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Raman Spectra of NH_4Cl and NH_4Br :
Dependence of the Librational and the Internal Modes
of the NH_4^+ Ion on Volume and on Nitrogen-Halogen Distance*

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ABSTRACT

The wavenumbers for the librational and the high frequency modes in the "disordered" NH_4Cl and NH_4Br were obtained from polarized Raman spectra with values for unresolved peaks obtained by fitting the Raman intensity to damped uncoupled oscillators. The high frequency and the librational modes were studied isothermally (296 K) as a function of volume or of nitrogen-halogen distance over a decrease in distance of 4.4% in NH_4Cl and 5.0% in NH_4Br . The librational frequency increases with decrease in volume in both halides with anharmonicity being given by the Grüneisen constants (γ_6): 1.30 ("disordered" NH_4Cl V); 0.29 (ordered NH_4Cl IV); 0.72 ("disordered" NH_4Br II) and 0.46 (NH_4Br V). The volume dependence of the librational motion do not show the behavior expected for a motion in a simple potential. The internal modes of the NH_4^+ ion are insensitive to phase transition in both halides but depend to a small degree on internuclear distance; for example, the Grüneisen constants for NH_4Br are: $\gamma_1 =$ (negative); $\gamma_2 = +0.022$; $\gamma_3 = -0.036$; $\gamma_4(\text{TO}) = -0.044$ and $\bar{\gamma}_4(\text{LO}) = -0.065$.

These interesting results on the internal modes provide direct evidence that anharmonic effects which can be attributed to strong proton-halogen coupling or hydrogen bonding effects are present in NH_4Cl and NH_4Br .

INTRODUCTION

Several recent studies indicate the importance of proton-halogen coupling in determining the librational and reorientational energy of the NH_4^+ ion in NH_4Cl and NH_4Br .¹⁻⁶ The coupling is expected to depend strongly on interionic distance. This dependence introduces a volume dependent anharmonicity of the librational and the internal mode frequencies of the NH_4^+ ion. The purposes of the present paper are to describe the dependence of the librational and the internal mode frequencies on volume and on the nitrogen-halogen distance in NH_4Cl and NH_4Br and to show that these modes are very anharmonic, consistent with strong proton-halogen interactions. To accomplish these purposes, accurate polarization spectra were obtained and precise mode frequencies were determined by fitting the Raman spectra with intensity calculations for uncoupled damped oscillators whenever the peaks could not be resolved experimentally. For the chloride, the study covers the "disordered" phase V (1 bar and 300 K)⁷⁻⁸, the ordered phase IV, and the changes that occur at the phase transition at 296 K between 9 and 10 kbar pressure.⁹ For NH_4Br , the internal modes are followed in the "disordered" phase II, through the phase transition at 19 ± 2 kbar and 296 K, and into the high pressure phase V.⁷ The relative position of the phases (NH_4Cl V, NH_4Cl IV, NH_4Br II and NH_4Br V) studied in the present report are shown schematically in Fig. 1.

The literature on proton-halogen coupling suggests that some hydrogen bonding has always been expected in crystalline NH_4Cl and NH_4Br . However, experimental evidence has never been especially definitive.¹¹⁻¹⁷ The CsCl-like structure of NH_4Cl and NH_4Br , with the NH_4^+ ion located in the body-centered position and the N-H bond pointing towards the halide ion, is considered to be ideal for hydrogen bonding and highly suggests its presence. The observed

nitrogen-halogen or better still hydrogen-halogen distances are considerably shorter than the sum of van der Waals radii.^{11,14,18} The experimental hydrogen-halogen distances are 2.32 Å and 2.49 Å (1 bar, 300 K) while the van der Waals radii sum to 3.0 Å and 3.2 Å for NH₄Cl and NH₄Br, respectively. Cohesive energy calculations also suggest the existence of hydrogen bonding and place the effect to be approximately 3% of the total lattice energy or 4.4 and 4.0 kcal mole⁻¹ in the chloride and bromide respectively.¹⁹ Deuteration often provides information about hydrogen bonding. In the presence of bonding, the smaller zero point energy of deuterium should lessen the amplitude of the hydrogen vibration, the repulsive potential, and the bond energy.²⁰ The lattice constant of ND₄Cl at room temperature and the volume change associated with the lambda phase transition are smaller than for NH₄Cl, consistent with weaker hydrogen bonding.²¹⁻²³ On the other hand at room temperature, the NH₄Br lattice expands upon isotopic substitution,²¹ Hydrogen bonding is also expected to increase the intensity, to broaden the peak and to decrease the frequency of the hydrogen stretching mode,²⁴ while the energies of the hydrogen deformation and the librational mode of the NH₄⁺ ion should increase. Effects characteristic of hydrogen bonding were observed in a preliminary high pressure Raman study of NH₄Cl.²⁵ On the other hand, hydrogen bonding is not supported by the near infrared studies (3000-7000 cm⁻¹) on NH₄Cl, where it is reported that the N-H bond strength increases (1.1% at 20 kbar) rather than weakening as the hydrogen-halogen distance decrease.²⁶⁻²⁷

An NH₄⁺ ion has T_d symmetry both in the isolated state and in the ordered phase IV. Four fundamental modes are allowed under the T_d point group with the following irreducible representations: 1 A₁ + 1 E + 2 F₂. ν₁(A₁) and ν₃(F₂) are the symmetric and the asymmetric hydrogen stretching modes, while ν₂(E)

and $\nu_4(F_2)$ refer to the two bending modes. Libration is another motion that the NH_4^+ ion undergoes and is characterized by F_1 symmetry in the ordered phase of $\text{NH}_4\text{Cl IV}$ and $\text{NH}_4\text{Br IV}$. The vibrational frequencies of the NH_4^+ ion would be independent of both temperature and volume if the motions were completely harmonic and the potential contained only terms quadratic in displacement of atoms.²⁸ However, one expects both the temperature and volume dependent anharmonicity to be quite large and important in the chloride and the bromide due to "disorder" and proton-halogen interactions. Volume dependent anharmonicity can be discussed in terms of microscopic or mode Grüneisen constant, γ_i , which is defined as:

$$\gamma_i = - \left(\frac{d \ln \nu_i}{d \ln V} \right)_T$$

or

$$= \left(\frac{1}{\beta \nu_i} \frac{d \nu_i}{d P} \right)_T \quad (1)$$

where ν_i , V and β are frequency, volume and compressibility respectively. Usually at ambient temperature γ_i is independent of temperature, although it is strongly temperature dependent near a phase transition and at a few tenths of the Debye temperature.

Anharmonicity in the internal modes rising from proton-halogen interaction in a crystal should be evaluated in terms of the free-ion frequencies, intensities and peak widths. In the absence of free-ion information, the strength of hydrogen bonding is often deduced from a comparison of different ammonium salts. The correlation is not very clear; difficulties arise due to changes of both the distance and ionicity of the surrounding anions.¹⁵ Investigation of the librational and internal mode frequencies as a function of proton-halogen or nitrogen halogen distance in the same compound is perhaps a more direct approach to the study of hydrogen bonding effects in these ammonium salts.

EXPERIMENTAL

Raman data were taken with 90° geometry using an argon ion laser (1.5 W) operating at 4880 and 5145 Å in conjunction with a Spex double monochromator and photon-counting system. All data recorded at atmospheric pressure were obtained from polarization spectra. Bands which could not be resolved experimentally were computed by fitting the Raman intensity to lineshapes calculated for uncoupled damped oscillators. Attempts were also made to fit the Raman intensity in certain cases to lineshapes for coupled oscillators; however, this did not improve the fit in the high frequency region of the internal modes. Polarization studies were not carried out in the high pressure cell due to the depolarization effect of the optical windows.

Only NH_4Cl crystals grown by a vapor deposition process were employed in the polarization studies; however, both vapor and solution grown samples were employed in the high pressure investigation. Most NH_4Cl crystals grown from the vapor phase were clearer than those grown from the solution, and the vapor-grown crystals gave sharper Raman peaks. No peaks were observed for these vapor-grown crystals assignable to either HCl or NH_3 .²⁹⁻³⁰ All NH_4Br crystals were grown from solution with the aid of urea as a habit modifier. Each crystal of both halides was carefully examined with a microscope for growth defects and occlusions, and defective crystals were discarded. No water peaks were observed in the Raman spectra of solution-grown NH_4Br samples; however, a weak peak at 1013 cm^{-1} , possibly arising from urea, was occasionally observed.³¹ These samples of NH_4Br were discarded. The high pressure spectra of solution-grown NH_4Br crystals were also compared with those of dry, compressed NH_4Br pellets. The same general features were observed with regard to the position of the phase transition and Raman peaks

in both types of NH_4Br samples. Thus impurities and crystal defect are not a problem in the present investigation.

The high pressure cell used in this work is a modified version of the optical cell originally designed by Drickamer.³² The cell was calibrated at room temperature with well established phase transitions and the linear variation of C-N stretch frequency. The cell is most reliable at 5 to 30 kbar region with the pressure accuracy being approximately ± 2 kbar. Each rectangular sample (2x2x3 mm) of ammonium halide was placed in the high pressure cell with the [100] direction perpendicular to the incident light. Wavenumber measurements were always initiated at low pressures and gradually the pressure was increased to 40 kbar over a period of several days. The system was allowed to equilibrate at each pressure for a half to several hours. The equilibration time appeared to have no marked effect on the wavenumbers, but peak intensities appear to increase with time at pressures lower than 10 kbar. Usually the solid-solid transition line was approached from lower pressure. However, the data were checked on recrossing the boundary from high pressures.

RESULTS

Atmospheric Pressure Spectra.

The high wavenumber polarization spectra ($1000-3400 \text{ cm}^{-1}$) of NH_4Cl and NH_4Br were carefully studied at atmospheric pressure and 296 K to determine accurate values of the wavenumbers. The upper two spectra in Fig. 2 are typical polarization spectra for "disordered" NH_4Cl in two scattering geometry, while the corresponding spectra of "disordered" NH_4Br are given in the lower two traces (Fig. 2). The Raman spectra of these two halides are quite similar

in this region. Also, the spillover (indicated by an asterisk) from modes inactive in the given geometry is surprisingly small and is of similar magnitude for an ordered crystal. The weak one-phonon libration (ν_6 , 350 cm^{-1} at 1 bar and 296 K) is active in all scattering geometries in the "disordered" NH_4Cl V and is the exception to the well behaved polarization results.^{7,33-34} The librational oscillation is not allowed in either the symmetry assigned to the "disordered" phase (O_h^1) or to the ordered phase (T_d^1).³⁵ The polarization of ν_6 and the strong pressure dependence of this mode (Fig. 4) suggests that the mode is Raman active due to the fact that the NH_4^+ ion is located in a very asymmetric potential well. The difference between the reported energy for the transition between the first and the second excited state (307 cm^{-1} at 1 bar and 300 K) and that between the ground and first excited state (350 cm^{-1}) also supports the asymmetry of the potential.³⁶ This observation of the second librational level suggests that the observed two-phonon librational mode (Fig. 4) is probably excited at a zone edge with the most likely position being M. This assignment of $2\nu_6$ is supported by the splitting of this mode at low temperatures in the ordered phase.^{10,37-38} The one-phonon librational excitation has only been observed in NH_4Br V at low temperatures. Raman tensors for the fundamental modes of the NH_4^+ ion (Table I) are consistent with tetrahedral symmetry; there also is no removal of degeneracy. These tensors do not support the selection rule expected for the space group, O_h^1 , that has been assigned to the "disordered" halides.

The wavenumbers for the fundamental modes (ν_1 to ν_4), combinations, and overtones were obtained from polarization studies and are listed in Table I and II. Values calculated by fitting the Raman intensity to uncoupled damped oscillators are indicated. Surprisingly, the symmetric hydrogen stretch mode ν_1 was at $3055 \pm 8 \text{ cm}^{-1}$ in both halides. The difference between this value for ν_1 and literature values appears to arise from the fact that polarization studies

were not employed to remove the nearly coincident combination ($\nu_2 + \nu_4$) which places the combined peak frequency ($\nu_1, \nu_2 + \nu_4$) at a lower value. ^{33,38-42}

The strongest peak with α_{xy} polarization in the 3100 cm^{-1} region is assigned to the triply degenerate ν_3 in NH_4Cl and NH_4Br . The values for ν_3 were obtained by fitting the Raman intensity to uncoupled oscillators. The literature values of the wavenumber indicate considerable scatter due to the difficulty of separating this mode from other peaks with the same polarization. ^{33,38-42}

The wavenumbers and assignment of the remaining peaks are in agreement with literature. ^{33,38-42} Since the primary purpose of this work is to report accurate wavenumbers at atmospheric pressure and their dependence on interatomic distance, further details on the polarization studies and assignment will be presented elsewhere. ¹⁰

Effects of Pressure and Phase Transition on the Spectra of NH_4Cl and NH_4Br .

The high wavenumber Raman peaks were studied to 40 kbar at 296 K. This compression decreases the lattice constant by 4.4% and 5.0% in NH_4Cl and NH_4Br , respectively. The variation of the wavenumbers of the fundamental modes with pressure are shown in Fig. 3 and 4. The wavenumber-pressure plots for the internal modes depart only slightly from linearity with the exception of ν_3 in NH_4Cl . The reason behind the response of ν_3 is not completely understood; however, it is felt that much of the nonlinearity at high pressures arises from difficulties in resolving ν_3 from other peaks. As already mentioned, the atmospheric pressure frequency of ν_3 was calculated by fitting the Raman intensity of the polarization spectra. However, no such calculations were attempted on the high pressure data owing to the complexity of the unpolarized spectra. The wavenumber-pressure plot of the librational phonon in NH_4Cl (Fig. 4) shows a large curvature with the two phases having different pressure dependence.

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.

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_0) 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_0 of 3.873 or N-X of 3.35 Å at 1 bar and 296 K), the differences ($\Delta\nu$) are:

$$\sim 7 (\nu_1); 15 (\nu_2); 30 (\nu_3); 12 (\nu_4(TO)); 23 (\nu_4(LO)) \text{ and } 15 \text{ cm}^{-1} (\nu_6).$$

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 $\text{cm}^{-1} \text{ kbar}^{-1}$ in NH_4Cl . The pressure derivatives with values greater than

$1 \text{ cm}^{-1} \text{ kbar}^{-1}$ usually belong to internal-lattice combination bands. These combination peaks show significant curvature in ν vs P plots (Fig. 7), and phase changes are reflected in the different values of pressure derivatives. This difference in response to pressure is a helpful aid for the vibrational assignment.¹⁰ The librational modes (ν_6) is often evaluated from the various combination bands, and these combination peaks are of special interest (Fig. 7). For NH_4Cl , three combination peaks with ν_6 occur at 1082 cm^{-1} ($\nu_4 - \nu_6$), 1765 cm^{-1} ($\nu_4 + \nu_6$) and 2008 cm^{-1} ($\nu_2 + \nu_6$) at 1 bar and 296 K. The intensity of the weak $\nu_4 - \nu_6$ band is very sensitive to temperature and is not ideal for obtaining a value for ν_6 . The other two peaks (1765 and 2008 cm^{-1}) are stronger and easier to follow, with preference usually being given to the former one.³⁸ In Raman studies, however, it is difficult to obtain a value for ν_6 from the combination peak ($\nu_4 + \nu_6$) due to the asymmetric nature of the band at ambient temperatures. The peak only splits at lower temperatures when the $\nu_4(\text{LO})$ becomes stronger than the $\nu_4(\text{TO})$ component. In both halides, the $\nu_4 + \nu_6$ peak is very likely to be a two-phonon, zone-edge excitation since the polarization results indicate only α_{xy} activity, whereas both α_{xx} and α_{xy} activity would be expected for zone-center process. Also the observed shift ($+1.5 \text{ cm}^{-1} \text{ kbar}^{-1}$) for the combination band ($\nu_4 + \nu_6$) is not that expected for the zone-center excitation.

Differences in the pressure dependence of a given phonon branch at various position in the Brillouin zone are well documented and this effect is apparent in the behavior of the different combination bands.^{46,47} Similar difficulties are met in the other two combination bands of ν_6 . The approximate value for ν_6 obtained from the combination bands are somewhat a drawback; nonetheless, these bands are an important source of information about ν_6 in many ammonium salts.

In NH_4Cl , the librational dispersion curve is known to be flat in both the ordered and "disordered" phase.^{37,48} These combination peaks in this case provide information about the dispersion of the internal modes of the NH_4^+ ion. For example in NH_4Cl , it can be seen that ν_2 and ν_4 have some dispersion when one subtracts the value of ν_6 (350 cm^{-1} at 1 atm and 296 K) from the combination band wavenumbers in Table II.

Another set of interesting two-phonon peaks characterized by the α_{xy} ($=\alpha_{xz} = \alpha_{yx}$) polarization are centered around the asymmetric hydrogen stretching mode, ν_3 . There are four and five peaks of α_{xy} polarization in this region of the spectrum in NH_4Br and NH_4Cl respectively. Here the interest is in ν_3 , $\nu_4 + \nu_2$ and $2\nu_4$ which are believed to form a strongly-resonating Fermi triplet.⁴¹ The peaks around ν_3 in NH_4Cl and NH_4Br are seen in Fig. 2 for the Z(XY)Y scattering geometry. The same peaks in NH_4Cl are shown in Fig. 8 for unpolarized light in the high pressure cell at 5.9 and 22.7 kbar. The peaks are considerably sharper in the ordered phase at 22.7 kbar than in the "disordered" NH_4Cl at 5.9 kbar. However, there is no appreciable change in the relative intensity, nor does the intensity of ν_3 change significantly with respect to the combination peak (ν_1 , $\nu_4 + \nu_2$) at 3050 cm^{-1} . No large relative intensity shift that might arise from Fermi resonance was observed in the 3100 cm^{-1} region of the spectra at 296 K in the entire pressure range in either halide. Small intensity changes, however, could not be evaluated due to the variation in transparency of high pressure windows with pressure. In fitting the intensity to uncoupled damped oscillators in NH_4Br for example, no unusual intensity behavior was noticed between any two of the three neighboring peaks around ν_3 which could be attributed to strong coupling.

In the high wavenumber region of the spectra, one observes only a few changes accompanying the phase transition in NH_4Cl (V-IV) and NH_4Br (II-V). The wavenumbers

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

NH_4Cl and thus is of interest.^{38,41,49} Unfortunately, it is difficult to observe ν_4' in Raman scattering. In NH_4Cl , $\nu_4(\text{LO})$ and ν_4' peaks could not be resolved experimentally, and their positions were determined through intensity analysis of the polarization spectra. In NH_4Br , ν_4' is separated from $\nu_4(\text{LO})$; however, it is much weaker and broader than in the chloride and difficult to place accurately. At 1 bar and 296 K, ν_4' is located at $1447 \pm 8 \text{ cm}^{-1}$ in NH_4Cl . It is easier to observe ν_4' in the high pressure phase of NH_4Br V, although it moves towards lower wavenumber with increasing pressure and becomes a shoulder on $\nu_4(\text{LO})$. Typical values of ν_4' in NH_4Br are 1445 ± 20 (1 bar), 1430 (26 kbar) and 1425 (30 kbar, 296 K).

The present atmospheric pressure data on $\nu_4(\text{LO})$, $\nu_4(\text{TO})$ and on ν_4' are quite different from those recently published by Wang and Wright.⁵⁰⁻⁵¹ In NH_4Cl , the most likely cause for the absence of ν_4' in the published work appears to be that no attempt was made to separate $\nu_4(\text{LO})$ and ν_4' peaks from the broad shoulder. The use of a lower intensity laser (140 mW as compared to 1.5 W in the present work) might explain the absence of details in Wang and Wright's work on NH_4Br . ν_4' which is characterized by α_{xy} polarization does not appear to arise from splitting of the degenerate $\nu_4(\text{T})$ since the latter is present with polarization expected for F_2 symmetry. ν_4' is thus assigned as a zone edge excitation of ν_4 in a manner similar to several of the lattice phonons with the point X in the Brillouin zone of the cubic lattice being a very likely position.^{7,34,52-53}

The results presented in this work represent observations of more than one thousand Raman bands of many different samples and in different high pressure cells. There are no conflicts in the direction of the wavenumber shifts with pressure from those reported in the preliminary work on NH_4Cl ;²⁵ however, there

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

lattice phonons, for which γ 's range from 2 to 3. The volume dependences of the librational mode is represented by the following values of the microscopic Grüneisen constant, γ_6 : 1.30 ± 0.17 (NH_4Cl V); 0.29 ± 0.06 (NH_4Cl IV); 0.72 ± 0.09 (NH_4Br II); and 0.46 ± 0.08 (NH_4Br V). The γ_i 's for the internal modes are listed in Table I. They are even smaller than the γ_6 's and are independent of the phase; in NH_4Br , for example, γ_1 is negative, and the others are: γ_2 , $+0.022$; γ_3 , -0.036 ; and γ_4 , -0.044 (TO), -0.065 (LO). Approximately the same values were obtained for the γ_i 's of NH_4Cl ; thus, the behavior of the internal modes is very similar in both halides. Although Grüneisen constants are a common measure of anharmonicity, for these halides, the ratio of the wavenumber change to the change of the nitrogen-halogen distance may be a more meaningful quantity for the internal modes; values of these ratios ($A_i = d \ln \nu_i / d \ln d_{\text{N-X}}$) also are given in Table I.

There is no detailed study of the potential or the force constants involved in the ammonium halides with which these observations may be quantitatively interpreted. However, some qualitative understanding of the frequency shifts and the γ_i 's can be obtained from available analyses of parts of the problem and general concepts of the expected change in the potential with interatomic distance. It should be remembered that force constants depend on the second derivative, while the Grüneisen constants depend on the third derivative, of the potential with interatomic distance. Generally, the repulsive term makes the dominant contribution to the force constant and is even more important for the γ_i 's. Thus, the wavenumbers of vibrational bands usually increase with a decrease of volume, which corresponds to positive γ_i 's.⁵⁴

The present results, especially the negative Grüneisen constant for the symmetric hydrogen stretching mode (ν_1) in NH_4Br , cannot be explained in terms of the dominance of repulsive interaction. It is necessary to consider contri-

butions from the attractive hydrogen-halogen coupling (hydrogen bonding effects) which would be important due to the large ionic polarizability of the halide ions.⁵⁵ Attractive forces also may arise from the van der Waals interaction between the NH_4^+ and the halide ion, from dynamic polarization effects introduced during vibration,⁵⁶ and as a result of the dipole induced on the halide ion by the hydrogens when the NH_4^+ ions are antiparallel.¹⁷ The last attractive potential is believed to be quite important in "disordered" NH_4Cl V and NH_4Br II.³⁵

The potential for the librational motion of the NH_4^+ ion is usually developed in terms of the spherical harmonics.¹⁷ In the disordered phase, the leading nonspherical term is the fourth-order term; and an approximate solution which relates the barrier height (V_0) to the first-order librational frequency is given by:⁵⁷

$$h\nu_6 = (8\hbar^2 V_0/I) - (5\hbar^2/2I) \quad (2)$$

Here, I is the moment of inertia, and ν_6 is the librational frequency. In this approximation, the barrier height should vary inversely as the fifth power of the lattice constant, a_0 . A potential for octapole-octapole interaction which varies inversely as the seventh power of lattice constant is usually added to the above expression for the potential when all the NH_4^+ ions are parallel to each other in the ordered phase. When the barrier height (V_0) for "disordered" NH_4Cl V is evaluated from the one-phonon librational frequency (Fig. 4) on the assumption of a cubic potential (Eq. 2) and a constant moment of inertia, V_0 is observed to be proportional to $a_0^{-6.7}$ rather than the expected a_0^{-5} . The barrier height for ordered NH_4Cl IV shows a weaker dependence on the lattice constant with V_0 now proportional to $a_0^{-2.5}$. Although the calculations for phase IV is based on librational frequency obtained from two-phonon excitation, it is felt that this is not the cause for the weak dependence on lattice constant in the ordered phase. The pressure dependence

of the zone-edge and zone-center phonons should be similar in the ordered phase since this was the case even in the "disordered" phase and also since the flat librational dispersion observed in neutron scattering experiments indicates little interaction between NH_4^+ ions.³⁷ This simple analysis on the librational frequency of NH_4Cl points to the inappropriateness of the electrostatic potential and of the barrier-height calculation based upon the cubic field approximation. The analysis also indicates the necessity of a repulsive potential, strongly dependent on interionic distance, in the "disordered" phase which becomes less important in the ordered phase. In the bromide, analysis of the two-phonon librational frequency shows that V_0 is proportional to $a_0^{-4.2}$ and $a_0^{-2.4}$ in $\text{NH}_4\text{Br II}$ and $\text{NH}_4\text{Br V}$, respectively.

A number of detailed potentials have been considered for the lattice modes of the ammonium halides. However, anharmonicity, especially of the librational mode, is not usually treated.⁵⁸⁻⁶³ Garland and Weiner's work is an exception. They have attempted to incorporate hydrogen bonding in NH_4Cl and NH_4Br by employing a semi-empirical potential similar to the potential proposed by Nagamiya.^{6,17} The absence of information about the volume anharmonicity for the one-phonon librational mode in NH_4Cl and NH_4Br made evaluation of constants depending on distance difficult.

When the high pressure Raman data for the librational and the internal modes are compared with data for other ammonium salts, a better perspective is obtained on the magnitude of anharmonicity of the internal modes, on the large contribution of proton-halogen interactions to the librational frequency, and on the barrier height preventing free rotation of the NH_4^+ ion. Literature values for the internal modes ($\nu_1 - \nu_4$), librational frequencies (ν_6), barrier heights (V_0) obtained from NMR studies, and internuclear distances for a series of ammonium compounds are listed in Table III. Examples were taken to cover the case where the librational motion of the NH_4^+ ion is highly hindered as in

NH_4F (ν_6 , 560 cm^{-1}) and also cases where the motion approximates free rotation as in NH_4PF_6 and NH_4ClO_4 .^{66,82,100-101} In NH_4PF_6 and NH_4ClO_4 , the NH_4^+ ion moves in a uniform force field created by symmetrically placed anions of low charge so that the cation behaves like a particle trapped in an almost spherical cell. The librational motions in NH_4Cl (350 cm^{-1}) and NH_4Br (310 cm^{-1}) lie between the two extremes. Table III also indicates some correlation between the internal mode frequencies and the librational frequency or the barrier height. The internal frequencies in NH_4Cl and NH_4Br are intermediate in value between those for compounds at the two extremes of rotational motion. When the internal modes of NH_4Cl are compared to those of an almost free rotator as in NH_4PF_6 , one observes that ν_1 (symmetric hydrogen stretch), ν_3 (asymmetric hydrogen stretch) and ν_4 (asymmetric hydrogen bend) are lower in NH_4Cl than in NH_4PF_6 , the differences are 200 cm^{-1} , 185 cm^{-1} , and 30 cm^{-1} and 30 cm^{-1} respectively. The symmetric hydrogen bending mode, ν_2 , is expected to have much lower value in NH_4PF_6 than in NH_4Cl , although no value is reported. The trend in the frequency of the low intensity, asymmetric hydrogen bending mode is not too clear in Table III; however, the negative $A_4(\gamma_4)$ observed in NH_4Cl and NH_4Br suggest that ν_3 frequency should be higher in ammonium salts with small NH_4 -anion interactions. The frequency shifts in NH_4Br are of similar value as those in NH_4Cl . The comparison of the different salts certainly show that the internal modes in NH_4Cl and NH_4Br are substantially different from those expected for a free ion with ν_1 , ν_3 and ν_4 values being smaller and ν_2 larger. Among several criteria that are employed to determine the presence of hydrogen bonding, determination of the volume anharmonicity, γ_1 (or A_1), of the internal modes of the NH_4^+ ion should be one useful approach to evaluation of the effects caused by hydrogen bonding. Such an evaluation is especially useful when free ion frequencies are not available.

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43. High Pressure Volume Data

There are several sources of high pressure volume measurements on NH_4Cl and NH_4Br at ambient temperature, however the most appropriate data for the present purposes are probably Kennedy and Bridgman's measurements.⁴⁴⁻⁴⁵ Their work covers the required pressure range (1 atm to 45 kbar) and also the relative volume changes show consistency. In NH_4Cl , for example at 5 kbar Bridgman's compressibility is 2% larger than Kennedy's while Bridgman's value is 4% smaller at 40 kbar. The present calculation of the high pressure nitrogen-halogen distances and Grüneisen constants (γ_i) were based on the x-ray lattice constants at 296 K and 1 atm and on Bridgman's relative volume measurements since there were more experimental values from this source. Unfortunately, the proton-halogen distance is only known at atmospheric pressure and is 2.32 Å and 2.49 Å at 300 K in NH_4Cl and NH_4Br respectively.³⁵

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Table I. The Fundamental Modes of the NH_4^+ Ion in NH_4Cl and NH_4Br
at 296 K

NH_4Cl			NH_4Br			
$\nu \text{ cm}^{-1}$ (1 atm)	γ_i (b)	A_i (c)	$\nu \text{ cm}^{-1}$ (1 atm)	γ_i	A_i	Assignment (d)
3055 ± 8			3055 ± 8	(negative)	(negative)	$\nu_1(A_1) (\alpha_{xx})$
1710 ± 2	$+0.026 \pm .004$	$+0.078$	1690 ± 2	$+0.022 \pm .003$	$+0.066$	$\nu_2(E) (\alpha_{xx})$
3150 ± 5 (a)	$-0.043 \pm .006$	-0.13	3135 ± 3 (a)	$-0.036 \pm .003$	-0.11	$\nu_3(F_2) (\alpha_{xy})$
1404 ± 3 (a)	$-0.047 \pm .006$	-0.14	1402 ± 3 (a)	$-0.044 \pm .003$	-0.13	$\nu_4(\text{TO}) \left. \begin{array}{l} (\alpha_{xy}) \\ (F_2) \end{array} \right\}$
1430 ± 5 (a)	$-0.058 \pm .008$	-0.17	1426 ± 5 (a)	$-0.065 \pm .01$	-0.20	$\nu_4(\text{LO}) \left. \begin{array}{l} (\alpha_{xy}) \\ (F_2) \end{array} \right\}$

(a) Frequencies which were calculated from fitting the Raman intensity to uncoupled damped oscillators.

(b) $\gamma_i = -\frac{d \ln \nu_i}{d \ln V}$ (mode Grüneisen constant)

(c) $A_i = -\frac{d \ln \nu_i}{d \ln d_{\text{N-X}}}$ (where $d_{\text{N-X}}$ is nitrogen-halogen distance)

(d) α_{ij} Raman tensor

Table II. Wavenumbers and isothermal pressure derivatives $(d\nu/dP)_T$ of the high frequency Raman peaks in NH_4Cl and NH_4Br at 296 K

NH_4Cl		NH_4Br		Assignment
$\nu \text{ cm}^{-1}$ (1 atm)	$(d\nu/dP)_T$ $\text{cm}^{-1} \text{ kbar}^{-1}$ Phase V	$\nu \text{ cm}^{-1}$ (1 atm)	$(d\nu/dP)_T$ $\text{cm}^{-1} \text{ kbar}^{-1}$ Phase II	
1082	-2.0	1110	-1.5	$\nu_4 - \nu_6$
1335	-2.7	1354	-1.4	$\nu_4(\text{TO}) - \nu_7$
1404(a)	-0.20	1402(a)	-0.27'	$\nu_4(\text{TO})(\text{F}_2)$
1430(a)	-0.52	1426(a)	-0.62	$\nu_4(\text{LO})(\text{F}_2)$
1447(a) [negative]		(1445) [negative]		ν_4
1710	+0.23	1690	+0.25	$\nu_2(\text{E})$
1765	+1.5	1725	+0.47	$\nu_6 + \nu_4$
2008	+1.2	1959	+0.56	$\nu_2 + \nu_6$
2823	+0.76	2807	-0.25	$2\nu_4$
3048(a)		3036(a) [negative]		$\nu_2 + \nu_4$
3055 [negative]		3055 [negative]		$\nu_1(\text{A}_1)$
(3100)(a)				
(3135)(a)		3075(a)		
3150(a) -1.3		3135(a) -0.37		$\nu_3(\text{F}_2)$
(3230)(a)		3199(a)		$\nu_1 + \nu_5(\text{TO})$

(a) Frequencies which were calculated from fitting the Raman intensity to uncoupled damped oscillators.

() Values in parentheses have large uncertainty.

Table III. Wavenumber for the librational (ν_6) and Internal modes ($\nu_1 - \nu_4$) of the NH_4^+ Ion in Various Ammonium Salts (300 K; 1 atm)

Crystal	Crystal Symmetry	Distance (Å)	Barrier Height, V_0 (kcal mole ⁻¹)	ν_6	ν_1	ν_2	ν_3	ν_4 (cm ⁻¹)	References
<u>FLUORIDE</u>		<u>dN-F</u>							
NH_4F	hex., C_{6V}^6 or C_{6V}^4	2.71	~10	555-568	2845	1750	3100	1408	15, 64-72
$(\text{NH}_4)_2\text{SiF}_6$	Cubic, O_h^5	3.00	~2	168	3233	1701	3314	1427	68, 73-76
$(\text{NH}_4)_2\text{BeF}_4$	Rhomb., V_h^{16}	2.86- 3.39	1.5, 2.7, 4.3		3247	1686 ⁺	3334	1431	15, 77, 81
NH_4PF_6	Cubic, O_h^5		0.2 (103K)		3252		3335	1433	15, 68, 82
<u>CHLORIDE</u>		<u>dN-Cl</u>							
NH_4Cl	Cubic, O_h^1	3.35	4.7	350	3055	1710	3150	1404(TO)	10, 18, 38, 57 83-84
$(\text{NH}_4)_2\text{SnCl}_6$	Cubic, O_h^5	3.55	1.2		3162	1670	3245	1407	76-77, 85
$(\text{NH}_4)_2\text{PtCl}_6$	Cubic, O_h^5	3.48					3240		68, 86
<u>BROMIDE</u>		<u>dN-Br</u>							
NH_4Br	Cubic, O_h^1	3.52	3.3, 4.0	310	3055	1690	3135	1402(TO)	10, 18, 38, 57, 83 87

(continuation)

<u>Crystal</u>	<u>Crystal Symmetry</u>	<u>Distance (A)</u>	<u>Barrier Height (kcal mole⁻¹)</u>	<u>ν_6</u>	<u>ν_1</u>	<u>ν_2</u>	<u>ν_3</u>	<u>ν_4</u>	<u>References</u>
<u>IODIDE</u>		<u>dN-I</u>							66, 71
NH ₄ I	Cubic, O _h ⁵	3.62			3075	1655	3130	1410	88-92
<u>OXIDE</u>		<u>dN-O</u>							68, 73, 77, 79
(NH ₄) ₂ SO ₄	Rhomb., V _h ¹⁶	2.93- 3.54	2.3, 3.9, 2.7 (305) doublet		3160	1672	3210	1417	93-96
NH ₄ NO ₃	Rhomb., V _h ¹³	2.05	2.4		3130	1656	3190, 3230, 3250	1414, 1462	77, 96-98
NH ₄ ClO ₄	Rhomb., V _h ¹⁶	2.93 - 3.08	0.1-0.2		3206		3290	1425	68, 96, 99-102

+The same temperature shift as that of NH₄Cl was assumed.

CAPTIONS

Fig. 1. Generalized phase diagram for NH_4Cl , NH_4Br and NH_4I . In this representation, three separate phase diagrams have been placed side by side. Each phase diagram starts on the left side at atmospheric pressure. The high temperature phase I has NaCl-like structure, while the remaining phases consist of CsCl-like arrangement of nitrogen and halogen atoms. The "disordered" phase of NH_4Cl "II" was relabeled as $\text{NH}_4\text{Cl V}$ in reference 7 for reasons cited herein. At 1 atm and 300 K, both $\text{NH}_4\text{Cl V}$ and $\text{NH}_4\text{Br II}$ are "disordered" whereas both halides have ordered structure with parallel arrangement of the NH_4^+ ion (T_d^1) in phase IV. $\text{NH}_4\text{Cl V}$ transforms into the higher temperature phase II at approximately 75°C at 1 atm.¹⁰ The relative position for II-V phase boundary in NH_4Cl is indicated by the dotted line (...). $\text{NH}_4\text{Br III}$ has a tetragonal structure with D_{4h}^7 space group. The present work reports changes accompanying isothermal compression in NH_4Cl (phase V and IV) and NH_4Br (phase II and V) at 296 K.

Fig. 2. High frequency polarization spectra for "disordered" $\text{NH}_4\text{Cl V}$ (upper two figures) and $\text{NH}_4\text{Br II}$ (lower two figures) are shown in two scattering geometries. The direction of incident and scattered light are given outside the parentheses while the corresponding polarization are placed inside. The asterisks indicate the spillover from peaks active in other scattering geometry.

Fig. 3. Shift of the internal mode frequencies (cm^{-1}) of the NH_4^+ ion in NH_4Br and NH_4Cl with increasing pressure at 296 K.

Fig. 4. Shift of the librational frequency (cm^{-1}) of NH_4Cl with increasing pressure at 296 K. The values obtained from one-phonon spectra are indicated by the light circles (O) while those obtained from two-phonon spectra are shown by the dark circles (●). The "order-disorder" phase transition occurs at 9-10 kbar.

Fig. 5. Shift of the internal mode frequencies of the NH_4^+ ion in NH_4Cl and NH_4Br with change in nitrogen-halogen distance, $d_{\text{N-X}}$, at 296 K. For the symmetric, hydrogen-stretching mode, ν_1 , only the wavenumber observed at 1 bar is indicated.

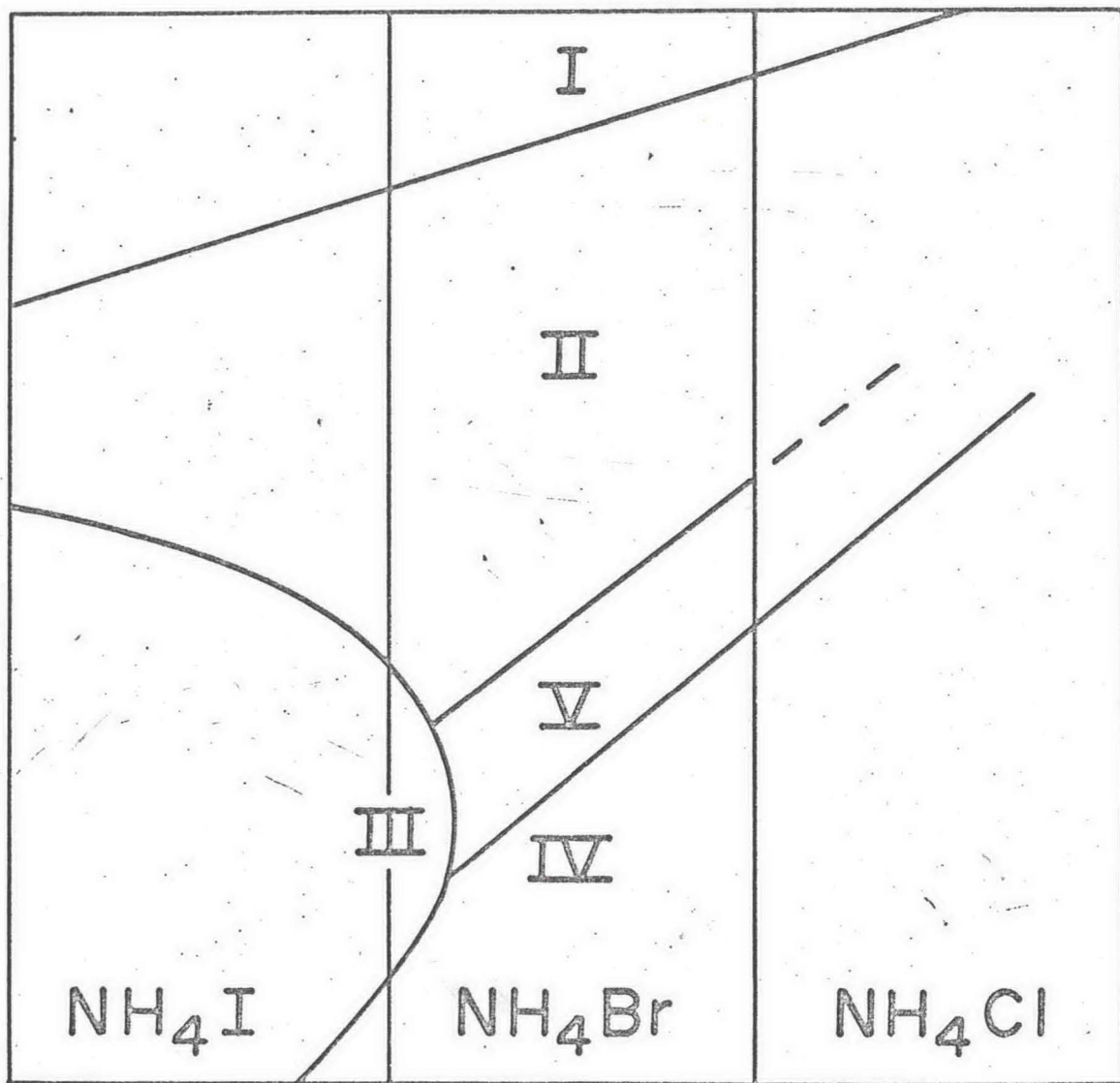
Fig. 6. Variation of the librational frequency (cm^{-1}) of NH_4Cl and NH_4Br with lattice constant a_0 . In NH_4Cl , values from both one-phonon (light circles, O) and two-phonon (dark circles, ●) spectra are shown, while those in NH_4Br were all obtained from two-phonon excitation process.

Fig. 7. Pressure induced frequency variation of the combination bands in NH_4Cl and NH_4Br at 296 K. Curves designated as A, B and C represent combination bands: $\nu_2 + \nu_6$, $\nu_4 + \nu_6$ and $\nu_4 - \nu_6$ respectively.

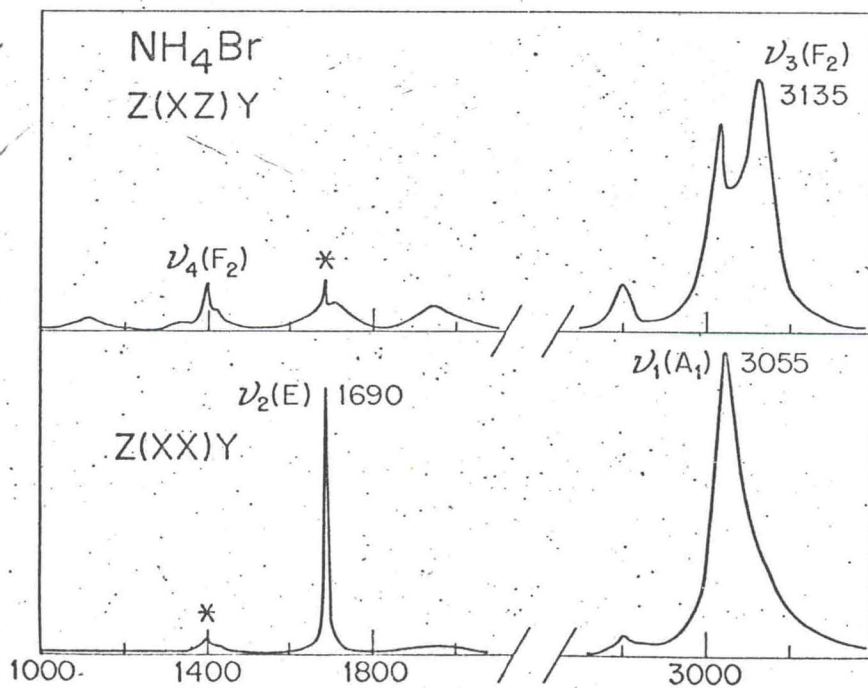
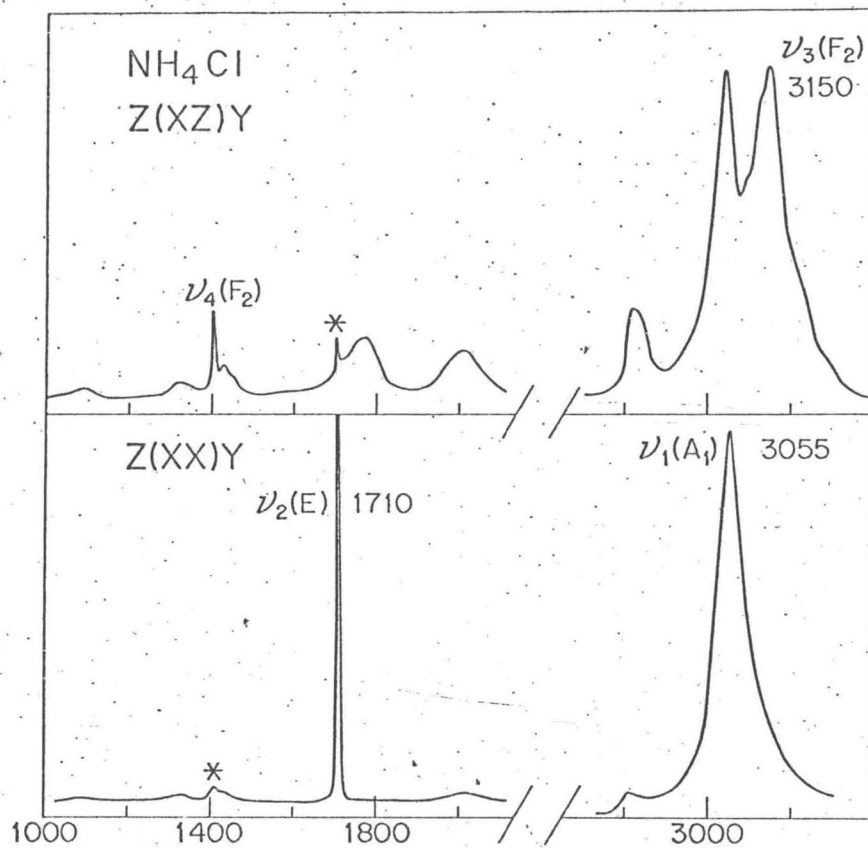
Fig. 8. Peaks centered around ν_3 (3150 cm^{-1} at 1 atm) in NH_4Cl are shown at 5.9 and 22.7 kbar pressure for unpolarized light. Polarization studies at atmospheric pressure show the presence of five peaks with α_{xz} and one with $\alpha_{xx}(\nu_1)$ polarization. These peaks could not be resolved in the high pressure spectra.

Fig. 9. Effect of isothermal (296 K) and isobaric (1 atm) "disorder-order" phase transition on the relative Raman intensity of $\nu_4(\text{TO})$ and $\nu_4(\text{LO})$ component in NH_4Cl .

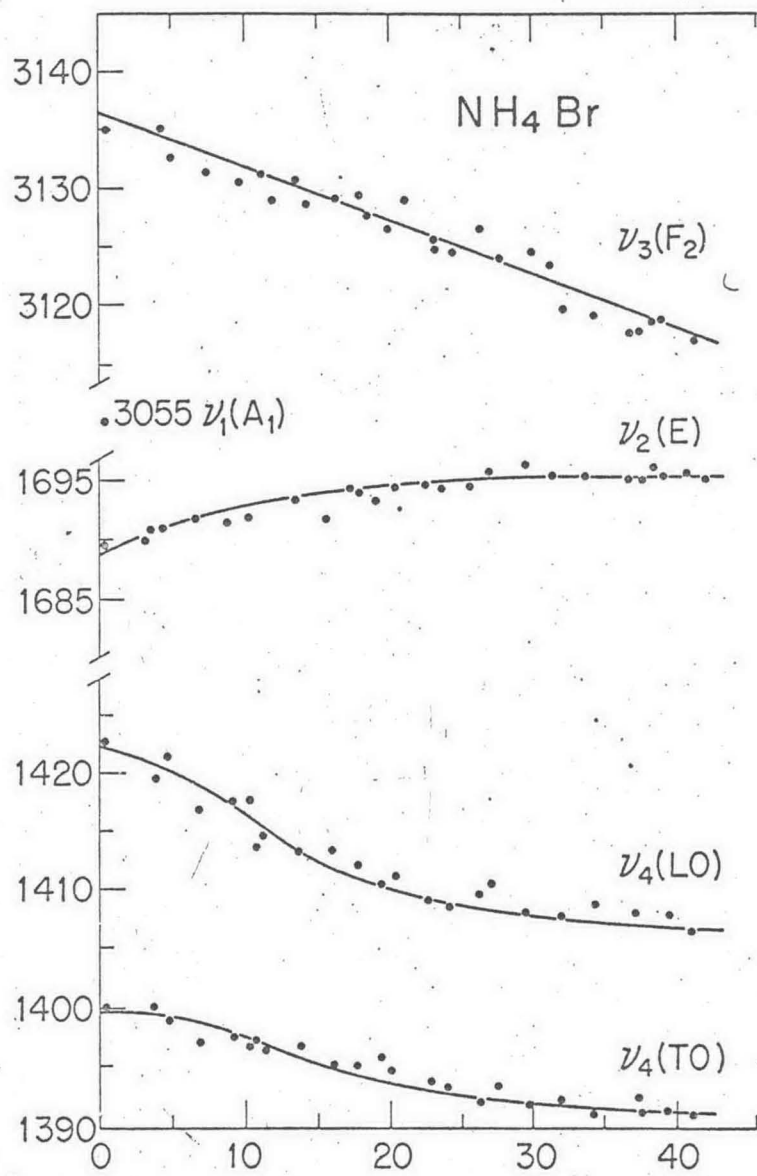
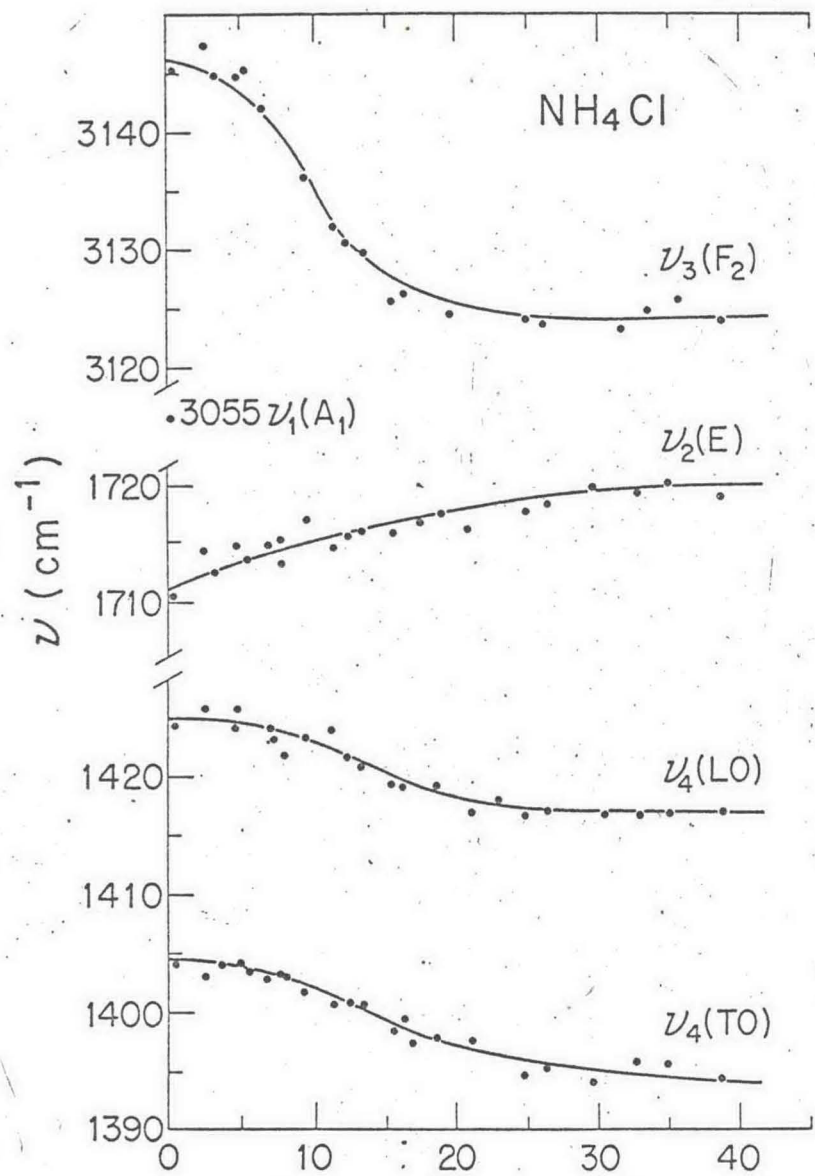
Temperature ↑



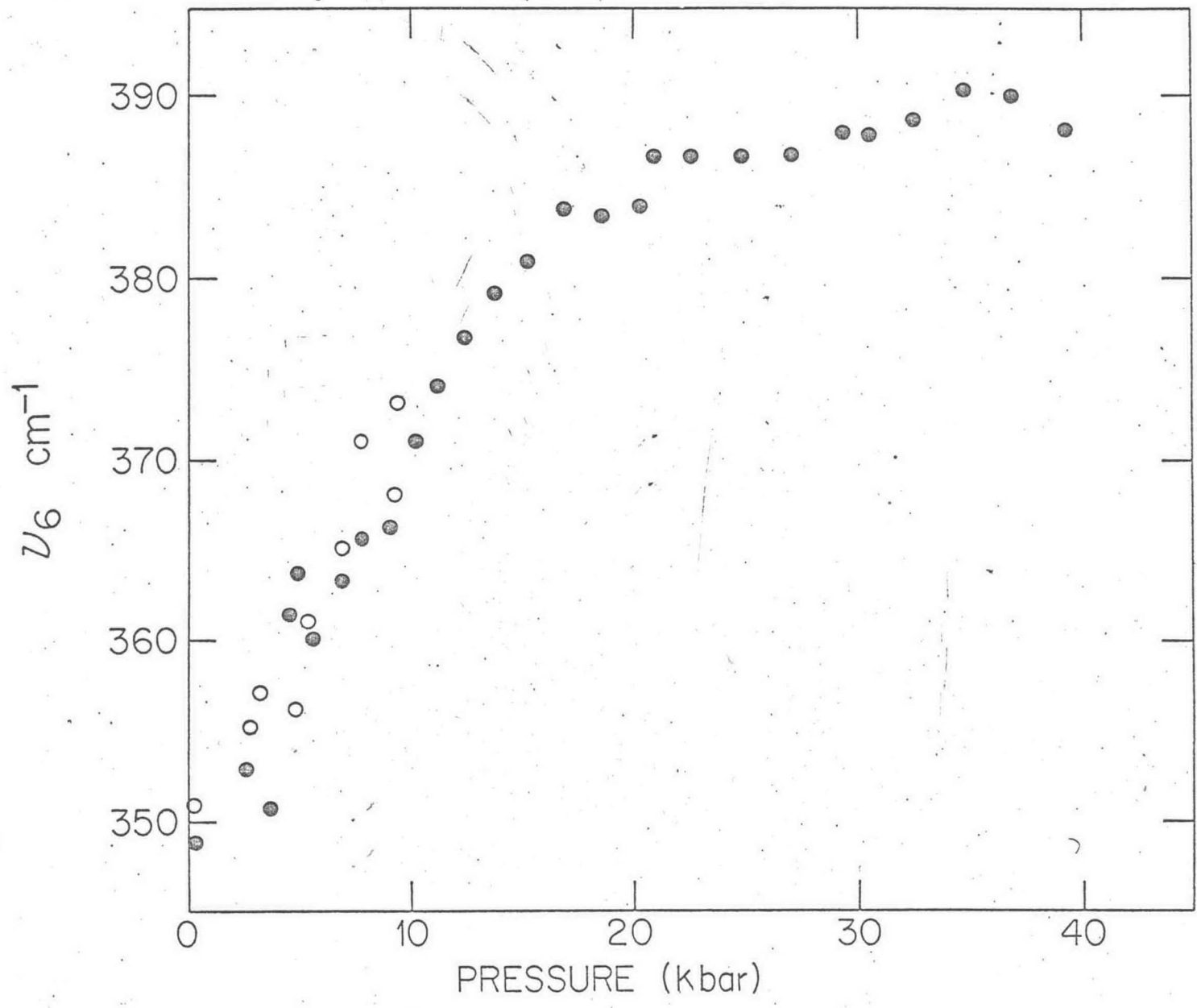
Pressure →

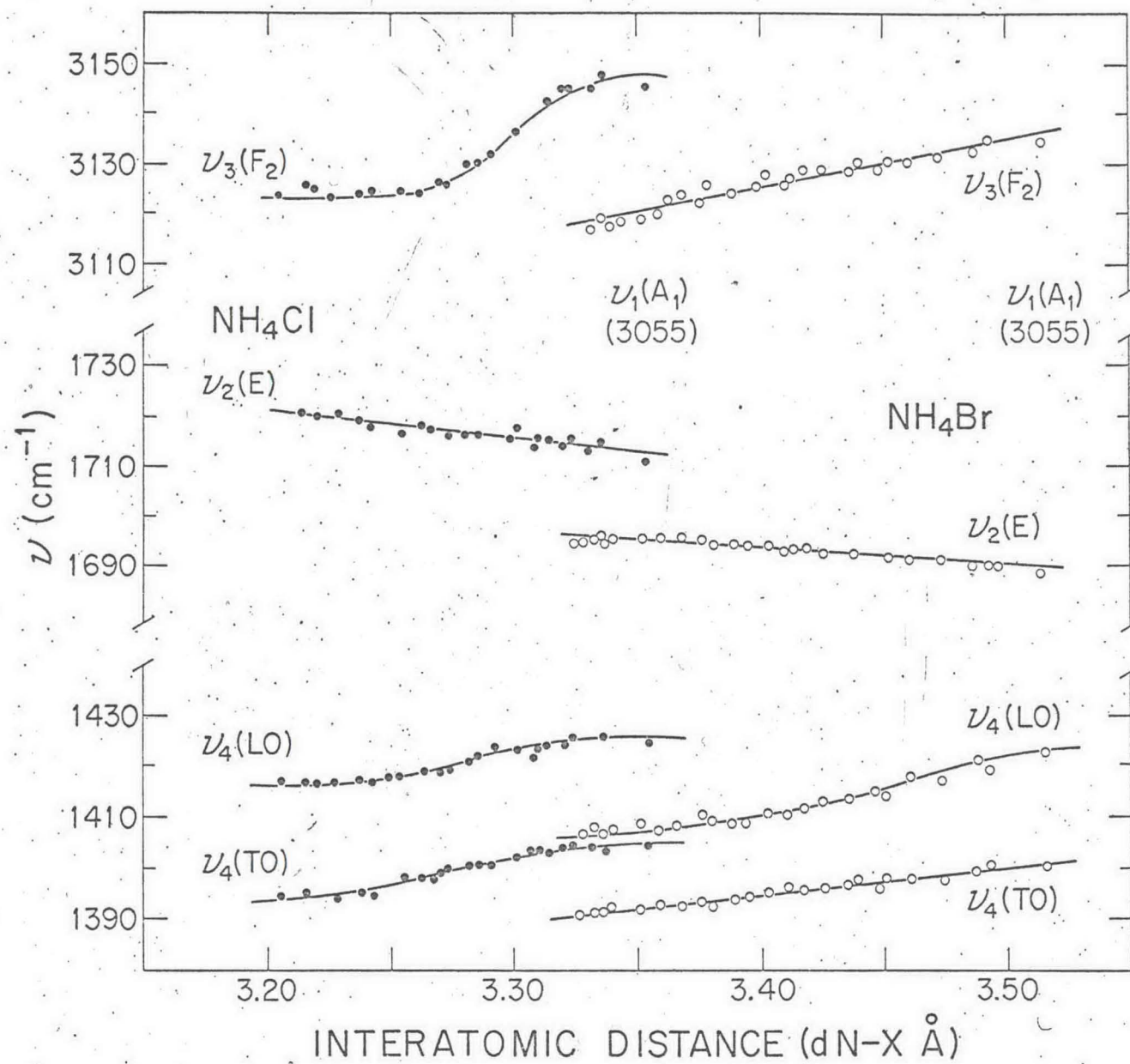


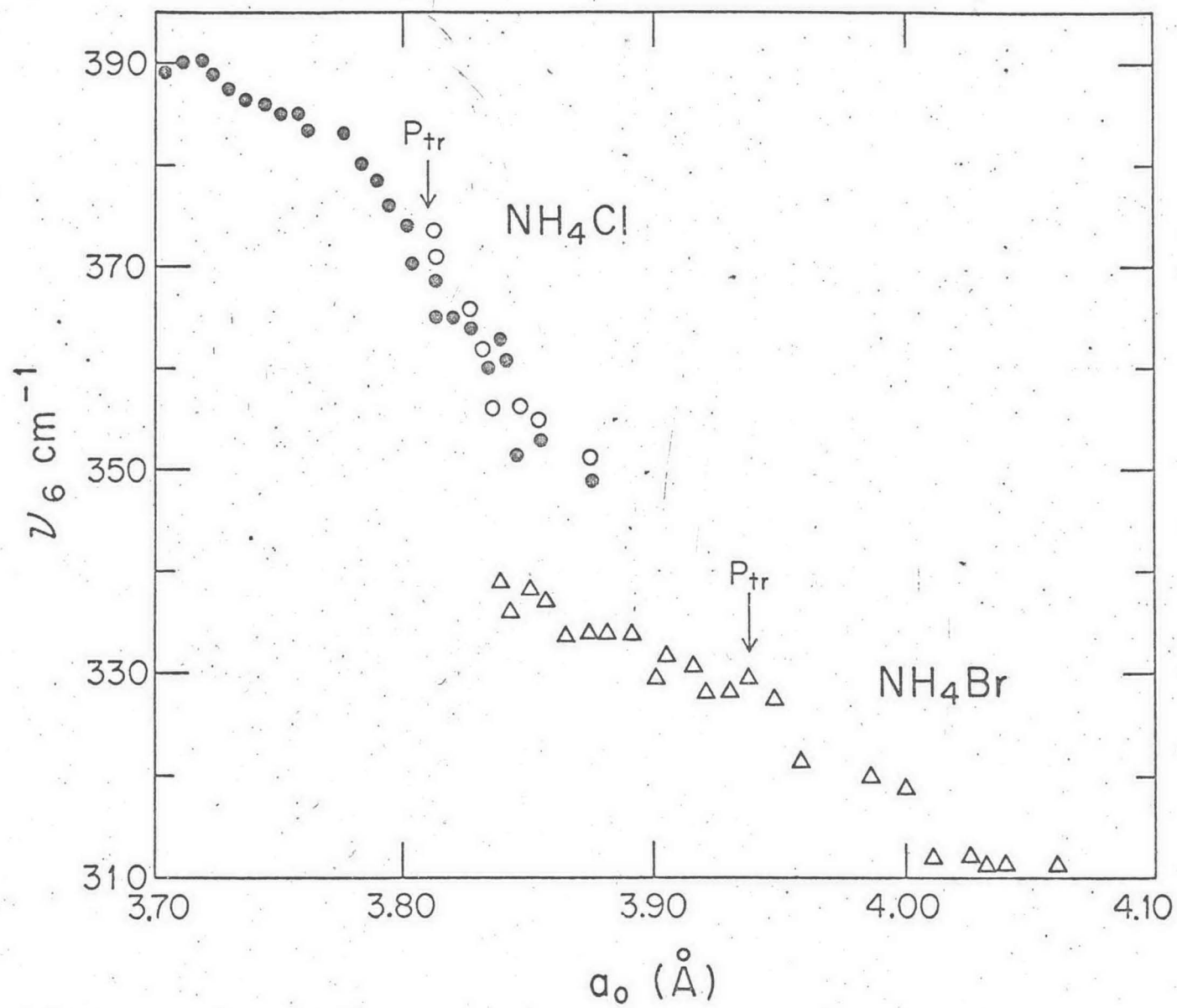
Wave Number Shift (cm^{-1})

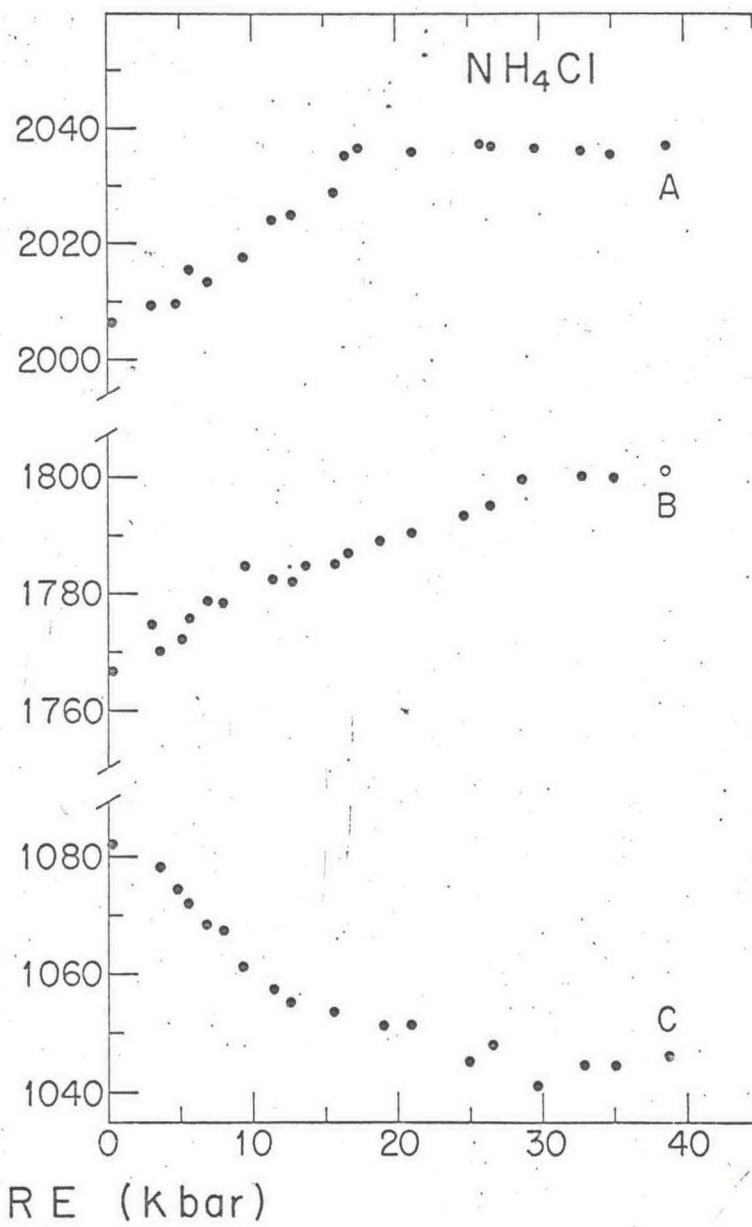
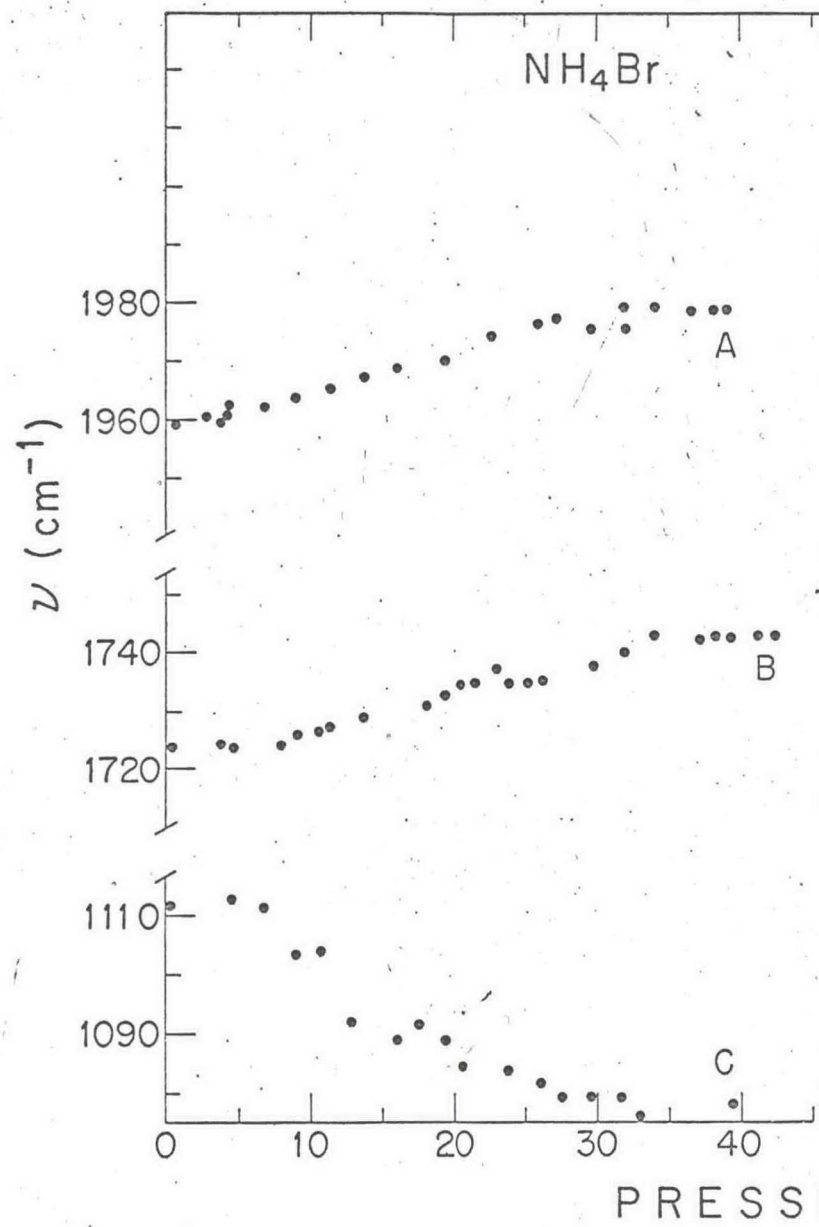


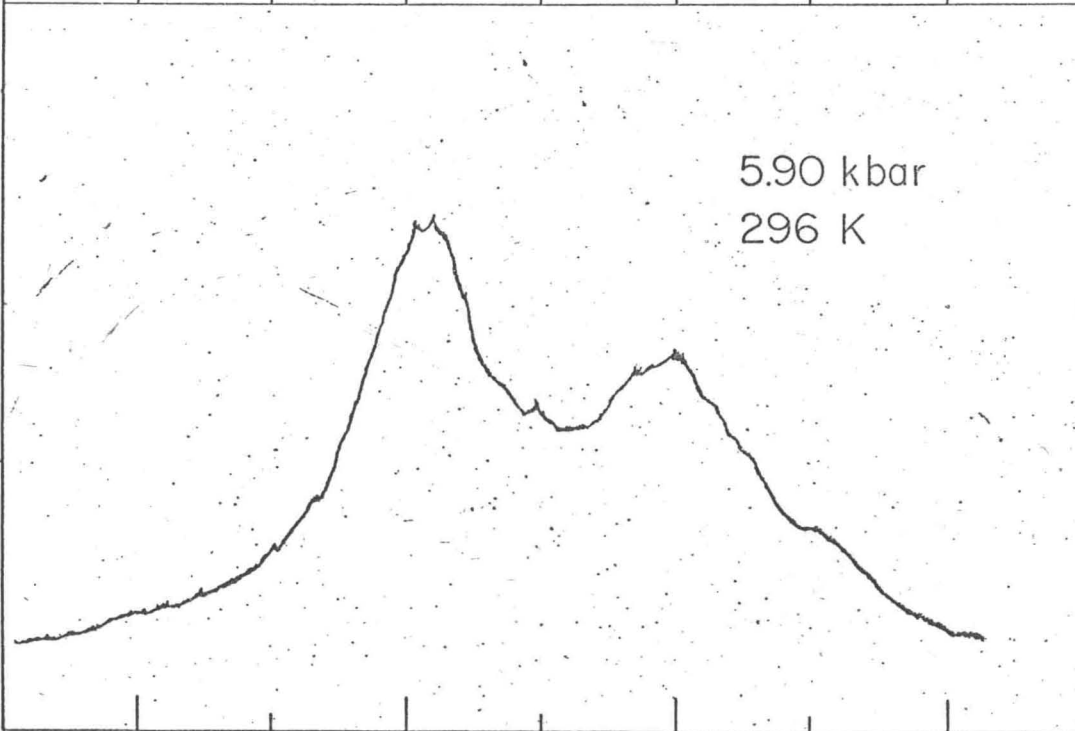
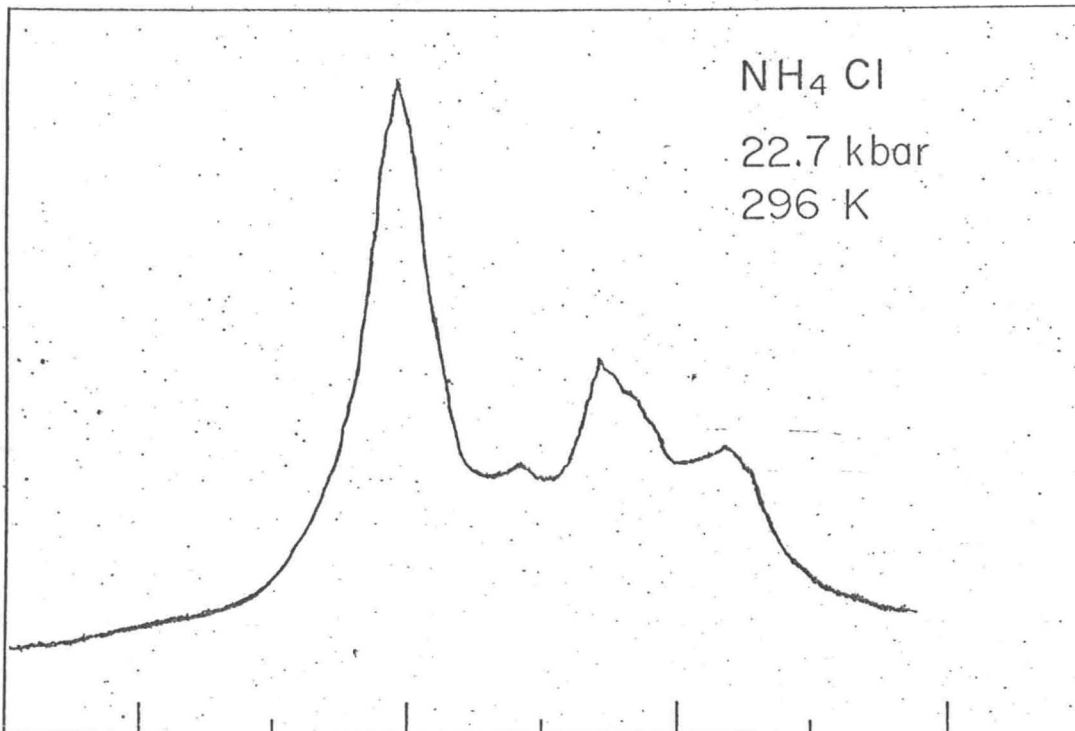
PRESSURE (kbar)







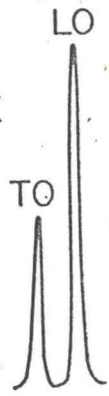




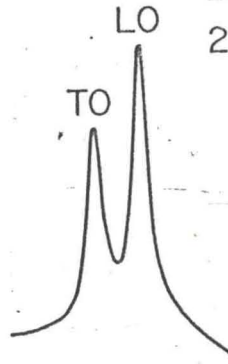
2950 3050 3150 3250

Wave Number Shift (cm⁻¹)

1 atm
130°K



23 kbar
296° K



ISOBARIC
TRANSITION

ISOTHERMAL
TRANSITION

1 atm
296° K

