CHAPTER-V

FIR REFLECTIVITY AND VIBRATIONAL SPECTRA OF (NH$_4$)$_2$ZnBr$_4$
FIR REFLECTIVITY AND VIBRATIONAL SPECTRA OF \((\text{NH}_4)_2\text{ZnBr}_4\)

5.1 INTRODUCTION

Ammonium tetrabromozincate, \((\text{NH}_4)_2\text{ZnBr}_4\), (hereafter referred to ATBZ) belongs to the class of crystals of the type \(A_2BX_4\), where \(A = \text{NH}_4, \text{N(CH}_3)_4, \text{K, Rb, Cs, B = Zn, Co, Cu, Fe, Mn or Cd and X = Cl, Br or I}\). Crystals of this type show ferroelectricity, ferroelasticity, incommensurability etc. [Pirnat et al 1980, Moskalev et al 1982, Broda 1984, Sawada et al 1981, Unruh 1981]. ATBZ is also known to undergo ferroelectric phase transition at 216 K [Osaka, Komukae and Makita 1982] and an incommensurate phase transition at 395 K [Sato, Osaka and Makita 1983]. Crystal structure at room temperature has been predicted by Asker, Scaife and Watts [1972] and Moskalev et al [1982] from preliminary x-ray and Br NQR measurements as orthorhombic. Moskalev et al [1982] have observed the two phase transitions mentioned above at 222.5 and 365 K respectively from the study of dielectric constant and Br NQR measurements. Osaka, Komukae and Makita [1982] have studied the dielectric and thermal properties of the crystal and observed another phase transition at 493 K. Bist and Agrawal [1986] have reported the temperature variation of Raman spectra of the crystal and found evidence for an additional phase transition at 130 K. They have recorded the Raman spectra of single crystals in different polarisation geometries for three different phases at 450, 300 and 85 K and suggested crystal's
symmetry as monoclinic at room temperature and not orthorhombic as reported by Asker, Scaife and Watts [1972]. The effect of temperature on Raman scattering in the low frequency region has also been studied by Moorthy, Chandrasekhar and Bhatnagar [1984]. They have observed anomalous change in bands' peak heights near the ferroelectric and incommensurate phase transition temperatures. No change in the frequency of bands with temperature was, however, observed.

We have measured the infrared reflectance of the single crystals for random orientation at 300 and 105 K in the far-infrared frequency region to study the behaviour of low frequency optical constants and frequencies of optical phonon modes in the two phases below room temperature. Our vibrational study of the crystal includes infrared absorption at room temperature in the NIR and FIR regions for powdered crystals. The room temperature Raman spectra of the crystal reported by Agrawal [1986] have been reproduced here for the completeness of vibrational spectra.

5.2 CRYSTAL STRUCTURE AND GROUP THEORETICAL ANALYSIS

An orthorhombic symmetry of the crystal at room temperature has been predicted by Asker, Scaife and Watts [1972] and Moskalev et al [1982] on the basis of preliminary x-ray study. Space group of the crystal is suggested as $D_{2h}^{16}$ (Pnmc) with unit cell parameters, $a = 9.66$ Å, $b = 13.2$ Å, $c = 7.605$ Å [Asker, Scaife and Watts 1972]. However, the detailed investigation of crystal
structure has not been made so far. The possible unit cell of
the crystal has been presented in figure 5.1 on the basis of the
symmetry of crystal. Total number of vibrational modes expected
for the crystal is 180, distributed among the species of $D_{2h}$
factor group as follows:

$$\Gamma_{180} = 24 A_g + 21 B_{1g} + 24 B_{2g} + 21 B_{3g} + 21 A_u + 24 B_{1u} + 21 B_{2u} + 21 B_{3u}.$$  

Vibrations belonging to species $A_g$, $B_{1g}$, $B_{2g}$ and $B_{3g}$
show Raman activity and those belonging to species $B_{1u}$, $B_{2u}$, $B_{3u}$
show infrared activity whereas the modes of $A_{1u}$ specy are
infrared-Raman inactive.

Vibrations of $A_g$ symmetry appear in the XX, YY and ZZ
polarisation geometries whereas those of $B_{1g}$, $B_{2g}$ and $B_{3g}$
symmetry appear in XY, ZX and YZ polarisation geometries
respectively in the Raman spectra. The infrared active vibrations
of $B_{1u}$, $B_{2u}$ and $B_{3u}$ symmetry are expected when the electric
vector of the incident radiation is made parallel to the Z, Y
and X axes of the crystal respectively.

For obtaining the number of vibrational modes belonging to
different symmetry species of the factor group, the site symmetry
of the ions in the crystal has been found out with help of table
given by Fateley et al [1972]. Possible site symmetries for the
factor group $D_{2h}$ are $C_1(8)$, $2C_1(4)$ and $C_s(4)$. The crystal has
Fig. 5.1 Schematic representation of structure of AT8Z at room temperature phase.
four formula units per unit cell. Therefore, there will be eight NH$_4^+$ ions and four ZnBr$_4^{2-}$ ions per unit cell. Eight NH$_4^+$ ions can be accommodated only on C$_1$ sites having multiplicity of 8. The ZnBr$_4^{2-}$ ions may have C$_s$ or C$_1$ site symmetry. Owing to the fact that site symmetry of a ion should be a subgroup of the free state point group the site symmetry of ZnBr$_4^{2-}$ ion is taken as C$_s$. Considering these site symmetries of the ions correlation between different symmetry species of T$_d$ point group, site symmetry point group and the factor group of the crystal has been obtained and presented in table 5.1. The number of phonon modes originating from a definite mode of free state point group of NH$_4^+$ and ZnBr$_4^{2-}$ ions along with the libratory and translatory modes of NH$_4^+$ and ZnBr$_4^{2-}$ ions under the different symmetry species of the crystal factor group are given in table 5.2.

5.3 RESULTS AND DISCUSSION

5.3.1 Reflectivity Spectra

FIR reflectivity spectra of ATBZ crystals have been recorded at 300 and 105 K for the two phases in random orientation of the crystal in the frequency range 50-500 cm$^{-1}$. Optical constants and frequencies of optical phonon modes have been evaluated from the classical oscillator fit to the reflectivity data as described earlier. The oscillator fit and experimental data are shown in figure 5.2. The variation in $\varepsilon'$ and $\varepsilon''$, $\sigma$ and Im($1/\varepsilon$), and n and k with frequency as evaluated
<table>
<thead>
<tr>
<th></th>
<th>Free state</th>
<th>Site group</th>
<th>Crystal factor group</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>$\text{NH}_4^+$</strong></td>
<td>$T_d$</td>
<td>$C_1$</td>
<td>$D_{16}^{16}$</td>
</tr>
<tr>
<td>$\nu_1(A_1)$</td>
<td>$\nu_2(E)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>$(A_g+B_1g+B_2g+B_3g+A_u+B_{1u}+B_{2u}+B_{3u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2A$</td>
<td>$2(A_g+B_1g+B_2g+B_3g+A_u+B_{1u}+B_{2u}+B_{3u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$3A$</td>
<td>$3(A_g+B_1g+B_2g+B_3g+A_u+B_{1u}+B_{2u}+B_{3u})$</td>
</tr>
<tr>
<td>translations</td>
<td></td>
<td>$3A$</td>
<td>$3(A_g+B_1g+B_2g+B_3g+A_u+B_{1u}+B_{2u}+B_{3u})$</td>
</tr>
<tr>
<td><strong>$\text{ZnBr}_4^{2-}$</strong></td>
<td>$T_d$</td>
<td>$C_s$</td>
<td>$D_{2h}$</td>
</tr>
<tr>
<td>$\nu_1(A_1)$</td>
<td>$\nu_2(E)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A'$</td>
<td>$(A_g+B_2g+B_{1u}+B_{3u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A'+A''$</td>
<td>$(A_g+B_2g+B_{1u}+B_{3u})+(B_2g+B_{3g}+A_u+B_{2u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2A'+A''$</td>
<td>$2(A_g+B_2g+B_{1u}+B_{3u})+(B_{1g}+B_{3g}+A_u+B_{2u})$</td>
</tr>
<tr>
<td>translations</td>
<td></td>
<td>$2A'+A''$</td>
<td>$2(A_g+B_2g+B_{1u}+B_{3u})+(B_{1g}+B_{3g}+A_u+B_{2u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A'+A''$</td>
<td>$(A_g+B_2g+B_{1u}+B_{3u})+2(B_{1g}+A_u+B_{2u})$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2 Classification of phonons in (NH$_4$)$_2$ZnBr$_4$ (Room temperature) 
(Site symmetry approach)

<table>
<thead>
<tr>
<th>Modes</th>
<th>Species under D$_{2h}$</th>
<th>N$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A$_g$</td>
<td>B$_1g$</td>
</tr>
<tr>
<td>I. Internal modes of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnBr$_4^{2-}$: Site C$_s$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(A$_1$)</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$\nu_2$(E)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_3$(F$_2$)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_4$(F$_2$)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>Total</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>II. Internal modes of</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_4^+$: Site C$_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu_1$(A$_1$)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\nu_2$(E)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\nu_3$(F$_2$)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>$\nu_4$(F$_2$)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>III. External modes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I) Translations of ZnBr$_4^{2-}$</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>(II) Librations of ZnBr$_4^{2-}$</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(III) Translations of NH$_4^+$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(IV) Librations of NH$_4^+$</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Total</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Grand Total</td>
<td>24</td>
<td>21</td>
</tr>
</tbody>
</table>

$^a$ Total number of phonon modes originating from a particular mode of vibration.
Fig. 5.2 Reflectance curve for ATBZ at 300 and 105 K (●, Experimental data, ——, classical oscillator fit).
from the fit has been plotted and is shown in figures 5.3, 5.4 and 5.5 respectively. The calculated variation in dielectric constant with frequency is shown in figure 5.6. The reflectance spectra show one strong reststrahlen band with a weak band at its higher frequency side. Values of classical oscillator parameters corresponding to these bands are given in table 5.3. Out of the 42 \((15B_{1u} + 12B_{2u} + 15B_{3u})\) infrared active modes expected to appear in the far-infrared region of the spectrum of ATBZ only two are observed. These 42 modes include 18 \((6B_{1u} + 6B_{2u} + 6B_{3u})\) external modes of \(\text{NH}_4^+\) ion, 15 \((6B_{1u} + 3B_{2u} + 6B_{3u})\) internal modes of \(\text{ZnBr}_4^{2-}\) ion and 9 \((3B_{1u} + 3B_{2u} + 3B_{3u})\) external modes of \(\text{ZnBr}_4^{2-}\) ion. As discussed earlier for TAHS in Chapter III, the number of external modes of \(\text{NH}_4^+\) to be observed in the spectrum is affected on account of the resolution of the order of 10 cm\(^{-1}\) near dispersion frequencies and the inactivity of libratory modes in the spectrum. Regarding the observation of internal modes of \(\text{ZnBr}_4^{2-}\) ion, it is to be noted that the internal modes of a molecular groups do not absorb in the reflection spectra as strongly as the external modes. The \(\nu_1^Z, \nu_3^Z\) and \(\nu_4^Z\) (to be described in the following section) modes of \(\text{ZnBr}_4^{2-}\) ion, of which \(\nu_1^Z\) is only weakly active in infrared lie close to the external modes of \(\text{NH}_4^+\) ion. In such a condition it is expected that internal modes of \(\text{ZnBr}_4^{2-}\) ion may not give separate strahlen bands and coalesce into the strahlen bands corresponding to the external modes of \(\text{NH}_4^+\) ion. The 9 external modes of \(\text{ZnBr}_4^{2-}\) ion will not
Fig. 5.3 Real ($\varepsilon'$) and imaginary ($\varepsilon''$) part of dielectric function vs frequency curve for ATBZ at 300 and 105 K.
Fig. 5.4 Conductivity and imaginary part of inverse dielectric function vs frequency for ATBZ at 300 and 105 K.
Fig. 5.5 Refractive index and extinction coefficient vs frequency for ATDZ at 300 and 105 K.
Fig. 5.6 Dielectric constant vs frequency for ATBZ at 300 and 105 K.
Table 5.3 Classical oscillator parameters at 300 and 105 K fitted to reflectivity data for (NH$_4$)$_2$ZnBr$_4$

$\varepsilon(\infty) = 1.4 \text{ cm}^{-1}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>300 K</th>
<th>105 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{t_1}$ (cm$^{-1}$)</td>
<td>162</td>
<td>178</td>
</tr>
<tr>
<td>$\omega_{q_1}$ (cm$^{-1}$)</td>
<td>238</td>
<td>258</td>
</tr>
<tr>
<td>$S_1$ (cm$^{-1}$)</td>
<td>240</td>
<td>250</td>
</tr>
<tr>
<td>$\gamma_1$ (cm$^{-1}$)</td>
<td>14.4</td>
<td>14.8</td>
</tr>
<tr>
<td>$\omega_{t_2}$ (cm$^{-1}$)</td>
<td>247</td>
<td>264</td>
</tr>
<tr>
<td>$\omega_{q_2}$ (cm$^{-1}$)</td>
<td>270</td>
<td>286</td>
</tr>
<tr>
<td>$S_2$ (cm$^{-1}$)</td>
<td>.45</td>
<td>45</td>
</tr>
<tr>
<td>$\gamma_2$ (cm$^{-1}$)</td>
<td>21.0</td>
<td>21.2</td>
</tr>
<tr>
<td>$\varepsilon(0)$</td>
<td>3.68</td>
<td>3.39</td>
</tr>
</tbody>
</table>
appear in the spectrum because they have frequencies below 50 cm\(^{-1}\), the range not covered here. Further, the number of expected modes will reduce due to the polarisation dependence of the modes of different symmetry.

The frequencies of TO modes at room temperature obtained from the fit are 162 and 247 cm\(^{-1}\). In the Raman spectra of the crystal [Agrawal 1986] no bands were observed around these frequencies. The Raman spectra show bands around 185 and 224 cm\(^{-1}\) identified with the internal modes of ZnBr\(_4\)\(^{2-}\) ion. However, a review of Raman spectra of various ammonium compounds shows the presence of bands around the frequencies of TO modes obtained from reflectance spectra. For example, in the spectra of TAHS crystal, described in Chapter III, bands around 160, 170, 234 and 258 cm\(^{-1}\), assigned to lattice modes of NH\(_4\)\(^+\) ion are observed. In the spectra of \((\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O} [\text{Gupta 1984}]\) and \((\text{NH}_4)_2\text{Cd}_2(\text{SO}_4\text{)}_2\) [Kreske and Devarajan 1982] bands around 160, 230 and 250 cm\(^{-1}\) appear and are assigned to lattice modes of NH\(_4\)\(^+\) ion. Similarly in \((\text{NH}_4)_2\text{SO}_4\) crystal [Torrie et al 1971] external translatory modes of NH\(_4\)\(^+\) ions are observed around 169, 234 and 247 cm\(^{-1}\). Therefore, the TO mode frequencies at 162 and 247 cm\(^{-1}\) are identified with the lattice modes of NH\(_4\)\(^+\) ion. This assignment is further corroborated by the behaviour of the modes with temperature in the spectrum. The TO mode frequencies observe a large blue shift (16 cm\(^{-1}\)) with the decrease in temperature. Since the external vibrations in the crystal are known to be
affected much with temperature, the large change in the frequencies of TO modes may be justified if they are identified with lattice modes. The fact that bands observed in the Raman spectrum of the crystal at 185 and 224 cm$^{-1}$, identified with internal modes of ZnBr$_4^{2-}$ do not show such a change with temperature confirms that the frequencies of TO modes in the reflectance spectrum do not correspond to the modes in the Raman spectrum. Therefore, the modes in the reflectance data are not assigned to internal vibrations of ZnBr$_4^{2-}$ ion.

The large increase mentioned above in the frequencies of lattice modes on cooling the crystal from 300 to 105 K may be attributed to the strengthening of hydrogen bonding in the crystal at lower temperatures. The slight increase in N-H stretching frequencies observed in the Raman spectrum [Agrawal 1986] as the crystal is cooled from 300 to 85 K is in consistency with this argument.

Further, the damping constant of the crystal do not show any significant change with change in temperature of the crystal. This indicates that the low temperature ferroelectric phase transition in the crystal does not affect the anharmonic behaviour of the crystal and the crystal bears the same anharmonicity in the two phases.
5.3.2 Vibrational spectra and assignments

Infrared spectra of ATBZ have been recorded for powdered crystal in the far-infrared and near-infrared regions. Spectra in the two regions are shown in figure 5.7 and 5.8 respectively. The Raman spectra of the crystal in different polarisation geometries recorded by Agrawal [1986] have been reproduced in figure 5.9. The observed band positions are presented in table 5.4. Superscript 'N' and 'Z' are used to distinguish between the modes of NH$_4^+$ and ZnBr$_4^{2-}$ ions respectively. Vibrational modes of ATBZ include the internal and external modes of NH$_4^+$ and ZnBr$_4^{2-}$ ions.

5.3.2.1 Internal modes of NH$_4^+$ ion

The NH$_4^+$ ion possesses tetrahedral symmetry in free state and has four fundamental internal vibrations, namely, $\nu_1^N$, $\nu_2^N$, $\nu_3^N$, $\nu_4^N$. The $\nu_1^N$ is the totally symmetric non-degenerate N-H stretch belonging to $A_1$ species of tetrahedral group whereas $\nu_3^N$ is the triply degenerate asymmetric N-H stretch mode. The $\nu_2^N$ is doubly degenerate symmetric bending (H - N-H) mode and $\nu_4^N$, the asymmetric bending is three-fold degenerate mode.

The internal modes of the NH$_4^+$ ion have been identified with the help of previous assignment for this crystal [Agrawal 1986]. A broad band is observed around 3200 cm$^{-1}$ having several weak components. The component at 3130 cm$^{-1}$ is assigned to the totally symmetric stretch $\nu_1^N (A_1)$ and the bands around 3195, 3206 and 3230 cm$^{-1}$ are identified with the components of asymmetric
Fig. 5.7: Infrared spectra of ATBZ at room temperature.
Fig. 6.8 Far-infrared spectra of ATBZ at room temperature.
Fig. 5.9 Raman spectra of \((\text{NH}_4)_2\text{ZnBr}_4\) crystal in phase III at 300K. The spectra in the low frequency region (0-450 cm\(^{-1}\)) have been taken at 10 times less sensitivity than the other regions.
<table>
<thead>
<tr>
<th>Infrared frequencies (cm$^{-1}$)</th>
<th>Raman frequencies</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Z(XY)Y</td>
<td>Z(YY)X</td>
</tr>
<tr>
<td>3385 w</td>
<td>3300 vw</td>
<td>3300 w</td>
</tr>
<tr>
<td>3330 vw</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3300</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3230 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3195 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3170 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3140 m,b</td>
<td>3144 m</td>
<td>3142 m</td>
</tr>
<tr>
<td>3060 w</td>
<td>3012 sh</td>
<td>3010 sh</td>
</tr>
<tr>
<td>3035</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2868 w</td>
<td>2788 vw</td>
<td>2786 vw</td>
</tr>
<tr>
<td>2830 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1745 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1710 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1680 m</td>
<td>1662 vw</td>
<td>1658 vw</td>
</tr>
<tr>
<td>1660 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1630 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1420 w</td>
<td>1410 w</td>
<td>1410 sh</td>
</tr>
<tr>
<td>1410 m</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1390 w</td>
<td>1390 w</td>
<td>1390 w</td>
</tr>
<tr>
<td>297 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>272 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>260 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>245 w</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>236 w</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$NH_4^+$ librations.
TABLE 5.4  Contd......

<table>
<thead>
<tr>
<th>217 w</th>
<th>224</th>
<th>224</th>
<th>224</th>
<th>224</th>
<th>224</th>
<th>224^2</th>
<th>Z_3^Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>192 m,b</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>185 m,b</td>
<td>1840</td>
<td>184</td>
<td>185</td>
<td>184</td>
<td>185</td>
<td>185</td>
<td>Z_1^Z</td>
</tr>
<tr>
<td>170 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>NH_4^+ translation.</td>
</tr>
<tr>
<td>160 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>132 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>90 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Z_4^Z</td>
</tr>
<tr>
<td>78 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Z_2^Z</td>
</tr>
<tr>
<td>62 w</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>ZnBr_4^{2-} lattice modes</td>
</tr>
<tr>
<td>56 w</td>
<td>52</td>
<td>55</td>
<td>52</td>
<td>54</td>
<td>55</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Abbreviations used - vw - very weak, w - weak, m - medium, b - broad, s - strong.
stretch mode, \( v_{3}^{N} (F_2) \). In the Raman spectrum these bands appear around 3140 and 3170 \( \text{cm}^{-1} \) respectively. Bands observed around 1390, 1410 and 1420 \( \text{cm}^{-1} \) are assigned to the components of \( v_{4}^{N} (F_2) \). The symmetric bending mode, \( v_{2}^{N} (E) \) has components at 1630, 1660 and 1680 \( \text{cm}^{-1} \) and observed around 1662 \( \text{cm}^{-1} \) in Raman spectra. The bands around 3300 \( \text{cm}^{-1} \) are identified with \( 2v_{2}^{N} \) and those around 2830 \( \text{cm}^{-1} \) and 3035 \( \text{cm}^{-1} \) are assigned to \( 2v_{4}^{N} \) and \( v_{2}^{N} + v_{4}^{N} \) respectively.

In the spectra two weak bands appear at 1710 and 1745 \( \text{cm}^{-1} \) which are not observed in the Raman spectra. A comparison of the spectra with those of other ammonium compounds [Acharya and Narayanan 1971, Alam and Srivastava 1982] suggests the identification of these bands as \( (v_{4}^{N} + v_{6}^{N}) \). \( v_{6}^{N} \) is the librational mode of \( \text{NH}_{4}^{+} \) ion. According to Hornig et al [1950a, b, 1953, 1955, 1961] the appearance of \( (v_{4}^{N} + v_{6}^{N}) \) in the spectra indicates the hindering of the reorientational motion of \( \text{NH}_{4}^{+} \) ion.

5.3.2.2 Internal modes of \( \text{ZnBr}_{4}^{2-} \) ion

The free \( \text{ZnBr}_{4}^{2-} \) ion also possesses tetrahedral symmetry. The four fundamental internal vibrations of the ion are the following. The \( v_{1}^{Z} (A_{1}) \) is the non-degenerate totally symmetric \( \text{Zn-Br} \) stretch vibration and \( v_{3}^{Z} (F_2) \) is triply degenerate asymmetric \( \text{Zn-Br} \) stretching vibration. The doubly degenerate, \( v_{2}^{Z} (E) \) vibration is totally symmetric (Br-Zn-Br) bending mode and triply degenerate \( v_{4}^{Z} (F_2) \) is the asymmetric bending mode.
The internal modes of ZnBr$_4^{2-}$ ion appear in the far-infrared frequency region. On comparing the frequencies observed in the spectrum with those observed in the Raman spectrum of ATBZ and the spectra of Cs$_2$ Zn Br$_4$ crystal [Lamba and Sinha 1986] the band at 185 cm$^{-1}$ is identified with the $\nu_1^Z$ ($A_1$) and those at 192, 215 and 232 cm$^{-1}$ with the components of $\nu_3^Z$ ($F_2$). The bands at 78 and 90 cm$^{-1}$ are identified with the bending modes $\nu_2^Z$ ($E$) and $\nu_4^Z$ ($F_2$) respectively.

5.3.3.3 External modes

The bands observed at 132, 160, 170 and 247 cm$^{-1}$ are assigned to the lattice translational modes of NH$_4^+$ ion whereas the bands observed at 260, 272 and 308 cm$^{-1}$ are assigned to librational modes on the basis of a comparison with the spectra of other ammonium compounds [Torrie et al 1972, Kreske and Devarajan 1982, Bist and Agrawal 1984].

5.4 CONCLUSIONS

1. The behaviour of optical phonon modes with temperature suggests a stronger hydrogen bonding in the low temperature phase.

2. The vibrational analysis indicates the hindering of reorientational motion of NH$_4^+$ ion in the crystal at room temperature.
REFERENCES


Hornig et al.


