High-Pressure in-situ XAFS-XRD Measurements of Liquid Iodine with MAX80

Upgrading the AR-NE5C beamline, we developed a new system with the large-volume press MAX80, which enables us to conduct high-pressure and high-temperature in-situ X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD) measurements. We succeeded in obtaining XAFS spectra and XRD profiles of liquid iodine up to about 9 GPa and 1100 K. Both types of data suggest that diatomic molecules persist up to the maximum pressure without dissociation. Detailed analyses, with the aid of the Reverse Monte Carlo modeling technique, clarified the structural transformation at 4–5 GPa characterized by the onset (or drastic increase in the probability) of rebonding among adjacent molecules.

Iodine has attracted considerable attention as a model material of diatomic molecules and its high-pressure behavior has long been studied in various research fields. In particular, numerous studies on metallization and molecular dissociation have been conducted since the discovery of the metallization of solid iodine at 16 GPa [1]. It has been found that a monoatomic phase appears above 30 GPa [2], and iodine is known as the first material whose pressure-induced molecular dissociation was observed experimentally. As for liquid iodine, it has been reported that its electrical conductivity jumps at 3–4 GPa [3]. Also, a possible molecular dissociation has been pointed out by XAFS measurements [4]. However, there is only one XAFS spectrum which could be evidence of molecular dissociation obtained at around 4.5 GPa; there are no spectra at higher pressures. Moreover, no XRD measurements that support the molecular dissociation have been reported.

XAFS and XRD provide complementary information on the local structure around an absorbing atom and the average structure including all atoms, respectively. There have been numerous reports of either XAFS or XRD measurements under high pressure, but there have been no cases in which both XAFS spectra and XRD profiles were obtained in a single run as far as we are aware. Upgrading the AR-NE5C beamline, we developed a high-pressure and high-temperature in-situ XAFS-XRD measurement system and obtained XAFS spectra and XRD profiles of liquid iodine up to about 9 GPa and 1100 K [5]. On the basis of the two types of data, we discuss the nature of the transformation in liquid iodine.

The large-volume press MAX80 installed at the beamline has long been used mainly for high-pressure in-situ energy-dispersive XRD measurements with white X-rays and a pure-Ge solid-state-detector (SSD) system. The existing double-crystal monochromator was reactivated to provide monochromatic X-rays. The transmission XAFS measurement system can be switched to the XRD measurement system with white X-rays within about 5 minutes by moving the first crystal of the monochromator (Fig. 1). In addition, the most appropriate thickness of sample is different between XAFS and XRD, and it is hard to obtain good data of the two kinds of measurements from one sample. Therefore, iodine-NaCl mixtures with a ratio of I_2 : NaCl = 1:9 and 1:3 in volume were prepared for XAFS and XRD, respectively, and the sample containers for the two measurements were located to achieve the same pressure and temperature conditions. XAFS spectra were obtained by scanning the energy of X-rays in the vicinity of the iodine K-absorption edge (33.169 keV) with a Si(111) double-crystal monochromator. Intensities of incident and transmitted X-rays were measured with two ionization chambers (IC) filled with Kr-Ar mixed gas and Kr gas, respectively. Samples were heated after being pressurized to predetermined press loads at room temperature. Electric power was supplied for heating to temperatures about 50 K above the melting point of each pressure.

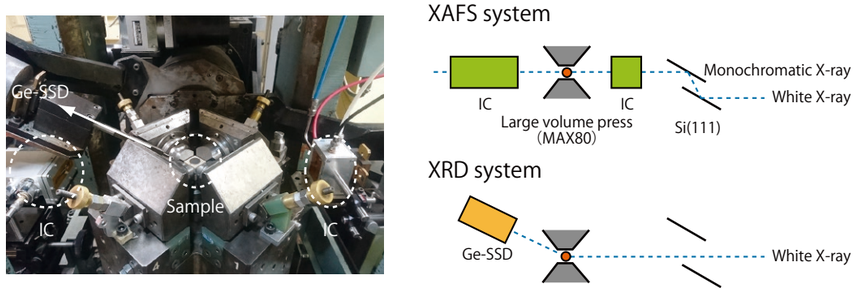

Figure 1: Image and schematic illustration of the experimental setup.

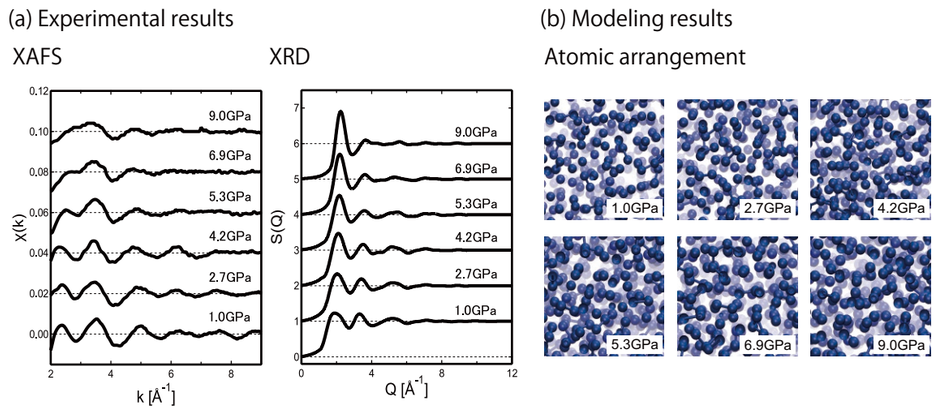

Figure 2: (a) EXAFS oscillation $\chi(k)$ and structure factor $S(Q)$ of liquid iodine obtained by XAFS and XRD measurements and (b) atomic arrangement by RMC modeling.

The pressure dependence of extended X-ray absorption fine structure (EXAFS) oscillation $\chi(k)$ and structure factor $S(Q)$ obtained from XAFS and XRD is shown in Fig. 2(a). The oscillation in $\chi(k)$ showed a significant decay above 4–5 GPa but persisted to the maximum pressure, suggesting that molecular bonds remain even at 9 GPa. Our results by XAFS are consistent with those by a previous study which suggested a possible molecular dissociation [4]. The significant decay of EXAFS oscillation might be misinterpreted as molecular dissociation. Detailed analyses of XRD data clarified that molecules get close to each other but persist even at 9 GPa, consistent with the results from XAFS. These observations suggest that the molecules in liquid iodine interact more strongly with each other with increasing pressure but do not dissociate even at 9 GPa. The atomic arrangement was determined with the Reverse Monte Carlo modeling technique to reproduce $\chi(k)$ and S(Q) well. The results of the modeling are shown in Fig. 2(b), demonstrating that molecules get close to each other with increasing pressure. Detailed analyses suggest that the structural transformation at 4-5 GPa is characterized by the abrupt increase in the probability that the distance between two atoms in different molecules is shorter than that between two atoms in the same molecule, and hence rebonding among adjacent molecules is enhanced.

REFERENCES

[1] A. S. Balchan and H. G. Drickamer, *J. Chem. Phys.* **34**, 1948 (1961).
[2] K. Takemura, S, Minomura, O. Shimomura and Y. Fujii, *Phys. Rev. Lett.* **45**, 1881 (1980).
[3] V. V. Brazhkin, S. V. Popova, R. N. Voloshin and A. G. Umnov, *High Press. Res.* **6**, 363 (1992).
[4] U. Buontempo, A. Filipponi, D. Martínez-García, P. Postorino, M. Mezouar and J. P. Itié, *Phys. Rev. Lett.* **80**, 1912 (1998).
[5] D. Wakabayashi, N. Funamori, T. Kikegawa, K. Watanabe, S. Kohara, H. Nitani, Y, Niwa, Y. Takeichi, H. Abe and M. Kimura, *Phys. Rev. B* **96**, 024105 (2017).

BEAMLINE

AR-NE5C

D. Wakabayashi[1], N, Funamori[1], T. Kikegawa[1], K. Watanabe[2], S. Kohara[3], H. Nitani[1], Y. Niwa[1], Y. Takeichi[1], H. Abe[1] and M. Kimura[1] ([1]KEK-IMSS-PF, [2]Mitsubishi Electric System & Service Co., Ltd., [3]NIMS)