in this region. Also, the spillover (indicated by an asterisk) from modes inactive in the given geometry is surprisingly small and is of similar magnitude for an ordered crystal. The weak one-phonon libration (ν_6, 350 cm^{-1} at 1 bar and 296 K) is active in all scattering geometries in the "disordered" NH_4Cl V and is the exception to the well behaved polarization results.[7,33-34] The librational oscillation is not allowed in either the symmetry assigned to the "disordered" phase (O_h^1) or to the ordered phase (T_d^1).[35] The polarization of ν_6 and the strong pressure dependence of this mode (Fig. 4) suggests that the mode is Raman active due to the fact that the NH_4^+ ion is located in a very asymmetric potential well. The difference between the reported energy for the transition between the first and the second excited state (307 cm^{-1} at 1 bar and 300 K) and that between the ground and first excited state (350 cm^{-1}) also supports the asymmetry of the potential.[36] This observation of the second librational level suggests that the observed two-phonon librational mode (Fig. 4) is probably excited at a zone edge with the most likely position being M. This assignment of $2\nu_6$ is supported by the splitting of this mode at low temperatures in the ordered phase.[10,37-38] The one-phonon librational excitation has only been observed in NH_4Br V at low temperatures. Raman tensors for the fundamental modes of the NH_4^+ ion (Table I) are consistent with tetrahedral symmetry; there also is no removal of degeneracy. These tensors do not support the selection rule expected for the space group, O_h^1, that has been assigned to the "disordered" halides.

The wavenumbers for the fundamental modes (ν_1 to ν_4), combinations, and overtones were obtained from polarization studies and are listed in Table I and II. Values calculated by fitting the Raman intensity to uncoupled damped oscillators are indicated. Surprisingly, the symmetric hydrogen stretch mode ν_1 was at 3055 ± 8 cm^{-1} in both halides. The difference between this value for ν_1 and literature values appears to arise from the fact that polarization studies