

butions from the attractive hydrogen-halogen coupling (hydrogen bonding effects) which would be important due to the large ionic polarizability of the halide ions.<sup>55</sup> Attractive forces also may arise from the van der Waals interaction between the  $\text{NH}_4^+$  and the halide ion, from dynamic polarization effects introduced during vibration,<sup>56</sup> and as a result of the dipole induced on the halide ion by the hydrogens when the  $\text{NH}_4^+$  ions are antiparallel.<sup>17</sup> The last attractive potential is believed to be quite important in "disordered"  $\text{NH}_4\text{Cl}$  V and  $\text{NH}_4\text{Br}$  II.<sup>35</sup>

The potential for the librational motion of the  $\text{NH}_4^+$  ion is usually developed in terms of the spherical harmonics.<sup>17</sup> In the disordered phase, the leading nonspherical term is the fourth-order term; and an approximate solution which relates the barrier height ( $V_0$ ) to the first-order librational frequency is given by:<sup>57</sup>

$$h\nu_6 = (8\hbar^2 V_0/I) - (5\hbar^2/2I) \quad (2)$$

Here,  $I$  is the moment of inertia, and  $\nu_6$  is the librational frequency. In this approximation, the barrier height should vary inversely as the fifth power of the lattice constant,  $a_0$ . A potential for octapole-octapole interaction which varies inversely as the seventh power of lattice constant is usually added to the above expression for the potential when all the  $\text{NH}_4^+$  ions are parallel to each other in the ordered phase. When the barrier height ( $V_0$ ) for "disordered"  $\text{NH}_4\text{Cl}$  V is evaluated from the one-phonon librational frequency (Fig. 4) on the assumption of a cubic potential (Eq. 2) and a constant moment of inertia,  $V_0$  is observed to be proportional to  $a_0^{-6.7}$  rather than the expected  $a_0^{-5}$ . The barrier height for ordered  $\text{NH}_4\text{Cl}$  IV shows a weaker dependence on the lattice constant with  $V_0$  now proportional to  $a_0^{-2.5}$ . Although the calculations for phase IV is based on librational frequency obtained from two-phonon excitation, it is felt that this is not the cause for the weak dependence on lattice constant in the ordered phase. The pressure dependence