

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 (H₂) 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-H₂ and high-pressure H₂ 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 H₂ 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_H to be the average nearest-neighbor intermolecular distance and assumed a packing of a hard sphere with diameter d_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_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_m .

$$V_m(P) = A \cdot N_A \cdot [d_H(P)]^3$$

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.

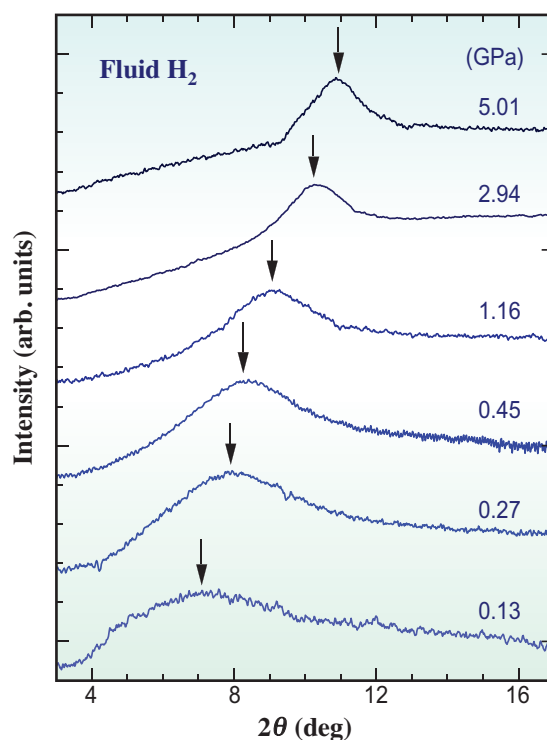


Fig. 1. Pressure evolution of the X-ray diffraction patterns for fluid H₂.

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_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 $P \sim V_m^{-3.11}$ above 1 GPa. Fluid O_2 and N_2 , which are the same homonuclear diatomic molecules as H_2 , followed the relational expression of $P \sim V_m^{-4.32}$ 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 O_2 and N_2 . Therefore, it was found that fluid H_2 behaves differently from fluid O_2 and N_2 and is more easily compressed. The reason why H_2 and He are easily compressed is that the wave function of the 2s electrons occupying the outer orbital of O_2 , N_2 , and Ne molecules is required to be orthogonal to the wave function of the 1s electron, but the 1s electron cloud surrounding H_2 and He molecules does not have this orthogonality constraint.

However, in the pressure region lower than ~ 1 GPa, the pressure dependence of H_2 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.

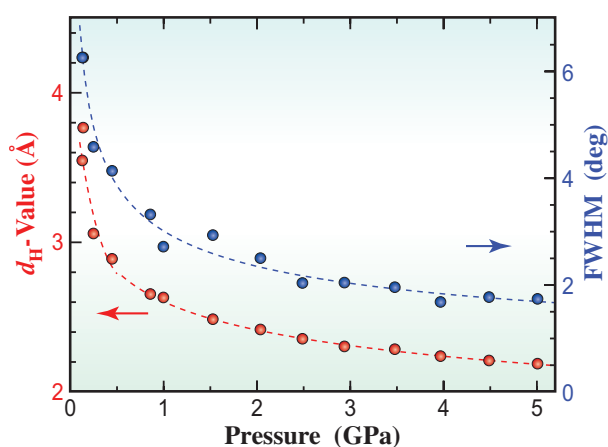


Fig. 2. Pressure dependence of the d_H value and FWHM of the first halo peak.

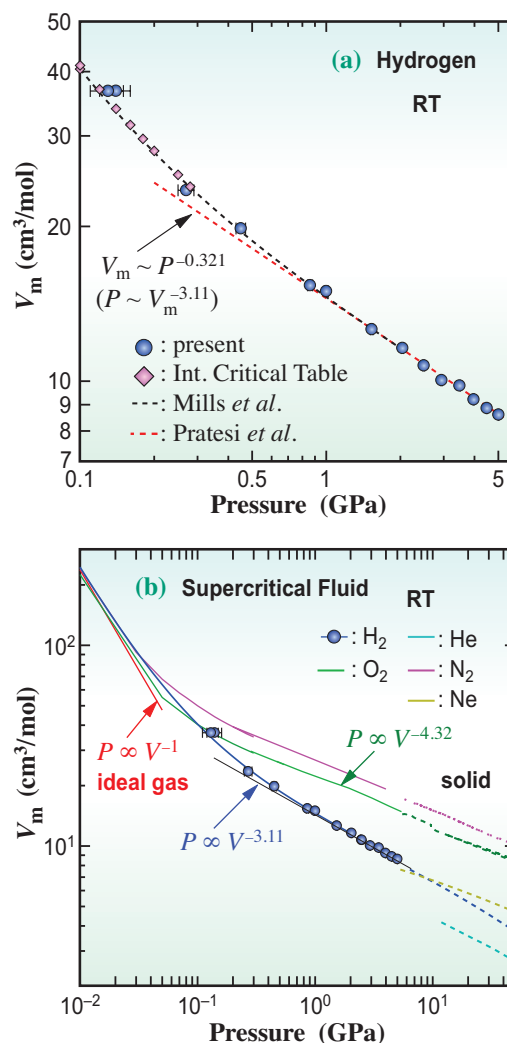


Fig. 3. Pressure dependence of V_m for the supercritical fluid of H_2 together with previous data (a) and for supercritical fluids (solid line) and solids (broken line) of H_2 , He, Ne, N_2 , and O_2 (b).

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References

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