

ternal modes of the ammonium ion and of comparable modes of other solids. Above 15 kbar in the ordered phase, $(\Delta\nu_5/\Delta P)$ is $+0.61 \text{ cm}^{-1} \times \text{kbar}^{-1}$.

When the observed frequency is plotted as a function of volume [2], a smooth curve is obtained throughout the 0-30 kbar region, with no noticeable break in the transition region. A $\log\nu$ - $\log V$ plot for the 0-30 kbar data can be fitted to a straight line of slope $-\gamma = \partial \ln\nu/\partial \ln V = -2.4$, where γ is the Grüneisen parameter. This value is perhaps fortuitously equal to that for KCl [8]. Neither plot, however, appears to be completely satisfactory above 30 kbar, and further data is being collected at higher pressures in an attempt to establish the precise volume dependence.

4. LIBRATIONAL MODE

Raman scattering at the librational fundamental, ν_6 , is allowed only by fluctuations of the local crystal symmetry in both phases. This fundamental is extremely weak, and it could be detected only in the low pressure (disordered) phase. However, the binary overtone, $2\nu_6$, is quite intense and could be followed in both phases, fig. 2. The pressure dependence of the overtone frequency, which is approximately $2(\Delta\nu_6/\Delta P)$, is $+5.0 \text{ cm}^{-1} \text{ kbar}^{-1}$ in the disordered phase. This implies that ν_6 in the disordered phase also is among the most pressure sensitive vibrational frequencies known.

The frequency of the overtone was used with Gutowsky, Pake, and Bersohn's potential function [9] for the libration of the NH_4^+ ion in a cubic field to calculate the potential barrier for rotation around a (100) axis. This barrier is found to increase with pressure from $4.4 \text{ kcal mole}^{-1}$

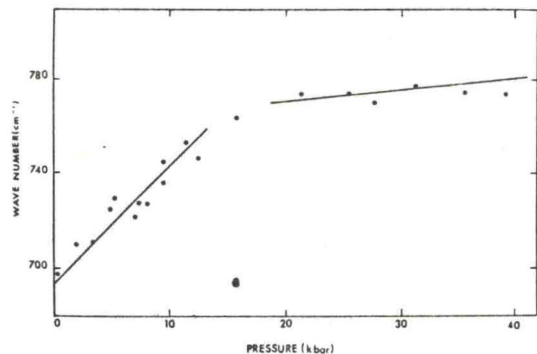


Fig. 2. A plot of $2\nu_6$ versus pressure. The slopes of the solid lines are $+5.0$ and $+0.48 \text{ cm}^{-1} \text{ kbar}^{-1}$.

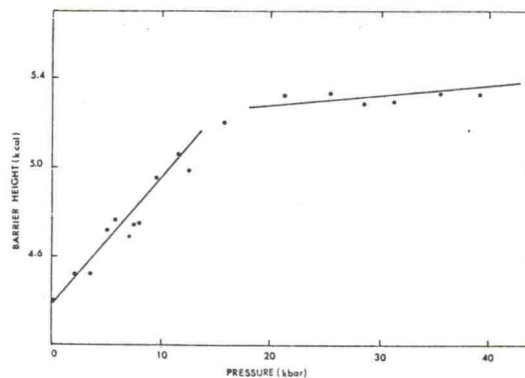


Fig. 3. A plot of the librational barrier height versus pressure.

at 1 atm to $5.3 \text{ kcal mole}^{-1}$ at 40 kbar, as shown in fig. 3. In this calculation, the moment of inertia was taken to be $4.826 \times 10^{-40} \text{ g cm}^2$ [10], and it was assumed that the N-H bond length and, thus, the moment of inertia does not change with the density of the crystal at these pressures. This assumption has been used successfully by Nagamiya in calculations of the ordering temperature of NH_4Cl [11].

5. INTERNAL MODES

The Raman active, symmetric stretching frequency, ν_1 , at 3052 cm^{-1} (1 atm) is the strongest peak of the spectrum and has the smallest pressure dependence [$(\Delta\nu_1/\Delta P) = -0.11 \pm 0.05 \text{ cm}^{-1} \times \text{kbar}^{-1}$] of all of the observed modes. This frequency also appears to be unaffected by the order-disorder transition; within the relatively large experimental uncertainty, its frequency variation with pressure can be fitted by a linear plot over the entire range studied, fig. 4. This is in sharp contrast to the other observed modes, all of which show a break of $(\Delta\nu_i/\Delta P)$ at the phase transition. The negative sign of the pressure dependence can perhaps be explained as arising from the decreasing distance between the hydrogen and chloride atoms and the resulting increase of hydrogen bonding. This lowering of the hydrogenic stretching frequency (-4 cm^{-1} for about 0.2 \AA decrease of the N-Cl bond length) by hydrogen bonding is consistent with data for other N-H...Cl systems [12, 13].

The doubly degenerate bending mode, ν_2 , is the only internal fundamental having a positive pressure dependence, fig. 5. The variation of this frequency can be fitted to straight lines of