

The one-phonon values are indicated as open circles (O) while the values obtained from two-phonon peaks are indicated as closed circles (●). Within experimental uncertainty, the two values are identical in the "disordered" phase (< 10 kbar at 296 K).

The symmetric hydrogen stretching mode, ν_1 , could not be resolved from the nearly coincident $\nu_2 + \nu_4$ by polarization studies at high pressures due to the depolarizing effect of the high pressure windows. In NH_4Br , ν_1 , was resolved from the combination band only above the II-V transition at 19 kbar which led to considerable decrease in the peak widths. The values of ν_1 are 3055 cm^{-1} (1 bar), 3050 cm^{-1} (27 kbar), and 3048 cm^{-1} (32 kbar) at 296 K in NH_4Br . Unfortunately, it was not possible to obtain values for ν_1 in NH_4Cl at other than at 1 bar.

The initial slope of the wavenumber-pressure plots (Fig. 3) or the isothermal pressure derivatives $(d\nu/dP)_T$ of the internal modes in "disordered" NH_4Cl V and NH_4Br II are given in Table II. The majority of the pressure derivatives in Table II show approximately 10% to 15% scatter; however, several shifts have larger error. The pressure derivatives for the internal modes of the NH_4^+ ion are quite small; for example, the values of $(d\nu/dP)_T$ in NH_4Br are: negative (ν_1), $+0.25$ (ν_2), -0.37 (ν_3), -0.27 ($\nu_4(\text{TO})$) and $-0.62 \text{ cm}^{-1} \text{ kbar}^{-1}$ ($\nu_4(\text{LO})$). The derivatives for the librational motion are $+2.21 \pm 0.15$ (phase V) and $+0.31 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ (phase IV) in NH_4Cl , with the values being obtained from the one-phonon (ν_6) and two-phonon ($2\nu_6$) processes respectively. In NH_4Br , the values of $(d\nu_6/dP)_T$ are $+1.14 \pm 0.08$ (phase II) and $+0.46 \pm 0.02 \text{ cm}^{-1} \text{ kbar}^{-1}$ (phase V) with both values being obtained from two-phonon excitation spectra.