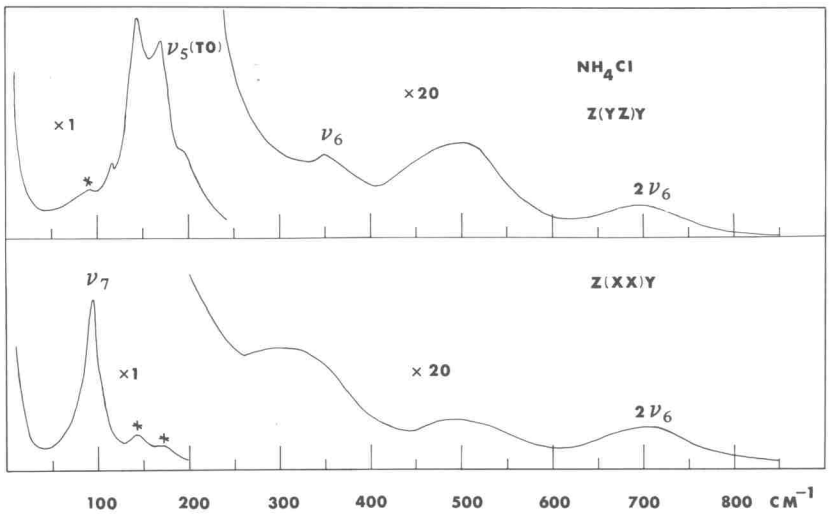

Fig. 1. Right-angle Raman scattering for the disordered phase (1 atm, 296 K) of NH_4Cl in two scattering geometry (see ref. 5 for notation). The asterisks indicate the spill-over of scattering from peaks active in other scattering geometry.

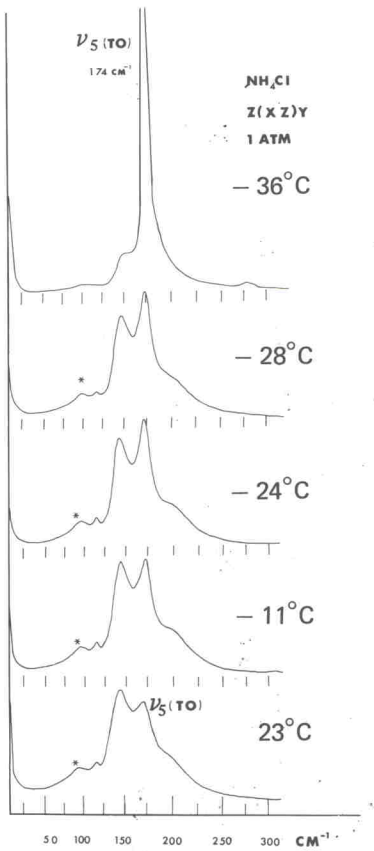

Fig. 2. Raman scattering intensities for modes centred around ν_5 (TO). The asterisks indicate peaks attributed to spill-over of scattering from other phenomena.

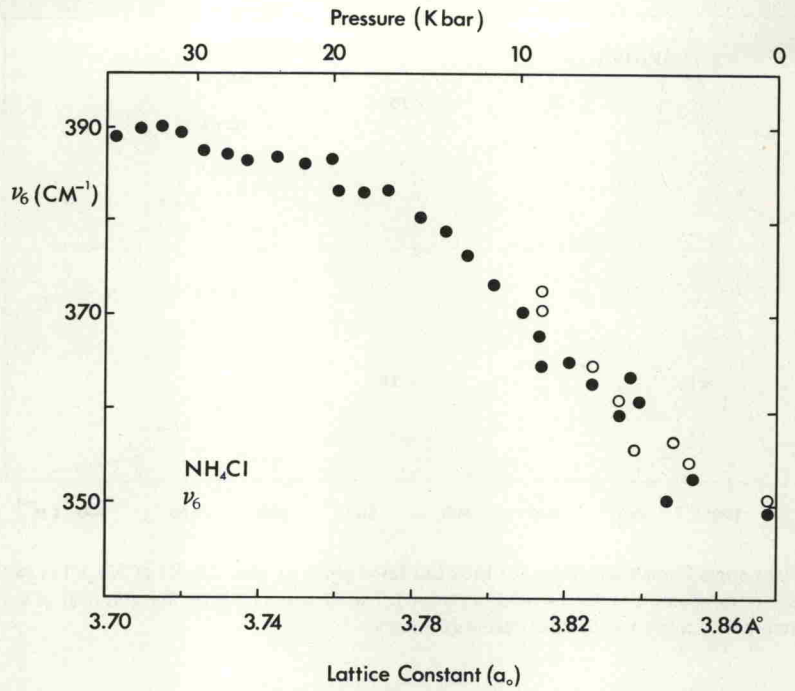

Fig. 3. The dependence of the librational frequency on pressure and lattice constant (a_0). Frequencies obtained from zone centre and as a two phonon process are indicated by open and solid circles, respectively.

characterized by well-defined polarizations; however, some modes such as the librational fundamental are active in all scattering geometries. The spill over from modes inactive in the particular scattering geometry (designated by asterisks) is quite small for both internal and lattice modes.

Figure 2 shows Raman peaks in the ν_5(TO) region with off-diagonal components in the polarization tensor. Of special interest is the observation that the total integrated intensity between 50 and 250 cm^{-1} remains constant while the intensity of ν_5(TO) itself depends strongly upon temperature and pressure. As the transition to the ordered phase[2] (−30.6°C, at 1 atm) is approached isobarically from higher temperatures, ν_5(TO) increases in intensity relative to others. The frequencies of ν_5(TO) and other modes shown in Fig. 2 are very volume sensitive in the disordered phase with large Grüneisen constants. The Grüneisen constant for ν_5(TO) is 3.1 and 2.5 for the disordered and ordered phases respectively.

Observation of ν_6 at the centre of the Brillouin zone (350 ± 15 cm^{-1} at 1 atm and 296 K) and as a two phonon process, $2\nu_6$, indicates that even in the disordered phase, the librational branch is flat within the precision of the experimental results. In the disordered phase, the frequency of ν_6 is very sensitive to change in the lattice constant (a_0); this is shown in Fig. 3. No differences can be distinguished between the frequency shift for the librational mode obtained as a fundamental and as a two phonon process.

The volume dependence or mode Grüneisen constants (γ_i) for the librational mode