

## InfraRed Absorption of Solid Ammonium Chloride and Ammonium Bromide

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Citation: [The Journal of Chemical Physics](#) **12**, 71 (1944); doi: 10.1063/1.1723918

View online: <http://dx.doi.org/10.1063/1.1723918>

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# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 12, NUMBER 3

MARCH, 1944

## Infra-Red Absorption of Solid Ammonium Chloride and Ammonium Bromide\*

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(Received January 7, 1944)

According to theoretical considerations based on specific heat, dielectric constant, coefficient of expansion, and other properties, the molecules of the solid ammonium halides, at room temperature, are thought to possess rotatory motion. This rotation is expected not to exist at temperatures below the transition temperature; namely,  $-30.4^{\circ}\text{C}$  for the chloride and  $-37.9^{\circ}\text{C}$  for the bromide. Molecular rotation, if present, should give rise to rotational fine structure superposed on the infra-red vibrational bands of the salts. Previous workers found evidence of this, but have not resolved the fine structure. The present investigation was undertaken in the hope of resolving this fine

structure, if any, and studying the changes in it resulting from lowering the temperature below the transition point. Fine structure in the  $5.6\text{-}\mu$  vibrational band of ammonium chloride and ammonium bromide was resolved. This structure was of the order of magnitude expected if the  $\text{NH}_4$  group rotating in the molecule were responsible for the fine structure. The fine structure existed practically unaltered to temperatures down to  $-20^{\circ}\text{C}$ . There was considerable change between  $-20^{\circ}\text{C}$  and  $-45^{\circ}\text{C}$ , but then the altered fine structure persisted down to at least  $-60^{\circ}\text{C}$  with little additional change.

### INTRODUCTION

THE study of the infra-red absorption spectra of many gases under high dispersion has yielded much valuable information about the structure and behavior of their molecules. The infra-red absorption bands of solids have not been studied as extensively with instruments of high resolving power, though such investigations should also yield valuable information.

Of particular interest are those crystals in which the molecules are believed to undergo some form of rotation. Typical of these are the ammonium halides, for which theory<sup>1</sup> predicts the existence of rotational motion of the  $\text{NH}_4$  group at room temperature. A review of the literature† reveals that experiments on specific

heats, dielectric constants, coefficients of expansion, crystal structure, and Raman spectra do not contradict the predicted molecular rotation, but neither do they furnish proof of its existence. However, the most recent report<sup>2</sup> of the numerous investigations of the infra-red spectra of the ammonium halides furnishes some evidence of the presence of rotational fine structure in the  $5.6\text{-}\mu$  vibrational band of the ammonium salts. Pohlman, with a prism spectrometer, studied the infra-red bands at temperatures both above and below the lower transition points (at, or near, which rotation is expected to cease—with decreasing temperature). He obtained differences in the bands at the two temperatures, but the resolving power of his instruments was not sufficiently great to allow conclusions regarding the rotatory state of the molecules to be drawn.

The present investigation, employing a grating spectrometer of higher resolving power than

\* Experiments performed in 1942.

\*\* Now a member of the scientific staff of Columbia University.

<sup>1</sup> L. Pauling, *Phys. Rev.* **36**, 430 (1930).

† A short bibliography of pertinent papers is attached to the end of this report.

<sup>2</sup> R. Pohlman, *Zeits. f. Physik* **79**, 394 (1932).

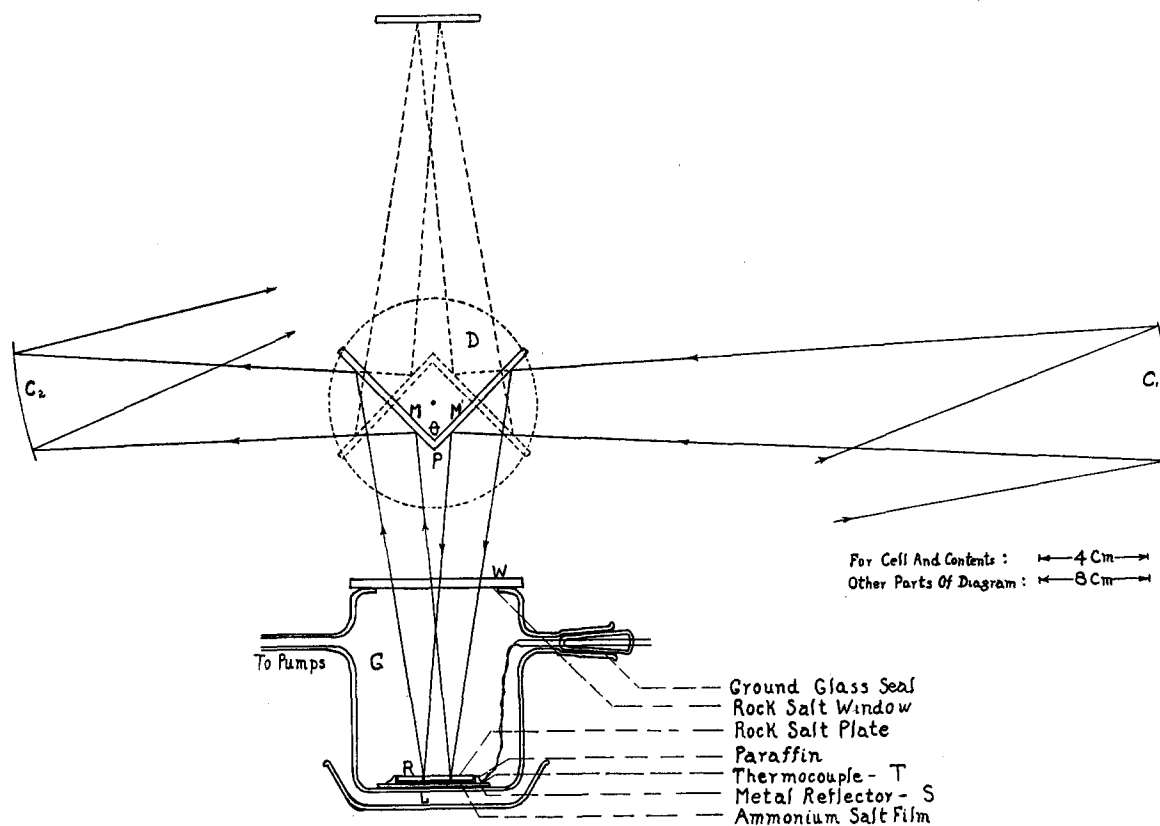


FIG. 1.

those used in the previous studies, was undertaken in the hope of resolving any rotational fine structure present in the vibrational bands of ammonium chloride and ammonium bromide at room temperature, and determining what changes occurred in this fine structure at temperatures below the transition point ( $-30.4^{\circ}\text{C}$  for the chloride and  $-37.9^{\circ}\text{C}$  for the bromide). There is a report in the literature of a successful experiment similar to the proposed one. Shearin,<sup>3</sup> using a grating spectrometer, was able to resolve clearly the fine structure in the near infra-red vibrational band of HCL after Hettner,<sup>4</sup> in a previous experiment with a prism instrument of lower resolving power, had found evidence of the existence of the rotational fine structure.

At room temperature in this investigation, attention was directed to the  $5.6\text{-}\mu$  and  $7\text{-}\mu$  bands of the two salts. The  $3.2\text{-}\mu$  bands were inaccessible

with the apparatus used here, because of high  $\text{CO}_2$  and water vapor absorption of the atmosphere at that wave-length. At low temperatures, attention was focused on the  $5.6\text{-}\mu$  band of ammonium bromide only. The latter procedure was adopted because Pohlman's investigation, and exploratory experiments in the present investigation, indicated (1) that little change occurred in the  $7\text{-}\mu$  bands in going to low temperature, and (2) that similar changes in the  $5.6\text{-}\mu$  bands of both ammonium chloride and ammonium bromide were to be expected in going to temperatures below the transition temperature. The ammonium bromide was chosen for this work.

This investigation, therefore, was divided into two parts. The first dealt with experiments at room temperature, which included studies of the  $5.6\text{-}\mu$  and  $7\text{-}\mu$  bands of ammonium chloride and ammonium bromide. The second part consisted of a study of the  $5.6\text{-}\mu$  band of ammonium bromide at four different temperatures ranging from  $27^{\circ}\text{C}$  to  $-60^{\circ}\text{C}$ .

<sup>3</sup> P. E. Shearin, Phys. Rev. 48, 299 (1935).

<sup>4</sup> G. Hettner, Zeits. f. Physik 78, 141 (1932).

## I. APPARATUS AND PROCEDURE

### A. Spectrometer and Optical Path at Room Temperature

The conventional type of infra-red grating spectrometer used in these experiments was calibrated by Shearin and Plyler<sup>5</sup> in 1938, and was rechecked during the present experiments by use of well-known  $\text{CO}_2$  and water vapor bands. The infra-red source was a Nernst glower, operating on 110 volts a.c. in series with a variable resistor by means of which the current was adjusted to 0.3 ampere.

For room temperature experiments, the radiation, after passing through a  $30^\circ$  rocksalt prism, was focused on, and passed through, a thin film of the solid ammonium salt under investigation. The latter was deposited on a plate of rocksalt which could be moved vertically out of the beam to allow for zero readings. After traversing the film and plate, the beam passed through a shutter into an insulated housing enclosing the grating (2060 lines per inch) and the vacuum-thermopile detector. The current from the detector, after amplification by a Moll thermorelay, went to a galvanometer from whose mirror a spot of light was reflected some four meters to a translucent scale on which readings were made. The slits in the optical path were 0.5 mm in width for all data, giving an equivalent slit-width of  $0.012\mu$ .

For each setting of the grating angle, the radiation first passed through the rocksalt plate and film of ammonium salt. This plate was then moved out of the beam and automatically replaced by a similar rocksalt plate having no deposited film. The ratio of the galvanometer deflection with the film in the beam to the deflection with the film out of the beam gave the percentage transmission of the ammonium salt for that wave-length. Prior to depositing the film on the plate, adjustments were made so that the beam in alternately traversing the two plates produced the same galvanometer deflection.

### B. Low Temperature Apparatus

For the low temperature experiments the optical path was altered to the form shown in

<sup>5</sup> E. K. Plyler and P. E. Shearin, J. Opt. Soc. Am. **28**, 61 (1938).

Fig. 1. The support for the rocksalt plates used in the room temperature experiments was replaced by two front-surfaced, plane mirrors  $M$  and  $M'$  (Fig. 1) mounted on a vertical disk  $D$  which could be rotated about its horizontal axis, the axis being perpendicular to the beam. The mirrors were mounted with their planes perpendicular to the face of the disk, with one pair of their ends  $P$  in contact, and with a dihedral angle of  $95^\circ$  between them. Directly below the mirrors was placed an evacuated cell  $G$  containing the rocksalt plate  $R$  which had the film under investigation deposited on its bottom face. The rocksalt plate  $R$  rested, with the film of ammonium halide downward, on a metal reflector  $S$  of polished stainless steel, to which it was firmly held by paraffin around the edges. The top of the cell was closed by a rocksalt window  $W$ .

The concave mirror  $C_1$  was adjusted so that, when the plane mirrors were turned with  $P$  pointing downwards, the light beam followed the arrows from  $C_1$  to  $M'$  to a focus on the reflector  $S$ ; thence to  $M$ ,  $C_2$ , and the detector. In the cell it passed twice through the rocksalt plate and the film of ammonium salt. When the disk was rotated through  $180^\circ$  so that  $P$  pointed upwards, the beam traversed a similar path from  $C_1$  to  $C_2$ , but one not containing the ammonium salt and the two rocksalt plates  $R$  and  $W$ . The ratio of the deflections of the galvanometer as the beam alternately travelled the two paths gave the percentage absorption of the film for that wave-length. Prior to depositing the film the apparatus was adjusted so that (with  $R$  and  $W$  in place) the beam, in alternately traversing the two paths, produced equal galvanometer deflections.

Close beside the plate of rocksalt  $R$  a copper constantan thermocouple  $T$  was securely fixed to the steel reflector. It is estimated that temperatures of the film, indicated by the nearby thermocouple, are not in error by more than  $\pm 3^\circ\text{C}$ . Beneath the steel reflector in the cell a thin layer of solder furnished thermal contact with the glass bottom of the cell. Underneath the cell was placed a small, shallow dish containing the cooling agents used to control the temperature of the film.

### C. Preparation of Films

The method of preparing films found most satisfactory consisted in suspending the rocksalt plate horizontally, face-downwards, inside a large-mouth flask, evacuated to about  $10^{-3}$  cm of mercury. A small flame underneath the flask caused part of the ammonium salt crystals, thinly scattered on the bottom of the flask, to vaporize. Some of the vapor condensed on the rocksalt

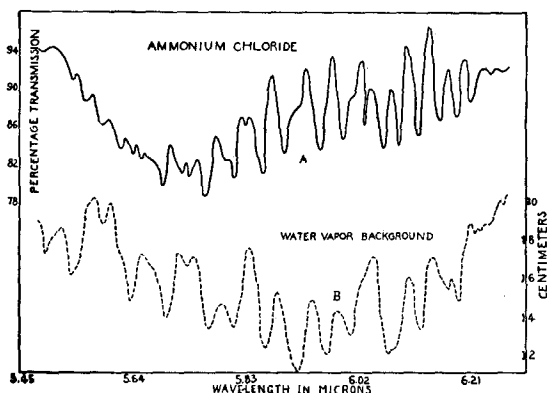


FIG. 2.

plate. Heating continued until enough vapor condensed on the plate to give a film of the desired opacity. Only films having a percentage transmission of  $80 \text{ percent} \pm 2 \text{ percent}$  at the center of the  $5.6\text{-}\mu$  band of that salt were used in these experiments. Microscopic examination revealed that the crystals in the films obtained by this "vacuum" method were so closely packed that it was impossible to determine where one crystal stopped and the next began. Thus, a practically continuous layer of salt was presented to the incident light, rather than many individual scattering particles.

## II. RESULTS

### A. Room Temperature

On three ammonium chloride films, deposited by the vacuum method described above, five complete runs through the  $5.6\text{-}\mu$  band and three through the  $7\text{-}\mu$  band were made. In each run, readings were taken at intervals of one minute of arc on the grating circle, corresponding to  $0.007\mu$ .

The percentage of incident radiation transmitted by the halide film as a function of wave-

length is shown in Fig. 2A for the  $5.6\text{-}\mu$  band. The fine structure lines shown in Fig. 2 were reproducible in successive experiments, with only small differences in depth of the absorption lines and irregularities on the higher percentage transmission "peaks" (see Section III B). The wavelengths and wave numbers of the prominent fine structure lines appearing in the  $5.6\text{-}\mu$  band of ammonium chloride are listed in columns 1 and 2, respectively, of Table I. Column 3,  $\Delta\nu$ , is the difference, in wave numbers, between the successive prominent fine structure lines.

The intensity of the  $7\text{-}\mu$  band of ammonium chloride (Fig. 3A) is so great that at the band center almost no radiation penetrates a film which allows 96 percent transmission on the sides of the band. No fine structure is present, but a few minor irregularities appear on the sides of the band.

In Fig. 4 the  $5.6\text{-}\mu$  band of ammonium bromide is shown. It is noticed that the intense, fairly regularly spaced fine structure lines throughout the band are more prominent than in the corresponding chloride band. The average spacing of these lines is about the same as in the chloride

TABLE I. Fine structure lines of the  $5.6\text{-}\mu$  band of  $\text{NH}_4\text{Cl}$ .

Wave-length microns	Wave numbers $\text{cm}^{-1}$	$\Delta\nu$ $\text{cm}^{-1}$	
5.69	1760		
5.76	1740	20	
5.81	1723	17	
5.86	1708	15	
5.90	1696	12	
5.96	1680	16	
6.00	1667	13	
6.06	1650	17	
6.12	1636	14	
6.16	1624	12	
6.19	1608	16	
			Average $\Delta\nu = 15.2 \text{ cm}^{-1}$

band. (See Tables I and II.) Between the intense lines, on the peaks of the curve, there are irregularities which indicate a much narrower, unresolved, fine structure similar to, though more pronounced than, that found in the corresponding chloride band. It was not possible to determine this smaller fine structure accurately with the instrument used here. Table II gives the information for the ammonium bromide corresponding to that listed in Table I for the chloride.

The  $7\text{-}\mu$  band of ammonium bromide (Fig. 5) was found to be similar in width and intensity to the corresponding chloride band. However, there was some difference in that the bromide band showed some very narrow fine structure of low intensity and a shape on the long wavelength side somewhat different from that shown in the corresponding band of the chloride.

### B. Ammonium Bromide at Various Temperatures

Only one film of ammonium bromide was used in these experiments, and all data were taken on the same day. On this film, two sets of data were taken through the  $5.6\text{-}\mu$  band at each of four temperatures, in the order named:  $27^\circ\text{C}$ ,  $-20^\circ\text{C}$ ,  $-45^\circ\text{C}$ ,  $-60^\circ\text{C}$ . At the end of the last run the temperature was allowed to return to  $27^\circ\text{C}$  and another set of data was taken (which duplicated almost exactly the previous data at  $27^\circ\text{C}$ ). All readings were taken at 2-minute intervals  $0.014\mu$  on the grating circle.

The two curves in Fig. 6 show the results obtained. The dotted curve represents the absorption at  $27^\circ\text{C}$  and  $-20^\circ\text{C}$ : The fine structure at these two temperatures was practically identical. This dotted curve appears slightly different from the curve in Fig. 4, which was also obtained at  $27^\circ\text{C}$ . The difference is due to the procedure of taking readings at 2-minute intervals (or  $0.0014\mu$ ) for the curve in Fig. 6, which fails to

reveal some of the less prominent lines shown in the curve of Fig. 4 (for which readings were taken at 1-minute intervals). The solid curve (Fig. 6) shows the absorption at  $-45^\circ\text{C}$  and  $-60^\circ\text{C}$ , for it was found that at both of these tempera-

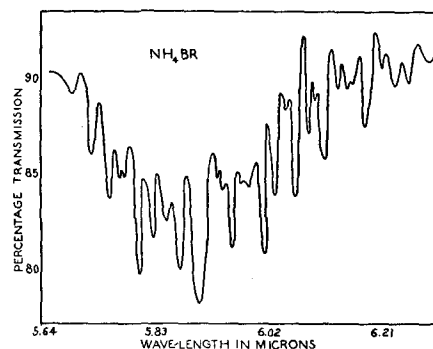


FIG. 4.

tures the band possessed the same fine structure. The alteration in fine structure occurred between  $-20^\circ$  and  $-45^\circ\text{C}$ .

Three points are to be noticed. First, the fine structure is much decreased in intensity at the lower temperature, but is still present, at the same wave-lengths. Second, the over-all shape of the band at the lower temperature is sharper and the charge is such that instruments of low resolving power would indicate a slight apparent shift of the band to shorter wave-lengths. Third, as mentioned above, the alteration takes place between  $-20^\circ\text{C}$  and  $-45^\circ\text{C}$ , a temperature range which includes the transition temperature of this salt ( $-37.9^\circ\text{C}$ ).

## III. DISCUSSION OF RESULTS

### A. Water Vapor in Atmosphere

The study of the infra-red spectra of the ammonium salts was complicated by the presence of numerous fine structure lines of the broad water vapor band having a center at  $6.26\mu$ .<sup>6</sup> The radiation from the Nernst glower has practically uniform intensity throughout this region. But the water vapor caused the galvanometer deflections through the air to vary from 4 to 30 centimeters, depending on the humidity and on the proximity of the grating setting to a

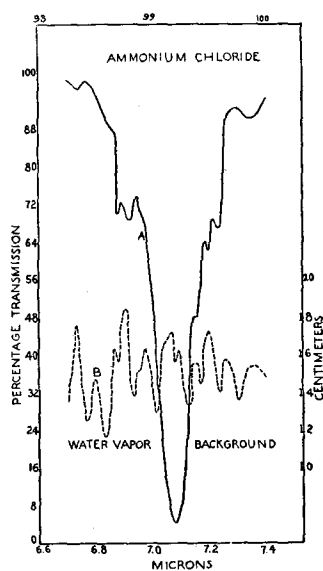


FIG. 3.

<sup>6</sup> E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

water vapor line. This explains the necessity of making two galvanometer readings for each wave-length in order to obtain the percentage transmission: one, that resulting when the radiation traversed the air path alone; the other,

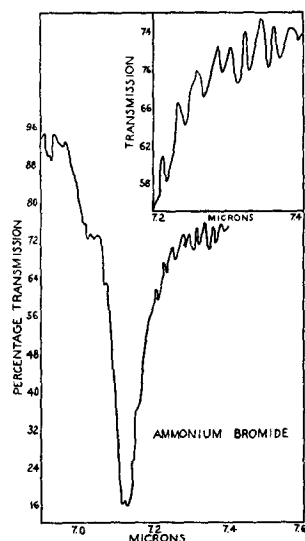


FIG. 5.

when both the air path and halide film were traversed. By simply plotting the air deflections of the galvanometer from any set of data as a function of wave-length the water vapor absorption spectrum could be shown (curve *B*, Fig. 2 and curve *B*, Fig. 3).

The wave-length spacing of the water fine structure is of the same order of magnitude as that of the ammonium chloride shown in curve *A* (Fig. 2). At first glance one might suspect that the apparent fine structure in the chloride band could be a result of the water vapor structure. But a careful scrutiny shows that there is no consistent correlation between peaks or dips on the two curves, as would be the case if the apparent fine structure on the halide curve were a result of the water vapor structure. Also the decidedly different structure of the  $\text{NH}_4\text{Cl}$  band on the low wave-length side, where the water structure is about the same, indicates that the water vapor is not responsible for the structure appearing on the  $\text{NH}_4\text{Cl}$  band. A similar bit of evidence comes from Fig. 3, which shows the band of  $\text{NH}_4\text{Cl}$  at  $7\mu$ , where the water structure (curve *B*) is more pronounced than at  $5.6\mu$ . But

there is no fine structure on the chloride band. Finally, it was found that similar fine structure of the ammonium salts was obtained on days of quite different absolute humidity. Thus it appears that the water vapor, though troublesome, did not affect the absorption spectra obtained for the ammonium salts.

### B. Errors and Accuracy

For any setting of the grating angle, consecutive measurements of percentage transmission of the ammonium salt agreed within  $\pm 0.5$  percent. The chief discrepancy in the data from film to film, or between different experiments on the same film, resulted from the inability to reproduce grating-angle settings exactly. With the aid of a low power microscope, it was possible to reproduce grating angle settings to within an estimated maximum error of 6 seconds of arc, which corresponds to a possible variation of  $0.0015\mu$  in wave-length. This is about 7 percent of the equivalent slit-width. If intense, closely spaced, fine structure lines were present, then an error of this magnitude in wave-length setting could cause an appreciable difference in the percentage transmission. This is apparently the case in the  $5.6\text{-}\mu$  bands, for, though successive measurements of transmission were constant for a given grating setting, the measurements frequently were not exactly the same when the grating angle was reset after having been moved. Thus, there was some uncertainty as to the absolute depth of a given line and the finer details on the "peaks" of the curves.

However, the prominent fine structure lines

TABLE II. Fine structure lines of the  $5.6\text{-}\mu$  band of  $\text{NH}_4\text{Br}$ .

Wave-length microns	Wave numbers $\text{cm}^{-1}$	$\Delta\nu$ $\text{cm}^{-1}$	Average $\Delta\nu = 14.8 \text{ cm}^{-1}$
5.71	1750		
5.75	1740	10	
5.80	1725	15	
5.87	1705	20	
5.91	1692	13	
5.96	1679	13	
6.02	1660	19	
6.07	1648	12	
6.11	1636	12	
6.18	1618	18	
6.24	1602	16	

shown in the bands at room temperature were reproducible from film to film. And in the low temperature experiments, the difference in fine structure between  $-20^\circ\text{C}$  and  $-45^\circ\text{C}$  (Fig. 6) was of such magnitude that the small variations were negligible in comparison. The wave-lengths of the absorption lines are accurate to within about  $0.006\mu$ ; approximately half the equivalent slit-width.

### C. Room Temperature

The results of this investigation of the  $7\text{-}\mu$  bands of ammonium chloride and ammonium bromide are in agreement with results of earlier investigations, and show little in addition. The irregularity on the long wave-length side of the  $7\text{-}\mu$  band of the bromide is more clearly shown in this investigation, but the explanation of its presence in the bromide band and its absence in the chloride band, or of the difference between the shapes of these corresponding bands of the two salts is not known.

The prominent fine structure in the  $5.6\text{-}\mu$  band of the ammonium bromide (Fig. 4) appears to be of the same nature as the structure in the corresponding band of ammonium chloride (Fig. 2), because the lines are similar in spacing and arrangement. However, there are two distinct differences. First, the shorter wave-length side of the band in the chloride has more irregularity, and was less resolvable, while in the bromide the fine structure lines were present on both sides of the band. Second, on the peaks of the curves, between the narrow fine structure absorption lines, the curve for the bromide shows more irregularity than is found on the corresponding curve for the chloride. The crystal structures of the two salts at room temperature, as pointed out earlier, are believed to be identical, and the tetrahedral arrangement of the  $\text{NH}_4$  radical in the crystals of both salts is assumed similar. The differences, therefore, in the fine structure of the corresponding band of the two salts are perhaps due to unequal influence of the different halogen atoms on the  $\text{NH}_4$  radical in the respective crystals.

### D. Low Temperature

It was hoped that examination of the fine structure of the  $5.6\text{-}\mu$  bromide band both above

and below the transition temperature would indicate whether or not rotation of the molecules was present at room temperature, and if so, whether this rotation ceased below the transition temperature. From the results obtained, if the resolved fine structure at the higher temperature is due to rotation, then the molecules continue to rotate below the transition temperature.

On the basis of a calculation of the kind outlined by Pohlman<sup>2</sup> for the fine structure obtained

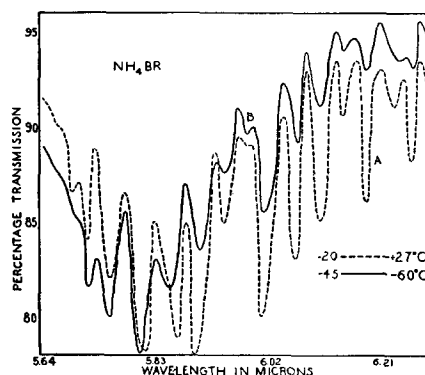


FIG. 6.

in  $\text{NH}_4\text{NO}_3$ , it is indicated that the fine structure obtained in the present investigation is due to rotation. We take

$$\Delta\nu = 15 \text{ cm}^{-1}$$

as the average spacing of the fine structure lines for the two salts, and assume an average wave-length

$$\lambda = 5.6\mu = 5.6 \times 10^{-4} \text{ cm.}$$

If one assumes that the rotation of the tetrahedral  $\text{NH}_4$  radical is responsible for these lines, it follows that the moment of inertia is independent of the direction of the axis of rotation. From this, one obtains for the moment of inertia

$$I = \frac{h}{4\pi^2\Delta\nu} = 3.69 \times 10^{-40} \text{ g cm}^2.$$

Then, from the geometry of the tetrahedron, it follows that the N-H distance indicated by these experiments is  $0.913 \times 10^{-8}$  centimeter. However, in this calculation, no consideration has been made of the possible influences of the neighboring atoms on the rotation groups. Therefore, the value stated above is to be taken as the



order of magnitude, and not as an absolute measure of the N—H distance in  $\text{NH}_4$ .

It is known from other studies of the structure of molecules that the value obtained here ( $0.913 \times 10^{-8}$  cm) for the intermolecular distance is approximately correct. Therefore, the calculation above indicates that the infra-red fine structure of these two ammonium salts is due to rotation of the  $\text{NH}_4$  group in the crystal. And the low temperature data indicate that this rotation continues, though quite altered, at temperatures below the transition temperature.

The author expresses his sincere thanks to Dr. Paul E. Shearin who suggested this investigation and gave unfailing interest and practical aid in the experiments, and to Dr. Nathan Rosen for his interest and helpful discussions.

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