2$ (D/Å)	$[\partial\Delta M/\partial r_2]$ (D/Å)	$[\partial\Delta M/\partial r_3]$ (D/Å)
(i) −+	1.43	2.01	0.58	−1.43
(ii) ++	0.63	4.15	3.52	−0.63

Table 4.

	Gas	Crystal
K(CH)	5.799	5.126
K(CN)	17.933	18.542
K(CH, CN)	−0.167	−0.158
H	0.271	0.204

mdyn/Å

$$2V=K(\mathrm{CH})r_2^2+K(\mathrm{CN})r_1^2+2K(\mathrm{CH,\,CN})r_1r_2+Hr_{\mathrm{CH}}r_{\mathrm{CN}}\Delta\phi^2.$$

the gas by the same procedure, Hyde and Hornig[7] adopted a somewhat different criterion in determining their force constants. In Table 4 are given the force constants thus obtained. The dipole moment derivatives $\partial M/\partial r$'s, are summarized in Table 2 and there compared with the corresponding gaseous quantity, $\partial\mu/\partial r$, where the proper choice of a relative sign for $\partial M/\partial q_1$ and $\partial M/\partial q_3$ is definitely (++).

It is remarkable that $\partial M/\partial r_1$ and $\partial M/\partial r_2$ have the same direction of polarity in the solid, while they are opposite in the gas. There may be two possibilities in accounting for the additional contribution, $\partial\Delta M/\partial r$. According to the choice of opposite or equal signs for $\partial M/\partial r_1$ (solid) and $\partial\mu/\partial r_1$ (gas), either (i) or (ii) in Table 3 is obtained.

Now, if an additional coordinate, r_3, is introduced to give the N⋯H stretching, the condition:

$$r_1+r_2+r_3=0 \tag{7}$$

is always realized for the optically-active modes in the crystal. Therefore, the dipole-moment derivatives dealt with thus far, which conform with this condition, of course, may be given by the expressions:

$$\begin{aligned}\frac{\partial\Delta M}{\partial r_1}&=\left[\frac{\partial\Delta M}{\partial r_1}\right]-\left[\frac{\partial\Delta M}{\partial r_3}\right]\\ \frac{\partial\Delta M}{\partial r_2}&=\left[\frac{\partial\Delta M}{\partial r_2}\right]-\left[\frac{\partial\Delta M}{\partial r_3}\right]\end{aligned} \tag{8}$$

where the bracketed derivatives imply that they have no connection with Eq. (7). In other words, the dipole-moment derivatives as given from Eq. (6) include inevitably a part which is properly attributable to a wholly intermolecular displacement, $[\partial\Delta M/\partial r_3]$.

As the C–N bonding electrons are supposed to be little involved in the hydrogen bonding, the $[\partial\Delta M/\partial r_1]$ in Eq. (8) may well be neglected in the following. Then, according to (i) or (ii) in Table 3,

$$\begin{aligned}&\qquad\qquad\qquad\quad\ \ (\mathrm{i})\qquad (\mathrm{ii})\\ &-[\partial\Delta M/\partial r_3]\approx\partial\Delta M/\partial r_1=1.43\ \text{or}\ 0.63\ \mathrm{D/Å}\\ &[\partial\Delta M/\partial r_2]\\ &\quad=\partial\Delta M/\partial r_2+[\partial\Delta M/\partial r_3]\approx 0.58\ \text{or}\ 3.52\ \mathrm{D/Å}\end{aligned}$$

where the positive value of the derivatives indicates that the moment is increased in the direction of $\overset{-}{\mathrm{N}}\equiv\mathrm{C}\text{–}\overset{+}{\mathrm{H}}$ for the stretching of the bond.

As is commonly recognized, the hydrogen-bond formation may be described properly in terms of electrostatic and charge-transfer interactions. That is, an appropriate wave function for the C–H⋯N system may be:[15]

$$\Psi=c_1\phi_1+c_2\phi_2+c_3\phi_3 \tag{9}$$

where ϕ_i represents these structures;

$$\begin{array}{lllll}\phi_1; & \mathrm{C—H} & \mathrm{N} & (\mathrm{I}) & \\ \phi_2; & \mathrm{C^-\ H^+} & \mathrm{N} & (\mathrm{II}) & \qquad(10)\\ \phi_3; & \mathrm{C^-\ H} & \!\!\!\text{——}\mathrm{N^+} & (\mathrm{III}). & \end{array}$$

Although the contribution of ϕ_2 may possibly be of greater importance in stabilizing the system, the vibrational change of the dipole moment is mainly ascribable to ϕ_3. This is because not only does the structure III have a much greater inherent moment than II, but also the weight of III in the Ψ is expected from theoretical consideration to be more susceptible to the vibrational displacement than that of II. This latter point is supported by the results of Coulson and Danielsson's[15] semi-empirical calculation of the O–H⋯O system. Therefore, the (i) set above corresponds to the case in which the approach of the H—N distance is far more effective in causing the charge transfer than the C–H stretching, and the (ii) set, *vice versa*.

Now, in order to obtain an approximate idea, the additional moment due to the contribution from the structure III may be given by:

$$\Delta M=c_3^2Re, \tag{11}$$

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[15] C. A. Coulson and U. Danielsson, *Ark. Fys.*, **8**, 239, 245 (1954).

where the intrinsic moment of the structure III is roughly equalized to the C–H⋯N distance, R, multiplied by the electronic charge, e. Then,

$$[\partial \Delta \boldsymbol{M}/\partial r] = e(c_3^2 + 2c_3R[\partial c_3/\partial r]), \tag{12}$$

where r may be either r_2 or r_3 and where the brackets imply the same as before. The size of c_3^2 has been estimated at a few per cent even in the O–H⋯O case, so ec_3^2 may be by far smaller than any possible $[\partial \Delta \boldsymbol{M}/\partial r]$ value given before. Therefore, the relationship:

$$\frac{[\partial \Delta \boldsymbol{M}/\partial r_2]}{[\partial \Delta \boldsymbol{M}/\partial r_3]} \simeq \frac{[\partial c_3/\partial r_2]}{[\partial c_3/\partial r_3]} \tag{13}$$

may be approximately valid in the present case.

The value of this ratio can not be estimated empirically. However, it can be shown that Coulson and Danielsson's findings on the O–H⋯O system[15] quated above give this ratio a negative value definitely less than unity in size. This fact suggests that the set (i) in Table 3 is preferable.

Finally, let us mention the polarity of the dipole-moment derivatives. Strictly speaking, the sign of those derivatives is significant only in a relative sense, as is obvious from Eq. (1). However, it is fairly conclusive from the above discussions that $[\partial \Delta \boldsymbol{M}/\partial r_3]$ has the polarity of $H^+ \cdots N^-$ for $r_3>0$, and that then, $[\partial \Delta \boldsymbol{M}/\partial r_2]$ is the reverse. Therefore, the set (i) adopted above implies the following polarities of individual derivatives for $r_1,r_2>0$:

$$\partial \boldsymbol{M}/\partial r_1 \text{ (solid)} = 1.03 \quad (\cdots\overset{-}{\mathrm{N}}\overset{+}{\mathrm{C}}\text{–H}\cdots)$$

$$\partial \boldsymbol{M}/\partial r_2 \text{ (solid)} = 3.08 \quad (\cdots\mathrm{N}\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{H}}\cdots)$$

$$\partial \mu/\partial r_1 \text{ (gas)} = 0.40 \quad (\mathrm{N}^+\equiv\mathrm{C}^-)$$

$$\partial \mu/\partial r_2 \text{ (gas)} = 1.07 \quad (\mathrm{C}^-\text{–}\mathrm{H}^+)$$

Critical Considerations

There may be some argument because the above interpretation ignored the possible influences on the intensities other than hydrogen bonding. In fact, there have been found several cases without hydrogen bonding which showed many-fold changes in intensity from a gas to a solid.[16] It may be noticed, however, that the absolute magnitude of such a change was generally much smaller than the present observations, althought it resulted in a remarkable change in ratio for the bands of a small intrinsic intensity. On the other hand, the field effect is of different category and may give some error in the numerical results, because Polo-Wilson's equation[17] employed in Table 1 may not be very satisfactory.[18]

It has been implicitly assumed so far that the sample films were composed of randomly-oriented polycrystals. There may be little doubt about the crystalline nature of the samples, because the observed spectra showed an excellent correspondence to the Raman spectra,[6] for which the samples were crystallized much more carefully. On the other hand, Hoffmann and Hornig observed an apparent change in the relative intensities of the splitted ν_2 components depending on the depositing condition; they attributed this change to the formations of oriented crystals.

In the present work, the features of the ν_2 bands were similar to those of the more scattering films of Hoffmann and Hornig which were looked on as less oriented, and were almost unchanged for various film thicknesses and different window materials. Accordingly, the orientation effect does not seem to be very significant even if it does occur. The close proximity of the gaseous and solid ν_2 intensities may possibly support the above inference.

Supposing the orientation effect to be considerable, the most probable case is one with molecular axes parallel to a window surface, because the parallel bands were observed to have a reasonably great intensity; also Hoffmann and Hornig observed only a single component of ν_2 in their more oriented films. When this is the case, the observed intensity, A, should be multiplied by 1.33 for ν_2 and by 0.67 for ν_1 and ν_3 before applying Eq. (1). Even in this case, however, the essential matter in the discussions so far may be little disturbed, because the stretching and bending vibrations were dealt with quite separately.

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[16] J. L. Hollenberg and D. A. Downs, *J. Chem. Phys.*, **37**, 1300 (1962); G. M. Wieder and D. A. Dows, *ibid.*, **37**, 2990 (1962).

[17] S. R. Polo and M. K. Wilson, *ibid.*, **23**, 2376 (1955).

[18] H. Yamada and W. B. Person, *ibid.*, **40**, 309 (1964).