

In NH_4Cl , the librational dispersion curve is known to be flat in both the ordered and "disordered" phase.^{37,48} These combination peaks in this case provide information about the dispersion of the internal modes of the NH_4^+ ion. For example in NH_4Cl , it can be seen that ν_2 and ν_4 have some dispersion when one subtracts the value of ν_6 (350 cm^{-1} at 1 atm and 296 K) from the combination band wavenumbers in Table II.

Another set of interesting two-phonon peaks characterized by the α_{xy} ($=\alpha_{xz}=\alpha_{yx}$) polarization are centered around the asymmetric hydrogen stretching mode, ν_3 . There are four and five peaks of α_{xy} polarization in this region of the spectrum in NH_4Br and NH_4Cl respectively. Here the interest is in ν_3 , $\nu_4 + \nu_2$ and $2\nu_4$ which are believed to form a strongly-resonating Fermi triplet.⁴¹ The peaks around ν_3 in NH_4Cl and NH_4Br are seen in Fig. 2 for the Z(XY)Y scattering geometry. The same peaks in NH_4Cl are shown in Fig. 8 for unpolarized light in the high pressure cell at 5.9 and 22.7 kbar. The peaks are considerably sharper in the ordered phase at 22.7 kbar than in the "disordered" NH_4Cl at 5.9 kbar. However, there is no appreciable change in the relative intensity, nor does the intensity of ν_3 change significantly with respect to the combination peak (ν_1 , $\nu_4 + \nu_2$) at 3050 cm^{-1} . No large relative intensity shift that might arise from Fermi resonance was observed in the 3100 cm^{-1} region of the spectra at 296 K in the entire pressure range in either halide. Small intensity changes, however, could not be evaluated due to the variation in transparency of high pressure windows with pressure. In fitting the intensity to uncoupled damped oscillators in NH_4Br for example, no unusual intensity behavior was noticed between any two of the three neighboring peaks around ν_3 which could be attributed to strong coupling.

In the high wavenumber region of the spectra, one observes only a few changes accompanying the phase transition in NH_4Cl (V-IV) and NH_4Br (II-V). The wavenumbers