

lattice phonons, for which  $\gamma$ 's range from 2 to 3. The volume dependences of the librational mode is represented by the following values of the microscopic Grüneisen constant,  $\gamma_6$ :  $1.30 \pm 0.17$  ( $\text{NH}_4\text{Cl}$  V);  $0.29 \pm 0.06$  ( $\text{NH}_4\text{Cl}$  IV);  $0.72 \pm 0.09$  ( $\text{NH}_4\text{Br}$  II); and  $0.46 \pm 0.08$  ( $\text{NH}_4\text{Br}$  V). The  $\gamma_i$ 's for the internal modes are listed in Table I. They are even smaller than the  $\gamma_6$ 's and are independent of the phase; in  $\text{NH}_4\text{Br}$ , for example,  $\gamma_1$  is negative, and the others are:  $\gamma_2$ ,  $+0.022$ ;  $\gamma_3$ ,  $-0.036$ ; and  $\gamma_4$ ,  $-0.044$ (TO),  $-0.065$  (LO). Approximately the same values were obtained for the  $\gamma_i$ 's of  $\text{NH}_4\text{Cl}$ ; thus, the behavior of the internal modes is very similar in both halides. Although Grüneisen constants are a common measure of anharmonicity, for these halides, the ratio of the wavenumber change to the change of the nitrogen-halogen distance may be a more meaningful quantity for the internal modes; values of these ratios ( $A_i = d \ln \nu_i / d \ln d_{\text{N-X}}$ ) also are given in Table I.

There is no detailed study of the potential or the force constants involved in the ammonium halides with which these observations may be quantitatively interpreted. However, some qualitative understanding of the frequency shifts and the  $\gamma_i$ 's can be obtained from available analyses of parts of the problem and general concepts of the expected change in the potential with interatomic distance. It should be remembered that force constants depend on the second derivative, while the Grüneisen constants depend on the third derivative, of the potential with interatomic distance. Generally, the repulsive term makes the dominant contribution to the force constant and is even more important for the  $\gamma_i$ 's. Thus, the wavenumbers of vibrational bands usually increase with a decrease of volume, which corresponds to positive  $\gamma_i$ 's.<sup>54</sup>

The present results, especially the negative Grüneisen constant for the symmetric hydrogen stretching mode ( $\nu_1$ ) in  $\text{NH}_4\text{Br}$ , cannot be explained in terms of the dominance of repulsive interaction. It is necessary to consider contri-