

Fig. 4. A plot of  $\nu_1$  versus pressure. The slope of the solid line is  $-0.11 \text{ cm}^{-1}\text{kbar}^{-1}$ .

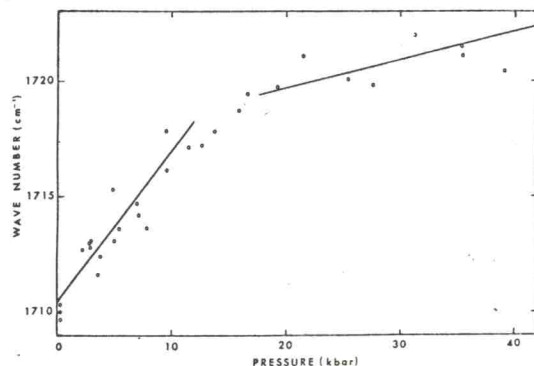


Fig. 5. A plot of  $\nu_2$  versus pressure. The slopes of the solid lines are  $+0.65$  and  $+0.12 \text{ cm}^{-1}\text{kbar}^{-1}$ .

slopes  $+0.65$  and  $+0.12 \text{ cm}^{-1}\text{kbar}^{-1}$  in the ordered and disordered phases respectively; the uncertainties in these numbers are estimated to be  $\pm 0.10 \text{ cm}^{-1}\text{kbar}^{-1}$ . This mode involves motion normal to the direction of the N-H...Cl bond. As the strength of the hydrogen bond increases, this motion might be expected to become more difficult, thus the positive shift.

The frequencies,  $\nu_3$  and  $\nu_4$ , of both triply degenerate modes of the "free" ion decrease as pressure increases. The variations of  $\nu_3$  with pressure are  $-1.20 \pm 0.10$  and  $-0.38 \pm 0.10 \text{ cm}^{-1} \times \text{kbar}^{-1}$  for the disordered and ordered phases respectively. The degeneracy of  $\nu_4$  is split by crystalline interactions into transverse and longitudinal components. The transverse component shows a larger pressure dependence than the longitudinal component with values of  $(\Delta\nu_4/\Delta P)$  of  $-0.35$  (transverse, disordered),  $-0.16$  (transverse, ordered),  $-0.29$  (longitudinal, disordered) and  $-0.17 \text{ cm}^{-1}\text{kbar}^{-1}$  (longitudinal, ordered). The uncertainties of these numbers are estimated to be  $\pm 0.10 \text{ cm}^{-1}\text{kbar}^{-1}$ . The motions associated

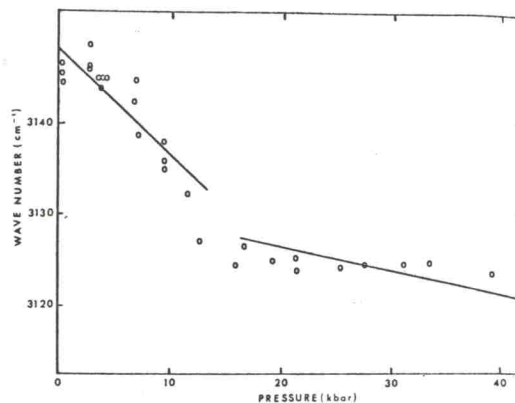


Fig. 6. A plot of  $\nu_3$  versus pressure. The slopes of the solid lines are  $-1.20$  and  $-0.39 \text{ cm}^{-1}\text{kbar}^{-1}$ .

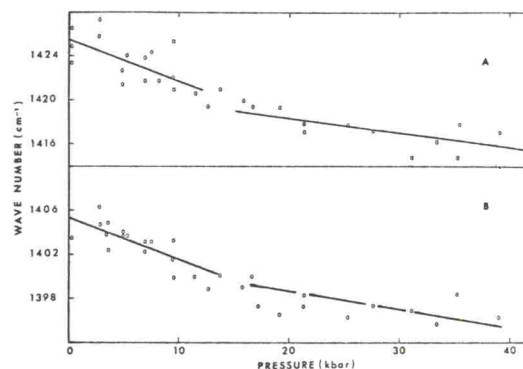


Fig. 7. A plot of the longitudinal (upper) and transverse (lower) components of  $\nu_4$  versus pressure. The slopes of the solid lines are:  $-0.35$  and  $-0.16$  (upper);  $-0.29$  and  $-0.16$  (lower)  $\text{cm}^{-1}\text{kbar}^{-1}$ .

with both  $\nu_3$  and  $\nu_4$  have components along the N-H...Cl axis, and the decrease of the frequencies with pressure, like that of  $\nu_1$ , can be attributed to the effects of increased hydrogen bond strength at high pressure.

Another interesting feature of the  $\nu_4$  mode is the increase of the intensity of the longitudinal component relative to that of the transverse component by about four times in the pressure range studied. The origin of this is not clear at present, but it may be related to the changing site symmetry. This and other unusual intensity effects in the 0-3000  $\text{cm}^{-1}$  region will be described in detail elsewhere [1] together with a detailed description of effects of pressure on the many combination and overtone bands of the spectra which are being studied. Preliminary results already suggest that several previous assignments [5] of these bands are incorrect.