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## Raman Spectrum of Crystalline Ammonium Chloride\*

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Crystalline  $\text{NH}_4\text{Cl}$  was studied in its room temperature and high temperature forms. Cylindrical crystals were grown by sublimation in a special furnace. At room temperature vibrational frequencies were observed at 3146, 3041, 2824, 2010, 1768, 1709, 1407 and subsidiary frequencies at 3300, 3232  $\text{cm}^{-1}$ . In the high temperature modification vibrational frequencies were observed at 3102, 2801, 1931, 1655, 1400  $\text{cm}^{-1}$ .

CRYSTALLINE ammonium salts have many curious physical properties,<sup>1</sup> some of which are ascribable to characteristics of the ammonium radical not yet fully understood. This work was undertaken in the hope that light would be thrown on some of these characteristics by more complete observations of the Raman effect in  $\text{NH}_4\text{Cl}$ .

The data obtained have been combined with the infrared observations of previous workers and interpreted with the help of two reasonable assumptions. Probably the most important result is the indication that the  $\text{NH}_4$  group in crystalline  $\text{NH}_4\text{Cl}$  either has not the geometrical structure of a tetrahedron of cubic symmetry or else has this structure but is strongly perturbed in a nongeometrical sense.

### GROWING CRYSTALS BY SUBLIMATION

A major difficulty was encountered in preparing a relatively pure and optically clear crystal of suitable size in the room temperature modification of this substance. Many attempts to grow crystals in the high temperature form and cool them through the 184°C transition<sup>1a</sup> produced merely mediocre crystals. However, it was found that an optically clear cylindrical crystal 3 cm long could be grown by sublimation, at a temperature below<sup>2</sup> 184°C, in about a month.

The essentials of the glass-walled furnace constructed for this purpose are shown in Fig. 1. The heating wire was wound directly on tube 1,

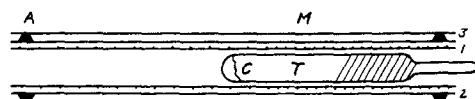


FIG. 1.

this assembly being separated from tube 2 by a coarse winding of asbestos string. Annular windings of asbestos, as at *A*, separated tubes 2 and 3. Heating current was obtained from a commercial power line, the voltage fluctuations being sufficiently reduced by the use of "ballast tubes."

The tube *T* was half filled with  $\text{NH}_4\text{Cl}$  (previously sublimed several times in vacuum), evacuated, heated for some time, and sealed off. It was inserted in the furnace as shown and moved toward the left. After the rounded end of *T* had passed *M*, the region of maximum temperature, a crystal *C* started to form. The rate of motion was then determined by the appearance of the surface of *C*, minute facets indicating dangerously fast growth.

For high temperature observations a similar furnace was inserted in the arc chamber. Essential modifications consisted in replacing 2 by a tube of Corning Red Ultra glass<sup>3</sup> and sealing a flat window on the end of *T*. Crystals were grown and then maintained at temperatures well above 184°C during exposures.

### ROOM TEMPERATURE RESULTS

Spectra of the room temperature modification were obtained by using Hilger constant deviation type instruments fitted with extra-dense flint prisms and long and short focus cameras. Commercial mercury and helium arcs were used

\* Portion of a dissertation presented for the degree of Doctor of Philosophy at Yale University.

<sup>1</sup> Most of the peculiarities of the ammonium halides are mentioned by A. C. Menzies and H. R. Mills, *Proc. Roy. Soc. A148*, 407 (1935).

<sup>1a</sup> *International Critical Tables*, Vol. 4, p. 7.

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

<sup>3</sup> L. J. Buttolph, *Rev. Sci. Inst.* **1**, 650 (1930).

with standard filters in the arc chamber described by Buttolph.<sup>3</sup>

The vibrational frequencies in  $\text{cm}^{-1}$ , with estimated relative visual intensities, are: 3146, 15; 3041, 20; 2824, 7; 2010, 2; 1768, 2; 1709, 5; 1407, 2 (average deviation 4  $\text{cm}^{-1}$  or less). The first three are inherently of intermediate width, the next two are broad<sup>4</sup> and without cores, 1709 is sharp, and 1407 is sharp on its low wave-length side, as is the wider line 2824 (and possibly 3146).

The infrared absorption frequencies observed by Wilberg<sup>5</sup> at approximately 2350 and 2250  $\text{cm}^{-1}$  were not found, although 2350 (He 3888A), if present, might have been masked by an observed Raman line assigned to 2824 (He 3819A).

Considering the widths of most lines, these results agree satisfactorily with the less complete results of Schaefer, Matossi, and Aderhold,<sup>6</sup> Kastler,<sup>7</sup> and Menzies and Mills,<sup>4</sup> and, except for 2824 and 1407, with weighted means of the infrared results of Wilberg<sup>5</sup> and Pohlman.<sup>2</sup> One should note, however, that 1709 is inactive in infrared absorption at room temperature.

Subsidiary frequencies were observed at  $3300 \pm 6$  and  $3232 \pm 5 \text{ cm}^{-1}$ . These may correspond to fine-structure lines observed by Pohlman at  $-80^\circ\text{C}$ .

### HIGH TEMPERATURE RESULTS

The spectrum of the high temperature modification was obtained only at low dispersion with helium excitation.

Observed frequencies in  $\text{cm}^{-1}$  are: 3102, 30; 2801, 4; 1931, 2; 1655, 2; 1400, 2 (average deviation 6  $\text{cm}^{-1}$  or less). The first, a very wide line, corresponds to one or both components of the high frequency pair which are well resolved in crystals at room temperature with this dispersion. On the basis of their intensities and

widths 1931 and 1655 correspond to 2010 and 1768. Apparently the room temperature 1709  $\text{cm}^{-1}$  frequency is much weaker or has shifted in the direction of shorter wave-lengths to an unobservable position. No asymmetries were observed.

### DISCUSSION

The 1407  $\text{cm}^{-1}$  frequency seems to be an unresolved doublet.<sup>2, 5</sup> This view is supported by the fact that the corresponding  $\text{NH}_4\text{Br}$  frequency is definitely double at low temperature.<sup>2</sup> Thus ten vibrational frequencies can be said to have been observed at room temperature in crystalline  $\text{NH}_4\text{Cl}$ .

Two assumptions will be applied throughout the rest of this paper: (1) That of most authors, namely, that all frequencies in this spectral region are produced by  $\text{NH}_4^+$ ; (2) that no  $\text{NH}_4^+$  frequency in crystalline  $\text{NH}_4\text{Cl}$  lies below<sup>8</sup> 1407  $\text{cm}^{-1}$ . These assumptions necessitate regarding at least one of the observed frequencies as due to a harmonic, a combination, or a perturbation. Consideration of all relevant data indicates that in  $\text{NH}_4\text{Cl}$  2824 may be the harmonic of 1407 and 3146 may be a combination frequency, possibly due to 1407 plus 1709.

The structure usually assumed for  $\text{NH}_4^+$  is that of a tetrahedron of cubic symmetry. Using this model Hettich<sup>9</sup> and Menzies and Mills<sup>4</sup> have presented explanations of the complex macroscopic phenomena in ammonium halide crystals. Also, Pohlman<sup>2</sup> has deduced from observed fine structure (without allowing for the possibility of vibration-rotation interaction<sup>10</sup>) a value for the N-H distance which agrees with that calculated by Laschkarew and Usyskin<sup>11</sup> from electron diffraction patterns. However, this structure is spectroscopically unsatisfactory unless seriously perturbed in a nongeometrical sense, since without such a perturbation only four fundamental vibrational frequencies could be observed.<sup>12</sup> Unfortunately the available spec-

<sup>4</sup> Compare A. C. Menzies and H. R. Mills, Proc. Roy. Soc. **A148**, 407 (1935).

<sup>5</sup> L. Wilberg, Zeits. f. Physik **64**, 304 (1930). See also O. Reinkober, *ibid.* **5**, 192 (1921).

<sup>6</sup> C. Schaefer, F. Matossi, and H. Aderhold, Zeits. f. Physik **65**, 289 (1930).

<sup>7</sup> A. Kastler, Proc.-verb. soc. sciences phys. natur. Bordeaux (1931-1932).

$\text{NH}_4\text{F}$	2830 m	3070 m	
$\text{NH}_4\text{Cl}$	2820 w	3050 s	3150 m
$\text{NH}_4\text{Br}$	2810 w	3030 s	3130 m
	w weak;	m medium;	s strong

<sup>8</sup> See, however, A. da Silveira, Comptes rendus **195**, 521 (1932) and Wilberg, reference 5.

<sup>9</sup> A. Hettich, Zeits. f. physik. Chemie **A168**, 353 (1934).

<sup>10</sup> D. M. Dennison and M. Johnston, Phys. Rev. **47**, 93 (1935), E. Teller and L. Tisza, Zeits. f. Physik **73**, 791 (1932).

<sup>11</sup> W. E. Laschkarew and I. D. Usyskin, Zeits. f. Physik **85**, 618 (1933).

<sup>12</sup> D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

troscopic data do not strongly indicate the correctness of any particular geometrical configuration.

Comparison of the Raman spectra of the room temperature and high temperature forms of  $\text{NH}_4\text{Cl}$  suggests various possibilities. Of these, the simplest are that the frequencies occurring at room temperature at 2010 and 1768  $\text{cm}^{-1}$  originate in similar types of vibration and that the

properties of  $\text{NH}_4^+$  undergo only minor changes at the high temperature transition point.

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## The Reaction Rates of Propionic and Acetic Propionic Anhydrides

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The infrared absorption spectra of mixtures of water and acetic propionic and of propionic anhydrides have been measured in the region from  $5\mu$  to  $6.4\mu$ . The intensity of the bands was found to decrease with time. By using the relative intensity of the anhydride band the reaction rate was calculated for three concentrations. The reactions were unimolecular but the value of the reaction constant

was different for each concentration, its value being approximately proportional to the concentration of the water. The value of the reaction constant of acetic propionic anhydride was about twice the value of the constant for propionic anhydride. A table is given of the values of the reaction constants for the different concentrations.

THE reaction velocity of acetic anhydride has been measured<sup>1</sup> recently by means of its infrared absorption spectra. The results showed that the reaction constant increased with temperature and that the value of the constant decreased in a given set of observations. The latter result may have been produced by the method of calculation. In order to study further the effect of concentration the work has been extended to propionic and acetic propionic anhydrides. Before the absorption spectra of different concentrations were measured the region from  $5\mu$  to  $6.5\mu$  was studied. It was found that the absorption spectra of acetic and of propionic acid were similar in this region and that the bands, which were at about  $5.7\mu$ , varied in position by about  $0.03\mu$ . The propionic and acetic propionic anhydrides were studied and it was found that there were two absorption bands at  $5.48\mu$  and  $5.66\mu$ , and  $5.50\mu$  and  $5.68\mu$ , respectively. When cells of about 0.01 mm in thickness were used, the two bands could be separated by the fluorite

prism. The two anhydrides have similar spectra, as can be seen by the absorption curves shown in Fig. 1. The fact that the  $5.50\mu$  band can be separated from the other anhydride band at  $5.68\mu$  and the acid bands at  $5.7\mu$  made it suitable for the study of reaction rates.

In the study of the reaction velocity, cells were made of three concentrations. The first solution had equivalent amounts of water and anhydride, the second two equivalent parts of water to one of anhydride, and the third three of water and one of anhydride. The actual concentrations of water and anhydride are given in Table I. The same concentrations were used for each anhydride. The reactions were allowed to progress in the absorption cell. After preliminary trials it was found that the reactions were slow and that the absorption curves should be measured at time intervals of from one to two hours. In this way six to eight sets of observations were obtained for each concentration. In Fig. 2 are shown the curves for the three concentrations of propionic anhydride. The bands in the section on the left are for equivalent amounts and the time of observation

<sup>1</sup> Plyler and Barr, J. Chem. Phys. 3, 679 (1935).