

**881. Infrared Spectra, Structure, and Hydrogen-bonding in Ammonium Salts.**

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Infrared spectra of a series of ammonium salts of monobasic acids have been examined. The spectra of the salts  $\text{NH}_4\text{N}_3$ ,  $\text{NH}_4\text{HF}_2$ ,  $\text{NH}_4\text{NCO}$ ,  $\text{NH}_4\text{NCS}$ ,  $\text{NH}_4\text{NO}_2$ ,  $\text{NH}_4\text{NO}_3$  show a combination frequency,  $\nu_4 + \nu_6$ , involving a torsional mode, and a multiplicity of lines at  $3000\text{ cm.}^{-1}$ ; all these salts have structures differing from those of the potassium and rubidium salts. It is concluded that in these salts the ammonium ion is locked in position in the crystal lattice by hydrogen bonding. No combination frequency,  $\nu_4 + \nu_6$ , or multiplicity of lines is found in  $\text{NH}_4\text{ClO}_4$ ,  $\text{NH}_4\text{BF}_4$ ,  $\text{NH}_4\text{B}(\text{C}_6\text{H}_5)_4$ , or  $\text{NH}_4\text{PF}_6$  and these salts are isomorphous with the corresponding potassium and rubidium salts. It is concluded that in these salts the  $\text{NH}_4^+$  ion is free to rotate. In  $\text{NH}_4\text{SO}_3\text{F}$  and  $\text{NH}_4\text{SO}_3\cdot\text{CH}_3$ , though a multiplicity of lines at  $3000\text{ cm.}^{-1}$  is found, no combination frequency of the torsional mode is detectable and the salts are isomorphous with the potassium and rubidium salts.

VARIOUS criteria have been used to determine whether the ammonium ion in an ammonium salt is freely rotating. They are: (1) The distortion of the crystal structure of the ammonium salt from that of the potassium and rubidium salts; (2) the line-width of the proton signal from the ammonium ion in the nuclear magnetic resonance spectrum; (3) specific-heat measurements on the salt; and (4) the infrared spectrum of the salt. Probably none of the criteria is sufficient to establish definitely the presence of free rotation and since in (2) and (3) particularly the experiments are difficult, evidence is only available from all four methods in the ammonium halides, in which the behaviour of the ammonium ion has been clearly established.

However the combination of X-ray evidence and infrared spectra can give much information about the behaviour of the ammonium ion in a crystal; we therefore investigated the infrared spectra of a series of ammonium salts of monobasic anions and, where it was unknown, tried to establish the isomorphism of the ammonium and potassium salts.

The ammonium ion has two fundamental frequencies active in the infrared region. They are  $\nu_3$ , which corresponds to N-H stretching and  $\nu_4$ , which is a deformation frequency of the ammonium ion. Both are triply degenerate in the freely rotating ion but this degeneracy will disappear if the ammonium ion is not rotating in the lattice, owing to the interaction of the symmetry of the site with that of the ion.

Apart from the thorough and extensive work of Wagner and Hornig<sup>1</sup> and Plumb and Hornig<sup>2</sup> on the infrared spectra of the ammonium halides, that of Dows, Whittle, and Pimentl<sup>3</sup> on ammonium azide and that of Cote and Thompson<sup>4</sup> on ammonium borofluoride, little systematic work has been done on the infrared spectra of the crystalline ammonium salts. Miller and Wilkins<sup>5</sup> have examined the spectra of a number of ammonium salts but theirs was mainly an analytical investigation and no attempt at a detailed assignment was made. Keller and Halford<sup>6</sup> have investigated the spectrum of ammonium nitrate but unfortunately their data are at variance with those of Miller and Wilkins.

<sup>1</sup> Wagner and Hornig, *J. Chem. Phys.*, 1950, **18**, 296, 305.

<sup>2</sup> Plumb and Hornig, *J. Chem. Phys.*, 1953, **21**, 366, 947.

<sup>3</sup> Dows, Whittle, and Pimentl, *J. Chem. Phys.*, 1955, **23**, 1258.

<sup>4</sup> Cote and Thompson, *Proc. Roy. Soc.*, 1952, *A*, **210**, 217.

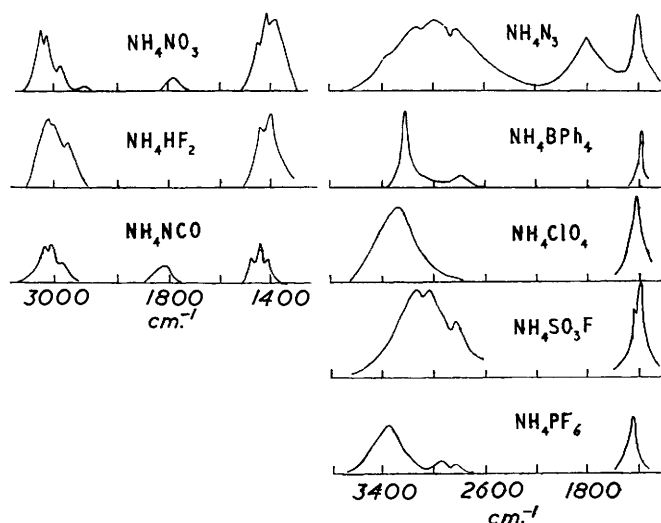
<sup>5</sup> Miller and Wilkins, *Ind. Eng. Chem. Anal.*, 1952, **24**, 1253.

<sup>6</sup> Keller and Halford, *J. Chem. Phys.*, 1949, **17**, 26.

## EXPERIMENTAL

**Materials.**—Ammonium azide was made by passing dry ammonia gas into an ethereal solution of hydrazoic acid. The precipitated ammonium azide was recrystallized from absolute ethyl alcohol and dried *in vacuo*. Ammonium cyanate was prepared by passing dry ammonia gas into a dry ethereal solution of cyanic acid, obtained by warming cyanuric acid in a stream of dry nitrogen and passing the gas through dry ether at  $-17^{\circ}$ . Ammonium hydrogen difluoride was made by adding a slight excess of hydrofluoric acid to aqueous ammonia; the solution was evaporated to dryness in a platinum dish and heated on a water-bath for several hours. Ammonium thiocyanate and nitrate were obtained by recrystallizing the "AnalaR" salt from water. Ammonium nitrite was prepared by treating aqueous barium nitrite with the stoichiometric quantity of aqueous ammonium sulphate, filtering, and freeze-drying the filtrate. Ammonium borofluoride was obtained as the "AnalaR" salt. Ammonium perchlorate was made by adding excess of aqueous ammonia to aqueous perchloric acid. Ammonium tetraphenylborate was precipitated by treating a filtered aqueous solution of the sodium salt with ammonium chloride. The precipitated salt was recrystallized from acetone. Ammonium fluorosulphate was prepared by treating aqueous fluorosulphonic acid with aqueous ammonia and evaporation. Ammonium methanesulphonate was made in the same manner. Ammonium hexafluorophosphate was kindly provided by Dr. W. G. Palmer.

**Apparatus and Methods.**—The infrared spectra were measured with a Perkin-Elmer 21 double-beam continuously recording infrared spectrophotometer. Most spectra were recorded



both with rock-salt and with fluorite optics. All solids were finely powdered and mullied with Nujol and with hexachlorobutadiene. In one or two cases a small amount of the powdered solid was mixed with powdered potassium bromide and pressed into a disc.

**Results.**—The observed frequencies are recorded in Table 1. Since the spectra were taken at room temperature in mulls, only the fairly strong bands were observable and all the features recorded by Hornig and his co-workers for the ammonium halides were not observed. The comparable bands found by Wagner and Hornig and Plumb and Hornig for  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$ , and  $\text{NH}_4\text{F}$  are also listed. The assignments were made largely on a basis of comparison with Hornig and his co-workers' results. The frequencies  $\nu_4$  and  $\nu_3$  are both infrared-active, and strong bands corresponding to these modes are found at about 1400 and 3200  $\text{cm}^{-1}$ . The first harmonic of  $\nu_4$ , *i.e.*,  $2\nu_4$ , is found at around 2800  $\text{cm}^{-1}$  in most of the spectra but its strength varies considerably; the band is very weak in some spectra and much stronger in others. An additional band at 3000–3100  $\text{cm}^{-1}$  is found in some of the spectra. Also in some spectra a band of moderate strength is found in the region 1600–2000  $\text{cm}^{-1}$ . This band, in the case of the ammonium and deuterioammonium halides, has been shown by Hornig and his

co-workers, to arise from the interaction of  $\nu_4$  with the torsional oscillation  $\nu_8$  of the ammonium on its lattice site. Some examples of the shapes of the  $\text{NH}_4^+$  bands in the spectra found are shown in the Figure. Only the spectra of the ammonium ions are shown; the spectra of the anions were eliminated by considering the bands common to the potassium and the ammonium salts.

## DISCUSSION

Table I shows that the variation in the values of the infrared-active fundamentals of the ammonium ion from salt to salt is quite considerable; thus the value of  $\nu_4$  ranges from 1484 to 1390  $\text{cm}^{-1}$  and of  $\nu_3$  from 3332 to 3100  $\text{cm}^{-1}$ . Hydrogen bonding should lengthen the N-H bond and thus shift  $\nu_3$  to a lower frequency; it should also raise the value of  $\nu_4$ . In agreement with this, ammonium fluoride, which might reasonably be expected to be the

TABLE I. Infrared frequencies ( $\text{cm}^{-1}$ ) of the ammonium ion in its monobasic salts.

Salt	Assignment				
	$\nu_4$	$\nu_4 + \nu_6$	$2\nu_4$	$\nu_3 + \nu_4$	$\nu_3$
$\text{NH}_4\text{Br}$ .....	1401 (1429)	1712	2833	3031	3137
$\text{NH}_4\text{Cl}$ .....	1403 (1445)	1762	2870	3044	3138
$\text{NH}_4\text{F}$ .....	1484 (1503)	2007	2830	3024	3100
$\text{NH}_4\text{N}_3$ .....	1414	1810	2830	3000	3140
$\text{NH}_4\text{NCO}$ .....	1408 1443 1475	1825	2840	3040	3140
$\text{NH}_4\text{HF}_2$ .....	1406 (1445)	*	2875	3050	3140
$\text{NH}_4\text{NCS}$ .....	1404 (1435)	1670	2810	3040	3160
$\text{NH}_4\text{NO}_2$ .....	1390 (1405)	1753	2785	3010	3150
$\text{NH}_4\text{NO}_3$ .....	1420 (1455)	1765	2860	3100	3160
$\text{NH}_4\text{ClO}_4$ .....	1425	—	2850	—	3290
$\text{NH}_4\text{BF}_4$ .....	1431	—	—	—	3332
$\text{NH}_4\text{BPh}_4$ .....	1396	—	2770	—	3222
$\text{NH}_4\text{PF}_6$ .....	1433	—	2920	—	3330
$\text{NH}_4\text{SO}_3\text{F}$ .....	1405 (1448)	—	2830	3500	3150
$\text{NH}_4\text{SO}_3\cdot\text{CH}_3$ .....	1414 (1446)	—	2820	2035	3130

\* A broad, strong  $\text{HF}_2$  band is found in the region 1500—1800  $\text{cm}^{-1}$  with overtones in the region 1800—2000  $\text{cm}^{-1}$  so that failure to identify a  $\nu_4 + \nu_6$  for  $\text{NH}_4^+$  is not regarded as significant.

( ) a weak side band occurring as a shoulder.

most heavily hydrogen-bonded salt, has the lowest value for  $\nu_3$  (3100  $\text{cm}^{-1}$ ) and the highest for  $\nu_4$  (1484  $\text{cm}^{-1}$ ). However the other ammonium salts do not fit closely into this simple pattern. Fortunately certain correlations do appear to exist and these are discussed below.

There appears to be a strong correlation between the occurrence of the combinational mode  $\nu_4 + \nu_6$  and the occurrence of structural differences between the ammonium salts and the corresponding rubidium and potassium salts. Also, in the few cases where nuclear magnetic resonance studies have been undertaken, the salts in which this technique indicates that the  $\text{NH}_4^+$  ion is not rotating,  $\text{NH}_4\text{Br}$ ,  $\text{NH}_4\text{Cl}$ ,<sup>7</sup> and  $\text{NH}_4\text{F}$ ,<sup>8</sup> the mode  $\nu_4 + \nu_6$  occurs in the infrared region. In the one salt in which nuclear magnetic resonance indicates that the ion  $\text{NH}_4^+$  is rotating,  $\text{NH}_4\text{BF}_4$ ,<sup>9</sup> no band corresponding to  $\nu_4 + \nu_6$  can be found in the infrared. All the ammonium salts in which  $\nu_4 + \nu_6$  does not occur are isomorphous with the corresponding potassium and rubidium salts. The results are summarized in Table 2.

It seems reasonable to ascribe the apparent lack of free rotation and the distortion of the crystal structure to hydrogen bonding. It is noteworthy that the frequency  $\nu_6$  is highest for the fluoride and lowest for the bromide and thiocyanate with the values for the azide, cyanate, and nitrate intermediate. Such an order would be expected from an *a priori* consideration of the abilities of the atoms concerned to form hydrogen bonds.

Both the frequencies  $\nu_4$  and  $\nu_3$  are triply degenerate in the freely rotating ammonium

<sup>7</sup> Gutowsky, Pake, and Bersohn, *J. Chem. Phys.*, 1954, **22**, 643.

<sup>8</sup> Drain, *Discuss. Faraday Soc.*, 1955, **19**, 200.

<sup>9</sup> Richards, *Trans. Faraday Soc.*, 1955, **51**, 468.

ion. However when the ion is locked in position in the crystal lattice the degeneracy is removed and a splitting is expected. The  $\nu_4$  band would be expected to produce a triplet with one  $A$  component and two  $B$  components. Such a splitting has indeed been observed at low temperatures by Hornig and Wagner for ammonium halides and by Dows, Whittle, and Pimentl for ammonium azide. However at room temperature the bands are considerably

TABLE 2.

Salt	Torsional oscillation $\nu_6$ (cm. <sup>-1</sup> )	Relation between structure.*		NMR data
		NH <sub>4</sub> <sup>+</sup> salt	K <sup>+</sup> and Rb <sup>+</sup> salts	
NH <sub>4</sub> F .....	523	Wurtzite	NaCl	Not rotating
NH <sub>4</sub> Cl .....	359	CsCl	NaCl	Not rotating
NH <sub>4</sub> Br .....	311	CsCl	NaCl	Not rotating
NH <sub>4</sub> I .....	None	NaCl	NaCl	Rotating
NH <sub>4</sub> N <sub>3</sub> .....	396	Orthorhombic	Tetragonal	—
NH <sub>4</sub> CNO .....	417	Tetragonal <sup>a</sup>	Tetragonal <sup>a</sup>	—
NH <sub>4</sub> HF <sub>2</sub> .....	—	Orthorhombic	Tetragonal <sup>b</sup>	—
NH <sub>4</sub> CNS .....	266	Not isomorphous * <sup>a</sup>		—
NH <sub>4</sub> NO <sub>2</sub> .....	363	Not isomorphous * <sup>a</sup>		—
NH <sub>4</sub> NO <sub>3</sub> .....	345	Not isomorphous		—
NH <sub>4</sub> ClO <sub>4</sub> .....	None	Isomorphous		—
NH <sub>4</sub> BF <sub>4</sub> .....	None	''	''	Rotating
NH <sub>4</sub> BPh <sub>4</sub> .....	None	'' <sup>a</sup>	''	—
NH <sub>4</sub> PF <sub>6</sub> .....	None	''	''	—
NH <sub>4</sub> SO <sub>3</sub> F .....	None	''	''	—
NH <sub>4</sub> SO <sub>3</sub> CH <sub>3</sub> .....	None	No data		—

\* All crystallographic data unless otherwise stated are taken from Landolt-Börnstein, Auflage 6, Band 1, Teil Kristalle 4.

<sup>a</sup> Waddington, unpublished results. <sup>b</sup> T. Davies and L. A. K. Stavely, *Trans. Farad. Soc.*, 1957, 53, 19. <sup>c</sup> D. W. A. Sharp, personal Communication.

broader and it is not always possible to resolve them. Thus the bands observed at 1441, 1428, and 1420 cm.<sup>-1</sup> for ammonium azide at 69° K appear as one band at 1415 cm.<sup>-1</sup> at room temperature. However in several of the ammonium salts even at room temperature it is possible to resolve a weak extra band as a shoulder on the high-frequency side of the principal 1400 cm.<sup>-1</sup> band. All ammonium salts in which it is possible to do this also show splitting of the 3000 cm.<sup>-1</sup> band.

The splitting of  $\nu_3$  in a fixed ammonium ion should be qualitatively similar to that of  $\nu_4$  but since the stretching frequency is much more sensitive to hydrogen bonding than  $\nu_4$  the splitting should be quantitatively much larger. Unfortunately the interpretation of these features is complicated by the presence of an overtone in the region 2800 cm.<sup>-1</sup> ( $2\nu_4$ ) and a combination band in the region 3000—3100 cm.<sup>-1</sup> ( $\nu_4 + \nu_2$ ). The intensity of the observed overtone band,  $2\nu_4$ , in the salts in which hydrogen bonding is inferred when compared with the intensity of the same band in NH<sub>4</sub>PF<sub>6</sub> or NH<sub>4</sub>ClO<sub>4</sub> suggests that this band is not caused solely by the overtone,  $2\nu_4$ , in the hydrogen-bonded salt. The combination  $\nu_2 + \nu_4$  does not appear in the spectrum of NH<sub>4</sub>BF<sub>4</sub>, NH<sub>4</sub>PF<sub>6</sub>, NH<sub>4</sub>ClO<sub>4</sub>, or NH<sub>4</sub>B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>. This suggests that, only when  $\nu_3$  is lowered in value and split by hydrogen bonding, can the line  $\nu_2 + \nu_4$  interact by Fermi resonance and so gain sufficient intensity to be observed. Also under these conditions the line  $2\nu_4$  appears to be able to borrow intensity from the main band.

Though the lowest value for  $\nu_3$  and the highest for  $\nu_4$  is observed in ammonium fluoride, the values in the other salts do not vary in a simple way. Thus the values of  $\nu_4$  for NH<sub>4</sub>ClO<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, and NH<sub>4</sub>PF<sub>6</sub> are higher than for the salts like NH<sub>3</sub>N<sub>3</sub>, but that for NH<sub>4</sub>B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> is lower. Apart from that for NH<sub>4</sub>F, the values all lie within a spread of 40 cm.<sup>-1</sup>. The values of  $\nu_3$  for NH<sub>4</sub>ClO<sub>4</sub>, NH<sub>4</sub>BF<sub>4</sub>, NH<sub>4</sub>PF<sub>6</sub>, and NH<sub>4</sub>B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> are all higher than for the salts which have been classed as hydrogen bonded but there is a considerable spread in their values, from 3332 for NH<sub>4</sub>BF<sub>4</sub> to 3220 for NH<sub>4</sub>B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>.

X-Ray studies have shown that the salt NH<sub>4</sub>SO<sub>3</sub>F is isomorphous with KSO<sub>3</sub>F and RbSO<sub>3</sub>F and indeed with NH<sub>4</sub>ClO<sub>4</sub>. The absence of a combination mode  $\nu_4 + \nu_6$  suggests

strongly that the ammonium ion is not completely locked in position in the lattice. However, a complex structure is found in the  $3000\text{ cm}^{-1}$  region of the infrared spectrum of this salt which is quite unlike that of  $\text{NH}_4\text{ClO}_4$ . Of course the local environment of the ammonium ion must be much less symmetrical than that in  $\text{NH}_4\text{ClO}_4$  and it is quite possible that this asymmetry is sufficiently strong to remove the degeneracy of the  $\nu_3$  mode. Perhaps the same type of behaviour is found in the ammonium ion here as exists in ammonium iodide at room temperature where the ion is hydrogen-bonded to an iodide ion along one bond and is free to rotate about this bond. Possibly a similar position exists in  $\text{NH}_4\text{SO}_3\cdot\text{CH}_3$  whose infrared spectrum is very similar to that of the fluorosulphate.

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[Received, June 24th, 1958.]

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