

are differences in the magnitude of the isothermal pressure derivatives. The differences lie mainly in the refinement of the data and in the use of a slightly different pressure scale.³²

When one compares the published high pressure infrared and the present Raman work, difficulties in experimentation and interpretation can be noticed in the near infrared (3000-7000 cm^{-1}) studies.²⁶ The selection rule is not favorable in the infrared for only two modes are active whereas all four internal modes of the NH_4^+ ion are Raman active. Pellets formed from powdered NH_4Cl and alkali halides allow only a single fundamental frequency (ν_3) to be observed in the infrared. A positive pressure derivative ($+ 0.07 \text{ cm}^{-1} \text{ kbar}^{-1}$) is reported for ν_3 in contrast to the negative value obtained in the Raman work (Table II). The smallness of the wavenumber for ν_3 in the reported infrared spectrum at 1 bar seems to indicate that the unequal intensity contribution from other peaks on either side were not taken into account in determining the position of ν_3 . The surrounding peaks differ in the relative shifts with pressure and thus again change the intensity contribution and lead to an error even in the value for the relative shift of ν_3 with pressure. Pressure dependences for the remaining internal modes in the infrared study were estimated from shifts of combination bands excited at different positions in the Brillouin zone. The difficulties of obtaining accurate wavenumbers for the fundamentals from many-phonon processes in the absence of dispersion relations for the internal modes has already been mentioned.

DISCUSSION

These studies show that the librational and internal modes of NH_4Cl and NH_4Br are less sensitive to volume or nitrogen-halogen distance than are most