Several interesting aspects of the behavior of the fundamentals are noted in Fig. 5 and 6. In Fig. 5 the wavenumbers for the internal modes of both halides are plotted against nitrogen-halogen distance (d_{N-X})[43], while the wavenumbers for the librational phonon, ν_6, are shown as a function of lattice constant (a_o) in Fig. 6. The wavenumber-distance relationships for the internal modes are almost linear with no evidence of discontinuity at the phase transition in NH_4Br (II-V; 19 kbar) and NH_4Cl (V-IV, 9 kbar). Fig. 5 shows that the corresponding modes in the chloride and bromide have similar wavenumber shifts $(d\nu/d_{N-X})_T$ with the exception of ν_3. The response of the librational phonon in the chloride and the bromide to change in interionic distance (Fig. 6) are quite different from those of the internal modes with the largest and the smallest wavenumber shift being observed in "disordered" phase V and ordered phase IV of NH_4Cl, respectively. Fig. 6 also shows that the librational phonon in NH_4Br is not so sensitive to the lattice constant as ν_6 in NH_4Cl. There is a substantial wavenumber gap between modes of NH_4Br and NH_4Cl at the same lattice constant; the values for the chloride are larger. For example, when the wavenumbers of the fundamentals of NH_4Br are compared to those of NH_4Cl at the same lattice constant (a_o of 3.873 or N-X of 3.35 Å at 1 bar and 296 K), the differences $(\Delta\nu)$ are:

~ 7 (ν_1); 15 (ν_2); 30 (ν_3); 12 $(\nu_4(TO))$; 23 $(\nu_4(LO))$ and 15 cm^{-1} (ν_6).

Wavenumbers and isothermal pressure derivatives for overtones and combination bands in NH_4Cl and NH_4Br are listed in Table II. No attempt was made at high pressures to follow weak peaks, shoulders and those peaks requiring polarization studies for resolution. In the 1 bar to 40 kbar pressure range, the overtone and combination bands show much larger changes with pressure than those of the fundamental internal modes of the NH_4^+ ion and range from -2.7 to +1.5 cm^{-1} $kbar^{-1}$ in NH_4Cl. The pressure derivatives with values greater than