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Raman Spectra of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ :  
Dependence of the Librational and the Internal Modes  
of the  $\text{NH}_4^+$  Ion on Volume and on Nitrogen-Halogen Distance\*

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ABSTRACT

The wavenumbers for the librational and the high frequency modes in the "disordered"  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  were obtained from polarized Raman spectra with values for unresolved peaks obtained by fitting the Raman intensity to damped uncoupled oscillators. The high frequency and the librational modes were studied isothermally (296 K) as a function of volume or of nitrogen-halogen distance over a decrease in distance of 4.4% in  $\text{NH}_4\text{Cl}$  and 5.0% in  $\text{NH}_4\text{Br}$ . The librational frequency increases with decrease in volume in both halides with anharmonicity being given by the Grüneisen constants ( $\gamma_6$ ): 1.30 ("disordered"  $\text{NH}_4\text{Cl}$  V); 0.29 (ordered  $\text{NH}_4\text{Cl}$  IV); 0.72 ("disordered"  $\text{NH}_4\text{Br}$  II) and 0.46 ( $\text{NH}_4\text{Br}$  V). The volume dependence of the librational motion do not show the behavior expected for a motion in a simple potential. The internal modes of the  $\text{NH}_4^+$  ion are insensitive to phase transition in both halides but depend to a small degree on internuclear distance; for example, the Grüneisen constants for  $\text{NH}_4\text{Br}$  are:  $\gamma_1 =$  (negative);  $\gamma_2 = +0.022$ ;  $\gamma_3 = -0.036$ ;  $\gamma_4(\text{TO}) = -0.044$  and  $\bar{\gamma}_4(\text{LO}) = -0.065$ .