

RAMAN SPECTRA AND THE DYNAMIC STRUCTURE OF THE HIGH PRESSURE PHASE OF NH_4Br (V) AND ND_4Br (V)*

Y. EBISUZAKI

*Department of Chemistry***, University of California, Los Angeles, California 90024, USA*

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Similar Raman spectra are observed at high pressures for phases II and V of ND_4Br and NH_4Br . Deuteration lowers the II-V phase transition from 20 to 9 kbar at 296 K. ND_4Br V and NH_4Br V are interpreted as mixed phases, and their spectra as the superposition of the spectra of two other phases, III (antiparallel arrangement of the NH_4^+ ions) and IV (parallel arrangement). The phonons which become Raman inactive at the V-IV phase transition are assigned to clusters or domains of phase V which have antiparallel arrangement.

1. Introduction

Five phases have been reported for NH_4Br . Four of these phases (II-V) are basically formed from the CsCl-like units with the NH_4^+ ions having a different orientational arrangement in each phase [1,2]. NH_4Br II is considered to be disordered, the NH_4^+ ions occupying the two possible orientations in a random fashion. In the tetragonal phase III, the NH_4^+ ions are ordered parallel along the *c* axis but ordered antiparallel to each neighbor in the *ab* plane. In addition, the neighboring rows of Br^- ions are displaced along the *c* axis in an opposite direction relative to the *ab* plane to compensate for the polarization of the halogen ion. The NH_4^+ ions show parallel ordering along each principal axis in the lowest temperature phase (IV) which has T_d^1 space group symmetry. NH_4Br V, which only exists at high pressures, has been observed in both Raman and acoustic studies, however, the structure of this phase is not known [1,2]. The purpose of this paper is to report the effects of deuteration on the II-V transition pressure and an assignment of the lattice phonons of NH_4Br V and ND_4Br V. The spectral differences between the disordered phase II and the

high pressure phase V are also pointed out. Extensive Raman data which establish the pressure-temperature phase boundaries, polarization characteristics, temperature (195-407 K) and pressure effects (1 bar-42 kbar) in the stability range of NH_4Br II, IV and V will be described in detail elsewhere [2].

NH_4Br IV (ND_4Br IV) has the simplest Raman spectrum of these phases, with the following representation for the fundamental mode:

$$\nu_1 (A_1) + \nu_2 (E) + \nu_3 (F_2) + \nu_4 (F_2) + \nu_5 (F_2) + \nu_6 (F_1).$$

ν_1 to ν_4 are internal vibrations of the NH_4^+ ion, while ν_5 and ν_6 are lattice phonons. All modes except the libration (ν_6) are Raman active. The Raman active fundamental modes of NH_4Br IV are also observed in NH_4Br II and V; therefore, the same designation will be employed for these modes in the three phases. The two molecular units in NH_4Br III (ND_4Br III) give rise to 36 vibrational degrees of freedom, the representation for the Raman active modes being: $(2A_{1g} + 1B_{1g} + 2B_{2g} + 2E_g)$ for the internal modes of the NH_4^+ and $(3E_g + 1A_{1g} + 1B_{2g})$ for the lattice phonons [3-5]. In NH_4Br III, the librational motion is designated as $\nu'_6 (E_g)$, while the translational motion of the NH_4^+ and Br^- ions are $\nu'_5 (E_g)$ and $\nu''_5 (B_{2g})$. One usually expects to observe excitations throughout the Brillouin zone in a disordered crystal such as NH_4Br II as a consequence of the breakdown in the *k*-conservation rule;

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however, many aspects of the Raman spectrum of NH_4Br II such as the origin of the Raman peaks and their polarization characteristics are still not completely understood.

2. Experimental

A high pressure optical cell designed for 90° scattering geometry and capable of 45 kbar was employed in this work. The NH_4Br crystal ($2 \times 2 \times 3$ mm) was placed in a high pressure cavity so that the (100) face was normal to the incident laser beam. Raman spectra were excited at 5145 and 4880 Å (1.5–1.8 W) and detected with a Spex monochromator in conjunction with a photon counting system. The temperature was altered by circulating a refrigerant through the casing of the cell and by immersing the cell in a cold temperature bath. Detailed description of the high pressure Raman experimental method can be found in a previous publication [2].

The deuterated ammonium bromide powder used in the phase transition study was prepared in a manner similar to that previously reported for ND_4Cl [6]. The powdered sample was compacted and placed in the high pressure cavity of the Raman cell. The results on ND_4Br are compared to both the single crystal and powdered NH_4Br data.

3. Results and discussion

The stability range of the phases in NH_4Br can be placed with the previously reported phase diagram [2]. Phase II extends from 235 to 411 K at 1 bar. Under isothermal compression, NH_4Br II becomes unstable and the II–V phase boundary is crossed, for example, at 11 and 20 kbar at 260 and 296 K, respectively. NH_4Br IV, which exists at lowest temperatures (<102 K at 1 bar) or at highest pressures of all the CsCl-like phases, is observed for example at pressures higher than 8 and 22 kbar at 195 and 260 K, respectively. NH_4Br V which is bordered by phase II at low pressures and by NH_4Br IV at high pressures has been detected in Raman studies from 195 K (<8 kbar) to 335 K (>23 kbar). The available phase diagram for ND_4Br covers a limited temperature–pressure range of phase II, III and IV; no observation of ND_4Br V has

previously been reported [7,8].

The Raman spectra of phase V is related to both NH_4Br II and to NH_4Br IV, the combination bands and the fundamental modes of the T_d^1 space group being Raman active in all three phases. The spectra for the lattice phonons of NH_4Br II, IV and V are shown in figs. 1 and 2. There are differences in the relative intensities, wavenumbers, Grüneisen constants, and number of the lattice modes in the different phases. NH_4Br IV has the simplest spectrum. If one approaches NH_4Br V from low pressures at 296 K (Figs. 2–4), the changes in the Raman activity accompanying the transition from phase II to V occur around 20 kbar with the appearance of a strong characteristic shoulder (182 cm^{-1} at 20 kbar) on the low energy side of ν_5 (TO) and the disappearance of an extremely weak mode (90 cm^{-1} at 1 bar). Figs. 1, 2 and 4 indicate that the low energy shoulder appears intense at 296 K. The anharmonicity of the crystal potential affecting the observed wavenumber shifts (fig. 3) of the

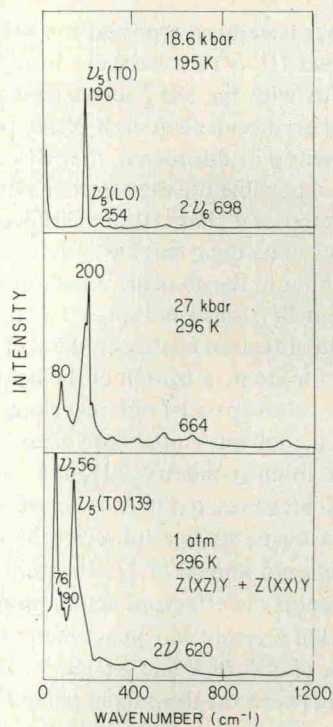


Fig. 1. Raman spectra of the lattice phonons of NH_4Br II (296 K and 1 bar), V (296 K and 27 kbar) and IV (195 K and 18.6 kbar). The spectrum at 1 bar was taken with the crystal outside the high pressure cell.