

## 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 ( $\nu_5$ ), the librational binary overtone frequency ( $\nu_6$ ), 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  $\pm 2$  kbar

from 5 to 40 kbar. Single crystals of  $\text{NH}_4\text{Cl}$  were grown from saturated aqueous solution of recrystallized  $\text{NH}_4\text{Cl}$  containing urea.

## 3. RESTSTRAHLEN FREQUENCY

In fig. 1, the Reststrahlen frequency, representing the vibration of the  $\text{NH}_4^+$  sublattice against the  $\text{Cl}^-$  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  $\text{NH}_4\text{Cl}$ . 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-

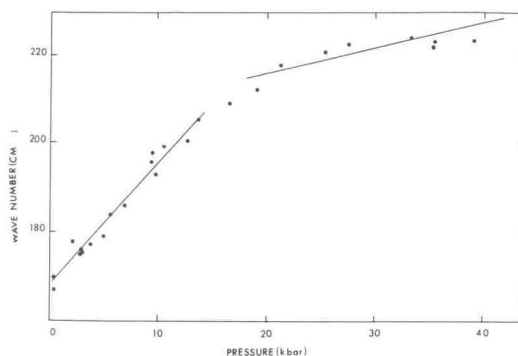


Fig. 1. A plot of  $\nu_5$  versus pressure. The slopes of the solid lines are  $+2.65$  and  $+0.61 \text{ cm}^{-1}\text{kbar}^{-1}$ .

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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  $\gamma$  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,  $\nu_6$ , 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  $\nu_6$  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  $\text{NH}_4^+$  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  $4.4 \text{ kcal mole}^{-1}$

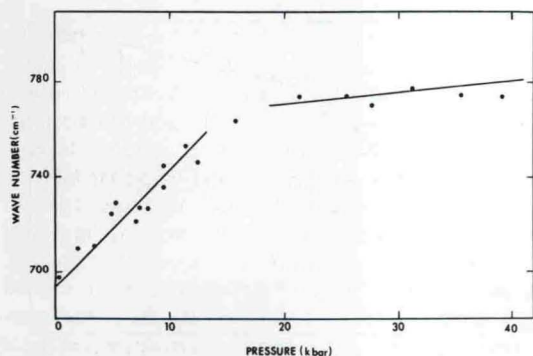


Fig. 2. A plot of  $2\nu_6$  versus pressure. The slopes of the solid lines are  $+5.0$  and  $+0.48 \text{ cm}^{-1} \text{ kbar}^{-1}$ .

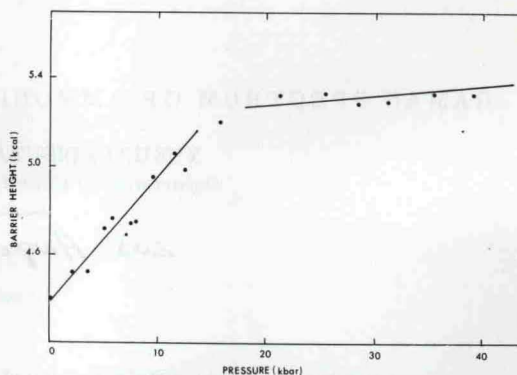


Fig. 3. A plot of the librational barrier height versus pressure.

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  $\text{NH}_4\text{Cl}$  [11].

#### 5. INTERNAL MODES

The Raman active, symmetric stretching frequency,  $\nu_1$ , at  $3052 \text{ cm}^{-1}$  (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 ( $-4 \text{ cm}^{-1}$  for about  $0.2 \text{ \AA}$  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,  $\nu_2$ , is the only internal fundamental having a positive pressure dependence, fig. 5. The variation of this frequency can be fitted to straight lines of