of the zone-edge and zone-center phonons should be similar in the ordered phase since this was the case even in the "disordered" phase and also since the flat librational dispersion observed in neutron scattering experiments indicates little interaction between NH_4^+ ions.[37] This simple analysis on the librational frequency of NH_4Cl points to the inappropriateness of the electrostatic potential and of the barrier-height calculation based upon the cubic field approximation. The analysis also indicates the necessity of a repulsive potential, strongly dependent on interionic distance, in the "disordered" phase which becomes less important in the ordered phase. In the bromide, analysis of the two-phonon librational frequency shows that V_o is proportional to $a_o^{-4.2}$ and $a_o^{-2.4}$ in NH_4Br II and NH_4Br V, respectively.

A number of detailed potentials have been considered for the lattice modes of the ammonium halides. However, anharmonicity, especially of the librational mode, is not usually treated.[58-63] Garland and Weiner's work is an exception. They have attempted to incorporate hydrogen bonding in NH_4Cl and NH_4Br by employing a semi-empirical potential similar to the potential proposed by Nagamiya.[6,17] The absence of information about the volume anharmonicity for the one-phonon librational mode in NH_4Cl and NH_4Br made evaluation of constants depending on distance difficult.

When the high pressure Raman data for the librational and the internal modes are compared with data for other ammonium salts, a better perspective is obtained on the magnitude of anharmonicity of the internal modes, on the large contribution of proton-halogen interactions to the librational frequency, and on the barrier height preventing free rotation of the NH_4^+ ion. Literature values for the internal modes (ν_1- ν_4), librational frequencies (ν_6), barrier heights (V_o) obtained from NMR studies, and internuclear distances for a series of ammonium compounds are listed in Table III. Examples were taken to cover the case where the librational motion of the NH_4^+ ion is highly hindered as in