

## INTRODUCTION

Several recent studies indicate the importance of proton-halogen coupling in determining the librational and reorientational energy of the  $\text{NH}_4^+$  ion in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ .<sup>1-6</sup> The coupling is expected to depend strongly on interionic distance. This dependence introduces a volume dependent anharmonicity of the librational and the internal mode frequencies of the  $\text{NH}_4^+$  ion. The purposes of the present paper are to describe the dependence of the librational and the internal mode frequencies on volume and on the nitrogen-halogen distance in  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  and to show that these modes are very anharmonic, consistent with strong proton-halogen interactions. To accomplish these purposes, accurate polarization spectra were obtained and precise mode frequencies were determined by fitting the Raman spectra with intensity calculations for uncoupled damped oscillators whenever the peaks could not be resolved experimentally. For the chloride, the study covers the "disordered" phase V (1 bar and 300 K)<sup>7-8</sup>, the ordered phase IV, and the changes that occur at the phase transition at 296 K between 9 and 10 kbar pressure.<sup>9</sup> For  $\text{NH}_4\text{Br}$ , the internal modes are followed in the "disordered" phase II, through the phase transition at  $19 \pm 2$  kbar and 296 K, and into the high pressure phase V.<sup>7</sup> The relative position of the phases ( $\text{NH}_4\text{Cl}$  V,  $\text{NH}_4\text{Cl}$  IV,  $\text{NH}_4\text{Br}$  II and  $\text{NH}_4\text{Br}$  V) studied in the present report are shown schematically in Fig. 1.

The literature on proton-halogen coupling suggests that some hydrogen bonding has always been expected in crystalline  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ . However, experimental evidence has never been especially definitive.<sup>11-17</sup> The CsCl-like structure of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ , with the  $\text{NH}_4^+$  ion located in the body-centered position and the N-H bond pointing towards the halide ion, is considered to be ideal for hydrogen bonding and highly suggests its presence. The observed