

$1 \text{ cm}^{-1} \text{ kbar}^{-1}$  usually belong to internal-lattice combination bands. These combination peaks show significant curvature in  $\nu$  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.<sup>10</sup> The librational modes ( $\nu_6$ ) is often evaluated from the various combination bands, and these combination peaks are of special interest (Fig. 7). For  $\text{NH}_4\text{Cl}$ , three combination peaks with  $\nu_6$  occur at  $1082 \text{ cm}^{-1}$  ( $\nu_4 - \nu_6$ ),  $1765 \text{ cm}^{-1}$  ( $\nu_4 + \nu_6$ ) and  $2008 \text{ cm}^{-1}$  ( $\nu_2 + \nu_6$ ) 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  $\nu_6$ . The other two peaks ( $1765$  and  $2008 \text{ cm}^{-1}$ ) are stronger and easier to follow, with preference usually being given to the former one.<sup>38</sup> In Raman studies, however, it is difficult to obtain a value for  $\nu_6$  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  $\nu_4(\text{LO})$  becomes stronger than the  $\nu_4(\text{TO})$  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  $\alpha_{xy}$  activity, whereas both  $\alpha_{xx}$  and  $\alpha_{xy}$  activity would be expected for zone-center process. Also the observed shift ( $+1.5 \text{ cm}^{-1} \text{ kbar}^{-1}$ ) 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.<sup>46,47</sup> Similar difficulties are met in the other two combination bands of  $\nu_6$ . The approximate value for  $\nu_6$  obtained from the combination bands are somewhat a drawback; nonetheless, these bands are an important source of information about  $\nu_6$  in many ammonium salts.