and $\nu_4(F_2)$ refer to the two bending modes. Libration is another motion that the NH_4^+ ion undergoes and is characterized by F_1 symmetry in the ordered phase of NH_4Cl IV and NH_4Br IV. The vibrational frequencies of the NH_4^+ ion would be independent of both temperature and volume if the motions were completely harmonic and the potential contained only terms quadratic in displacement of atoms.[28] However, one expects both the temperature and volume dependent anharmonicity to be quite large and important in the chloride and the bromide due to "disorder" and proton-halogen interactions. Volume dependent anharmonicity can be discussed in terms of microscopic or mode Grüneisen constant, γ_i, which is defined as:

$$\gamma_i = - \left.\frac{d\ln \nu_i}{d\ln V}\right)_T$$

or (1)

$$= \left.\frac{1}{\beta\nu_i} \frac{d\nu_i}{dP}\right)_T$$

where ν_i, V and β are frequency, volume and compressibility respectively. Usually at ambient temperature γ_i is independent of temperature, although it is strongly temperature dependent near a phase transition and at a few tenth of the Debye temperature.

Anharmonicity in the internal modes rising from proton-halogen interaction in a crystal should be evaluated in terms of the free-ion frequencies, intensities and peak widths. In the absence of free-ion information, the strength of hydrogen bonding is often deduced from a comparison of different ammonium salts. The correlation is not very clear; difficulties arise due to changes of both the distance and ionicity of the surrounding anions.[15] Investigation of the librational and internal mode frequencies as a function of proton-halogen or nitrogen halogen distance in the same compound is perhaps a more direct approach to the study of hydrogen bonding effects in these ammonium salts.