

## EXPERIMENTAL

Raman data were taken with 90° geometry using an argon ion laser (1.5 W) operating at 4880 and 5145 Å in conjunction with a Spex double monochromator and photon-counting system. All data recorded at atmospheric pressure were obtained from polarization spectra. Bands which could not be resolved experimentally were computed by fitting the Raman intensity to lineshapes calculated for uncoupled damped oscillators. Attempts were also made to fit the Raman intensity in certain cases to lineshapes for coupled oscillators; however, this did not improve the fit in the high frequency region of the internal modes. Polarization studies were not carried out in the high pressure cell due to the depolarization effect of the optical windows.

Only  $\text{NH}_4\text{Cl}$  crystals grown by a vapor deposition process were employed in the polarization studies; however, both vapor and solution grown samples were employed in the high pressure investigation. Most  $\text{NH}_4\text{Cl}$  crystals grown from the vapor phase were clearer than those grown from the solution, and the vapor-grown crystals gave sharper Raman peaks. No peaks were observed for these vapor-grown crystals assignable to either  $\text{HCl}$  or  $\text{NH}_3$ .<sup>29-30</sup> All  $\text{NH}_4\text{Br}$  crystals were grown from solution with the aid of urea as a habit modifier. Each crystal of both halides was carefully examined with a microscope for growth defects and occlusions, and defective crystals were discarded. No water peaks were observed in the Raman spectra of solution-grown  $\text{NH}_4\text{Br}$  samples; however, a weak peak at  $1013\text{ cm}^{-1}$ , possibly arising from urea, was occasionally observed.<sup>31</sup> These samples of  $\text{NH}_4\text{Br}$  were discarded. The high pressure spectra of solution-grown  $\text{NH}_4\text{Br}$  crystals were also compared with those of dry, compressed  $\text{NH}_4\text{Br}$  pellets. The same general features were observed with regard to the position of the phase transition and Raman peaks