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Technical Report No. 21

**Ia and Ib. EVIDENCE FOR ONE-DIMENSIONAL ROTATION IN  
AMMONIUM IODIDE**

**By**

**R. C. Plumb and D. F. Hornig**

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**By**

**C. C. Ferriso and D. F. Hornig**

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COMPLEX IONS IN CRYSTALS. VII. THE RAMAN SPECTRUM  
OF CRYSTALLINE NH<sub>3</sub> and ND<sub>3</sub>**

**By**

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## Evidence for One-Dimensional Rotation in Ammonium Iodide

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(Received December 8, 1952)

PREVIOUSLY it has been demonstrated spectroscopically that the  $\lambda$ -point transitions in ammonium halides cannot involve free rotation since the torsional oscillation frequency of the ammonium ion in the lattice occurs in the phase above (*II*) as well as beneath (*III*) the transition temperature.<sup>1</sup> These results were subsequently confirmed by neutron diffraction studies.<sup>2</sup> However, it was noted by Wagner<sup>3</sup> and confirmed by the careful studies by Dinsmore<sup>4</sup> that in the face-centered cubic modification of  $\text{NH}_4\text{I}$  (*I*), which is stable above the first-order transition at  $-17.6^\circ\text{C}$ , the combination of the triply degenerate bending vibration  $\nu_4$  at  $1400\text{ cm}^{-1}$  with the lattice torsion  $\nu_6$  which occurs at  $1685\text{ cm}^{-1}$  in phases *II* and *III* was absent. Instead the spectra showed only a weak diffuse absorption maximum at  $1600\text{--}1650\text{ cm}^{-1}$  which persisted without much change in films in which phase *I* was supercooled to  $-195^\circ\text{C}$ . We have repeated this work with care and found the diffuse region mentioned before at approximately  $1600\text{ cm}^{-1}$  and, in addition, noted that there were roughly exponential wings at the base of  $\nu_4$  in phase *I*. The width at half-height of the central peak changed from about  $23\text{ cm}^{-1}$  in phases *II* and *III* to about  $30\text{ cm}^{-1}$  in phase *I*.

These observations are consistent neither with a statically disordered model nor the 3-dimensional freely rotating structure suggested by the heat capacity studies of Stephenson *et al.*<sup>5</sup> The latter would require *P* and *R* branch maxima which do not exist.

According to a rough electrostatic calculation, the minimum potential energy occurs when one  $\text{N-H}$  bond is directed at an iodine ion. Such a model with free rotation about this  $\text{N-H}\cdots\text{I}^-$  axis is consistent with the observed spectrum. The height of the barrier to this rotation, the frequency of the zero-point vibration, and the frequency of the perpendicular torsional oscillation were all computed from the electrostatic potential of an ammonium ion, represented with a charge  $+0.43e$  located at the proton positions. This same model has been used successfully to calculate the torsional frequencies in  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , low  $\text{ND}_4\text{Br}$ , and  $\text{NH}_4\text{I}$  (*II* or *III*) and in no case did the effective charge vary outside the limits  $0.42e\text{--}0.50e$ .<sup>6</sup> The calculated torsional frequency was  $203$

$\text{cm}^{-1}$ , in good agreement with the experimental combination band at  $1600\text{ cm}^{-1}$ . The height of the barrier to rotation thus calculated was  $35\text{ cm}^{-1}$ , with a zero-point vibrational level at  $20\text{ cm}^{-1}$ . Consequently, the very first excited level would be above the barrier, and to a good approximation the ion can be thought of as freely rotating when  $T > 75^\circ\text{K}$ .

The selection rules for this model allow only the *Q* branch of the parallel component of  $\nu_4$ , and only *P* and *R* branches of the perpendicular component, to appear in the infrared spectrum. However, the *P* and *R* branches of a one-dimensional rotator have no maxima; the band envelope is an error function with a missing central line. The predicted envelope of the line fits the experimental curve to within the experimental error and shows the correct effect of temperature on the wings. The diffuse nature of the combination band is roughly accounted for by rotational structure and rotation-vibration interaction.

Consequently, we conclude that the spectrum strongly indicates a structure for phase *I* of  $\text{NH}_4\text{I}$  in which one hydrogen bond is formed to  $\text{I}^-$ , and the ammonium ion rotates freely about this bond. A more detailed description of this work will appear at a later date.

Recent neutron diffraction studies of  $\text{ND}_4\text{Br}$  and  $\text{ND}_4\text{I}$  have also led Levy and Peterson to eliminate the model with 3-dimensional free rotation<sup>7</sup>; they find that two different static models and the one-dimensional rotator all give equally good agreement with their data.

The authors are indebted to Dr. C. C. Stephenson and Dr. H. A. Levy for conversations regarding their work.

\* duPont Fellow in Chemistry, 1951-1952.

<sup>1</sup> E. L. Wagner and D. F. Hornig, *J. Chem. Phys.* **18**, 296 (1950); *ibid.* **305** (1950).

<sup>2</sup> H. A. Levy and S. W. Peterson, *Phys. Rev.* **86**, 766 (1952).

<sup>3</sup> E. L. Wagner (unpublished data).

<sup>4</sup> H. L. Dinsmore (unpublished data). See also L. F. H. Bovey, *J. Opt. Soc. Am.* **41**, 836 (1951).

<sup>5</sup> Stephenson, Landers, and Cole, *J. Chem. Phys.* **20**, 1044 (1952).

<sup>6</sup> D. F. Hornig and S. Millman (unpublished work).

<sup>7</sup> H. A. Levy and S. W. Peterson, *J. Chem. Phys.* **21**, 366 (1953).

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### Evidence for One-Dimensional Rotation in $\text{NH}_4\text{I}$

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(Received April 1, 1953)

**I**N a previous communication under this same title<sup>1</sup> it was pointed out that in the NaCl-like phase of  $\text{NH}_4\text{I}$  which exists at room temperature the only reasonable interpretation of the infrared absorption spectrum in the  $7\mu$  region led to a model in which the ammonium ion underwent one-dimensional free rotation. It was further concluded that the rotation took place about the hydrogen bond formed from one apex of the  $\text{NH}_4^+$  tetrahedron to an adjacent  $\text{I}^-$  ion.

At the time that note was written we had, unfortunately, overlooked the beautiful investigations of the Raman spectrum of single crystals of  $\text{NH}_4\text{I}$  which had previously been published by L. C. Mathieu and J. P. Mathieu.<sup>2</sup> From measurements of the polarization of the Raman radiation they showed quite definitely that the threefold axis of the  $\text{NH}_4^+$  ion coincided with the fourfold axis of the crystal. They did not reach any conclusions regarding rotation of the ion, but their prior evidence is probably less ambiguous than either the infrared spectrum or the neutron diffraction results<sup>3</sup> in demonstrating the one-bond model. Taken together the three investigations make this structure nearly certain.

<sup>1</sup> R. C. Plumb and D. F. Hornig, *J. Chem. Phys.* 21, 366 (1953).

<sup>2</sup> L. Couture-Mathieu and J. P. Mathieu, *J. chim. phys.* 49, 226 (1952).

<sup>3</sup> H. A. Levy and S. W. Peterson, *J. Chem. Phys.* 21, 366 (1953).

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### THE INFRARED SPECTRUM OF THE OXONIUM ION

Sir:

The infrared absorption spectra of films of oxonium chloride and oxonium bromide have been observed at  $-195^{\circ}$  and spectra which are typical of those obtained are reproduced in Fig. 1. The films were prepared by condensing an equimolar mixture of gaseous  $H_2O$  and  $HX$  on a previously cooled  $KBr$  plate. The  $OH_3^+$  must be the source of the four absorption bands at  $1050\text{ cm.}^{-1}$ ,  $1700\text{ cm.}^{-1}$ ,  $2100\text{ cm.}^{-1}$  and  $2570\text{ cm.}^{-1}$  in  $OH_3Cl$  (similarly, at  $1100\text{ cm.}^{-1}$ ,  $1700\text{ cm.}^{-1}$ ,  $2100\text{ cm.}^{-1}$  and  $2610\text{ cm.}^{-1}$  in  $OH_3Br$ ). In addition, some films of both salts show an absorption maximum near  $3200\text{ cm.}^{-1}$  as part of the broad absorption region which extends to frequencies above  $3500\text{ cm.}^{-1}$ . Very little of the observed spectrum can be attributed to ice, whose intense bands<sup>1</sup> at  $812\text{ cm.}^{-1}$  and  $2150\text{ cm.}^{-1}$ ,<sup>2</sup> do not appear. Except for the peaks at  $2770\text{ cm.}^{-1}$  in  $OH_3Cl$  and  $2410\text{ cm.}^{-1}$  in  $OH_3Br$ , the halides cannot be responsible either since the same bands occur in both salts.

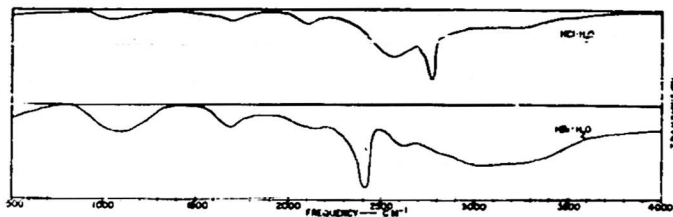
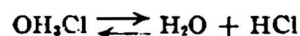


Fig. 1.—The infrared absorption spectrum of oxonium chloride and oxonium bromide at  $-195^{\circ}$ .

To confirm these conclusions we have, in addition to the equimolar compounds, condensed five gas mixtures with composition ranging from 90%  $HCl$ -10%  $H_2O$  to 20%  $HCl$ -80%  $H_2O$ , and these

(1) F. P. Reding, Thesis, Brown University, 1951.  
(2) J. J. Fox and A. E. Martin, *Proc. Roy. Soc. (London)*, **A174**, 234 (1940).

showed the expected  $HCl$  or ice spectrum superimposed on that of the  $OH_3^+$  ions. The compositions containing excess  $HCl$  showed two peaks very close to those reported for pure crystalline  $HCl$  at  $2704\text{ cm.}^{-1}$  and  $2746\text{ cm.}^{-1}$ .<sup>3,4</sup> Therefore the  $HCl$  responsible for the  $2770\text{ cm.}^{-1}$  peak in the  $OH_3Cl$  sample must be in a different environment, *e.g.*, as  $HCl$  molecules in the  $OH_3Cl$  lattice. In this case they may be produced by the equilibrium



but we have not yet investigated this possibility. Altogether, the general outlines of the experimental situation seem clear, but some details still need clarification. A number of films have been prepared and the spectra were not completely reproducible, differing chiefly in two respects: (a) the shape of the diffuse absorption region between  $2350\text{ cm.}^{-1}$  and  $3500\text{ cm.}^{-1}$  and (b) the height of the peak we have ascribed to free  $HX$  molecules. Further studies are continuing.

Whereas the observed spectrum is different from either ice or the hydrogen halides, it is closely parallel to that of ammonia. The hydrogen stretching frequencies are lower and the bands broader but both of these features may be attributed to strong hydrogen bonds. It may therefore be concluded that the  $OH_3^+$  ion which is isoelectronic with  $NH_3$ , also exists in a symmetrical pyramidal configuration. This conclusion agrees with that derived from proton resonance measurements.<sup>5-6</sup>

(3) G. Hettner, *Z. Physik*, **76**, 141 (1932).  
(4) Lee, Sutherland and Wu, *Proc. Roy. Soc. (London)*, **A176**, 493 (1940).  
(5) Y. Kakiuchi, *et al.*, *J. Chem. Phys.*, **19**, 1069 (1951).  
(6) R. E. Richards and J. A. S. Smith, *Trans. Far. Soc.*, **47**, 1261 (1951).

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THE VIBRATIONAL SPECTRA OF MOLECULES AND COMPLEX IONS IN CRYSTALS  
VII. THE RAMAN SPECTRUM OF CRYSTALLINE AMMONIA  
AND 3-DEUTERO-AMMONIA

F. P. Reding and D. F. Hornig

ABSTRACT

The Raman spectra of crystalline  $\text{NH}_3$  and  $\text{ND}_3$  were measured at  $-32^\circ\text{C}.$ , using Hg 2536.5 Å exciting radiation. The fundamentals  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  were observed but  $\nu_4$  was not.  $\nu_2$  was split into two components by intermolecular coupling. Lattice frequencies of both translational and rotational origin were observed and there was evidence of very little coupling between them.

# THE VIBRATIONAL SPECTRA OF MOLECULES AND COMPLEX IONS IN CRYSTALS

## VII. THE RAMAN SPECTRUM OF CRYSTALLINE AMMONIA

### AND 3-DEUTERO-AMMONIA

F. P. Reding and D. F. Hornig

#### INTRODUCTION

The Raman spectrum of crystalline ammonia and 3-deutero-ammonia has been observed in conjunction with the previously reported infrared study of these crystals.<sup>1</sup>

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1. F. P. Reding & D. F. Hornig, J. Chem. Phys. 19, 594 (1951)  
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In that paper it was pointed out that on the basis of the present theory of crystalline spectra<sup>2,3</sup>

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2. D. F. Hornig, J. Chem. Phys. 16, 1063 (1948)  
3. H. Winston and R. S. Halford, J. Chem. Phys. 17, 607 (1949)  
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the motions of the four molecules in the unit cell of the cubic ammonia crystal (symmetry  $T^4$ ) may be expected to couple so that the symmetrical vibrations of  $NH_3$  or  $ND_3$ ,  $\nu_1$  and  $\nu_2$ , each yield one component of species A and one of species F. Similarly, the doubly degenerate vibrations,  $\nu_3$  and  $\nu_4$ , should each yield one component of species E and two of species F in the crystals. Only the species F components may be active in the infrared spectrum whereas all three (A,E,F) may be active in the Raman spectrum. Actually, although all four fundamentals were observed in the infrared spectrum, only one component arising from each degenerate vibration was observed. In addition, evidence was produced that the second, Raman active, component of  $\nu_1$  was displaced by  $10\text{ cm}^{-1}$  from the infrared

active component.

Since all ten components arising from the four internal vibrations may be Raman active, it was hoped that the frequency separation between components originating in the different phases of coupling of the four molecules could be determined. This splitting would give a quantitative measure of the intermolecular interaction. In addition, it was hoped that the limiting lattice vibrations, five of which originate in molecular rotation and four in molecular translation, might be observed at low frequencies.

In previous work on the Raman spectrum of crystalline  $\text{NH}_3$  Sutherland<sup>4</sup>

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4. G. B. B. M. Sutherland, Proc. Roy. Soc., 141A, 546 (1933)  
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reported lines at 3369, 3303, and 1585  $\text{cm}^{-1}$  with relative intensities of 4, 1, and 0 respectively. The Raman spectrum of  $\text{ND}_3$  was not found in the literature.

#### EXPERIMENTAL

The ultraviolet absorption spectrum of crystalline  $\text{NH}_3$  begins at 2345Å.<sup>5</sup>

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5. A. Prikhotko, Acta Physicochimica U.S.S.R. 12, 559 (1940)  
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Consequently the Hg 2536.5Å proved most satisfactory as an exciting line. The mercury arc used was an eight turn quartz helix. The vapor pressure of the mercury in the lamp was kept low by using amalgamated gold foil electrodes. No evidence of resonance absorption by the cool mercury vapor along the wall of the tube was noted. The exciting line was filtered from the Raman radiation by filling the spectrograph with mercury vapor.

A diagram of the sample tube and cooling jacket is shown in Figure 1. Nitrogen which had been cooled by bubbling through liquid nitrogen was used to cool the Raman tube. In preparation for an investigation, the system was evacuated and the sample condensed from a storage flask into the Raman tube. The liquid was slowly crystallized and a highly cracked semi-transparent crystal was obtained. Since this proved to be satisfactory, no attempt was made to form a flawless single crystal. The  $\text{NH}_3$  used\*

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 \* Mathieson Alkali Works  
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was stated to be 99.97 per cent pure. The  $\text{ND}_3$  was prepared by the procedure described in the previous paper.

A medium Hilger E-3 303 Spectrograph with quartz optics was used to record the spectra. Depending upon the intensity desired, exposure times varied from 20 minutes to two hours, using a slit of 0.01 mm. The resolution of the spectrometer was approximately three  $\text{cm}^{-1}$  in the region employed. For wave length determinations, an iron arc spectrum was recorded using a Hartman diaphragm. The error in the measurement of the Raman line displacement was approximately  $\pm 5 \text{ cm}^{-1}$ .

### RESULTS

The Raman spectra obtained from crystalline  $\text{NH}_3$  and  $\text{ND}_3$  at  $-82^\circ\text{C}$ ., reproduced from the microphotometer tracings, are shown in Figures 2 and 3, respectively. The mercury lines included are marked and the  $2536.5\overset{\circ}{\text{A}}$  exciting line is indicated by  $\Lambda$ . The frequencies of the band centers and approximate intensities are shown in Table 1. For comparison the fundamental bands observed in the

infrared spectrum are also listed.

Two components of the symmetrical bending vibration  $\nu_2$  at 1048 and 1058  $\text{cm}^{-1}$  were clearly resolved in the  $\text{NH}_3$  spectrum. A corresponding doublet was indicated in the  $\text{ND}_3$  spectrum by the shoulder at 817  $\text{cm}^{-1}$  on the high frequency side of the peak at 810  $\text{cm}^{-1}$ . From the very near coincidence of the bands at 1058 and 817  $\text{cm}^{-1}$  with the corresponding bands for  $\nu_2$  in the infrared spectrum, it is safe to conclude that these Raman components arise from the species F vibration. The other two components at 1048 and 810  $\text{cm}^{-1}$  in  $\text{NH}_3$  and  $\text{ND}_3$  must therefore be the species A components.

The symmetric stretching frequency,  $\nu_1$ , could not be determined for  $\text{NH}_3$  because it lies in the broad intense band which extends from 3160  $\text{cm}^{-1}$  to 3330  $\text{cm}^{-1}$  and has a maximum at approximately 3210  $\text{cm}^{-1}$ . This difficulty did not arise for the corresponding line in the  $\text{ND}_3$  spectrum at 2330  $\text{cm}^{-1}$  which is sharp. It is seen in Table 1 that  $\nu_1$  in the infrared spectrum of crystalline  $\text{ND}_3$ , which must be of species F, has the band center at 2318  $\text{cm}^{-1}$ . The 12  $\text{cm}^{-1}$  frequency separation between the infrared and Raman components of this fundamental in  $\text{ND}_3$  is outside of the experimental error in this region. Consequently these Raman lines probably arise from the species A rather than the species F vibration.

The Teller-Redlich product ratio for the F components of the symmetric vibrations was found to be 1.808 (harmonic value = 1.842). If the product ratio is the same for the A components,  $\nu_1$  of  $\text{NH}_3$  would occur at 3240  $\text{cm}^{-1}$ . The broad band in which it is located is apparently the first overtone region corresponding to the intense infrared absorption running from 1575  $\text{cm}^{-1}$  to the fundamental  $\nu_4$

at  $1648\text{ cm}^{-1}$ . A similar band in  $\text{ND}_3$  would be expected in the region  $2350\text{-}2400\text{ cm}^{-1}$  which underlies the Hg line adjacent to  $\nu_1$ .

A component of the antisymmetrical stretching vibration  $\nu_3$  was observed at  $3375\text{ cm}^{-1}$  in  $\text{NH}_3$  and  $2507\text{ cm}^{-1}$  in  $\text{ND}_3$ . This vibration gives rise to a species E and two species F phases of coupling. Since the observed lines occur so near the corresponding infrared active vibrations at  $3378$  and  $2500\text{ cm}^{-1}$ , they may arise from the same F component observed in the infrared spectrum. However, since in all cases the observed splitting between components was very small, it may be that the bands arise from either of the other components or from a superposition of the three. The frequency found for  $\nu_3$  in the crystal in this and the previous paper are in accord with that recently found in the gas from its Raman spectrum.<sup>6</sup>

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 6. C. Cumming & H. L. Welsh, J. Chem. Phys., 21, 1119 (1953)  
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The lines at  $3303$  and  $3369\text{ cm}^{-1}$  reported by Sutherland<sup>2</sup> certainly correspond to those at  $3160\text{-}3330\text{ cm}^{-1}$  and  $3375\text{ cm}^{-1}$  in the work reported here. Sutherland assigned the line he observed at  $1585\text{ cm}^{-1}$  to  $\nu_4$ , which like  $\nu_3$  may have three active Raman components in the crystal. No line was observed in this region in the present work. Since Sutherland did not observe the lines at  $1058$  and  $1048\text{ cm}^{-1}$  at all, any comparable Raman scattering in the present study in the vicinity of  $1585\text{ cm}^{-1}$  would be expected to be more intense than the lines around  $1050\text{ cm}^{-1}$ . Sutherland observed the spectrum at  $-185^\circ\text{C}$ . whereas the present study was performed at  $-82^\circ\text{C}$ .; therefore the possibility remains that the relative intensities of the lines around  $1050\text{ cm}^{-1}$  and  $1585\text{ cm}^{-1}$  change enough with temperature to account for the apparent discrepancy,

although this seems highly improbable.

In addition to the well-defined features, the microphotometer trace shows a broad band with a maximum at about  $2700 \text{ cm}^{-1}$  ( $2730\text{\AA}$ ) which can be ascribed to  $\nu_2 + \nu_4$ . There may also be other diffuse bands running from  $2630\text{\AA}$  to  $2670\text{\AA}$  and from  $2670\text{\AA}$  to  $2700\text{\AA}$ . ( $1300\text{-}1900 \text{ cm}^{-1}$ ,  $1900\text{-}2300 \text{ cm}^{-1}$ ).

### Lattice Vibrations

As pointed out before, there are five fundamental lattice vibrations originating in molecular torsion, three of symmetry species F and one each of species A and E, and four fundamental lattice vibrations originating in molecular translation, two of species F and one each of species A and E. (There are actually three species F translational vibrations but one of them is the zero frequency motion corresponding to translation of the crystal as a whole.) Because of its small moments of inertia, one expects the translational motions in these molecules to be of lower frequency than the torsional motions, although the two types of motion of a given symmetry species may be coupled. These motions may also be coupled to the internal vibrations of the molecules of the same symmetry species, but because of the large frequency separation it is doubtful if such coupling is of any consequence.

As seen in Table 1, a number of lattice vibrations were observed. A complete assignment of the observed bands is not possible but several features should be noted. From the low frequency and the small frequency separation between  $\text{NH}_3$  and  $\text{ND}_3$  the bands at  $99$  and  $129 \text{ cm}^{-1}$  in  $\text{NH}_3$  and  $91$  and  $121 \text{ cm}^{-1}$  in  $\text{ND}_3$  are certainly translational modes. The Teller-Redlich ratios of the species A and E translations are both  $1.084$  and the ratio for the two species

F translations is 1.177. The observed ratios of the above two bands are both 1.08. Although the symmetry of the bands cannot be determined, the observed ratios indicate that there is very little coupling between the translational and torsional lattice modes.

From the high intensity, relatively high frequency and large frequency shift in going from  $\text{NH}_3$  to  $\text{ND}_3$ , the bands at  $284 \text{ cm}^{-1}$  in  $\text{NH}_3$  and  $213 \text{ cm}^{-1}$  in  $\text{ND}_3$  are almost certainly fundamental torsional modes. The observed frequency ratio of these bands is 1.33. The Teller-Redlich product ratio for the species A torsion is 1.41, for the species E torsion is 1.39 and for the three species F torsions is 2.736. Although again it is not possible to determine the symmetry of the motion, the observed ratio indicates that it is a nearly uncoupled torsion.

The band between  $325$  and  $375 \text{ cm}^{-1}$  in  $\text{NH}_3$  almost certainly arises in part from the species F torsion observed at  $362 \text{ cm}^{-1}$  in the infrared spectrum<sup>1</sup>. The high frequency shoulder of the corresponding band in  $\text{ND}_3$  was observed in the infrared spectrum but the position of the band center could not be determined because the low frequency limit of the spectrometer used was  $300 \text{ cm}^{-1}$ . The band between  $245$  and  $270 \text{ cm}^{-1}$  in the Raman spectrum of  $\text{ND}_3$  corresponds to the band between  $325$  and  $375 \text{ cm}^{-1}$  in  $\text{NH}_3$ . This indicates that the band center of the species F torsion in  $\text{ND}_3$  is approximately  $260 \text{ cm}^{-1}$ .

There was no evidence of Raman scattering corresponding to the bands observed at  $527$  and  $406 \text{ cm}^{-1}$  in the infrared spectrum of  $\text{NH}_3$  and  $\text{ND}_3$  respectively. These bands must be of species F but it is doubtful if they are fundamental vibrations. The remaining low frequency bands in the Raman spectrum of  $\text{NH}_3$  and  $\text{ND}_3$  are probably

combinations and overtones of lattice fundamentals.

In conclusion, the interaction between the molecules in the  $\text{NH}_3$  and  $\text{ND}_3$  crystals must be small. Not only is the separation between the different phases of coupling of the internal vibrations small but also it appears that the low frequency translational and torsional modes are only slightly coupled.

TABLE 1

## Observed Raman Bands of Crystalline Ammonia and 3-Deutero-Ammonia

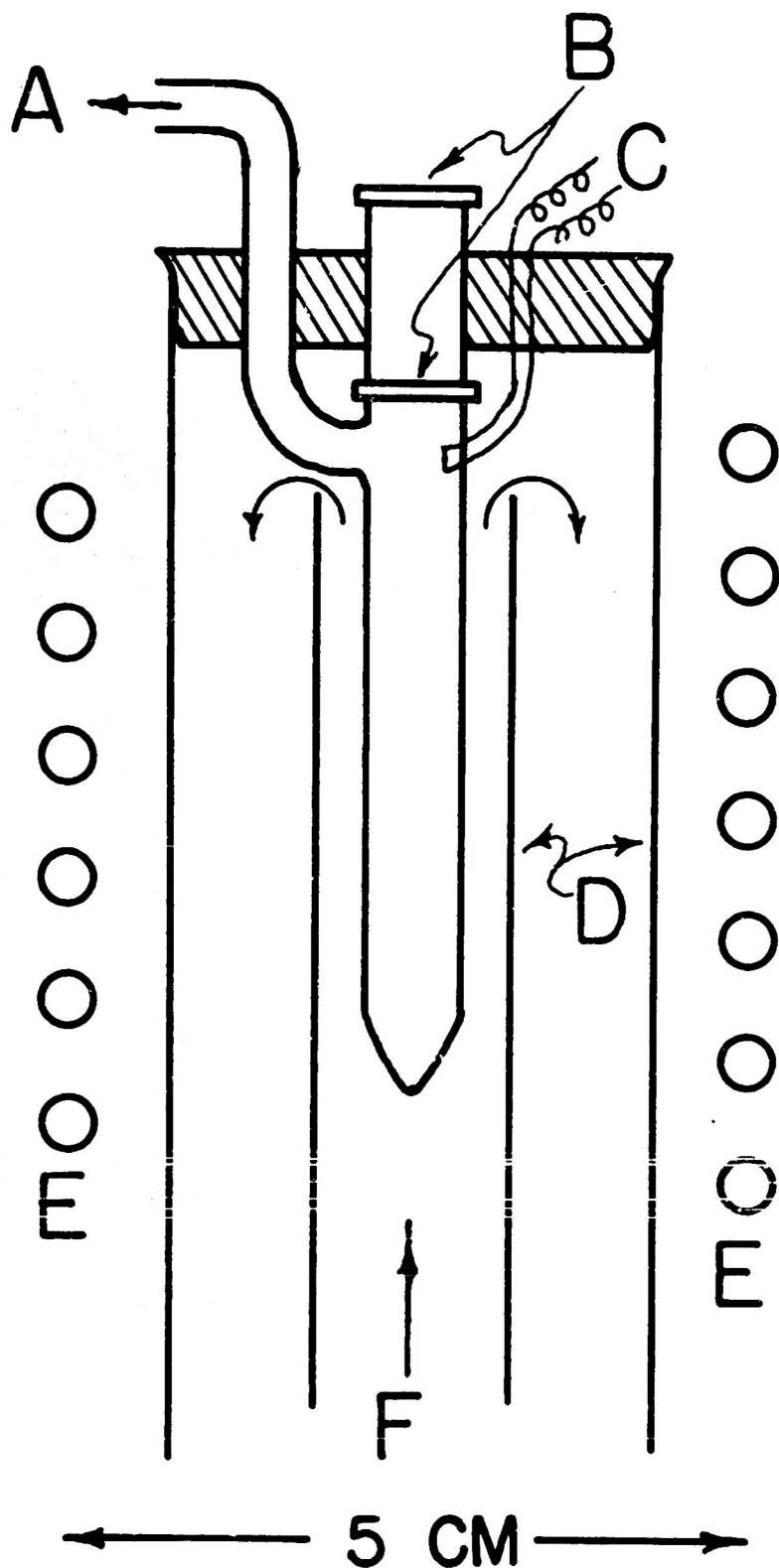
NH<sub>3</sub>ND<sub>3</sub>

Assignment*	Observed Frequency, Raman (cm <sup>-1</sup> )	Observed Frequency, Infrared (cm <sup>-1</sup> )	Assignment*	Observed Frequency, Raman (cm <sup>-1</sup> )	Observed Frequency, Infrared (cm <sup>-1</sup> )
lattice vibrations	99	53 <sup>+</sup>	lattice vibrations	91.5	41 <sup>+</sup>
	129	52 <sup>+</sup>		121	--
	284	-- <sup>+</sup>		142-161	--
	325-375	250 <sup>+</sup>		213	-- <sup>+</sup>
	~386	362 <sup>+</sup>		245-270	200
	430-462	--		280-312	< 300 <sup>+</sup>
	--	527	330-380	--	
			--	406	
			505-540	--	
$\nu_2'$	1048	--	$\nu_2'$	810	--
$\nu_2$	1058	1060	$\nu_2$	817	815
$\nu_4$	--	1646	$\nu_4$	--	1196
$\nu_{1,2,4}'$	3160-3330	--	$\nu_1'$	2330	--
$\nu_1$	--	3223	$\nu_1$	--	2318
$\nu_{3, \nu_3' \text{ or } \nu_3''}$	3375	3378 ( $\nu_3$ )	$\nu_{3, \nu_3' \text{ or } \nu_3''}$	2507	2500 ( $\nu_3$ )

\*  $\nu_1, \nu_2, \nu_3, \nu_4$  refer to the internal modes of NH<sub>3</sub>, species F if unprimed, species A if single primed and species E if double primed.

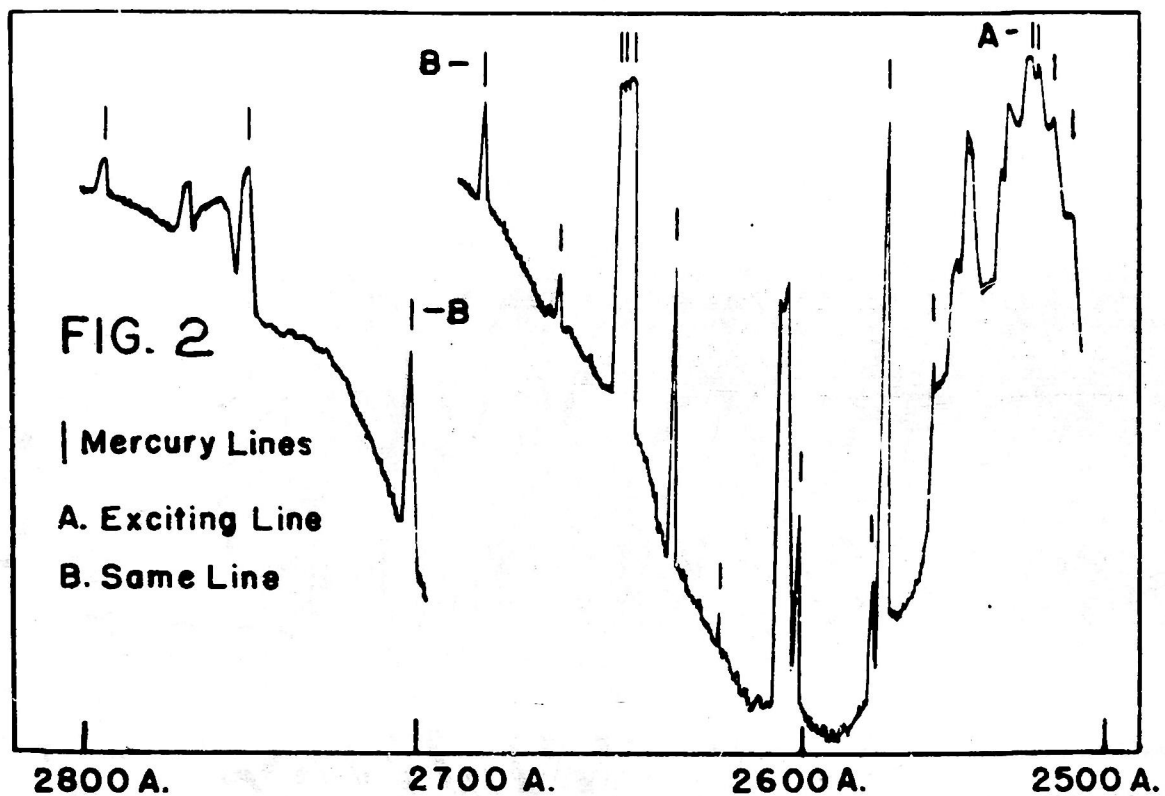
<sup>+</sup> From Combination bands in the infrared spectrum.

Figure 1



- A. To  $\text{NH}_3$  Reservoir.
- B. Double quartz window with dead air space to avoid frosting.
- C. Thermocouple.
- D. Quartz baffle.
- E. Helical quartz lamp.
- F. Cold nitrogen.

## RAMAN SPECTRUM OF NH<sub>3</sub>



## RAMAN SPECTRUM OF ND<sub>3</sub>

