

of the internal modes are insensitive to these phase transitions, although lattice-internal combination bands have different isothermal pressure derivatives with the value for the higher pressure phase being smaller. Noticeable sharpening of the high wavenumber peaks occurs in NH_4Cl at the "disorder-order" transition; while the changes at the II-V transition in NH_4Br are basically limited to the lattice modes and to small decreases in all peak widths. The high pressure transition in NH_4Br (V-IV) was not observed, although it is expected at approximately 30 kbar at room temperatures. This is probably due to the gradual nature of the spectral changes that accompany the transition and also due to experimental difficulties at these pressures. The spectra were not often observed beyond 30 kbar since the cell would require rebuilding as the metal in the high pressure cavity begins to show relaxation. Transmission of the optical windows also begins to deteriorate around 30 kbar. To avoid these experimental difficulties, the V-IV phase transition in NH_4Br was observed at lower temperatures and pressures.⁷

The V-IV bromide transition is accompanied by changes similar to "disorder-order" transition in NH_4Cl , and one observes the sharpening of the Raman peaks and several changes in the region of the hydrogen bending mode, ν_4 .⁷ At 1 bar and 296 K, ν_4 is decomposed into a weak $\nu_4(\text{LO})$ component observed in back reflection studies ($Z(\text{XY})\bar{Z}$) and into a much stronger $\nu_4(\text{TO})$ component. However, $\nu_4(\text{LO})$ becomes stronger than $\nu_4(\text{TO})$ component in the ordered phase IV. This change in intensity of ν_4 is shown in Fig. 9 for both isobaric transition at 1 bar and for the isothermal transition (296 K) in the chloride. The weak anomalous satellite, ν_4' , on the high wavenumber side of ν_4 is the only internal mode which becomes Raman inactive at the V-IV transition in NH_4Cl and NH_4Br . This mode (ν_4') has been associated with the lambda transition in