

$\text{NH}_4\text{F}$  ( $\nu_6$ ,  $560 \text{ cm}^{-1}$ ) and also cases where the motion approximates free rotation as in  $\text{NH}_4\text{PF}_6$  and  $\text{NH}_4\text{ClO}_4$ .<sup>66,82,100-101</sup> In  $\text{NH}_4\text{PF}_6$  and  $\text{NH}_4\text{ClO}_4$ , the  $\text{NH}_4^+$  ion moves in a uniform force field created by symmetrically placed anions of low charge so that the cation behaves like a particle trapped in an almost spherical cell. The librational motions in  $\text{NH}_4\text{Cl}$  ( $350 \text{ cm}^{-1}$ ) and  $\text{NH}_4\text{Br}$  ( $310 \text{ cm}^{-1}$ ) lie between the two extremes. Table III also indicates some correlation between the internal mode frequencies and the librational frequency or the barrier height. The internal frequencies in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  are intermediate in value between those for compounds at the two extremes of rotational motion. When the internal modes of  $\text{NH}_4\text{Cl}$  are compared to those of an almost free rotator as in  $\text{NH}_4\text{PF}_6$ , one observes that  $\nu_1$  (symmetric hydrogen stretch),  $\nu_3$  (asymmetric hydrogen stretch) and  $\nu_4$  (asymmetric hydrogen bend) are lower in  $\text{NH}_4\text{Cl}$  than in  $\text{NH}_4\text{PF}_6$ , the differences are  $200 \text{ cm}^{-1}$ ,  $185 \text{ cm}^{-1}$ , and  $30 \text{ cm}^{-1}$  and  $30 \text{ cm}^{-1}$  respectively. The symmetric hydrogen bending mode,  $\nu_2$ , is expected to have much lower value in  $\text{NH}_4\text{PF}_6$  than in  $\text{NH}_4\text{Cl}$ , although no value is reported. The trend in the frequency of the low intensity, asymmetric hydrogen bending mode is not too clear in Table III; however, the negative  $A_4(\gamma_4)$  observed in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  suggest that  $\nu_3$  frequency should be higher in ammonium salts with small  $\text{NH}_4$ -anion interactions. The frequency shifts in  $\text{NH}_4\text{Br}$  are of similar value as those in  $\text{NH}_4\text{Cl}$ . The comparison of the different salts certainly show that the internal modes in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  are substantially different from those expected for a free ion with  $\nu_1$ ,  $\nu_3$  and  $\nu_4$  values being smaller and  $\nu_2$  larger. Among several criteria that are employed to determine the presence of hydrogen bonding, determination of the volume anharmonicity,  $\gamma_1$  (or  $A_1$ ), of the internal modes of the  $\text{NH}_4^+$  ion should be one useful approach to evaluation of the effects caused by hydrogen bonding. Such an evaluation is especially useful when free ion frequencies are not available.