

High-pressure X-ray diffraction studies of the supercritical fluid of hydrogen

Hydrogen has high potential as a next-generation clean energy source. One of the challenges facing the realization of a hydrogen society is the establishment of safe and efficient hydrogen transportation and storage technology. For this purpose, it is important to have information on the basic physical properties of high-pressure hydrogen (H_2) gas, such as its aggregation state and density.

Normal hydrogen (n-H₂) has a critical point at 32.97 K and 1.293 MPa and solidifies under a high pressure of 5.4 GPa at room temperature. Up to now, Mills *et al.* [1] have proposed an equation of state up to 2 GPa through volume compression and ultrasonic velocity measurements using a piston cylinder device. Pratesi *et al.* [2] have proposed a pressure dependence of density up to 5.4 GPa at room temperature on the basis of Brillouin scattering experiments.

In this study, synchrotron radiation X-ray diffraction experiments were performed to collect halo patterns within a wide pressure range (0.1 to 5 GPa) to obtain information on the density and structure of the supercritical fluid phase [3].

A diamond anvil cell (DAC) was used to generate high pressure. The sample was $n-H_2$ and high-pressure H_2 gas of 180 MPa (or 50 MPa) was loaded into the DAC using a high-pressure gas filling apparatus. High-pressure X-ray diffraction experiments were performed at room temperature at SPring-8 **BL10XU**. The incident X-ray energy was 30 keV and an image plate was used as a two-dimensional detector. In these one-dimensional data, the halo pattern from the fluid H_2 was overlaid by the relatively strong Compton scattered X-ray background from the diamond anvil. To subtract this background numerically, the background pattern of an empty cell containing no sample was measured.

During this X-ray diffraction experiment, we succeeded in observing the halo pattern of the hydrogen supercritical fluid phase within a wide pressure range from 0.12 to 5.1 GPa. Figure 1 shows the pressure change of a typical diffraction pattern. The first halo was observable, but the second was undetectable. A spectral analysis was performed to estimate the 2θ value and FWHM of the first halo peak. The *d*_H value was calculated from the 2θ value. The *d*_H value and FWHM decreased as the pressure increased (Fig. 2). The FWHM corresponds to a measure of the correlation of intermolecular distance in fluid.

We considered $d_{\rm H}$ to be the average nearestneighbor intermolecular distance and assumed a packing of a hard sphere with diameter $d_{\rm H}$. Herein, the molar volume was estimated using the equation of state proposed on the basis of the ultrasonic measurement by Mills *et al.* [1] That is, assuming that the cube of the $d_{\rm H}$ value at 2 GPa is proportional to the molar volume reported by Mills *et al.*, i.e., 11.593 cm³/mol. At this pressure, the proportional constant *A* of the following formula was determined to estimate the molar volume $V_{\rm m}$.

$$V_{\rm m}(P) = A \cdot N_{\rm A} \cdot [d_{\rm H}(P)]^3$$

Here, N_A is Avogadro's number and A is 1.37, which corresponds to the reciprocal of the packing factor. If A was 1.0, it would correspond to the hexagonal coordinate of a simple cubic lattice. In our previous study on supercritical fluid phases of O₂ and N₂, A was 1.47, indicating that the filling rate of H₂ is higher than those of O₂ and N₂. Figure 3 shows the pressure dependence of the molar volume together with the results of previous studies.





The pressure dependence in this study was in good agreement with the data of Mills et al. up to 2 GPa and the data of Pratesi et al. above 1 GPa. Therefore, the validity of the hard sphere model assumed in this study was demonstrated. That is, it was considered that the $d_{\rm H}$ value corresponded to the average intermolecular distance and that the average coordination number (packing factor: A) of the molecules was constant and did not change in the pressure range of 0.1 to 5 GPa. There was a change in compressibility at around 1 GPa, i.e., the dependence followed the relational expression of $P \sim V_{\rm m}^{-3.11}$ above 1 GPa. Fluid O₂ and N₂, which are the same homonuclear diatomic molecules as H_2 , followed the relational expression of $P \sim V_{\rm m}^{-4.32}$ at a pressure higher than 0.2 GPa. The repulsive term of the Lennard-Jones potential, which is applied to molecular solids, became dominant for fluid O₂ and N_2 . Therefore, it was found that fluid H_2 behaves differently from fluid O₂ and N₂ and is more easily compressed. The reason why H₂ and He are easily compressed is that the wave function of the 2s electrons occupying the outer orbital of O₂, N₂, and Ne molecules is required to be orthogonal to the wave function of the 1s electron, but the 1s electron cloud surrounding H₂ and He molecules does not have this orthogonality constraint.

However, in the pressure region lower than ~1 GPa, the pressure dependence of H₂ deviates from the relationship of $P \sim V^{-3.11}$. It seems that the repulsive term of the intermolecular potential becomes dominant in the pressure region higher than ~1 GPa. That is, the compressibility of the supercritical phase of hydrogen changes from gas-like to liquid- or solid-like at around 1 GPa.



Fig. 2. Pressure dependence of the $d_{\rm H}$ value and FWHM of the first halo peak.



Fig. 3. Pressure dependence of V_m for the supercritical fluid of H₂ together with previous data (a) and for supercritical fluids (solid line) and solids (broken line) of H₂, He, Ne, N₂, and O₂ (b).

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References

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