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RAMAN SPECTRUM OF AMMONIUM CHLORIDE AT HIGH PRESSURES *

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Raman spectra of single crystals of ammonium chloride have been studied to 40 kbar at room temperature. Effects of pressure on the frequencies of the Reststrahlen, librational, and internal modes are described, and the origins of these shifts are discussed.

1. INTRODUCTION

Room temperature, Raman spectra of single crystals of ammonium chloride have been studied to 40 kbar. This halide is an interesting candidate for such an investigation owing to the presence in its Raman spectrum of lines associated with many lattice and internal vibrational normal modes [1], to its large compressibility [2, 3], and to phenomena associated with an order-disorder transition that occurs at about 10 kbar at room temperature [4]. A few of the salient features of these spectra will be outlined in this communication including the effects of pressure on the Reststrahlen frequency (ν_5), the librational binary overtone frequency (ν_6), and the frequencies of internal modes of the ammonium ion ($\nu_1 - \nu_4$) [5].

2. EXPERIMENTAL

The technique for Raman spectroscopy of crystals under high pressures used in this work has been described elsewhere [6]. Recent calibration studies in this laboratory confirm that the pressure of the sample is about 20% less than the "pressure" calculated from the applied load and the area of the piston that has been used in our earlier work. The revised pressure scale, that will be reported elsewhere [7], is used in this work; it is probably accurate within ± 2 kbar

from 5 to 40 kbar. Single crystals of NH_4Cl were grown from saturated aqueous solution of recrystallized NH_4Cl containing urea.

3. RESTSTRAHLEN FREQUENCY

In fig. 1, the Reststrahlen frequency, representing the vibration of the NH_4^+ sublattice against the Cl^- sublattice, is plotted as a function of pressure. The plot can be roughly divided into two regions; this division is typical of the shifts of almost all of the vibrational modes of NH_4Cl . In the disordered phase below 10 kbar, the shift can be fitted to a straight line of slope ($\Delta\nu_5/\Delta P$) of $+2.65 \text{ cm}^{-1}\text{kbar}^{-1}$. This slope is of similar magnitude to those of the transverse optic modes of alkali halides [8], and it is among the largest known for lattice or internal vibrations, being two to twenty times larger than those of the in-

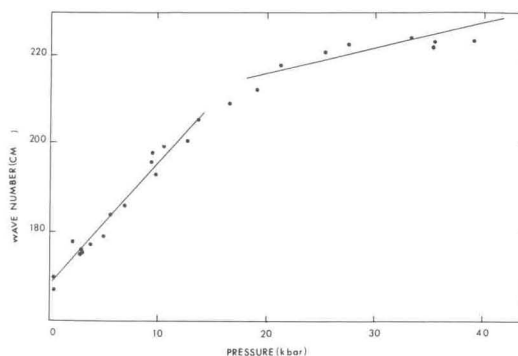


Fig. 1. A plot of ν_5 versus pressure. The slopes of the solid lines are $+2.65$ and $+0.61 \text{ cm}^{-1}\text{kbar}^{-1}$.

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ternal modes of the ammonium ion and of comparable modes of other solids. Above 15 kbar in the ordered phase, $(\Delta\nu_5/\Delta P)$ is $+0.61 \text{ cm}^{-1} \times \text{kbar}^{-1}$.

When the observed frequency is plotted as a function of volume [2], a smooth curve is obtained throughout the 0-30 kbar region, with no noticeable break in the transition region. A $\log\nu$ - $\log V$ plot for the 0-30 kbar data can be fitted to a straight line of slope $-\gamma = \partial \ln\nu/\partial \ln V = -2.4$, where γ is the Grüneisen parameter. This value is perhaps fortuitously equal to that for KCl [8]. Neither plot, however, appears to be completely satisfactory above 30 kbar, and further data is being collected at higher pressures in an attempt to establish the precise volume dependence.

4. LIBRATIONAL MODE

Raman scattering at the librational fundamental, ν_6 , is allowed only by fluctuations of the local crystal symmetry in both phases. This fundamental is extremely weak, and it could be detected only in the low pressure (disordered) phase. However, the binary overtone, $2\nu_6$, is quite intense and could be followed in both phases, fig. 2. The pressure dependence of the overtone frequency, which is approximately $2(\Delta\nu_6/\Delta P)$, is $+5.0 \text{ cm}^{-1} \text{ kbar}^{-1}$ in the disordered phase. This implies that ν_6 in the disordered phase also is among the most pressure sensitive vibrational frequencies known.

The frequency of the overtone was used with Gutowsky, Pake, and Bersohn's potential function [9] for the libration of the NH_4^+ ion in a cubic field to calculate the potential barrier for rotation around a (100) axis. This barrier is found to increase with pressure from $4.4 \text{ kcal mole}^{-1}$

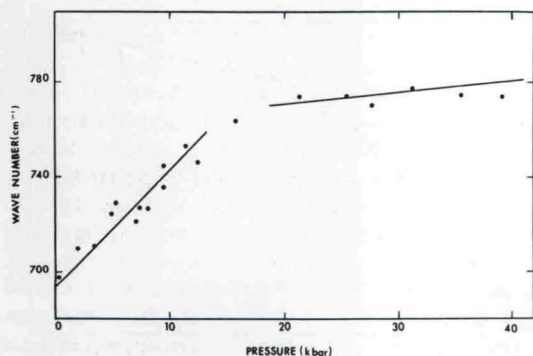


Fig. 2. A plot of $2\nu_6$ versus pressure. The slopes of the solid lines are $+5.0$ and $+0.48 \text{ cm}^{-1} \text{ kbar}^{-1}$.

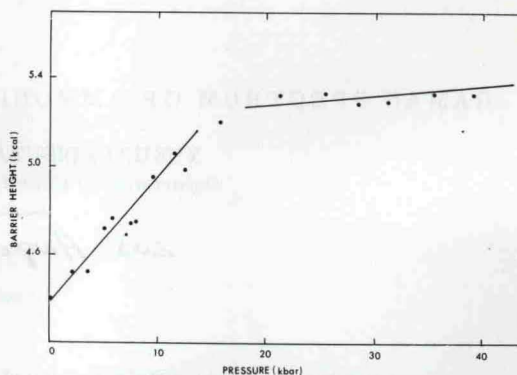


Fig. 3. A plot of the librational barrier height versus pressure.

at 1 atm to $5.3 \text{ kcal mole}^{-1}$ at 40 kbar, as shown in fig. 3. In this calculation, the moment of inertia was taken to be $4.826 \times 10^{-40} \text{ g cm}^2$ [10], and it was assumed that the N-H bond length and, thus, the moment of inertia does not change with the density of the crystal at these pressures. This assumption has been used successfully by Nagamiya in calculations of the ordering temperature of NH_4Cl [11].

5. INTERNAL MODES

The Raman active, symmetric stretching frequency, ν_1 , at 3052 cm^{-1} (1 atm) is the strongest peak of the spectrum and has the smallest pressure dependence [$(\Delta\nu_1/\Delta P) = -0.11 \pm 0.05 \text{ cm}^{-1} \times \text{kbar}^{-1}$] of all of the observed modes. This frequency also appears to be unaffected by the order-disorder transition; within the relatively large experimental uncertainty, its frequency variation with pressure can be fitted by a linear plot over the entire range studied, fig. 4. This is in sharp contrast to the other observed modes, all of which show a break of $(\Delta\nu_i/\Delta P)$ at the phase transition. The negative sign of the pressure dependence can perhaps be explained as arising from the decreasing distance between the hydrogen and chloride atoms and the resulting increase of hydrogen bonding. This lowering of the hydrogenic stretching frequency (-4 cm^{-1} for about 0.2 \AA decrease of the N-Cl bond length) by hydrogen bonding is consistent with data for other N-H...Cl systems [12, 13].

The doubly degenerate bending mode, ν_2 , is the only internal fundamental having a positive pressure dependence, fig. 5. The variation of this frequency can be fitted to straight lines of

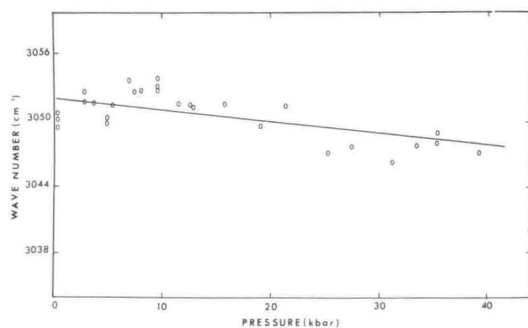


Fig. 4. A plot of ν_1 versus pressure. The slope of the solid line is $-0.11 \text{ cm}^{-1}\text{kbar}^{-1}$.

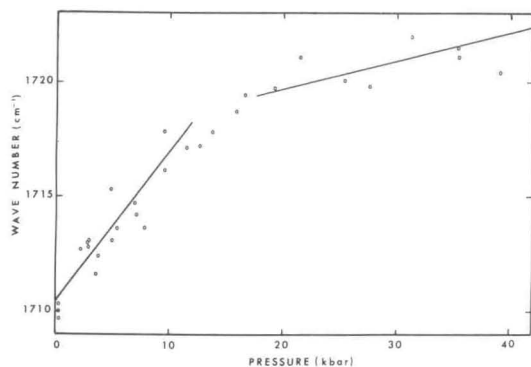


Fig. 5. A plot of ν_2 versus pressure. The slopes of the solid lines are $+0.65$ and $+0.12 \text{ cm}^{-1}\text{kbar}^{-1}$.

slopes $+0.65$ and $+0.12 \text{ cm}^{-1}\text{kbar}^{-1}$ in the ordered and disordered phases respectively; the uncertainties in these numbers are estimated to be $\pm 0.10 \text{ cm}^{-1}\text{kbar}^{-1}$. This mode involves motion normal to the direction of the N-H...Cl bond. As the strength of the hydrogen bond increases, this motion might be expected to become more difficult, thus the positive shift.

The frequencies, ν_3 and ν_4 , of both triply degenerate modes of the "free" ion decrease as pressure increases. The variations of ν_3 with pressure are -1.20 ± 0.10 and $-0.38 \pm 0.10 \text{ cm}^{-1} \times \text{kbar}^{-1}$ for the disordered and ordered phases respectively. The degeneracy of ν_4 is split by crystalline interactions into transverse and longitudinal components. The transverse component shows a larger pressure dependence than the longitudinal component with values of $(\Delta\nu_4/\Delta P)$ of -0.35 (transverse, disordered), -0.16 (transverse, ordered), -0.29 (longitudinal, disordered) and $-0.17 \text{ cm}^{-1}\text{kbar}^{-1}$ (longitudinal, ordered). The uncertainties of these numbers are estimated to be $\pm 0.10 \text{ cm}^{-1}\text{kbar}^{-1}$. The motions associated

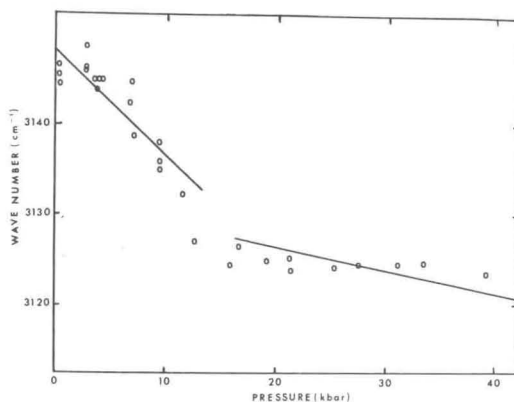


Fig. 6. A plot of ν_3 versus pressure. The slopes of the solid lines are -1.20 and $-0.39 \text{ cm}^{-1}\text{kbar}^{-1}$.

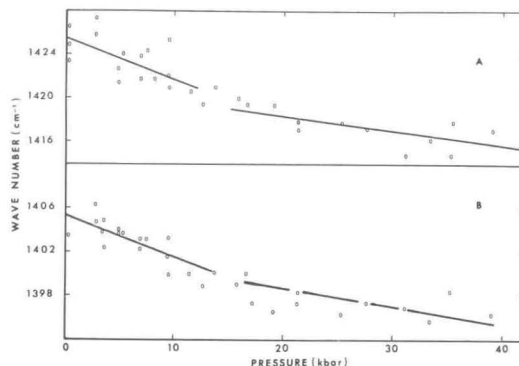


Fig. 7. A plot of the longitudinal (upper) and transverse (lower) components of ν_4 versus pressure. The slopes of the solid lines are: -0.35 and -0.16 (upper); -0.29 and -0.16 (lower) $\text{cm}^{-1}\text{kbar}^{-1}$.

with both ν_3 and ν_4 have components along the N-H...Cl axis, and the decrease of the frequencies with pressure, like that of ν_1 , can be attributed to the effects of increased hydrogen bond strength at high pressure.

Another interesting feature of the ν_4 mode is the increase of the intensity of the longitudinal component relative to that of the transverse component by about four times in the pressure range studied. The origin of this is not clear at present, but it may be related to the changing site symmetry. This and other unusual intensity effects in the $0-3000 \text{ cm}^{-1}$ region will be described in detail elsewhere [1] together with a detailed description of effects of pressure on the many combination and overtone bands of the spectra which are being studied. Preliminary results already suggest that several previous assignments [5] of these bands are incorrect.

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