

NH_4F (ν_6 , 560 cm^{-1}) and also cases where the motion approximates free rotation as in NH_4PF_6 and NH_4ClO_4 .^{66,82,100-101} In NH_4PF_6 and NH_4ClO_4 , the 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 NH_4Cl (350 cm^{-1}) and NH_4Br (310 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 NH_4Cl and NH_4Br are intermediate in value between those for compounds at the two extremes of rotational motion. When the internal modes of NH_4Cl are compared to those of an almost free rotator as in NH_4PF_6 , one observes that ν_1 (symmetric hydrogen stretch), ν_3 (asymmetric hydrogen stretch) and ν_4 (asymmetric hydrogen bend) are lower in NH_4Cl than in NH_4PF_6 , the differences are 200 cm^{-1} , 185 cm^{-1} , and 30 cm^{-1} and 30 cm^{-1} respectively. The symmetric hydrogen bending mode, ν_2 , is expected to have much lower value in NH_4PF_6 than in NH_4Cl , 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 NH_4Cl and NH_4Br suggest that ν_3 frequency should be higher in ammonium salts with small NH_4 -anion interactions. The frequency shifts in NH_4Br are of similar value as those in NH_4Cl . The comparison of the different salts certainly show that the internal modes in NH_4Cl and NH_4Br are substantially different from those expected for a free ion with ν_1 , ν_3 and ν_4 values being smaller and ν_2 larger. Among several criteria that are employed to determine the presence of hydrogen bonding, determination of the volume anharmonicity, γ_i (or A_i), of the internal modes of the 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.