1 cm^{-1} $kbar^{-1}$ usually belong to internal-lattice combination bands. These combination peaks show significant curvature in ν vs P plots (Fig. 7), and phase changes are reflected in the different values of pressure derivatives. This difference in response to pressure is a helpful aid for the vibrational assignment.[10] The librational modes (ν_6) is often evaluated from the various combination bands, and these combination peaks are of special interest (Fig. 7). For NH_4Cl, three combination peaks with ν_6 occur at 1082 cm^{-1} ($\nu_4 - \nu_6$), 1765 cm^{-1} ($\nu_4 + \nu_6$) and 2008 cm^{-1} ($\nu_2 + \nu_6$) at 1 bar and 296 K. The intensity of the weak $\nu_4 - \nu_6$ band is very sensitive to temperature and is not ideal for obtaining a value for ν_6. The other two peaks (1765 and 2008 cm^{-1}) are stronger and easier to follow, with preference usually being given to the former one.[38] In Raman studies, however, it is difficult to obtain a value for ν_6 from the combination peak ($\nu_4 + \nu_6$) due to the asymmetric nature of the band at ambient temperatures. The peak only splits at lower temperatures when the ν_4(LO) becomes stronger than the ν_4(TO) component. In both halides, the $\nu_4 + \nu_6$ peak is very likely to be a two-phonon, zone-edge excitation since the polarization results indicate only α_{xy} activity, whereas both α_{xx} and α_{xy} activity would be expected for zone-center process. Also the observed shift (+1.5 cm^{-1} $kbar^{-1}$) for the combination band ($\nu_4 + \nu_6$) is not that expected for the zone-center excitation.

Differences in the pressure dependence of a given phonon branch at various position in the Brillouin zone are well documented and this effect is apparent in the behavior of the different combination bands.[46,47] Similar difficulties are met in the other two combination bands of ν_6. The approximate value for ν_6 obtained from the combination bands are somewhat a drawback; nonetheless, these bands are an important source of information about ν_6 in many ammonium salts.