

Infrared spectra of $(\text{NH}_4)_2\text{BeF}_4$

Y S JAIN

Department of Physics, Aligarh Muslim University, Aligarh 202 001

MS received 19 May 1977

Abstract. The infrared spectra ($4000\text{-}250\text{ cm}^{-1}$) of $(\text{NH}_4)_2\text{BeF}_4$ powder have been recorded at $\sim 300\text{K}$ (paraelectric phase) and 120K (ferroelectric phase). Observed bands have been consistently attributed to different internal modes of NH_4^+ and BeF_4^{-2} ions; a few bands also arise due to combination of these modes. The frequencies of librational modes of NH_4^+ and BeF_4^{-2} ions have been estimated to be ~ 370 and $\sim 100\text{ cm}^{-1}$, respectively, from combination modes.

Keywords. Infrared spectrum; $(\text{NH}_4)_2\text{BeF}_4$.

1. Introduction

$(\text{NH}_4)_2\text{BeF}_4$ (henceforth abbreviated as AFB) crystal becomes ferroelectric below 176K (Pepinsky and Jona 1957). However, due attention was not paid to the study of this phenomenon and its related properties of the crystal. Only recently we have reported the transition mechanism (Jain 1975) and laser-Raman spectra (Jain 1976) of AFB. Blinc and Levstek (1960) and Tedenac and Cot (1969) have reported prominent bands of the IR spectrum of AFB powder but have discussed very little of the analysis. In this paper a sufficiently detailed analysis of IR spectra of AFB powder has been reported both in its paraelectric and ferroelectric phases.

2. Experimental

AFB was obtained from Alfa inorganics USA. It was purified by its repeated crystallization from a solution in distilled deionized water by slow evaporation at about 300K . Good transparent pieces of crystals were used to prepare samples. Spectra were recorded on PE-521 spectrophotometer for nujol mull, KBr pellet and microcrystalline low scattering thin film (Jain *et al* 1973) prepared on AgCl window at room temperature (RT); low temperature (LT) spectra were recorded for only the film using a Wagner-Hornig type low temperature cell fitted with CsBr windows. The spectrum obtained for KBr pellet does not resemble exactly with those recorded for other samples most probably because of possible ion exchange phenomenon as observed in case of isomorphous $(\text{NH}_4)_2\text{SO}_4$ (Jain 1974).

3. Results and discussion

The infrared spectra recorded for nujol mull and the low scattering film of the sample are shown in figure 1. The peak frequency values of observed bands are given in

table 1 along with our assignments. The values are accurate up to ± 2 cm^{-1} for sharp bands and up to ± 10 cm^{-1} for broad ones. The notations ν_i ($i=1, 2, 3$ and 4) used in this report are after Herzberg (1945) for a tetrahedral molecule like XY_4 ; librational mode has been represented by l . Modes of NH_4^+ and BeF_4^{2-} ions have been distinguished respectively using superscripts n and b on the notations.

Table 1. Infrared band frequencies (ν , in cm^{-1}) of $(\text{NH}_4)_2\text{BeF}_4^a$ powder at room temperature (RT $\simeq 300\text{K}$) and low temperature (LT $\simeq 120\text{K}$) in 4000–250 cm^{-1} range.

$\nu(\text{RT})$	Assignment ^b	$\nu(\text{LT})$
3240	$\nu_3^n/\nu_3^n + \nu_4^n$	$\left\{ \begin{array}{l} 3315 \\ 3260 \\ 3180 \end{array} \right.$
3040	$\nu_3^n + \nu_4^n/\nu_3$	$\left\{ \begin{array}{l} 3100 \\ 3035 \\ 2980 \end{array} \right.$
2860	$2\nu_4^n$	$\left\{ \begin{array}{l} 2920 \\ 2850 \end{array} \right.$
2040	$\nu_2^n + l^n$	2065
1795	$\nu_4^n + l^n$	$\left\{ \begin{array}{l} 1845 \\ 1805 \\ 1780 \end{array} \right.$
1675	ν_2^n	1675
1465 } 1415 } 1372 }	ν_4^n	$\left\{ \begin{array}{l} 1484 \\ 1456 \\ 1436 \\ 1420 \\ 1397 \\ 1370 \end{array} \right.$
930	$\nu_1^b + \nu_4^b$	$\left\{ \begin{array}{l} 950 \\ 920 \end{array} \right.$
790	ν_3^b	$\left\{ \begin{array}{l} 845 \\ 800 \\ 750 \end{array} \right.$
655	$\nu_2^b + \nu_4^b$	670
553	ν_1^b	553
472	$\nu_4^b + l^b$	$\left\{ \begin{array}{l} 474 \\ 430 \end{array} \right.$
370	ν_4^b	370

^aFrequencies of SO_4^{2-} ion impurity (1%) bands i.e. 1105 (RT), 1122, 1109 and 1092 (LT) cm^{-1} arising due to $\nu_3(\text{SO}_4^{2-})$ and 620 (RT) and 627 (LT) cm^{-1} arising due to $\nu_4(\text{SO}_4^{2-})$ cm^{-1} have not been included in this table.

^bSuperscripts n and b refer to the modes of NH_4^+ and BeF_4^{2-} ions, respectively; ν_i ($i=1, 2, 3$ and 4) represents the internal mode having the same description as given by Herzberg (1945) and l represents the librational modes.

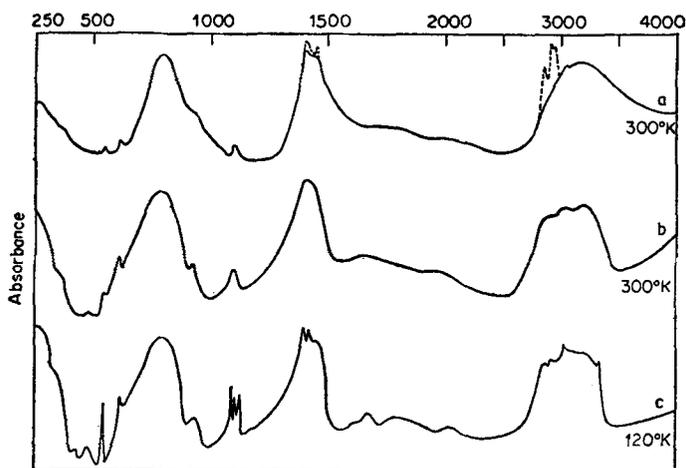


Figure 1. Infrared spectra of $(\text{NH}_4)_2\text{BeF}_4$ powder of (a) nujol mull (b) and (c) microcrystalline low scattering their film on AgCl plate.

In N—H stretching region of the spectrum, a broad and intense band, having three components at 3240, 3040 and 2860 cm^{-1} is observed at RT. Following the arguments and observations reported earlier (Jain 1976) for the analysis of Raman spectra of AFB single crystal, the first two bands have been attributed to two mixed modes arising due to strong Fermi resonance between $\nu_3(\text{F}_2)$ fundamental and $\nu_2 + \nu_4(\text{F}_1 + \text{F}_2)$ combination modes. The 2860 cm^{-1} band has been associated with $2\nu_4$ overtone. At LT, each of the 3240 and 3040 cm^{-1} bands splits into three components at 3315, 3260 and 3180 cm^{-1} ; and at 3100, 3035 and 2980 cm^{-1} , respectively. The $2\nu_4$ mode splits into 2920 and 2850 cm^{-1} components. The ν_1 mode, which is infrared forbidden for perfect T_d structure, is expected to appear weakly because of its low site symmetry (C_s in RT phase and C_1 in LT phase) (Mukherjee 1944, Nozik and Tokar 1969; Udalova 1961). In Raman spectra ν_1 is observed as a strong band around 3185 cm^{-1} (Jain 1976), while in our IR spectra it seems to have quite low intensity. Consequently, its presence is obscured by strong bands in the region. This indicates that NH_4^+ ions (like those in isomorphous $(\text{NH}_4)_2\text{SO}_4$ crystal) (Jain 1974) have almost a tetrahedral structure in both phases of AFB. This observation is also corroborated by the low IR intensity of ν_2 (1675 cm^{-1}) mode which is also forbidden under T_d symmetry. The ν_4 mode appears as a strong broad band between 1400–1500 cm^{-1} having indications of three components at RT and six components at LT.

The centre of ν_4 band shifts by about 10 cm^{-1} towards higher frequency side on going to LT. This could be an indication of H-bonds becoming stronger. However, the centre of N—H stretching band does not shift noticeably towards low frequency side as might be expected as an obvious effect. This reveals that H-bond strength does not increase appreciably on cooling up to our recorded LT.

Among the remaining bands for analysis two more bands at 2040 and 1795 cm^{-1} most likely arise due to $\nu_2^n + l^n$ and $\nu_4^n + l^n$ combinations respectively. In LT spectrum the former band shifts to 2065 cm^{-1} while the latter one splits into three components at 1845, 1805 and 1780 cm^{-1} . These data provide an opportunity to estimate the frequency of NH_4^+ libration to be around 370 and 385 cm^{-1} respectively

at RT and LT. These values are of the same order of magnitude as observed for NH_4^+ libration in isomorphous $(\text{NH}_4)_2\text{SO}_4$ (Venkateswarlu *et al* 1975) and other NH_4^+ compounds (Wagner and Hornig 1950). The increase in the librational frequency on lowering the temperature also indicates the strengthening of H-bonds in ferroelectric phase.

Strong bands at 790 and 370 cm^{-1} have correctly been attributed to ν_3^b and ν_4^b modes. The former band seems to show three components in LT spectrum, while the latter one shows a considerably increased intensity. ν_1^b and ν_2^b are IR forbidden for perfect T_d symmetry of BeF_4^{2-} . But the low site symmetry (C_s at RT and C_1 at LT (Mukherjee 1944, Nozik and Tokar 1969 and Udalova 1961) allows these modes in the spectrum. As a result the former mode appears very weakly at 553 cm^{-1} at RT and gets considerably enhanced (about 10 times) intensity at LT; the major change in intensity occurs in the vicinity of transition temperature (176K) (Jain 1975). The ν_2^b (Raman frequency=273 cm^{-1}) (Jain 1976) mode is however obscured by strong IR band around 200 cm^{-1} due to NH_4^+ translatory modes.

Three weak but well developed bands are observed at 930, 655 and 472 cm^{-1} . The most appropriate assignment for these bands seem to be $\nu_1^b + \nu_4^b$, $\nu_2^b + \nu_4^b$ and $\nu_4^b + l^b$ modes. The good intensity of 930 and 655 cm^{-1} bands may be attributed to the effect of possible Fermi-interaction of these modes and strongly IR active $\nu_3^b(\text{F}_2)$ fundamental having a full width at half the maximum intensity of the order of 200 cm^{-1} . The librational frequency of BeF_4^{2-} ion may be estimated to be around 100 cm^{-1} from $\nu_4^b + l^b$ (472 cm^{-1}) and ν_4^b (372 cm^{-1}).

Our sample of AFB was found to have 1% impurity of SO_4^{2-} ion which results in two weak bands at 1105 and 620 cm^{-1} due to its strongly IR active ν_3 and ν_4 modes. However, it should not affect the reliability and usefulness of our data as argued and established in our earlier papers (Jain 1975 and 1976) on the same sample.

Acknowledgements

The author is thankful to Dr H D Bist for his valuable suggestions on the work and his kind hospitality during the author's stay at IIT, Kanpur. Thanks are also due to CSIR for financial help.

References

- Blinc R and Levstek I 1960 *J. Phys. Chem. Solids* **12** 295
 Herzberg G 1945 *Molecular Spectra and Molecular Structure* (New York: Van Nostrand) Vol. 2
 Jain Y S, Bist H D and Upreti G C 1973 *Chem. Phys. Lett.* **22** 572
 Jain Y S 1974 *Spectra Structure Correlation in Certain Polyatomic Systems* Ph.D. Thesis IIT, Kanpur
 Jain Y S 1975 *Phys. Status Solidi* **B71** 61k
 Jain Y S 1976 *Indian J. Phys.* **50** 206
 Mukherjee P L 1944 *Indian J. Phys.* **18** 148
 Nozik Yu Z and Tokar L F 1969 *Latv. PSR Zinat. Akad. Vestis Fiz. Techn. Ser (SSSR)* **4** 75
 Pepinsky R and Jona F 1957 *Phys. Rev.* **105** 344
 Tedenac J C and Cot L 1969 *CR Acad. Sci. Paris* **C268** 1687
 Udalova V V 1961 *Sov. Phys. Crystallogr.* **6** 504
 Venkateswarlu P, Bist H D and Jain Y S 1975 *J. Raman Spectrosc.* **3** 143
 Wagner E L and Hornig D F 1950 *J. Chem. Phys.* **18** 296, 305