

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,  $\nu_1$ , 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  $\text{NH}_4\text{Br}$ ,  $\nu_1$ , 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  $\nu_1$  are  $3055 \text{ cm}^{-1}$  (1 bar),  $3050 \text{ cm}^{-1}$  (27 kbar), and  $3048 \text{ cm}^{-1}$  (32 kbar) at 296 K in  $\text{NH}_4\text{Br}$ . Unfortunately, it was not possible to obtain values for  $\nu_1$  in  $\text{NH}_4\text{Cl}$  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"  $\text{NH}_4\text{Cl}$  V and  $\text{NH}_4\text{Br}$  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  $\text{NH}_4^+$  ion are quite small; for example, the values of  $(d\nu/dP)_T$  in  $\text{NH}_4\text{Br}$  are: negative ( $\nu_1$ ),  $+0.25$  ( $\nu_2$ ),  $-0.37$  ( $\nu_3$ ),  $-0.27$  ( $\nu_4(\text{TO})$ ) 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  $\text{NH}_4\text{Cl}$ , with the values being obtained from the one-phonon ( $\nu_6$ ) and two-phonon ( $2\nu_6$ ) processes respectively. In  $\text{NH}_4\text{Br}$ , 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.