

## Phase study on solid hydrogen bromide by high-pressure and low-temperature Raman spectroscopy

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Pressure-temperature ( $P$ - $T$ ) phase diagram for solid hydrogen bromide (HBr) was determined over a wide region up to 15 GPa in pressure and down to 20 K in temperature, by means of Raman spectroscopy. From the change in Raman spectra, the stability regions of the cubic phases (I and I') and the orthorhombic phases (II and III) were clarified. Ferroelectric phase III is stable in a wide  $P$ - $T$  range and phase II does not exist at room temperature. The triple point of phases I', II, and III exists around  $P=7.5$  GPa and  $T=230$  K.

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### I. INTRODUCTION

Hydrogen bromide (HBr) is one of the simplest molecules forming hydrogen bonds in solid states. A great deal of attention has been paid to the interesting structure characterized by the hydrogen bond, e.g., quasi-one-dimensional zig-zag chains of the molecules in the low-temperature phase III. At ambient pressure, HBr shows four solid phases. As the temperature decreases, HBr freezes from the liquid into cubic phase I ( $Fm\bar{3}m$ ) (Ref. 1) at 186.3 K, and undergoes transitions successively to the cubic phase I' ( $Pa\bar{3}$ ) (Ref. 1) at 116.9 K, orthorhombic phase II ( $Cmca$ ) (Ref. 2) at 113.7 K, and orthorhombic phase III ( $Cmc2_1$ ) (Ref. 2) at 89.7 K. The solid phases I, I', and II are orientationally disordered phases. The hydrogens are randomly distributed among 12, 6, and 2 equivalent positions in phases I, I', and II, respectively. In those disordered phases, the molecules are believed to undergo rapid flipping, temporarily forming the hydrogen bond to one of the nearest neighbors. On the other hand, in the low-temperature phase III, the hydrogens are fully ordered, forming planar zig-zag chains of the molecules. This phase is well known to show ferroelectricity.<sup>3</sup>

Several authors<sup>4-6</sup> characterized these phases by Raman spectra: phase I; a broad stretching band, phase II; two broad stretching bands of nearly equal intensity, and phase III; two sharp stretching bands and several lattice peaks. For phase I', the Raman spectrum is still not clear.

Although many kinds of experiments have been made for solid HBr, the pressure-temperature ( $P$ - $T$ ) phase diagram is still little known. Johannsen, Helle, and Holzapfel,<sup>7</sup> have investigated the  $P$ - $T$  phase diagram of HBr by Raman spectroscopy, and suggested that phase IV, showing symmetric hydrogen bonds exists at pressures above 32 GPa and at 100 K. However, their experiments were limited in a narrow temperature range between 100 and 250 K. In particular, the regions of phases II and I' were not clear at all. In this paper, we present a phase study on the molecular solid HBr up to about 15 GPa in pressure and from room temperature down to 20 K by Raman spectroscopy using a diamond-anvil cell. The Raman spectral changes corresponding to the phase transitions among I, I', II, and III were clearly observed,

which allowed us to determine the  $P$ - $T$  regions of those phases.

### II. EXPERIMENTS

A HBr specimen was loaded into a diamond-anvil cell (DAC) by spraying its vapor into a hole of the gasket of the DAC that was cooled by liquid N<sub>2</sub>. The HBr solidified on the gasket was sealed by translating the lower diamond. The loading of HBr was done in a sealed vessel filled with dry nitrogen gas to avoid inclusion of contamination. After the appropriate pressure was applied, the DAC was warmed to room temperature. The coexistence pressure of liquid and solid phase I was about 0.3 GPa at room temperature. Raman-scattering measurements of the specimen were carried out in a backscattering geometry. The spectra were excited by a 514.5 nm line of an Ar ion laser and recorded by a spectrometer (JASCO NR1800) equipped with a triple monochromator and a liquid-nitrogen-cooled charge-coupled device detector.

To measure the Raman spectra under various temperatures and pressures, we controlled the temperature of the specimen that was pressurized at room temperature. The specimen in the DAC was cooled by a closed-cycle-type He cryostat (Iwatani Cryomini) and the temperature was monitored and stabilized with a controller (Iwatani TCU-4). Temperature fluctuations during the present experiment were within  $\pm 0.5$  K. The pressure applied to the specimen was measured with the ruby-scale method, which was extended to low-temperature experiments.<sup>8</sup>

When the Raman spectra of H-Br stretching vibration were measured, the second-order Raman signal arising from the diamond anvil was superimposed around 2500 cm<sup>-1</sup> as a background, which prevented data analyses. To remove the background, the broad diamond signals were measured by focusing the beam on the gasket under the same condition, and was subtracted from the spectra.

### III. RESULTS

The Raman spectra of intramolecular stretching and intermolecular (lattice) vibrations were measured for the

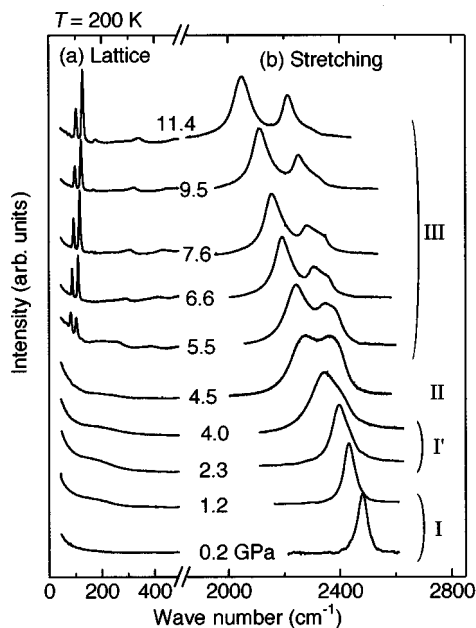


FIG. 1. Raman spectra measured for various pressures at 200 K. (a) and (b) correspond to the frequency regions of lattice and stretching vibrations, respectively. With increasing pressure, phases I, I', II, and III appear sequentially.

pressure-induced crystalline HBr in DAC up to about 15 GPa and down to 20 K. Figure 1 shows typical Raman spectra of the solid HBr obtained under various pressures at 200 K. In this figure, (a) and (b) correspond to the frequency regions of lattice and stretching vibrations, respectively. At 0.2 GPa, we can see a symmetric-shape Raman band of stretching mode, which indicates the existence of phase I. With increasing pressure the weak shoulder is found to appear at higher frequency side. Although the Raman spectra of phase I' has not been identified, we believe that the growth of the shoulder is due to the phase transition to phase I'. The discussion on phase I' will be made later. Next, the phase transition to phase II is clearly observed around 4.5 GPa by the spectral changes into the two broad stretching bands with almost the same intensity<sup>4</sup> and by discontinuous shift of the peak frequencies. In these orientationally disordered phases (I, I' and II), we could observe no distinct peak in the lattice vibrational region. Broad and weak bands observed around 200  $\text{cm}^{-1}$  have been suggested to arise from vibrational lattice modes in the zig-zag chains forming temporarily.<sup>6</sup> In Fig. 1(a), we can observe the sudden appearance of the lattice peaks above 5.5 GPa, which corresponds to the transition to the fully ordered phase III.<sup>5,6</sup> We also find that the low-frequency band of the stretching modes ( $A_1$  mode) is stronger in intensity than the high-frequency band ( $B_1$  mode). These data points for phases I, I', II, and III are plotted in the  $P$ - $T$  phase diagram as shown in Fig. 2.

Previously, several authors<sup>1,9</sup> reported the existence of a cubic phase (denoted here as I') at a narrow temperature range between I and II. According to the neutron-diffraction experiment made at ambient pressure by Cockcroft, Simon, Ziebeck,<sup>1</sup> the intermediate phase has a cubic structure in which the bromine atoms are positioned at fcc lattice points and the hydrogens are located between the bromine atoms in sixfold disordered arrangements. In contrast to phase I with

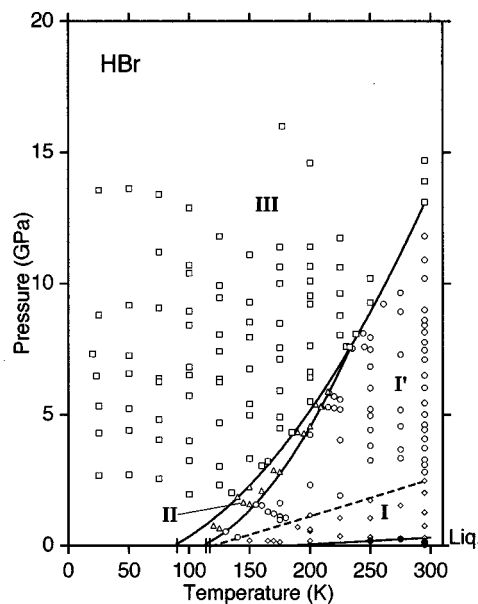


FIG. 2. Pressure-temperature phase diagram of HBr. The data point at which Raman spectra were measured, are plotted by open squares (phase III), open triangles (phase II), open circles (phase I'), open diamonds (phase I) and solid circles (liquid).

one molecule in the primitive cell, phase I' possesses four molecules in the primitive cell, which can give rise to vibrational Davydov splitting for the stretching mode. According to a recent x-ray study,<sup>10</sup> the solid phase at room temperature shows a cubic structure up to about 13 GPa, suggesting that the solid phase at higher pressures above phase I is a cubic phase if it exists. Therefore, we believe at present that the growth of the shoulder [Fig. 1(b)] is attributed to the transition from cubic phase I to cubic phase I'.

Figures 3(a) and 3(b) show the Raman spectra measured around 5 and 8 GPa, respectively, as a function of temperature in quasi-isobaric process. With decreasing temperature,

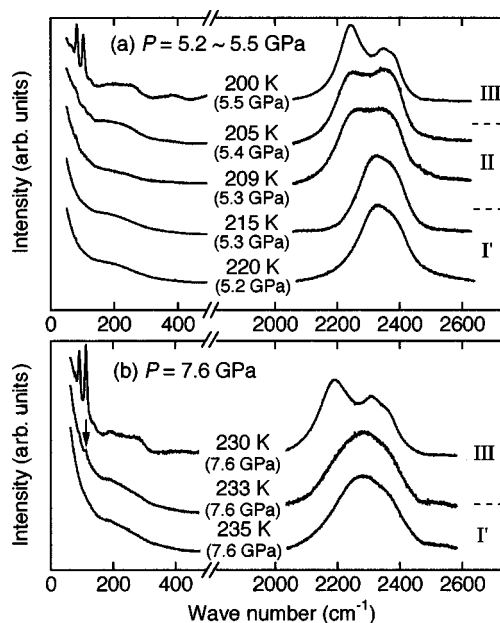


FIG. 3. Temperature dependence of Raman spectra in solid HBr around (a) 5 GPa and (b) 8 GPa.

the pressure in the DAC increases as indicated in these figures, which is probably due to the contraction of the DAC. Around 5 GPa [Fig. 3(a)], we observed the successive spectral changes corresponding to the  $I' \rightarrow II$  and  $II \rightarrow III$  transitions as the temperature decreases. The asymmetric stretching band characterizing phase  $I'$  changes suddenly to the broad-doublet band of phase II below 209 K. Further spectral changes in stretching and lattice modes take place at 200 K, demonstrating the transition to phase III. On the other hand, around 8 GPa [Fig. 3(b)] the spectra of phase II were not obtained. The spectra obtained at 233 K shows the stretching band corresponding to phase  $I'$  and also indicates the small lattice peak, which suggests the coexistence of phase  $I'$  and III. Therefore, we find that phase  $I'$  undergoes the transition to phase III not via phase II.

As seen in Figs. 1 and 3, the  $I'$ -II, II-III, and  $I'$ -III transitions give rise to the rapid and drastic changes in the spectral feature, which allowed us to determine easily those phase boundaries. As is noted in Fig. 1, however, it is rather difficult to determine the  $I$ - $I'$  phase boundary because the stretching bands of phase I and  $I'$  are similar to each other and the shoulder grows gradually. To identify the pressure at which the shoulder appears, we deconvoluted all the spectra of phases I and  $I'$  into two bands that are the combination of Gaussian and Lorentzian lines, as shown in Fig. 4(a). The frequencies of the separated bands are plotted as a function of pressure at 200 and 295 K in Figs. 4(b) and 4(c), respectively. The peak frequencies in phase II and III are also plotted with triangles and squares, respectively. (Although the shoulder is associated with the  $B_1$  mode for phase III, only the peak frequencies are plotted.) In the low-pressure region, the shoulder (open circles) is located at almost the same frequency as the main peak (solid circles), suggesting that the stretching band consists of only one band. However, above a particular pressure indicated by dashed lines, the separation between the main peak and shoulder becomes remarkable, demonstrating that one stretching mode splits into two. From the analyses mentioned above, we determined the transition pressure between phases I and  $I'$  at each temperature.

Combining the phase transition points determined from the present Raman results with the transition temperatures at ambient pressure reported previously, the phase boundaries were drawn, as shown in Fig. 2. As seen in the obtained  $P$ - $T$  phase diagram, phase III is stable in a wide  $P$ - $T$  region. On the other hand, phase II shows only a small stability region and does not exist at temperatures higher than about 230 K. The triple point of  $I'$ , II, and III was found to exist around

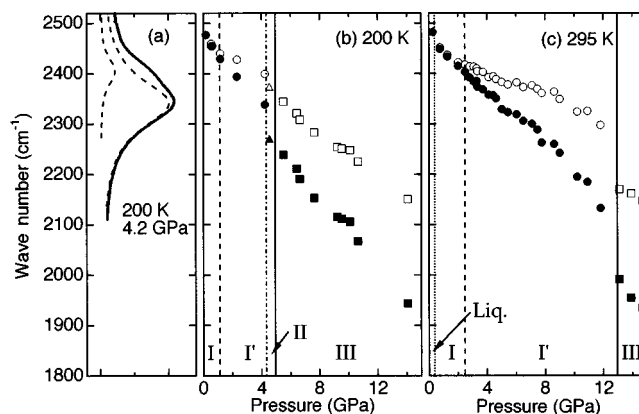


FIG. 4. (a) Typical result of the deconvolution of the stretching band of phase  $I'$  into two bands. The observed stretching band and two bands obtained by the deconvolution are shown by solid and dashed curves, respectively. (b) and (c) Pressure dependence of the frequencies of the separated bands at (b) 200 K and (c) 295 K. Solid and open circles correspond to the main peak and the shoulder, respectively. The peak frequencies for phase II and III are also shown by triangles and squares, respectively.

$P = 7.5$  GPa and  $T = 230$  K. The phase boundary between phase I and  $I'$  determined from the spectral analyses is indicated by a dashed line. We can see that phase  $I'$ , which exists in the narrow temperature range at ambient pressure, occupies a wide  $P$ - $T$  range. In order to confirm the region of phase  $I'$ , detailed structural analyses, which can determine the positions of hydrogens, or NMR studies, which can obtain the information of the molecular motion, are needed under high pressures.

In conclusion, we made the  $P$ - $T$  phase study of the molecular solid HBr by high-pressure Raman spectroscopy using a diamond-anvil cell. From the the spectral changes in the stretching- and lattice-vibrational modes, the phase diagram was obtained at pressures up to about 15 GPa and temperatures from room temperature down to 20 K. Consequently, the stability regions of phases I,  $I'$ , II, and III were clarified. Phase III is stable in a wide  $P$ - $T$  range, but phase II exists in a small region and vanishes above 7.5 GPa. The triple point of phases  $I'$ , II, and III exists around  $P = 7.5$  GPa and  $T = 230$  K. Since the present experiments were limited below 15 GPa, the phase transition to phase IV suggested by Johannsen, Helle, and Holzapfel<sup>7</sup> was not confirmed. To determine the  $P$ - $T$  region of the high-pressure phase IV and to explore the new phase, a further phase study has been currently in progress in our laboratory.

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