

The Vibrational Spectra of Molecules and Complex Ions in Crystals. V. Ammonia and DeuteroAmmonia

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J. Chem. Phys. **18**, 296 (1950); 10.1063/1.1747622



the dielectric constant of several concentrations of the polymer in benzene solutions. The cell was composed of three concentric metal cylinders enclosed in a glass tube. This cell has been used for a number of years in this laboratory for the determination of the dipole moments of low molecular weight compounds. Its capacitance was measured by the heterodyne beat method at a frequency of 1.5 Mc, which is well outside the dispersion range.

If M is the molecular weight of each chain unit, that is to say, the molecular weight of the polymer molecule is N_0M , then, providing N_0 is large compared with unity, it may be shown that

$$\bar{\mu}^2/N_0 = (9kT/4\pi A)[P_\infty - M(n^2 - 1)/d_1(n^2 + 2)],$$

where A is Avogadro's number, n is the index of refraction of the solute, and P_∞ is the value at infinite dilution of

$$P = M \frac{100 - x}{x} \left[\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} \frac{100}{(100 - x)d_{12}} - \frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{1}{d_0} \right].$$

In this expression, x is the weight percent of polymer, ϵ is the

dielectric constant and d is the density. The subscripts 0, 1, and 12 refer to solvent, polymer, and solution, respectively.

Complete dielectric measurements were taken on two different batches of polymer. The average results obtained were 1.45 D at 30°C and 1.46 D at 50°C with an estimated error of about 1 percent.⁸

To find the quantity desired, $\bar{\mu}^2/N_0\mu^2$, we need yet the moment of the free chain unit. This was assumed to be the same as that for *p*-chlorotoluene, and a value of 1.93 D was used. Although the values given in the literature do not agree too well with each other, this value was taken as an average of what appears to be the most reliable values. Assuming this value, we then obtain an experimental value of 0.56 for $\bar{\mu}^2/N_0\mu^2$.

⁸ The monomer, parachlorostyrene, was kindly furnished by the Dow Chemical Company. Their analysis showed it to be 99.6 percent of the para isomer. The dipole values stated have been corrected for a small amount of chlorine lost during polymerization.

The Vibrational Spectra of Molecules and Complex Ions in Crystals. V. Ammonia and Deutero-Ammonia*

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Infrared spectra of thin non-scattering films of NH_3 and ND_3 were obtained at -190°C . All four fundamentals of both compounds were observed with no evidence of inversion doubling of ν_2 . The crystal spectrum of NH_3 suggests a frequency near 3450 cm^{-1} for ν_3 in the gas. The spectra are in agreement with a molecular crystal having the reported x-ray symmetry T^4 . Two of the five torsional lattice vibrations were probably observed directly and one more strongly indicated in combination bands. A fourth lattice frequency of 53 cm^{-1} also occurs in combination bands. Since the coupling between the various internal vibrations and between the lattice and internal vibrations proved to be small, the potential function of the crystal was assumed to be separable into an internal and a lattice problem. A normal coordinate treatment of the internal vibrations fits all frequencies to better than one percent.

INTRODUCTION

AMMONIA is an example of a simple molecule which forms crystals of high symmetry in which the forces between the molecules are relatively large. It has been well studied in the gas phase; the additional features in the spectrum of the crystal arise from the effect of the crystalline field on the molecule and from coupling of the motions of the molecules. Since the

intermolecular field arises largely from hydrogen bonding, these effects are of some interest in that they afford a tool for the more detailed study of the hydrogen bond. Furthermore, it has been reported that it is necessary to postulate dimerization of the molecules in the crystal in order to interpret the Raman spectrum.^{1,2} It seems likely that the complications in the spectrum which this hypothesis was meant to explain are due instead to crystalline interaction and, indeed, it seems possible that a quantitative measure of such interaction may be obtained.

The ammonia crystal has been reported by x-ray investigators to be cubic, having space group symmetry $T^4(P2_13)$, with four molecules per unit cell.^{3,4} On the basis of present theory,^{5,6} the spectrum of fundamental vibrations should be interpretable in detail, and it should be possible to determine whether the hydrogen atoms conform to the x-ray symmetry.

Vibration	Gas Symmetry	Local Crystal Symmetry	Space Group	Activity In Crystal
ν_1, ν_2, T_z	A_1	A	A	R
R_z	A_2	E	E	R
ν_3, ν_4 R_x, R_y T_x, T_y	E	F	F	R, I

FIG. 1. Relation of the symmetry characteristics of the gas and the crystal for NH_3 and ND_3 . The ν 's are normal vibrations, the T 's and R 's translational and torsional lattice vibrations, and R and I indicate Raman and infrared activity, respectively.

* This work was supported in part by ONR, under contract N6ori-88, Task Order I.

¹ G. B. M. Sutherland, Proc. Roy. Soc. (London) **141A**, 546 (1933).

² A. Dadiou and K. Kohlrausch, Naturwiss. **18**, 154 (1930).

³ H. Mark and E. Pohland, Z. Krist. **61**, 532 (1925).

⁴ J. de Smedt, Bull. classe. sci. Acad. roy. Belg. **11**, 655 (1925).

⁵ D. F. Hornig, J. Chem. Phys. **16**, 1063 (1948).

⁶ H. Winston and R. S. Halford, J. Chem. Phys. **17**, 607 (1949).

The relation between the symmetry species of the free molecule (C_{3v}), the symmetry about the center of gravity of each molecule in the crystal (C_3), and the symmetry of the entire unit cell[†] containing four molecules (T) is given in Fig. 1.[‡] If the coupling between molecules is weak, it may be assumed that only vibrations of the same frequency in every molecule will couple; then Fig. 1 applies to the individual vibrations as well.

Only vibrations of species F may be active in the infrared spectrum of the crystal; consequently, vibrations of species A in the free molecule yield only one infrared active vibration in the crystal while each vibration of the doubly degenerate species E yields two infrared active vibrations. It should be noted that the appearance of doublets in this case is not owing to a removal of the degeneracy but to the fact that two different phases of coupling of the molecular motions give rise to infrared active fundamentals. All symmetry species may be active in the Raman spectrum so that vibrations of species A in the gas may give rise to two components in the Raman spectrum and vibrations of species E may give rise to three.

In addition to the internal vibrations of the molecules, the lattice vibrations, both motions of the center of gravity and torsional oscillations, may give rise to an infrared spectrum. Since the motions are strongly coupled, it is not strictly correct to separate the two categories, but it may be anticipated that the higher lattice frequencies are primarily torsions and the lower primarily translations. In particular, two infrared active vibrations may arise from the torsions about an axis perpendicular to the symmetry axis and one from the torsion about the symmetry axis. Similarly, there may be three infrared active vibrations arising from the translational motions; one of them, however, is the zero frequency limit of the acoustical branch of the lattice spectrum, so that only two may occur in the infrared spectrum.

EXPERIMENTAL METHOD

The ammonia and deuterio-ammonia films were studied at -190°C , using the apparatus and techniques successfully employed by Hoffman in the study of crystalline HCN and BF_3 .⁷ The low temperature cell employed was a transmission type cell similar to that previously described⁸ except that a side arm was attached to the outer jacket facing the cooling block. When gas was admitted through the side arm condensation took place, not only on the carrier plate but also on the surface of the cooling block and coolant reservoir. Using this procedure, it did not prove possible to obtain

any information as to the thickness of the films obtained. This technique is extremely simple and convenient and makes it possible to adjust the film thickness readily. It is applicable to any material which has a sufficiently low vapor pressure at the temperature of liquid nitrogen and permits full recovery of the material when the cell is warmed.

Following the method of Hoffman, the NH_3 and ND_3 were admitted into the cell in small bursts through a stopcock connecting the cell with a storage bulb in which they were kept at a pressure of up to 20 cm Hg. The gas condensed on a one mm thick KBr (or KRS-5) plate held in the cooling block by a rectangular ring. If thermal contact of the plate to the block was maintained with a small amount of Apiezon "M" grease applied to the edge of the plate, the temperature of the center of the plate, measured with a thermocouple inserted into a small hole drilled into the KBr, was only 5°C above that of the copper block after ten minutes of cooling. The films obtained by this procedure were essentially non-scattering, except in the case of the thickest film studied, and it transmitted 90 percent of the radiation at 2500 cm^{-1} .

The NH_3 used was obtained from the Mathieson Alkali Company and was rated at 99.98 percent pure. No evidence of impurities was found in the spectra.

The ND_3 was prepared by passing D_2O vapor over two U-tubes filled with Mg_3N_2 .⁹ It was found necessary to space the Mg_3N_2 with plugs of glass wool to keep it from packing so tightly that the D_2O vapor could not flow through. The tube containing the D_2O and the U-tubes of Mg_3N_2 were separated by a U-tube filled with mercury, whose level was controlled by a leveling bulb. This enabled the D_2O to be stored for extended periods of time without being in contact with hydrogen containing greases. Before generation of the ND_3 , the Mg_3N_2 was evacuated and heated to 350°C for two hours in order to remove traces of H_2O . The D_2O used[§] was rated as 99.57 percent pure. The resultant ND_3 was found to be approximately 98 percent pure by comparing the relative intensities of ν_2 of ND_3 (815 cm^{-1}) and ND_2H (909 cm^{-1}).

The spectra were obtained with a double beam spectrophotometer¹⁰ whose monochromator was taken from a Perkin-Elmer Model 12B spectrometer. CaF_2 , NaCl , KBr , and KRS-5 prisms were utilized in these investigations.

The investigation in the KRS-5 region was complicated by the presence of a high percentage of stray light. In order to attenuate it, a stainless steel plate, roughened with aluminex grinding compound No. 120, was employed as the mirror before the entrance slit. This scattering filter reduced the stray light from 65 percent to 8 percent, at 450 cm^{-1} and from 87 percent to 31 percent at 310 cm^{-1} . The reflectivity of this

[†] This is not the symmetry of the isolated unit cell but the effective symmetry in the crystal for active fundamental vibrations. Details are given in reference 5.

[‡] In deriving Fig. 1, it is necessary to consider the separable degeneracy of species E encountered in C_3 and T individually.

⁷ R. E. Hoffman, thesis, Brown University, 1949.

⁸ E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950).

⁹ Smits, Muller, and Kröger, *Z. physik. Chem.* **B38**, 177 (1937).

[§] Obtained from Norsk Hydro-Elektrisk Kvaelfstofaktieselskab.

¹⁰ Hornig, Hyde, and Adcock, *J. Opt. Soc. Am.* **40**, 497 (1950).

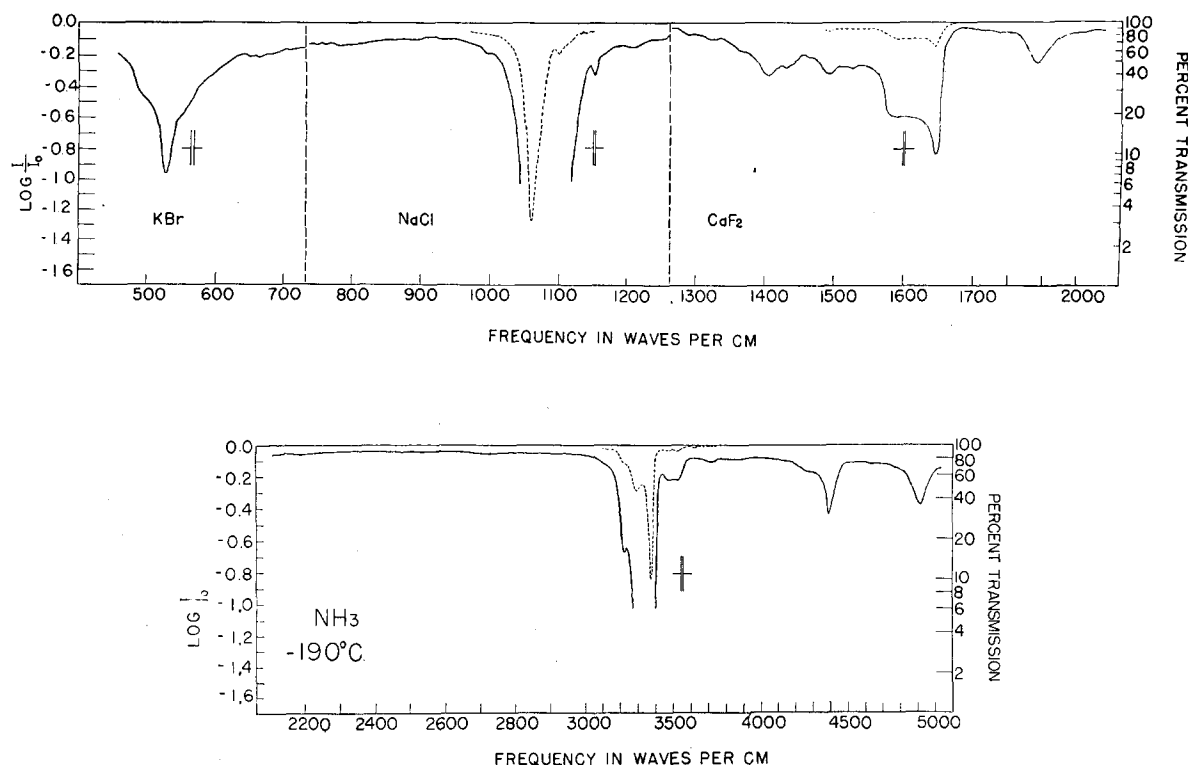


FIG. 2. Infrared transmission spectrum of crystalline NH₃ at -190°C .

mirror was 85 percent throughout the region 450 to 300 cm^{-1} . Except for the one mm thick KBr window on the thermocouple, KRS-5 optics were used exclusively in this region; under these conditions, spectra could be obtained to 300 cm^{-1} .

EXPERIMENTAL RESULTS

The spectra obtained for NH₃ and ND₃ at -190°C from 500 cm^{-1} to 5000 cm^{-1} and 500 cm^{-1} to 3800 cm^{-1} , respectively, are shown in Figs. 2 and 3. These are experimental curves and have not been corrected for scattering nor has the noise level been appreciably smoothed. The solid line refers to a thick film, and the dotted line in regions of great absorption refers to a much thinner film. The absorption peak at 815 cm^{-1} in the thin ND₃ film shifts to a higher frequency in going to the thick film; we have studied a series of films of intermediate thickness and found that the frequency of the peak increases continuously to 820 cm^{-1} for a film with a peak absorption of 98 percent, although the line width remains approximately constant. The reason for this shift is not certain. Upon investigation of this phenomenon with a number of films of varying thickness and degree of scattering, the shift was found to depend only on the thickness. Consequently, it cannot result from an orientation effect which, of course, would be inconsistent with a cubic symmetry for the crystal. The shift resembles that of the ammonium salts which

has been shown to be caused by the rapid increase of reflection intensity with film thickness.¹¹

The spectra obtained in the KRS-5 region for NH₃ and ND₃ are shown in Figs. 4 and 5, respectively. Again these curves are experimental and no correction for stray light has been made, with the result that the bands are actually more intense than they appear to be in these figures. Curve A in Fig. 4 was obtained on the same thick film employed for Fig. 2. Comparing the relative intensities of the band at 527 cm^{-1} in curves A and B, it is seen that the band at 362 cm^{-1} is by far the most intense in the entire spectrum.

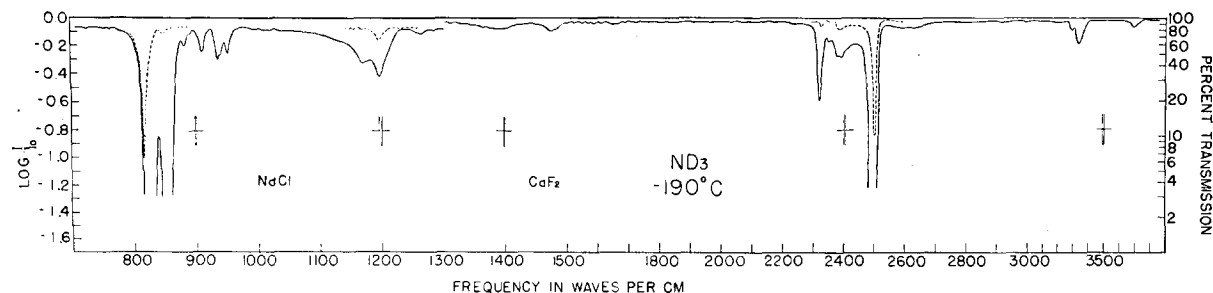
The band center of the ND₃ counterpart of this intense band lies, as may be seen in Fig. 5, below 300 cm^{-1} ; and by comparison with the NH₃ curve, it is estimated to have its minimum at approximately 250 cm^{-1} .

FUNDAMENTAL FREQUENCIES IN THE CRYSTAL

The fundamental frequencies and relative integrated intensities found in the infrared spectrum of both NH₃ and ND₃ crystals, as well as the corresponding Raman bands for solid NH₃ as reported by Sutherland,¹ are shown in Table I. For comparison, the frequencies of the fundamentals in the gas¹² are also included. The error of the relative intensities is of the order of 10

¹¹ L. F. H. Bovey, *J. Chem. Phys.* **18**, 1684 (1950).

¹² See G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 295.

FIG. 3. Infrared transmission spectrum of crystalline NH_3 at -190°C .

percent. The average width at half-height of the resolved fundamentals is 22 cm^{-1} and none exceeds 35 cm^{-1} . It is, therefore, safe to conclude that the crystal is well ordered.^{5,13}

The totally symmetric bending mode ν_2 occurs at 1060 cm^{-1} in NH_3 and 815 cm^{-1} in ND_3 . This fundamental, which is split by 36 cm^{-1} in gaseous NH_3 , has been observed in a number of films with no evidence of splitting and, consequently, of inversion doubling. This is to be expected, since hydrogen bonding certainly raises the potential barrier to the inversion by several kilocalories per mole.

The doubly degenerate bending vibration ν_4 occurs at 1646 cm^{-1} in NH_3 and 1196 cm^{-1} in ND_3 . According to Fig. 1, it may have two components in the crystal. This may account for some of the absorption on the low frequency side of the observed peak in both NH_3 and ND_3 , but absorption due to other causes, which will be discussed later, may also be expected in this region.

The only real question in the assignment concerns the hydrogen stretching vibrations, ν_1 and ν_3 . The totally symmetric vibration ν_1 has been assigned to the shoulder at 3223 cm^{-1} in NH_3 and to the sharp peak at 2318 cm^{-1} in ND_3 . The perpendicular stretching vibration ν_3 has been assigned to the very intense peaks at 3378 cm^{-1} and 2500 cm^{-1} in NH_3 and ND_3 , respectively. If this assignment is correct, it is seen in Fig. 3 that ν_1 is only about $\frac{1}{10}$ as intense as ν_3 at 2500 cm^{-1} . Similarly, ν_1 in Fig. 2, although partially obscured, is not nearly as intense as ν_3 . This assignment points to a complete reversal in the relative intensities of the two fundamentals in going from the gas to the crystal, since in the gas ν_1 is so intense that it completely obscures ν_3 .¹⁴ However, similarly great changes in relative intensity in going from the gas to the crystal have been observed before, for example, in HCN .¹⁵

The key to this assignment is the frequency 2318 cm^{-1} in ND_3 which is almost certainly a fundamental, both because of its sharpness and because no combination assignment fits it. Moreover, the corresponding

line in NH_3 at 3223 cm^{-1} also appears to be sharp in the thick film and can be fitted only as $\nu_2 + \nu_4 + \nu_5$. It may be objected that the line at 2318 cm^{-1} appears to change intensity relative to its neighbor at 2390 cm^{-1} in going from thin to thick films, suggesting an impurity effect. However, in a number of films of varying thickness, the intensity ratio between it and the peak at 2500 cm^{-1} is constant so the variation must reside in the line at 2390 cm^{-1} . Undoubtedly the reason for this variation is that both of the partially deuterated ammonias also have lines in this vicinity. Since the lines at 2390 cm^{-1} and 3297 cm^{-1} in ND_3 and NH_3 , respectively, fit their assignment to $2\nu_4$ and no satisfactory assignment based on their being fundamentals was possible, this alternative was eliminated.

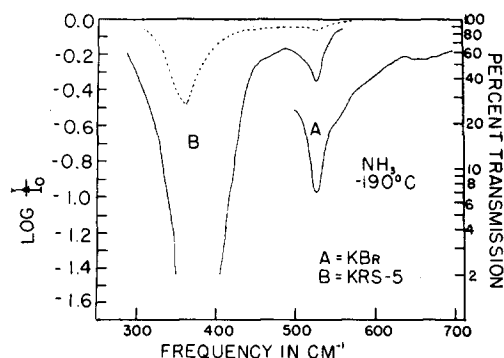
The assignment of fundamental frequencies given in Table I yields the following values for the Teller-Redlich product ratios. ||

Species A:

$$\frac{\nu_1^H \nu_2^H}{\nu_1^D \nu_2^D} = \frac{3223 \times 1060}{2318 \times 815} = 1.808 \text{ (harmonic value, 1.842).}$$

Species E:

$$\frac{\nu_3^H \nu_4^H}{\nu_3^D \nu_4^D} = \frac{3378 \times 1646}{2500 \times 1196} = 1.860 \text{ (harmonic value, 1.871).}$$

FIG. 4. Infrared transmission spectrum of crystalline NH_3 at -190°C in KRS-5 region.

¹³ D. F. Hornig, J. Chem. Phys. **17**, 1346 (1949).

¹⁴ E. F. Barker, Phys. Rev. **55**, 657 (1939).

¹⁵ R. E. Hoffman and D. F. Hornig, J. Chem. Phys. **17**, 1163 (1949).

|| The moments of inertia used in calculating the harmonic values were those of the gas, taken from reference 25.

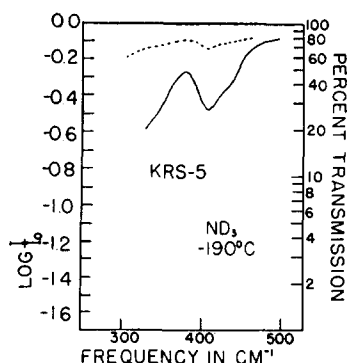


FIG. 5. Infrared transmission spectrum of spectrum of crystalline ND_3 at -190°C in KRS-5 region.

The agreement is as good as is usually obtained with deuterium substitution.

In order to consider the symmetry species separately, it is necessary to assume that the coupling between the molecules is weak so that there is no appreciable mixing of the A_1 and E vibrations (free molecule), which are both of species F in the crystal. It would be somewhat more rigorous to compare the product of all four vibrations of species F ; this yields an experimental ratio of 3.363 compared to a theoretical ratio of 3.446. Rigorously it would be necessary to include the lattice frequencies of species F as well, but in this case it is probably safe to assume negligible interaction because of the wide frequency separation.

An alternate assignment in which the previous designations of ν_1 and ν_3 are interchanged was also considered. In this case, the Teller-Redlich product ratios would be:

$$\text{Species } A: \frac{3378 \times 1060}{2500 \times 815} = 1.757.$$

$$\text{Species } E: \frac{3223 \times 1646}{2318 \times 1196} = 1.914.$$

These ratios are not so far from the theoretical values as to rule out this possibility. Nevertheless, the ratio for species A is 5 percent low, somewhat more than might be expected, and the ratio for species E is 2

TABLE I. Fundamental frequencies of ammonia and deuterio-ammonia.

Vibration	NH_3 frequencies (cm^{-1})			ND_3 frequencies	
	Infrared	Raman*	Gas Infrared	Crystal Infrared	Gas Infrared
ν_1	3223(?)	3202(1)	3336	2318(1)	2419
ν_2	1060(12)	—	931.6	815(9)	748.6
ν_3	3378(10)	3369(4)	968.1	2500(12)	749.0
ν_4	1646(1)	1585(0)	3414(?)	1196(1)	2555
ν_5	527	—	1627.5	406	—
ν_5'	362	—	—	(250) ^b	—
ν_5''	(250) ^b	—	—	(200) ^b	—
ν_6	(53) ^b	—	—	—	—

* See reference 1.

^b Not directly observed. ν_5 , ν_5' , ν_5'' —Limiting perpendicular torsional oscillation in lattice; ν_6 —Limiting parallel torsional oscillation in lattice or translational lattice vibration.

percent high, whereas anharmonicity usually produces a ratio lower than the harmonic value.

Other considerations also lead to the assignment given in Table I. Unless the crystalline field produces large interaction terms in a valence force potential function, ν_1 would remain lower in frequency than ν_3 in going from the gas to the crystal. Furthermore, in all cases of simple hydrogen bonded molecules which have been observed to date,¹⁶ the frequency of hydrogen stretching vibrations decreases in passing from the gas to the crystal. If the alternate assignment were correct, however, ν_1 would increase in frequency by 42 cm^{-1} .

A knowledge of the polarization properties of the Raman spectrum in this region would assist in deciding the assignment; unfortunately, no polarization measurements on the crystal are yet available. However, the Raman spectrum of liquid ammonia^{17,18} shows three lines, at 3220 cm^{-1} , 3300 cm^{-1} , and 3380 cm^{-1} , which have essentially the same frequencies as the lines observed in the infrared and Raman spectra of the crystal in the same region; it seems likely that the assignment in the liquid is the same as in the crystal. According to Bhagavantam, the line at 3220 cm^{-1} is strongly polarized, indicating an A type vibration, and that at 3380 cm^{-1} is only slightly polarized, indicating an E type vibration. These conclusions are in accord with the assignment arrived at here.

Although none of the four arguments presented are in themselves conclusive, they all point to the assignment of ν_3 to the higher of the frequencies in question and of ν_1 to the lower. This leads to the further conclusion that the relative intensities of the two vibrations in the infrared spectrum change enormously on crystallization.

Two Raman lines at 3202 cm^{-1} and 3369 cm^{-1} have been observed in the ammonia crystal in this region.¹ Since they apparently do not coincide with the infrared lines, they probably are the A component of ν_1 and the E component of ν_3 (under the unit cell group). It seems most likely then that the weak Raman line at 3202 cm^{-1} arises from ν_1 and that the strong line at 3369 cm^{-1} arises from ν_3 , pointing to a reversal of the Raman intensities as well.

FREQUENCY OF ν_3 IN THE GAS

Since the fundamental frequencies in the crystal seem to be established, it may be possible to use them to help ascertain the frequency of the asymmetric stretching frequency ν_3 which is not certain in the gas. This frequency has been given as 3414 cm^{-1} by Barker¹⁴ who considered the band at 2450 cm^{-1} to be $\nu_3 - \nu_2$. However, this value is 85 cm^{-1} (2.5 percent) below that predicted by the Teller-Redlich product rule and the ND_3 frequencies, a greater deviation than might be expected

¹⁶ D. F. Hornig, Trans. Faraday Soc., to be published.

¹⁷ P. Daure, Trans. Faraday Soc. **25**, 825 (1929).

¹⁸ S. Bhagavantam, Indian J. Phys. **5**, 54 (1930).

from the usual effect of anharmonicity. Consequently, Sutherland¹⁹ chose the alternative value, 3450 cm^{-1} , taken from an absorption maximum which is not explained by the ν_1 band in this same region, which fits the product rule better.

The results of the crystalline investigation favor Sutherland's value. The shift in ν_3 for ND_3 , where the gas frequency seems well established,¹¹ is -55 cm^{-1} or 2.2 percent. A proportionate shift in NH_3 would yield a frequency of 3452 cm^{-1} for ν_3 in the gas.

TORSIONAL VIBRATIONS

It seems highly probable that the two low-frequency peaks at 527 cm^{-1} and 362 cm^{-1} in NH_3 (Fig. 4) originate in the torsional oscillations perpendicular to the threefold axis. This motion, corresponding to the perpendicular rotation of the free molecule (Species *E*), may be expected to give two components in the crystal (Species *F*), which have been designated ν_5 and ν_5' in Table I. That they are so widely separated is a natural consequence of the fact that intermolecular coupling is a first order effect in lattice vibrations rather than a small perturbation, as in the case of the internal vibrations. A corresponding pair of lines occurs in ND_3 (Fig. 5), one at 406 cm^{-1} , and one at $<300 \text{ cm}^{-1}$, which, from the shape of the high frequency side of the band, is estimated to be approximately at 250 cm^{-1} .

None of the three remaining infrared active fundamentals were observed directly, but the spectrum of NH_3 contains a series of sum and difference bands with a spacing of 53 cm^{-1} (Table II) which are centered about a frequency of 1048 cm^{-1} . This frequency must be the second, infrared inactive, component of ν_2 which is of species *A* in the crystal. The selection rules then require that the combining mode be of species *F*, identifying the frequency 53 cm^{-1} (ν_6) as one of the infrared active fundamentals. Preliminary observations of the Raman spectrum[¶] of crystalline NH_3 confirm the deduction regarding the frequency 1048 cm^{-1} in that ν_2 has been resolved into two components at 1050 cm^{-1} and 1060 cm^{-1} .

The first component of a similar combination series in ND_3 is indicated by the band at 849 cm^{-1} . The band at 880 cm^{-1} , which at first sight appears to be the second component of the series, is probably an impurity, as will be discussed later. Furthermore, since no corresponding difference band was observed, it is not possible to place the inactive component of ν_2 (Species *A*) and, consequently, calculate the frequency of this lattice motion in ND_3 .

Another torsional mode** is indicated by the bands at 1888 cm^{-1} in NH_3 and 1390 cm^{-1} in ND_3 . These

TABLE II. Combination and overtone bands of crystalline NH_3 and ND_3 .

NH_3 (cm^{-1})		ND_3 (cm^{-1})		Assignment
obs	calc	obs	calc	
640-750	724	—	—	$2\nu_5'$
995	—	—	—	$\nu_2 - \nu_6$
1100	—	849	—	$\nu_2 + \nu_6$
1151	—	—	—	$\nu_2 + 2\nu_6$
1207	—	—	—	$\nu_2 + 3\nu_6$
1350-1600	—	1050-1180	—	$\nu_2 + \text{lattice modes}$
1600	1587	—	—	$\nu_2 + \nu_6$
1888	—	1390	—	$\nu_2 + \nu_5''$
3297	3292	2390	2392	$2\nu_4$
3450-3550	—	2550-2650	—	ν_1 or $\nu_3 + \text{lattice modes}$
4397	4438	3335	3315	$\nu_2 + \nu_3$
4923	5024	3686	3696	$\nu_4 + \nu_3$

bands seem to require frequencies of about 250 cm^{-1} and 200 cm^{-1} in combination with the fundamentals at 1646 cm^{-1} and 1196 cm^{-1} in NH_3 and ND_3 , respectively. This observation is substantiated by the fact that in the previously mentioned Raman spectrum of NH_3 a strong line was observed at 261 cm^{-1} . This vibration cannot yet be assigned; it may be the *E* type component of the perpendicular torsion, ν_5'' (Table I), a component of the parallel torsion, or it may be the vibration ν_6 which was previously assigned to 527 cm^{-1} . In the latter case the absorption at 527 cm^{-1} would be ascribed to its first overtone.

COMBINATION AND OVERTONE BANDS

The combination and overtone bands observed are listed in Table II. They all differ from the characteristically sharp fundamentals in that they are broader and more diffuse, as is to be expected since the entire frequency branches arising from each of the combining fundamentals yield active combinations.^{5,6}

The most interesting region of the spectrum is the broad region of tremendous integrated absorption intensity extending from 1350 cm^{-1} to 1650 cm^{-1} in the case of NH_3 . It almost certainly arises in large part from the combination of the fundamental ν_2 at 1060 cm^{-1} with the torsional oscillations of the lattice. The complete frequency spectrum of these vibrations has not been calculated but it obviously extends from the vicinity of the limiting mode of this type at approximately 250 cm^{-1} (ν_5'') to the vicinity of the limiting mode at 527 cm^{-1} (ν_5). It is not possible to discuss the details of this band without knowing the complete frequency distribution function of the torsional vibration branches, but it is probably significant that the regions of maximum absorption, 1422 cm^{-1} and 1587 cm^{-1} , are approximately coincident with the frequencies of combination with the observed limiting modes at 362 cm^{-1} and 527 cm^{-1} . This region is further complicated by the fact that the distribution $3\nu_5$ may be superimposed on it, as well as by the possibility that a second component of ν_4 may be contained in the shoulder between 1585 and 1640 cm^{-1} . The corre-

¹⁹ G. B. M. Sutherland, Phys. Rev. **56**, 836 (1939).

[¶] To be described in detail in another publication.

** Although it cannot be demonstrated that the vibrations discussed in this paragraph are torsions, the frequencies are all higher than expected for translations, so it is assumed that they are largely torsional motions.

TABLE IIIa. Force constants in the most general potential function for the internal vibrations of crystalline ammonia.

Symmetry		Valence force	
F_1	5.998×10^6 dynes/cm	f_d	6.130×10^6 dynes/cm
F_2	0.4852×10^6 dynes/cm	f_{dd}	-0.0712×10^6 dynes/cm
F_3	6.201×10^6 dynes/cm	f_α	0.5835×10^6 dynes/cm
F_4	0.6377×10^6 dynes/cm	$f_{\alpha\alpha}$	-0.0492×10^6 dynes/cm
F_{12}	0.00×10^6 dynes/cm	$f_{\alpha d}$	0.00×10^6 dynes/cm
F_{34}	0.00×10^6 dynes/cm	$f'_{\alpha d}$	0.00×10^6 dynes/cm

sponding region in ND_3 has only one clearly defined absorption maximum, while there are several in NH_3 . This may possibly be due to the fact that $3\nu_6$ and $\nu_5 + \nu_2$ fall some 50 cm^{-1} below ν_4 in NH_3 , whereas in ND_3 they are slightly higher in frequency than ν_4 .

The bands at 909, 1263, and 1475 cm^{-1} in ND_3 have been identified as partially deuterated ammonia bands by observing the spectrum of a two to one mixture of ND_3 and NH_3 . This leaves only the bands at 880, 934, and 950 cm^{-1} in ND_3 to be accounted for, and from their varying relative intensity with respect to other bands in the spectra in going from one film to another, it seems highly probable that they are caused by some impurity. In two films they were absent altogether.

FORCE CONSTANTS IN THE AMMONIA CRYSTAL

Following the first paper in this series,⁵ the potential function for the ammonia crystal may be written in the form

$$V = V_l + \sum_j V_j + V_{mm'} + V_{ml}, \quad (1)$$

where V_l includes only lattice coordinates (e.g., coordinates of the center of gravity and principal axes of each molecule), V_j includes the internal coordinates of the j th molecule, $V_{mm'}$ includes cross terms between the internal coordinates of different molecules, and V_{ml} represents cross terms between lattice and internal coordinates.

Because of the considerable frequency separation between lattice frequencies and internal frequencies, the effect of the term V_{ml} is probably small and in first approximation may be neglected. The small difference between the frequencies observed in the Raman and infrared spectra as well as the failure to find a second component of ν_3 and ν_4 suggest that the contribution of the coupling term $V_{mm'}$ is not great. In this case the potential function may be written in first approximation as

$$V = V_l + \sum_j V_j. \quad (2)$$

The problem of the lattice vibrations and the internal vibrations of the individual molecules now separates and the latter can be treated by the usual methods. The potential function V_j of each molecule differs from that of the free molecule only in that the crystalline field resulting from the equilibrium configuration of the crystal changes the effective valence force constants.

TABLE IIIb. Comparison of calculated and observed frequencies using potential constants of Table IIIa.

	NH_3 freq. (cm^{-1})		ND_3 freq. (cm^{-1})	
	calc	obs	calc	obs
ν_1	3224	3223	2316	2318
ν_2	1069	1060	809	815
ν_3	3381	3378	2496	2500
ν_4	1649	1646	1194	1196

Since all four frequencies in both NH_3 and ND_3 were observed, it should be possible to evaluate the six force constants in the most general valence force potential function^{20,21} given below:

$$2V = f_d \sum d_j^2 + d_0^2 f_\alpha \sum \alpha_{ij}^2 + 2f_{dd} \sum d_i d_j + 2d_0^2 f_{\alpha\alpha} \sum \alpha_{ij} \alpha_{ik} + 2d_0 f'_{\alpha d} \sum \alpha_{ij} d_k + 2d_0 f_{\alpha d} \sum \alpha_{ij} d_i. \quad (3)$$

This potential function differs from that of the references cited in that it explicitly includes the factor of two in all cross terms whereas they include it in the interaction force constants. In Eq. (3), the equilibrium N—H distance is d_0 and the valence force constants are bond stretching (f_d), angle bending (f_α), bond-bond interaction (f_{dd}), angle-angle interaction ($f_{\alpha\alpha}$), bond adjacent angle interaction ($f_{\alpha d}$), and bond opposite angle interaction ($f'_{\alpha d}$).

Following the method of Wilson,²² the changes in N—H bond lengths (d_j) and H—N—H bond angles (α_{ij}) were used as internal coordinates. Since the local symmetry about each molecule in the crystal is C_3 , which contains two species, A and E , symmetry was used to factor the F and G matrices. The blocks of the factored F matrix are of the form given below, the latter block occurring twice.

$$\begin{array}{cc|cc} \text{Species } A & & \text{Species } E & \\ \hline F_1 & d_0 F_{12} & F_3 & d_0 F_{34} \\ d_0 F_{12} & d_0^2 F_2 & d_0 F_{34} & d_0^2 F_4 \end{array}$$

The F 's are the various symmetry force constants, given explicitly in terms of the valence force constants by the following relations:

$$\begin{array}{ll} F_1 = f_d + 2f_{dd} & F_3 = f_d - f_{dd} \\ F_2 = f_\alpha + 2f_{\alpha\alpha} & F_4 = f_\alpha - f_{\alpha\alpha} \\ F_{12} = f'_{\alpha d} + 2f_{\alpha d} & F_{34} = f'_{\alpha d} - f_{\alpha d} \end{array} \quad (4)$$

These symmetry force constants are like those used by Hemptinne and Delfosse,²⁰ except that their constants for Species E are twice those given above.

The G matrix elements were taken from those tabulated by Decius,²³ and the elements of the factored G -matrix contain the same linear combinations as the F matrix, Eq. (4).

²⁰ M. de Hemptinne and J. Delfosse, Ann. soc. sci. Bruxelles 56, 373 (1936).

²¹ J. Duchesne and I. Otellet, J. Chem. Phys. 17, 1354 (1949).

²² E. B. Wilson, Jr., J. Chem. Phys. 7, 1047 (1939); 9, 76 (1941).

²³ J. C. Decius, J. Chem. Phys. 16, 1025 (1948).

There are eight possible sets of force constants which may be obtained for the general potential function; since all eight observed frequencies are needed to calculate the six force constants (one in each symmetry class is determined by the product rule and is independent of the specific potential function), no mathematical elimination is possible. The set which corresponds to normal coordinates in which the high frequencies are all N—H stretching frequencies and the low frequencies are bends is the only set which is physically reasonable and is given in Table IIIa. The frequencies calculated from this potential function are compared with those observed in Table IIIb. The discrepancy is less than 1 percent and is as good as the product rule in all cases.

It is of great interest that the best fit is obtained when the symmetry factored F matrix is diagonal. However, F_{12} and F_{34} cannot be determined with any precision, since they enter the equations for the frequencies either as squares or with very small coefficients. Conversely, the calculated frequencies are very insensitive to these constants. This is illustrated in Table IV by a set of force constants which are not quite a best fit (but which were obtained as a best fit in preliminary calculations) together with calculated and observed frequencies. Although the force constants are substantially different from those of Table IIIa, the maximum frequency deviation is still but 1.1 percent and the general fit is very nearly as good as with the force constants of Table IIIa. This same difficulty occurs, of course, in determining the potential function for gaseous ammonia.²⁰

Because of the insensitivity to F_{12} and F_{34} , and because the best fit of the most general potential function was obtained when $F_{12}=F_{34}=0$, these constants were set equal to zero, and the four NH_3 frequencies were used to calculate the remaining four force constants. Four sets were obtained, one of them being the set of Table IIIa, but when they were used to calculate the four ND_3 frequencies, two of them, the expected number, gave a bad fit and were eliminated. The remaining set fitted almost as well as that of Table IIIa but was physically unreasonable, corresponding to the assignment of the high frequencies to bond bending coordinates and the low frequencies to bond stretching.

Two other more simplified potential functions were tried. The first included only the diagonal force con-

TABLE IV. Comparison of calculated and observed frequencies using a slightly varied most general potential function.

Force constants ($\times 10^{-5}$ dyne/cm)		NH ₃ freq. (cm ⁻¹)		ND ₃ freq. (cm ⁻¹)	
		calc	obs	calc	obs
$F_1 = 5.911$	ν_1	3220	3223	2321	2318
$F_2 = 0.500$	ν_2	1069	1060	806	915
$F_3 = 6.075$	ν_3	3374	3378	2502	2500
$F_4 = 0.655$	ν_4	1654	1646	1192	1196
$F_{12} = -0.24$					
$F_{34} = 0.23$					

stants f_d and f_a , and the second included f_d , f_a , and the off diagonal constant f_{aa} . In both cases the correlation between the observed and calculated frequencies was poor and their deviation greater than the deviation of the experimental from the theoretical product ratios.

Until reliable values of all of the fundamental frequencies are available in gaseous ammonia, the potential function in the crystal cannot be compared in detail with that of the gas. Nevertheless, the effective N—H stretching force constant is certainly lowered about 5 percent, and the effective bending force constant is raised by approximately 40 percent.²⁴ This large apparent change is due chiefly to the failure to include the correction for the anharmonicity of ν_2 in the calculation of the gas force constants. Dennison²⁵ has calculated the harmonic value of ν_2 to be 1055 cm⁻¹ in NH_3 and 803 cm⁻¹ in ND_3 . The bending force constants for the crystal are only about 5 percent higher than gas force constants calculated from these values. It is apparent then that the greatest effect of the crystalline field is to raise the barrier to inversion and largely eliminate the anharmonicity, a conclusion which agrees with that previously arrived at from the absence of any evidence of splitting of ν_2 .

CONCLUSION

It appears then that the infrared spectra of crystalline NH_3 and ND_3 can be interpreted in terms of the motions of monomeric molecules, coupled weakly in a crystal lattice having the x-ray structure previously reported. There is no indication of the presence of dimers or higher polymers, except in the sense that any crystal is an infinite polymer.

²⁴ See reference 12, p. 177, for comparison with gas values

²⁵ D. M. Dennison, Revs Modern Phys. 12, 175 (1940).