were not employed to remove the nearly coincident combination ($\nu_2 + \nu_4$) which places the combined peak frequency (ν_1, $\nu_2 + \nu_4$) at a lower value.[33,38-42] The strongest peak with α_{xy} polarization in the 3100 cm^{-1} region is assigned to the triply degenerate ν_3 in NH_4Cl and NH_4Br. The values for ν_3 were obtained by fitting the Raman intensity to uncoupled oscillators. The literature values of the wavenumber indicate considerable scatter due to the difficulty of separating this mode from other peaks with the same polarization.[33,38-42] The wavenumbers and assignment of the remaining peaks are in agreement with literature.[33,38-42] Since the primary purpose of this work is to report accurate wavenumbers at atmospheric pressure and their dependence on interatomic distance, further details on the polarization studies and assignment will be presented elsewhere.[10]

Effects of Pressure and Phase Transition on the Spectra of NH_4Cl and NH_4Br.

The high wavenumber Raman peaks were studied to 40 kbar at 296 K. This compression decreases the lattice constant by 4.4% and 5.0% in NH_4Cl and NH_4Br, respectively. The variation of the wavenumbers of the fundamental modes with pressure are shown in Fig. 3 and 4. The wavenumber-pressure plots for the internal modes depart only slightly from linearity with the exception of ν_3 in NH_4Cl. The reason behind the response of ν_3 is not completely understood; however, it is felt that much of the nonlinearity at high pressures arises from difficulties in resolving ν_3 from other peaks. As already mentioned, the atmospheric pressure frequency of ν_3 was calculated by fitting the Raman intensity of the polarization spectra. However, no such calculations were attempted on the high pressure data owing to the complexity of the unpolarized spectra. The wavenumber-pressure plot of the librational phonon in NH_4Cl (Fig. 4) shows a large curvature with the two phases having different pressure dependence.