

Reprinted from
ADVANCES IN RAMAN SPECTROSCOPY, VOLUME 1
(Proceedings of Third International Conference on Raman Spectroscopy,
Reims, France, September 1972)
Heyden & Son Ltd., London

OCT 8 1974

18. RAMAN SCATTERING INVESTIGATION OF THE COOPERATIVE ORDER-DISORDER PHASE TRANSITION IN AMMONIUM CHLORIDE AND AMMONIUM BROMIDE

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INTRODUCTION

Extensive studies on NH_4Cl show a strong volume dependence of the temperature for the cooperative order-disorder transition.¹ This suggests a relationship between volume and the ordering process of the NH_4^+ ion. Thus a knowledge of the volume and temperature dependence of the vibrational spectra would be most useful for a better understanding of this transition.

This chapter reports the most recent results on the volume and temperature dependence of the libration and translational motion of the NH_4^+ ion and changes of Raman activity due to the ordering process. The existence of the direct cooperative phase transition in NH_4Br also is reported.

EXPERIMENTAL

At low temperatures, both NH_4Cl and NH_4Br have ordered cubic phases in which the NH_4^+ ions have parallel orientations. The fundamental modes and their representations are

$$\nu_1(A_1) + \nu_2(E) + \nu_3(F_2) + \nu_4(F_2)$$

[internal modes of the NH_4^+ ion] and

$$\nu_5(F_2) + \nu_6(F_1)$$

[lattice modes]. Only the lattice modes are of immediate interest. These are the translational motion of the NH_4^+ against the Cl^- sublattice, ν_5 , and the librational motion about the four-fold axes of the cube, ν_6 . In the ordered phase, the librational mode is the only Raman-inactive fundamental, and it must be observed as a two-phonon process. However, in the disordered phase, NH_4Cl shows a complex spectrum with all fundamentals being Raman active.

Figure 1 shows the polarization spectra of the lattice modes for several scattering geometries of the disordered phase of NH_4Cl (296 K, 1 atm). The internal modes also are

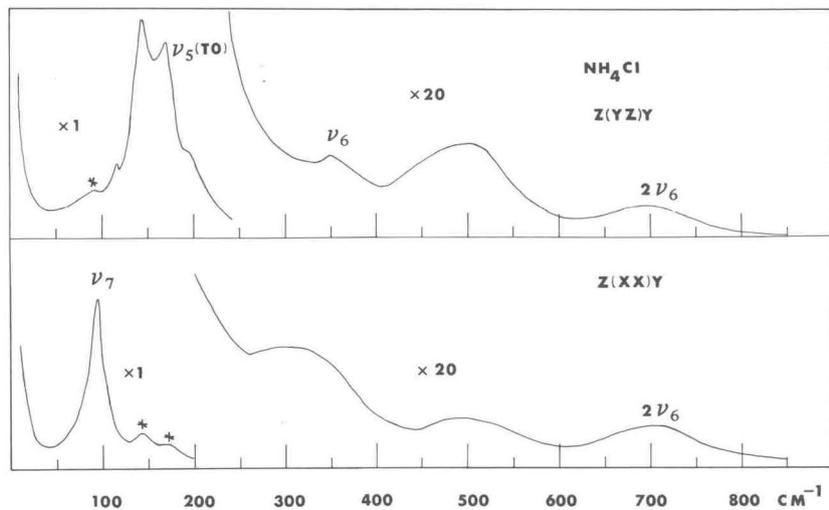


Fig. 1. Right-angle Raman scattering for the disordered phase (1 atm, 296 K) of NH_4Cl in two scattering geometry (see ref. 5 for notation). The asterisks indicate the spill-over of scattering from peaks active in other scattering geometry.

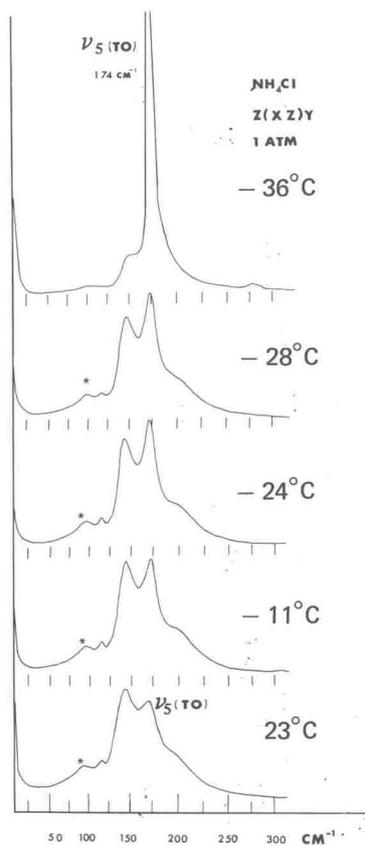


Fig. 2. Raman scattering intensities for modes centred around $\nu_5(\text{TO})$. The asterisks indicate peaks attributed to spill-over of scattering from other phenomena.

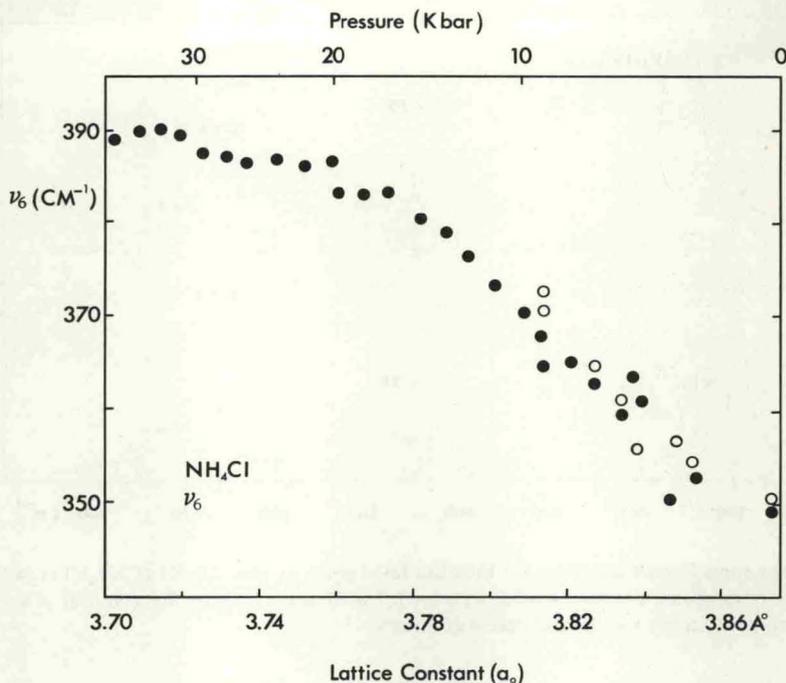


Fig. 3. The dependence of the librational frequency on pressure and lattice constant (a_0). Frequencies obtained from zone centre and as a two phonon process are indicated by open and solid circles, respectively.

characterized by well-defined polarizations; however, some modes such as the librational fundamental are active in all scattering geometries. The spill over from modes inactive in the particular scattering geometry (designated by asterisks) is quite small for both internal and lattice modes.

Figure 2 shows Raman peaks in the $\nu_5(\text{TO})$ region with off-diagonal components in the polarization tensor. Of special interest is the observation that the total integrated intensity between 50 and 250 cm^{-1} remains constant while the intensity of $\nu_5(\text{TO})$ itself depends strongly upon temperature and pressure. As the transition to the ordered phase² (-30.6°C , at 1 atm) is approached isobarically from higher temperatures, $\nu_5(\text{TO})$ increases in intensity relative to others. The frequencies of $\nu_5(\text{TO})$ and other modes shown in Fig. 2 are very volume sensitive in the disordered phase with large Grüneisen constants. The Grüneisen constant for $\nu_5(\text{TO})$ is 3.1 and 2.5 for the disordered and ordered phases respectively.

Observation of ν_6 at the centre of the Brillouin zone ($350 \pm 15 \text{ cm}^{-1}$ at 1 atm and 296 K) and as a two phonon process, $2\nu_6$, indicates that even in the disordered phase, the librational branch is flat within the precision of the experimental results. In the disordered phase, the frequency of ν_6 is very sensitive to change in the lattice constant (a_0); this is shown in Fig. 3. No differences can be distinguished between the frequency shift for the librational mode obtained as a fundamental and as a two phonon process.

The volume dependence or mode Grüneisen constants (γ_i) for the librational mode

Table 1. Modes which become Raman inactive upon 'cooperative disorder-order' transition in NH_4Cl and NH_4Br .

NH_4Cl (cm^{-1}) ^a	NH_4Br (cm^{-1}) ^a
96 (ν_7) [Z(XX)Y]	56 (ν_7) [Z(XX)Y]
119 ^b [Z(YZ)Y, Z(XZ)Y]	80 [Z(YZ)Y, Z(XZ)Y]
144 ^b [Z(YZ)Y, Z(XZ)Y]	141 ^b [Z(YZ)Y, Z(XZ)Y] (low energy shoulder appearing on this peak in phase V)
198 ^b [Z(YZ)Y, Z(XZ)Y]	180 ^b [Z(YZ)Y, Z(XZ)Y] (found at low T in phase V weak, broad, unresolved)
310 ^c [Z(XX)Y]	
350 (ν_6) [Z(XX)Y, Z(XZ)Y, Z(XZ)Y]	

- ^a Frequencies are given at 1 atm and 296 K. [] Indicate scattering geometry in which the mode is Raman active.
^b Modes fitted to an uncoupled damped harmonic oscillator.
^c Frequency has a large uncertainty.

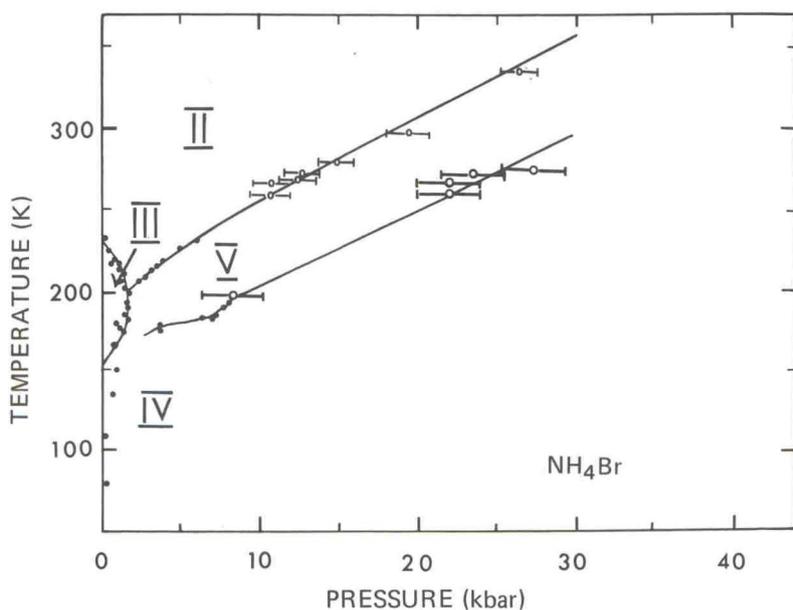


Fig. 4. Phase diagram for NH_4Br . Open circles with error bars represent data obtained in the present study; solid circles represent the literature values (ref. 4).

are 1.30 and 0.29 for the disordered and the ordered phase respectively. The magnitude of γ_i for the disordered phase indicates that there is a fair amount of anharmonicity associated with the librational mode. This anharmonicity probably arises from repulsive interactions between hydrogens on adjacent NH_4^+ ions. The large frequency increase in ν_6 as the transition temperature is approached isobarically from room temperature cannot

be accounted for with the room temperature Grüneisen constant. That is the self-energy or explicitly temperature dependent shift is larger than the volume shift.

The phase diagram⁴ for NH_4Br is shown in Fig. 4. Both II–V and V–IV transitions are disorder-order transitions with slopes of 5.0 ± 0.8 and 5 ± 1 K/kbar respectively. Experimental evidence for identifying V–IV transition as the cooperative disorder-order phase transition consists in the fact that at this transition, the Raman spectrum shows the same characteristic changes as at the disorder-order transition in NH_4Cl . This is true in the change of the number of Raman active peaks (Table 1), intensity increase of $\nu_5(\text{TO})$ and decrease of the Grüneisen constants upon ordering. The II–V transition is accompanied by a decrease of the Grüneisen constants, with typical changes being: 3.2 to 0.75 (ν_7); 0.72 to 0.46 ($2\nu_6$); and 0.036 to 0.003 ($\nu_2(E)$). These decreases of the γ 's suggest that there must be some type of ordering which leads to a decrease in anharmonicity. This is especially true for the librational overtone ($2\nu_6$) where the orientation-dependent part of the force constant between the NH_4^+ ions would be expected to decrease upon ordering.

The interesting implication of the studies on NH_4Br is that both NH_4Br V and NH_4Cl II are ordered. Also, the possible existence of another high temperature phase in NH_4Cl is suggested; and this aspect is now being explored.

The present Raman data give no indication of a disorder-order transition mechanism involving a soft or other low-energy mode. However, the experimental data indicate the presence of volume- and temperature-dependent anharmonicity associated with the librational mode in the disordered state. There are also modes coupled to the translation motion of the NH_4^+ ion in the disordered phase, but their role in the phase transition is not known.

ACKNOWLEDGEMENT

The author wishes to express her appreciation to Dr. M. F. Nicol for encouragement and for the use of the equipment. She also wishes to acknowledge helpful discussions with Dr. R. S. Katiyai. This work is supported in part by the U. S. Atomic Energy Commission.

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