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Infrared Intensities of Crystalline NH_3 and ND_3

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The infrared spectra of crystalline ammonia were investigated by Reding and Hornig,[1] by Anderson and Walmsley,[2] and by Wolf, Rollar, and Wolf[3] for films deposited on a cold window, and interpreted on the basis of the cubic structure of the space group T^4, as given by X-ray diffraction.[4] However, Mauer and McMurdie[5] have reported that the X-ray pattern of such a deposited film can not be solely attributed to the cubic structure; they have suggested the intermixing of one or two non-cubic phases. Staats and Morgan[6] observed rather remarkable changes in the infrared spectra when they annealed the film or deposited it at a higher temperature, but they came to no definite conclusion concerning the structure of the film. The spectral changes mentioned above are so spectacular that the investigation of its origin is of great interest in connection with the role of hydrogen bonding in this crystal. In the present paper, the absolute infrared intensities of crystalline NH_3 and ND_3 films will be reported, and then the intensity behavior in the course of annealing will be described.

Experimental

Commercial NH_3 gas of a reagent grade was used without purification. The ND_3 was obtained by the reaction of Mg_3N_2 with D_2O; it was distilled several times to remove all traces of water. In both samples, no evidence of the impurities was observed in the infrared spectra except for a small amount of H-species remaining in the ND_3 sample, whose deuterium concentration was determined from the intensity of a remaining NH_3 band to be 95—97%. The measurement of the absolute intensity was made using a conventional vacuum cell with a KRS-5 window for depositing the sample. Another metal cell equipped with a wire heater and an extra chamber sealed with Ge and KRS-5 windows was used in observing the spectral changes by annealing. The sample films were formed on the inside surface of the Ge window, and the chamber was filled with helium gas (20—30 Torr) to suppress the dissipation of the film.

Results

The spectral features of the films deposited at 77°K were, in general the same, as those reported by Reding and Hornig,[1] as is shown in Fig. 1 (i). In evaluating the intensity, the density was assumed to be equal to the cubic value (NH_3; 0.861 gr cm^{-3} at 77°K) calculated from the X-ray data.[7] The refractive index at the wavelength of 1 micron, where the interference

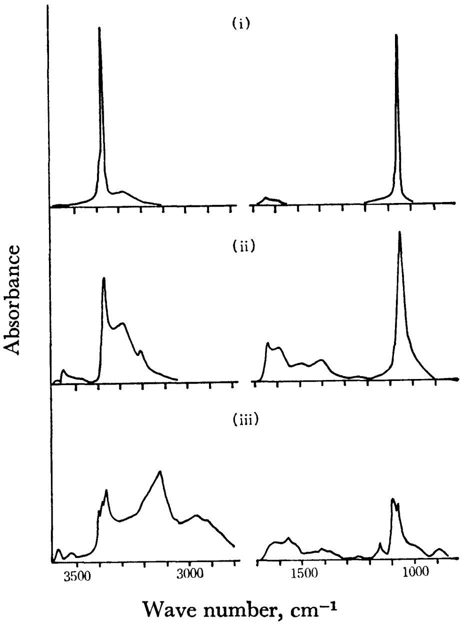

Fig. 1. Spectra of crystalline NH_3.
(i): Deposited at 77°K.
(ii): Deposited at 77°K and annealed to 180°K with suppressive gas.
(iii): Annealed up to a temperature higher than 180°K without suppressive gas.

TABLE 1.

	Cryst. (77°K)			Gas (Ref. 8)		
	Freq. cm^{-1}	A_i[a] $\times 10^4$ darks	$\lvert\partial\mu/\partial Q_i\rvert$ $\times 10^2$ cm$^{3/2}$sec^{-1}	Freq. cm^{-1}	A_i $\times 10^4$ darks	$\lvert\partial\mu/\partial Q_i\rvert$ $\times 10^2$ cm$^{3/2}$sec^{-1}
NH_3						
$\nu 1$	3223	1.92	1.65[b]	3337	0.045	0.31[b]
$\nu 3$	3378			3444	0.029	
$\nu 2$	1060	0.83	1.09	950	1.24	1.39
$\nu 4$	1646	0.12	0.29	1627	0.15	0.42
ND_3						
$\nu 1$	2318	1.08	1.24[b]			
$\nu 3$	2500					
$\nu 2$	815	0.53	0.87			
$\nu 4$	1196	0.097	0.26			

a) Values corrected for effective field by Polo-Wilson's equation with $n=1.47$ (Ref. 15).

b) Given as a quantity $\{(\partial\mu/\partial Q_1)^2+2(\partial\mu/\partial Q_3)^2\}^{1/2}$.

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1) F. P. Reding and D. F. Hornig, *J. Chem. Phys.*, **19**, 594 (1951); *ibid.*, **23**, 1053 (1955).

2) A. Anderson and S. H. Walmsley, *Mol. Phys.*, **9**, 1 (1965).

3) H. Wolf, H.-G. Rollar, and E. Wolf, *J. Chem. Phys.*, **55**, 1373 (1971).

4) H. Mark and H. F. Pohland, *Z. Krist.*, **61**, 532 (1925).

5) F. A. Mauer and H. F. McMurdie, reported at the 1958 meeting of the American Crystallographical Association, Milwaukee, Wisconsin.

6) P. A. Staats and H. W. Morgan, *J. Chem. Phys.*, **31**, 553 (1959).

7) I. Olovsson and D. H. Templeton, *Acta Crystallogr.*, **12**, 823 (1959).

8) D. C. McKean and P. N. Schatz, *J. Chem. Phys.*, **24**, 316 (1956).

TABLE 2.

	$\lvert\partial\mu_{(NH)}/\partial r_{NH}\rvert$	$\lvert\partial\mu/\partial S_2\rvert$	$\lvert\partial\mu/\partial S_4\rvert$
Gas (Ref. 8)			
NH_3	0.24	1.53	0.34
Cryst. (77°K)			
NH_3	1.20	1.38	(+) 0.29[c] (−) 0.24
ND_3	1.24	1.45	(+) 0.37 (−) 0.28
Average	1.22	1.42	0.26
	D/Å	D/rad	D/rad

c) Two possihle choices of relative sign in $|\partial\mu/\partial Q_3|$ and $|\partial\mu/\partial Q_4|$ are denoted by (+) and (−), where (−) combination gives better agreement in NH_3 and ND_3.

fringes were recorded for measuring the film thicknesses,[9] was estimated to be 1.47, on the basis of the data in the visible region. Linear Beer's law plots were obtained; the resulting intensities and dipole-moment derivatives are given in Tables 1 and 2. Since the two stretching absorptions were not well separated, the results were interpreted by assuming the vector addition of NH(ND) bond moment derivatives.[10] It is equivalent to assume that:[11]

$$|\partial\mu_{(NH)}/\partial r| = (3L_{11}^{2})^{-1/2}\{(\partial\mu/\partial Q_1)^2+2(\partial\mu/\partial Q_3)^2\}^{1/2}.$$

The derivatives with respect to the bending coordinate, *i.e.*, $(\partial\mu/\partial S_2)$ and $(\partial\mu/\partial S_4)$, are given by the following equations:

$$|\partial\mu/\partial S_2| = L_{22}^{-1}|\partial\mu/\partial Q_2| \pm L_{12}^{-1}|\partial\mu/\partial Q_1|$$
$$|\partial\mu/\partial S_4| = L_{34}^{-1}|\partial\mu/\partial Q_3| \pm L_{44}^{-1}|\partial\mu/\partial Q_4|.$$

In these expressions the contributions from stretching modes are relatively small and $|\partial\mu/\partial Q_1|$ is estimaed to be by far smaller than $|\partial\mu/\partial Q_3|$, so that the $|\partial\mu/\partial S|$'s were evaluated by ignoring $|\partial\mu/\partial Q_1|$ and assuming that the stretching intensities are to be attributed solely to $|\partial\mu/\partial Q_3|$. In general, the observed intensity change from gas to crystal shows the characteristic features of hydrogen-bonded systems.

When the films were annealed up to about 180°K,[12] the spectra showed rather striking changes, as was also found by Staats and Morgan[6] mentioned above, although the present observations were not quite consistent with theirs. Figure 1 (ii) shows the spectra of NH_3 when the film deposited at 77°K[12] was annealed to 180°K[12] with the suppressive gas in the chamber, while (iii) shows the spectra when the film was annealed to a somewhat higher temperature than (ii) without suppressive gas.[13] Similar behavior was observed for ND_3 too. Although Staats and Morgan attributed the (iii) to the cubic phase, the preliminary results on the Raman spectra[14] seem to suggest that the (ii) is more likely to be cubic.

As the sample dissipation on annealing was considerable, no measurement of the absolute intensity was possible for (ii) and (iii). It may be pointed out, however, that the relative intensities in the various phases are appreciably different; the enhancement of the stretching band in the (iii) is particularly notable, suggesting still stronger hydrogen bonding in this phase than in the others.

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

[10] S. Ikawa and S. Maeda, *Spectrochim. Acta*, **24A**, 655 (1968).

[11] Symbols and subscrips are the same in Ref. 8.

[12] Temperature of the copper block holding the window.

[13] When the vacuum seal of the sample chamber was poor.

[14] Will be published shortly.

[15] S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).