

## Infrared spectroscopic study of the rotation of the $\text{NH}_4^+$ ion in ammonium halides\*

SOMNATH GANGULY

Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore 560 012, India

MS received 16 June 1980

**Abstract.** Infrared correlation functions have been obtained from the analysis of band shapes of the  $1400\text{ cm}^{-1}$  bending mode of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  in both the Pm3m and Fm3m phases. The  $\text{NH}_4^+$  ion seems to undergo relatively free rotation in the high temperature Fm3m phases of these halides.

**Keywords.** Ammonium halides ; phase transitions ; infrared correlation functions.

### 1. Introduction

$\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  undergo a low temperature  $\lambda$  type transition followed by a transition at a higher temperature when the symmetry changes from CsCl type (Pm3m) to NaCl type (Fm3m) (Rao and Natarajan, 1972). Thermodynamic data on the transitions are shown in table 1. The  $\lambda$  transition has been shown to be of the order-disorder type (Frenkel 1935; Levy and Peterson 1952, 1953a) above the  $\lambda$  transition, the  $\text{NH}_4^+$  tetrahedra are randomly distributed between two possible orientations.  $\text{NH}_4^+$  ions behave as torsional oscillators, both, above and below the  $\lambda$  transition (Wagner and Hornig 1950). Above the first order Pm3m-Fm3m transition, however, the  $\text{NH}_4^+$  ions appear to show relatively free rotation (Leung *et al* 1968). Thus, the  $\text{NH}_4^+$  ion in  $\text{NH}_4\text{I}$  rotates freely about the hydrogen bond formed by  $\text{I}^-$  in the high temperature phase (Plumb and Hornig 1953). Rotation of the  $\text{NH}_4^+$  ion has been examined by NMR (Gutowsky *et al* 1954; Woessner and Snowden, 1967) neutron scattering and other techniques (Leung *et al* 1968; Levy and Peterson 1953b; Wagner and Hornig 1950; Krishnan 1948) generally in the low temperature phases. We have investigated the rotation of  $\text{NH}_4^+$  ion in these ammonium halides in both the Pm3m and Fm3m phases by the method of infrared correlation functions (Gordon 1965).

---

\* Communication No. 73 from the Solid State and Structural Chemistry Unit.

Table 1. Thermodynamics of phase transitions of ammonium halides.

| Compound           | $T_{\lambda}$ , (K)      | $T_{tr}$ , (K)<br>(Pm3m-Fm3m) | $\Delta H_{tr}$ , (kJ mol <sup>-1</sup> )<br>(Pm3m-Fm3m) |
|--------------------|--------------------------|-------------------------------|--|
| NH <sub>4</sub> Cl | 243<br>(Pm3m-Pm3m)       | 456                           | 4.3  |
| NH <sub>4</sub> Br | 235<br>(Tetragonal-Pm3m) | 411                           | 3.7  |
| NH <sub>4</sub> I  | 231<br>(Tetragonal-Pm3m) | 257                           | 3.4  |

## 2. Method of study

Dipole correlation functions were determined by Fourier analysing infrared band shapes and is given by

$$G(t) = \langle \mu(0) \cdot \mu(t) \rangle = \int_{-\infty}^{\infty} \hat{I}(\omega) \exp(-i\omega t) d\omega \quad (1)$$

where  $\hat{I}(\omega) = I(\omega) / \int_{-\infty}^{\infty} I(\omega) d\omega$ .

Here  $\mu$  is the vibrational transition moment vector whose direction in the molecule depends upon molecular symmetry and on the symmetry species of the infrared band;  $\hat{I}(\omega)$  is the transition probability. The correlation function  $G(t)$  describes the time behaviour of  $\mu$  with respect to its position at time  $t = 0$  and so it yields the characteristics of reorientational motion of the molecule around some specific molecular axis. Infrared correlation times were determined from the band half-widths,  $\Delta\nu$  using the relation,

$$\tau_c = 1/\pi c \Delta\nu. \quad (2)$$

## 3. Experimental

Infrared spectra were recorded on a Perkin Elmer 580 IR spectrophotometer. The ammonium halide samples were sublimed on to a KRS-5 plate. Temperatures were set and controlled using a Specac temperature controller in conjunction with a variable temperature cell. The temperature control was as accurate as 1K and the spectrometer resolution varied between 1 and 2 cm<sup>-1</sup> and the scan speed employed was about 10 cm<sup>-1</sup> per minute.

Numerical calculation of spectra for Fourier inversion was performed by reading off the linear transmission relative to the zero absorption line and computing  $\log(I/I_0)$  in steps of 1 cm<sup>-1</sup>. Integration was extended over the entire observable frequency range of the band.

#### 4. Results and discussion

In figures 1–3 we show plots of the correlation functions for the  $1400\text{ cm}^{-1}$  N–H bending mode of  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$  in the Pm3m and Fm3m phases. Infrared correlation times in the two phases are tabulated in table 2. A comparison of the correlation functions for the two phases of these halides shows a marked change in the rotational behaviour of the  $\text{NH}_4^+$  ion. The correlation function in the high temperature Fm3m phase for each of these halides decays much more rapidly than the correlation function in the low temperature phase. The  $\text{NH}_4^+$  ion which undergoes torsional oscillations in the Pm3m phase seems to be rotating essentially freely in the high temperature Fm3m phase. The large decrease in the infrared correlation times supports this conclusion. Furthermore, we find that  $\tau_c$  values in the Pm3m and Fm3m phases remain the same in the three ammonium halides.

In figure 4 we have plotted the logarithm of the infrared correlation time against the reciprocal of absolute temperature for the ammonium halides in the Fm3m

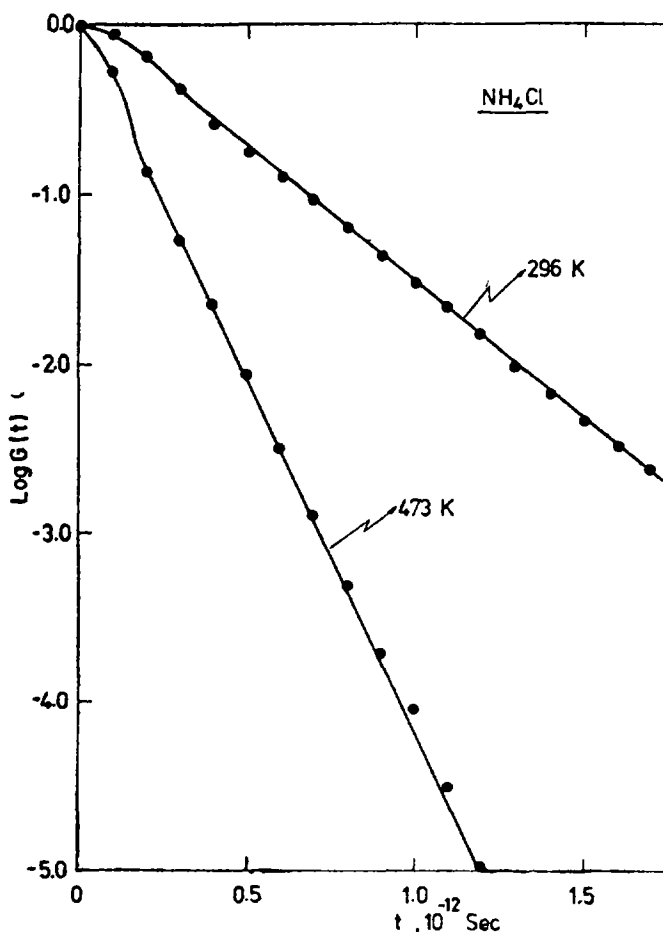


Figure 1. Logarithm of infrared correlation functions for the  $1400\text{ cm}^{-1}$  mode in  $\text{NH}_4\text{Cl}$  at 296 and 473 K.

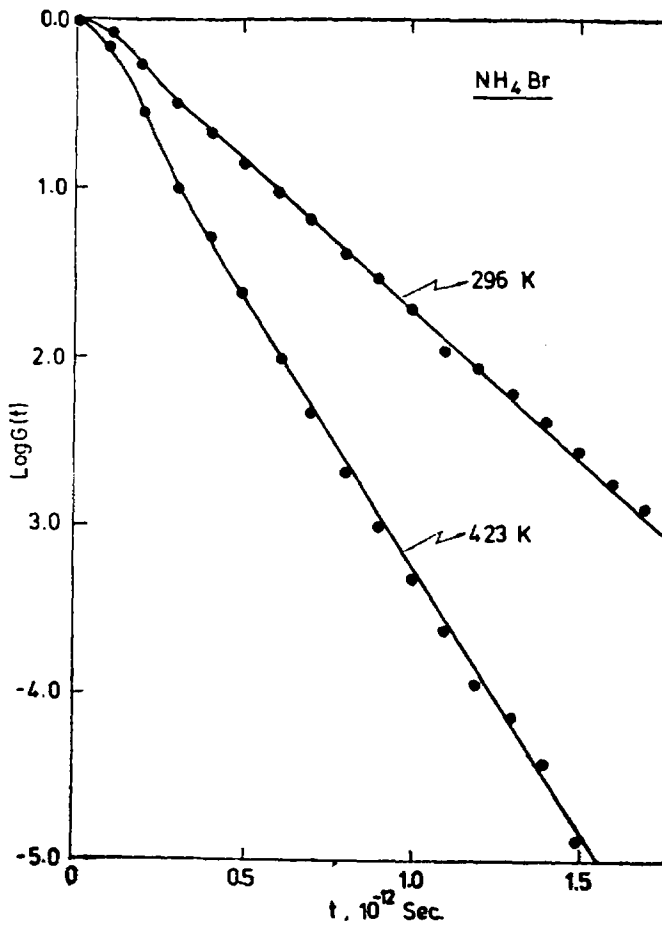


Figure 2. Logarithm of infrared correlation functions for the  $1400\text{ cm}^{-1}$  mode in  $\text{NH}_4\text{Br}$  at 296 and 423 K.

Table 2. Infrared correlation times in ammonium halides.

| Compound               | Phase | Temp. (K) | $\tau_c$ ( $10^{-12}$ sec) | $E_a$ ( $\text{kJ mol}^{-1}$ ) |
|------------------------|-------|-----------|----------------------------|--------------------------------|
| $\text{NH}_4\text{Cl}$ | Fm3m  | 296       | 0.65                       | 19.7 <sup>a</sup>              |
|                        | Fm3m  | 473       | 0.23                       | 7.2                            |
| $\text{NH}_4\text{Br}$ | Fm3m  | 296       | 0.56                       | 15.1 <sup>a</sup>              |
|                        | Fm3m  | 423       | 0.28                       | 5.2                            |
| $\text{NH}_4\text{I}$  | Fm3m  | 243       | 0.62                       | 12.1 <sup>b</sup>              |
|                        | Fm3m  | 293       | 0.42                       | 4.8                            |
|                        |       | (423)     | (0.27)                     |                                |

<sup>a</sup> From NMR studies of Woessner and Snowden (1967).

<sup>b</sup> From NMR studies of Gutowsky *et al* (1954).

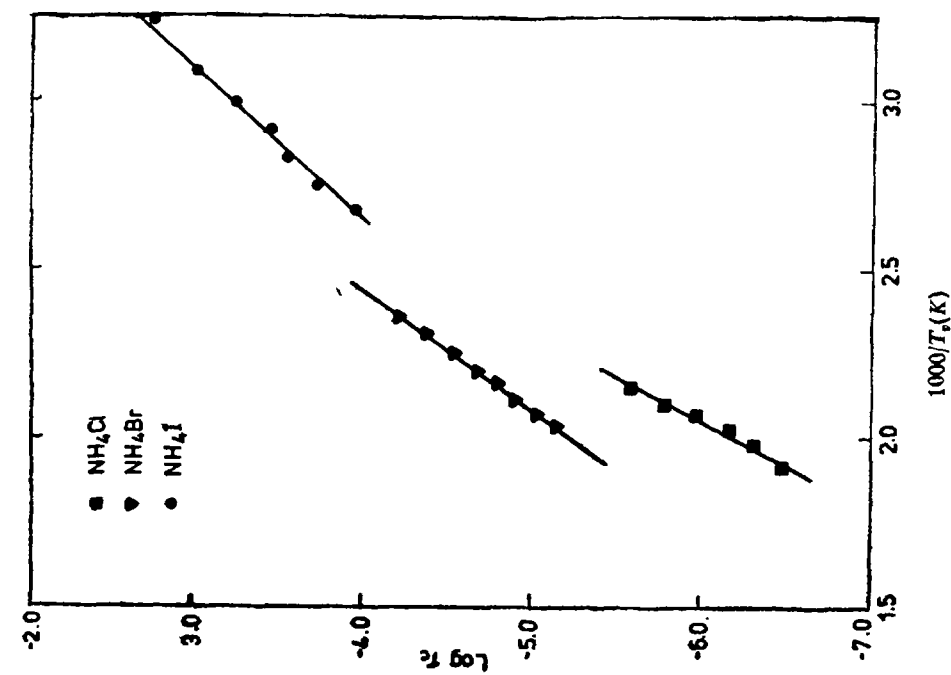


Figure 4. Logarithm of infrared correlation times against reciprocal of absolute temperature for  $NH_4Cl$ ,  $NH_4Br$  and  $NH_4I$  in the Fm3m phases.

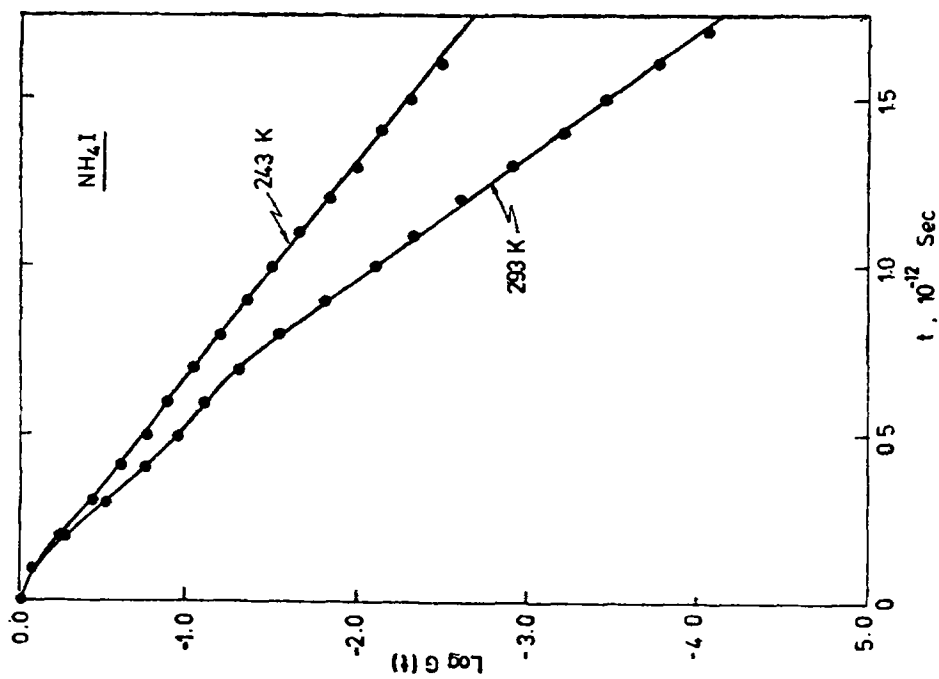


Figure 3. Logarithm of infrared correlation functions for the  $1400\text{ cm}^{-1}$  mode in  $NH_4I$  at 243 and 293 K.

phase. Activation energies  $E_a$  calculated from these plots are tabulated in table 2. We find that the activation energy for rotation increases in the order  $\text{NH}_4\text{Cl} > \text{NH}_4\text{Br} > \text{NH}_4\text{I}$ . The activation energies found from NMR studies also show the same trend (table 2). The  $E_a$  values are, however, much greater in the Pm3m phase than in the high temperature Fm3m phase, again suggesting ease of rotation in the latter phase.

### Acknowledgement

The author's thanks are due to Professor C N R Rao for suggesting the problem and guidance. His thanks are due to the NCERT for the National Science Talent Scholarship.

### References

- Frenkel J 1935 *Acta Physicochem.* **3** 23  
Gordon R G 1965 *J. Chem. Phys.* **43** 1307  
Gutowsky H S, Pake G E and Bersohn R 1954 *J. Chem. Phys.* **22** 643  
Krishnan R S 1948 *Proc. Indian Acad. Sci.* **A27** 327  
Levy H S and Peterson S W 1952 *Phys. Rev.* **86** 766  
Levy H S and Peterson S W 1953a *J. Am. Chem. Soc.* **75** 1536  
Levy H S and Peterson S W 1953b *J. Chem. Phys.* **21** 366  
Leung P S, Taylor T I and Havens Jr W W 1968 *J. Chem. Phys.* **48** 4912  
Plumb R C and Hornig D F 1953 *J. Chem. Phys.* **21** 366  
Rao C N R and Natarajan M 1972 *Crystal structure transformations in binary halides*, NSRDS--NBS Monograph 41, National Bureau of Standards, Washington DC  
Wagner E L and Hornig D F 1950 *J. Chem. Phys.* **18** 296, 305  
Woessner D E and Snowden Jr B S 1967 *J. Chem. Phys.* **47** 378  
Woessner D E and Snowden Jr B S 1967 *J. Phys. Chem.* **71** 952