

Evidence for Molecular Dissociation in Bromine near 80 GPa

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Synchrotron x-ray diffraction studies using a diamond-anvil cell and an imaging plate reveal that solid bromine begins to undergo a molecular-to-monatomic phase transition near 80 GPa. The structure of the high-pressure phase is found to be body-centered orthorhombic ($D_{2h}^{25}-Immm$), as previously observed in iodine above 21 GPa. These results on bromine plus previous data on iodine and iodine monobromide show that the molecular dissociation takes place when the scaled unit-cell volume $\bar{v} = v/8r_s^3$ in the molecular phase (r_s is the intramolecular bond length in the solid) reaches $\bar{v}_c = 1.29$. We also observe universal behavior of the scaled lattice constants versus \bar{v} in all solid halogens.

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A diatomic molecular crystal loses its molecular character in the limit that the intermolecular distance becomes equal to the intramolecular bond length. This phenomenon, called molecular dissociation, is predicted in densely compressed hydrogen; however, in this case no experimental evidence has been obtained at the high pressures accessible in the laboratory. The solid halogens are also prototypical diatomic molecular crystals analogous to hydrogen. Their crystal structure is shown in Fig. 1(a) (space group $D_{2h}^{18}-Cmca$). In the early 1960s pressure-induced metallization was discovered in iodine.¹ Such pioneering work motivated structural studies to explore the possible molecular dissociation in its metallic state above about 16 GPa.² By using an x-ray diffraction technique, we made a direct observation of such a molecular dissociation in iodine, I_2 , at 21 GPa³⁻⁵ and later in iodine monobromide, $I\text{Br}$, at 39 GPa.⁶ Our structure analysis of iodine^{5,7} revealed that prior to the molecular dissociation the nearest-neighbor intermolecular distance becomes close to the intramolecular bond length while the angle between two adjacent molecules approaches 90° . Thus the culmination of these trends results in the high-pressure structure formed by monatomic iodine as shown in Fig. 1(b) ($D_{2h}^{25}-Immm$). It is also noted that in its monatomic phase further successive phase transitions take place at 43 and 55 GPa, eventually leading to the face-centered-cubic structure.^{8,9} In other halogens and interhalogen compounds, no phase transition has been reported so far, with the exception of $I\text{Br}$.

Recently, Düsing, Grosshans, and Holzapfel¹⁰ introduced the asymmetry parameter defined as $\Delta = [(2b_L)^2 + c_L^2]^{1/2}/4r - 1$, where b_L and c_L are the lattice constants in the low-pressure (LP) molecular phase and r is the intramolecular bond length in the gaseous state. This quantity is a measure for describing the deviation from a simple quadratic lattice like the high-pressure (HP)

monatomic phase. Then they proposed a scaling rule¹⁰⁻¹³ that all isostructural solid halogens undergo molecular dissociation when Δ reaches its critical value Δ_c , which was deduced from our previous data on iodine.⁵ They further predicted the molecular dissociation pressures for Br_2 and Cl_2 as $P_c = 58 \pm 6$ and 140 ± 30 GPa, respectively, by extrapolating their lattice-parameter data.

The purpose of the present x-ray diffraction study on Br_2 is to survey its molecular dissociation in an unexplored high-pressure region and to examine such a scaling rule. The establishment of the scaling rules is expected to offer a key idea in order to clarify the micro-

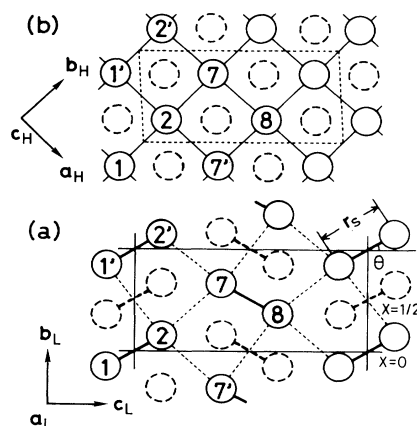


FIG. 1. Crystal structure of solid halogens. (a) The low-pressure (LP) molecular phase ($D_{2h}^{18}-Cmca$) and (b) the high-pressure (HP) monatomic phase ($D_{2h}^{25}-Immm$). A rectangle drawn with solid thin lines is a crystallographic unit cell, in which solid and dashed circles shows halogen atoms separated by half of the lattice constant along the direction perpendicular to the sheet. Some atoms are labeled for easy understanding of the interrelationship between the two structures.

scopic mechanism of the molecular dissociation not only in halogens but also in other analogous diatomic molecular crystals.

Bromine samples with a purity of 99.8% were commercially available from Merck. In order to avoid sublimation and any chemical reaction, all the processes for grinding and mounting the sample in a diamond-anvil cell (DAC) were carried out in an argon atmosphere and at low temperature. The gasketed DAC used below 70 GPa in the present study was the same as that used in the previous work on iodine.^{5,8,9} Above 70 GPa, on the other hand, beveled diamond anvils were used to generate higher pressures. The pressure was determined by the wavelength of the fluorescence line from ruby chips enclosed with the sample in a gasket hole of 0.2 mm (regular anvils) or 0.08 mm (beveled ones) in diameter. No pressure transmitting fluid was used. The pressure distribution was measured to be ± 3 GPa at 70 GPa in the former DAC and ± 5 GPa at 88 GPa in the latter one. Synchrotron x-ray powder diffraction was performed on beam line 6B of the Photon Factory. The incident x-ray energy was chosen to be 20.00 keV ($\lambda = 0.6199$ Å) monochromatized with a Si(111) sagittally focusing double-crystal monochromator. Diffracted beams were recorded by a flat imaging plate with special capabilities such as high sensitivity, wide dynamic range, and two dimensionality.^{14,15} After the absence of any preferred orientation was ensured, the uniform intensity of all Debye-Scherrer rings recorded on the imaging plate was integrated along the arcs.¹⁶ Thus, an extremely small fluctuation in the noise level was obtained in the diffraction patterns. All measurements were made at room temperature.

At first the regular DAC was used to reach the target pressure of 58 ± 6 GPa, where molecular dissociation was predicted for Br₂.¹⁰ Each of the lattice constants a_L , b_L , and c_L in the LP phase, which were obtained from the observed diffraction patterns, lies well on a smooth curve. However, no phase transition was detected at pressures up to 70 GPa. In order to survey any phase transition beyond 70 GPa, the DAC was switched to that with beveled anvils to generate higher pressures. Figure 2 displays diffraction patterns observed in the higher-pressure region. The patterns are partly contaminated with the reflections from the gasket (*G* in the figure); however, the key reflections do not deteriorate. At 82 GPa new peaks begin to emerge as indicated with arrows and become stronger at 88 GPa, which was the highest pressure reached in the present experiment. As indexed in the top figure, these new reflections can be explained by a body-centered orthorhombic lattice [D_{2h}^{25} -*Immm* in Fig. 1(b)], which is identical to that previously assigned to the high-pressure phase of iodine between 21 and 43 GPa.^{4,5} However, the coexistence of two phases leaves more detailed structure analysis to further work that realizes the single HP phase. The lattice constants at 82 GPa, where the coexistence of two phases is seen, are

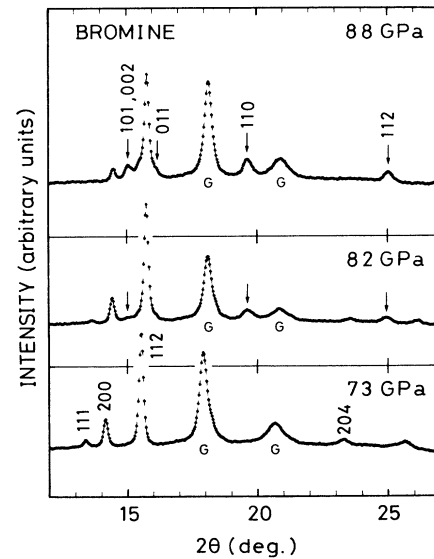


FIG. 2. Emergence of a HP phase (indicated with arrows) in x-ray diffraction patterns. Reflection indices in the bottom and top figures are based on the structures shown in Figs. 1(a) and 1(b), respectively.

determined to be the following: $a_L = 4.76$, $b_L = 3.22$, and $c_L = 7.61$ Å (LP phase) and $a_H = 2.63$, $b_H = 2.36$, and $c_H = 4.57$ Å (HP phase). The resultant volume change is $\Delta v/v = -0.028$. These figures are accompanied by an uncertainty of about 0.3%. Thus in bromine the first-order phase transition associated with the molecular dissociation begins to take place at 80 ± 5 GPa.

Since the lattice constants in the LP phase are fully known not only in the previous cases of I₂ and IBr but also in the present case of Br₂, we can examine the critical values of the asymmetry parameter Δ_c introduced by Düsing, Grosshans, and Holzapfel¹⁰ upon the onset of the molecular dissociation. If we use the intramolecular bond length in the gaseous state r_g [2.666 (I₂), 2.485 (IBr), 2.281 Å (Br₂)],¹⁷ $\Delta_c = 0.13$ for I₂ and 0.11 for both IBr and Br₂. In the case that the bond length in the solid state r_s is used [2.715 (I₂),¹⁸ 2.521 (IBr),¹⁹ 2.27 Å (Br₂)¹⁷], the same value $\Delta_c = 0.11$ is obtained for all three cases. Therefore, r_s turns out to be the more relevant scaling parameter compared to r_g . The unit-cell volume is also scaled as $\tilde{v} = v/8r_s^3$ ($v = a_L b_L c_L$) and plotted in Fig. 3 as a function of pressure. One can see from Fig. 3 that in all three cases the molecular dissociation takes place at $\tilde{v}_c = 1.29$. Holzapfel^{12,13} also proposed that each of the lattice constants scaled as $\tilde{a} = a_L/r_g$, $\tilde{b} = b_L/r_g$, and $\tilde{c} = c_L/r_g$ lies on its own universal curve as a function of \tilde{v} for all three of the halogens I₂, Br₂, and Cl₂. Since r_g is found not to be the relevant parameter for scaling, each lattice constant is scaled by r_s as $\tilde{a} = a/2r_s$, $\tilde{b} = b/2r_s$, and $\tilde{c} = c/2r_s$ in the present analysis and the scaled lattice constants are plotted in Fig. 4 as a function of \tilde{v} . The vertical solid lines represent the scaled volume at atmospheric pressure. One can see that

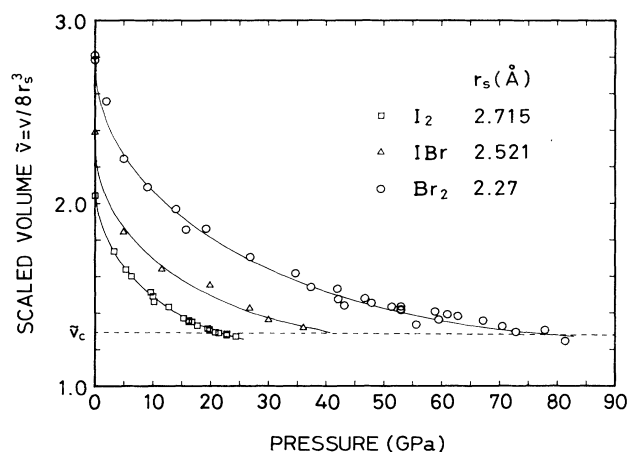


FIG. 3. Scaled unit-cell volume vs pressure observed for I_2 , IBr , and Br_2 . Onset of the molecular dissociation is observed at $\tilde{v}_c = 1.29$ in all three systems.

the three sets of available data for I_2 , IBr , and Br_2 can be fitted remarkably well by a universal curve for each scaled lattice constant, particularly in the vicinity of \tilde{v}_c . The data for Cl_2 available at atmospheric pressure ($\tilde{a} = 1.576$, $\tilde{b} = 1.132$, $\tilde{c} = 2.086$, $\tilde{v} = 3.720$, $r_s = 1.980$ Å) are also located well on the smoothly extrapolated curves beyond the limit of this figure. This fact shows that at a given value of \tilde{v} the shape of the unit cell is similar among all of these crystals. At \tilde{v}_c the following relation is commonly observed in I_2 , IBr , and Br_2 : $a_L:b_L:c_L:r_s = 2.12:1.46:3.38:1$.

Previous measurements of Raman scattering²⁰ and infrared reflectivity²¹ of I_2 revealed that the librational phonon mode with the Ag symmetry softens significantly above about 15 GPa as a precursor to the molecular dissociation and that the reflectivity increases abruptly at P_c . In the case of Br_2 , on the other hand, the pressure region previously investigated turns out not to be high enough to detect any anomaly in the Raman scattering (≤ 33 GPa)²² and infrared reflectivity (≤ 60 GPa).²³ Therefore, it would be interesting to proceed with these measurements of Br_2 in an extended pressure region to study whether other common features can be observed in these systems. Applying the Goldhammer-Herzfeld criterion²⁴ to I_2 and Br_2 , for which the density is now fully known throughout the LP phase, the molar refractivity reaches its metallic limit at about 20 and 80 GPa in I_2 and Br_2 , respectively. In each case such a metallization pressure agrees well with the corresponding molecular dissociation pressure P_c . It is not clear if such an agreement is accidental or necessary.

It is attractive to deduce a unified view from the pressure-induced phase transitions observed in different halogens. Holzapfel and co-workers¹⁰⁻¹³ made the first such attempt even when only iodine had been known to undergo molecular dissociation. Based on both our previous data of I_2 and their x-ray data of Br_2 and Cl_2 ob-

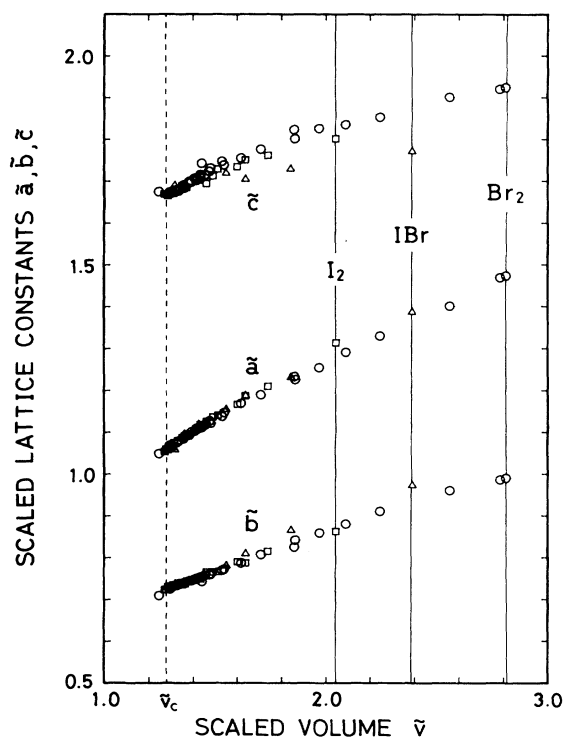


FIG. 4. Scaled lattice constants vs scaled volume observed for I_2 , IBr , and Br_2 . Solid vertical lines represent the location of \tilde{v} at atmospheric pressure.

tained in a relatively low-pressure region of the LP phase, they found a universal behavior of the lattice constants and unit-cell volume scaled by the intramolecular bond length in the gaseous state r_g . However, in the present analysis, with the addition of the new data for Br_2 , it turns out that the bond length in the solid state r_s is a more relevant scaling parameter than r_g . Since the intramolecular bond length changes significantly due to the intermolecular charge transfer upon solidification, r_s is more relevant for characterizing the solid-state property. In this paper we use experimental r_s values at atmospheric pressure and low temperature. In our previous structure analysis⁵ of I_2 and the preliminary one of Br_2 , r_s does not change appreciably throughout the LP phase in either crystal. This fact also supports the use of r_s at atmospheric pressure for scaling.

The universal behavior of the scaled lattice constants demonstrated in Fig. 4 reveals similarities of the unit cells. At $\tilde{v} = 2.1$, for example, the shape of the unit cell for I_2 at atmospheric pressure is similar to that for Br_2 at 5.0 GPa. Such a similarity further implies the similarity of the molecular arrangement in the unit cell. In fact, our preliminary structure analysis of Br_2 based on the present reliable intensity data proves that the atomic coordinates (y and z specifying the $8f$ site of the space group D_{2h}^{18}) at $\tilde{v} = 2.1$ are nearly the same for both I_2 at atmospheric pressure¹⁸ and Br_2 at 5.0 GPa. It is also

commonly observed that just before the molecular dissociation at $\bar{v}_c = 1.29$, the molecules are aligned in such a manner that the angle between the molecular axis and the principal c axis becomes $\theta = 39^\circ \pm 2^\circ$ and the interatomic distances are $r_{17}/r_s = 1.13 \pm 0.02$ and $r_{12}/r_s = 1.15 \pm 0.02$ [see Fig. 1(a)]. These common features of the molecular arrangements necessarily lead to the universal behavior of the scaled unit-cell volume and lattice constants as originally proposed by Holzapfel and co-workers. The detailed structure analysis of Br_2 and its comparison with that of I_2 are now under way and offer important information for understanding the microscopic mechanism of the molecular dissociation systematically observed in halogens.

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