

Changes in the structure of water deduced from the pressure dependence of the Raman OH frequency

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We report on the Raman spectra of water under high temperature and pressure conditions and show a discontinuity in the pressure dependence of the OH stretching frequency. As pressure increases, the strength of hydrogen bonding increases rapidly in the pressure ranges up to 0.4 ± 0.1 GPa at 25 °C, 1.0 ± 0.1 GPa at 100 °C, and 1.3 ± 0.1 GPa at 300 °C and slowly above these pressures. This finding clearly demonstrates the existence of discontinuities in the pressure response of the hydrogen bonds of water, which suggests a possible structural change under these conditions.

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In addition to the 12 polymorphs of ice,¹ experimental and theoretical studies have revealed the existence of polyamorphism in H₂O as glass forms.^{2,3} A first-order phase transition was observed under supercooled conditions between low-density amorphous ice (LDA) and high-density amorphous ice (HDA).² *In situ* neutron diffraction studies^{3,4} found similarities between LDA and ice Ih and HDA and ice VI/VII/VIII; HDA is characterized by interpenetrating hydrogen bond networks and coordination with four hydrogen bonding and four nonhydrogen bonding oxygen atoms. Direct information on the structure of liquid H₂O by neutron diffraction at -5 °C in the pressure range from 0.02 to 0.4 GPa suggests that the structure of water *gradually* changes from low-density water (LDW) to high-density water (HDW),⁵ which may represent high-temperature analogs of LDA and HDA, respectively.² Classical molecular dynamics simulations also suggest the possibility of a phase transition between LDW and HDW at higher temperatures up to 127 °C (Ref. 6). We have investigated the Raman spectra of liquid H₂O in order to explore the structural change from LDW to HDW under higher-pressure and -temperature conditions.

Raman spectra of liquid H₂O were obtained over pressure ranges up to 1.6, 2.9, and 5.7 GPa at 25, 100, and 300 °C, respectively. Some data at 25 and 100 °C were collected under supercooled conditions. The high-pressure and -temperature experiments were performed with a Bassett-type externally heated diamond anvil cell,⁷ which was placed within a gear box allowing a continuous compression. Pure (Mili-Q) water was placed in a rhenium gasket together with small ruby chips and a few grains of cubic boron nitride as a

secondary pressure marker. Temperature was monitored and controlled by means of two Chromel–Almel thermocouples attached to the diamonds. Pressure was estimated by means of the ruby fluorescence using established equations^{8,9} with a precision better than 0.1 GPa. For the pressure calculation, the temperature and pressure dependences of the ruby fluorescence are assumed to be independent of each other. Unpolarized Raman spectra of water were collected with a Raman microscope (Kaiser HoloLab 5000) using a 532-nm YAG laser (17 mW at the sample surface), holographic transmission grating, and charge-coupled-device (CCD) detector of 2048 pixels for the range of 291–4573 cm⁻¹ in Raman shift. The spectral resolution in the present system is approximately 2 cm⁻¹ and the Raman shift was calibrated with fluorescence lines of a neon lamp. We obtained the Raman spectrum for water with an exposure for 15 s and took a fluorescence spectrum from a ruby chip at each measurement. A series of data points was measured at each temperature successively without a tea break. A linear base line between 2800 and 3800 cm⁻¹ was subtracted for the spectrum of water.

Curve fitting was applied to the broad Raman bands resulting from the OH stretching vibrations of liquid H₂O (Fig. 1). Initially, two Gaussian curves with approximate peak heights and peak positions were given, and the peak heights and positions were optimized using the least-squares method. For this procedure, two commercial softwares (Origin and PeakFit) were used and the results were carefully compared. The peak frequencies obtained from these two curve fittings were identical.

With increasing pressure, peak intensities of the lower-frequency band increase at each temperature (Fig. 1). Raman spectra of liquid water in the OH stretching region show a complex profile of several broad and overlapping bands. Although the interpretation is still controversial, the individual

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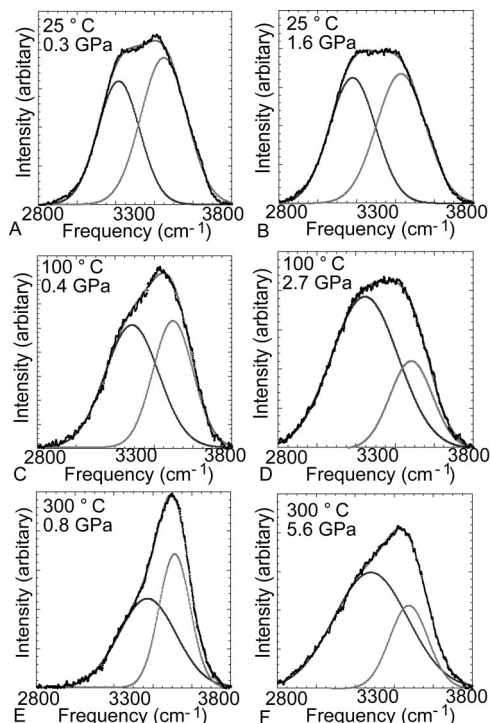


FIG. 1. Representative band component analyses on Raman spectra of water at 0.3 GPa, 25 °C (A), 1.6 GPa, 25 °C (B), 0.4 GPa, 100 °C (C), 2.7 GPa, 100 °C, (D), 0.8 GPa, 300 °C (E), and 5.6 GPa, 300 °C (F). Black dots represent raw data and are deconvoluted into two Gaussian peaks which sums up to produce gray dots.

bands are thought to result from a particular configuration of the hydrogen-bonded molecules. The high-frequency components are attributable to the least-associated molecules, whereas the lower-frequency components are due to more hydrogen-bonded molecules.^{10,11} Based on this assignment, Fig. 1 indicates that the ratio of more hydrogen-bonded molecules increases with increasing pressure. An alternative interpretation is that the lower-frequency peak may be attributed to the overtone of the bending vibration of molecular water and that the other high-frequency peaks are due to the symmetric and asymmetric stretching vibrations.^{12,13} Fermi resonance can also play a role in the spectra of liquid water.¹³ An effect of Fermi resonance between the stretching vibration mode and the bending overtone was observed in ice VII at a pressure range from 17 to 30 GPa (Ref. 14). It is not easy to preclude this possibility to explain the increase of the lower-frequency components with increasing pressure (Fig. 1).

At constant temperature, the frequencies of Raman peaks show a negative correlation with pressure, and the peak frequencies increase with increasing temperature [Figs. 2(A) and 2(B)]. This suggests that the strength of hydrogen bonding increases with increasing pressure and decreases with increasing temperature as shown in previous experiments.^{15–19} At a given temperature, the slopes of frequency as a function of pressure change significantly at 0.4 ± 0.1 GPa, 25 °C, 1.0 ± 0.1 GPa, 100 °C, and 1.3 ± 0.1 GPa, 300 °C [Figs. 2(A) and 2(B)]. The peak widths at half maximum and also the areas of those decomposed peaks also show a change in their pressure dependence at identical P – T

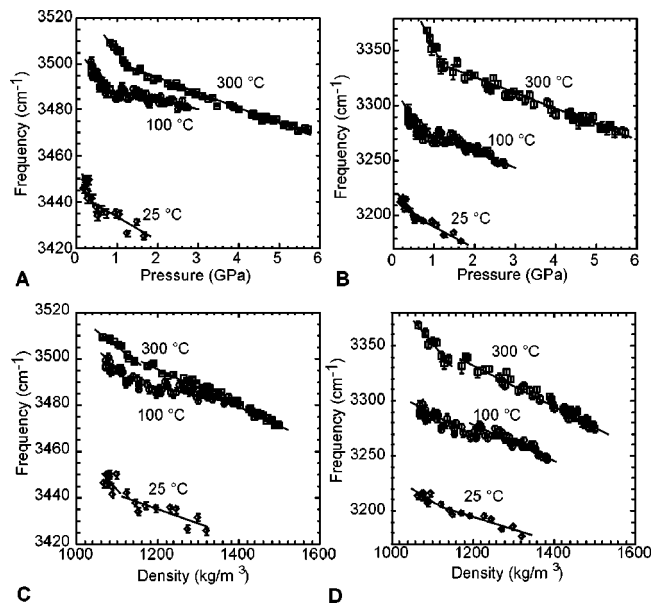


FIG. 2. Raman frequencies of two peaks of OH vibration of water at 25, 100, and 300 °C as a function of pressure [(A), (B)] and density [(C), (D)]. Raman frequencies show discontinuity in pressure dependence at 0.4 ± 0.1 GPa at 25 °C, 1.0 ± 0.1 GPa at 100 °C, and 1.3 ± 0.1 GPa at 300 °C. Lines are guides for the eyes.

conditions. The Raman frequency also changes, reflecting density changes. There are cusps in the Raman frequency as a function of isothermal density²⁰ at P – T conditions identical to those observed in the pressure dependence: 1160 kg/m^3 , 25 °C, 1200 kg/m^3 , 100 °C, and 1175 kg/m^3 , 300 °C [Figs. 2(C) and 2(D)]. This change in the pressure dependence of the Raman frequency reflects different compression behavior of liquid water, which may suggest a structural change. Alternatively, this change could be explained as a result of the Fermi resonance between the stretching vibration mode and the bending overtone *without any structural change*. It is, however, unlikely that Fermi resonance becomes effective when the frequency difference between the higher- and lower-frequency components increases with increasing pressures [Figs. 2(A) and 2(B)]. These pressure and temperature conditions are plotted in a phase diagram of H_2O (Refs. 1 and 21) (Fig. 3). This curvature is interpreted to represent a phase transition between low-pressure water (sparse water) and high-pressure water (dense water) forms.

The structural regimes observed may be identical to LDW and HDW, because HDW was proposed to be stable at pressures greater than 0.4 GPa at -5 °C (Ref. 5), which seems to be consistent with the phase boundary measured here (Fig. 3). However, our Clapeyron curve is inconsistent with the slightly negative curve of the boundary between LDW and HDW calculated by molecular dynamic simulations.⁶ HDW has an estimated density (1200 kg/m^3 at -5 °C) (Ref. 5) similar to the dense water at the phase transition boundary measured here (1160 – 1200 kg/m^3).

The structural boundary inferred from the different pressure dependences of Raman frequencies (Fig. 3) can be related to a structural change from a low-pressure icelike structure (Ih, III, V) to high-pressure icelike structure (VI, VII, VIII). There is a structural difference between lower-pressure

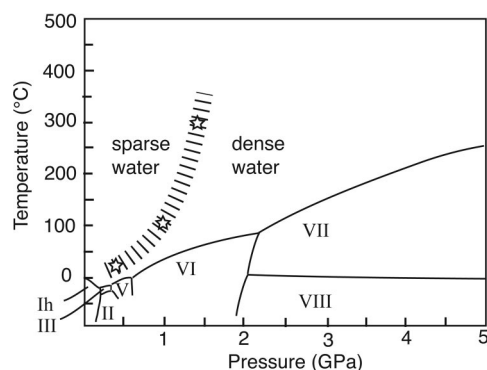


FIG. 3. Pressure and temperature diagram showing stability of ice Ih, II, III, V, VI, VII, and VIII (Refs. 1 and 21) and a possible phase transition of liquid H_2O from sparse water to dense water, which can be identical to low-density water and high-density water determined at -5°C (Ref. 5). The interrupted curve does not mean a first-order liquid-liquid transition here, but suggests a region where water gradually changes its structure. See text.

ices (Ih, III, V) and higher-pressure ices (VI, VII, VIII). With increasing pressure, ice Ih changes its form to III and then V by changing hydrogen bonding and consequently decreasing distance between H_2O molecules.^{22,23} In contrast, ice VI/VII/VIII have structures consisting of two hydrogen bonding structural units that interpenetrate each other^{22,23} with no hydrogen bonding between those two interpenetrating units. Mishima and Suzuki²⁴ reported Raman spectra during the phase transition from LDA to HDA under atmospheric pressure with increasing temperature and reported an increase of Raman peak frequency of about 100 cm^{-1} . Differences in the Raman frequency between ice I and ice VI/VII are 120 and 250 cm^{-1} , respectively.²² LDA and HDA, therefore, seem to behave like ice I and ice VI, respectively. These characteristics are consistent with the solidlike features observed in LDA and HDA.^{25,26} Such a large jump in Raman frequency is not observed at the transition from sparse water to dense water (Fig. 2). Our Raman data indicate that the structural change of the liquid water is not abrupt as observed for LDA-HDA, but suggest that sparse water gradually changes hydrogen bonding with increasing pressure and then changes to dense water. Whether the dense water has some interpenetrating structural units or not remains to be investigated by neutron diffraction experiments.

Ultrasonic velocities of water have been measured under high-pressure conditions and at room temperature.²⁷⁻³⁰ The available velocity data are plotted as a function of pressure in Fig. 4(A). Those data may be fitted by a single equation. By contrast, recent high-frequency sound velocity data for liquid water show an anomaly at 1120 kg/m^3 , 0.37 GPa [Fig. 4(B)].³¹ Krisch and co-workers have suggested that the high-frequency sound velocity is more sensitive to the microscopic dynamical and structural properties of water due to the strength of the relaxation.³¹ Although this anomalous behavior can be observed at a pressure range from 0.37 to 0.76 GPa , their data can be also interpreted as the result of a phase transition starting at 0.37 GPa [Fig. 4(B)]. The Brillouin scattering frequency of water under high-pressure conditions and at room temperature also shows a cusp at around 0.4 GPa (Ref. 32). These data sets support the present hypothesis of a

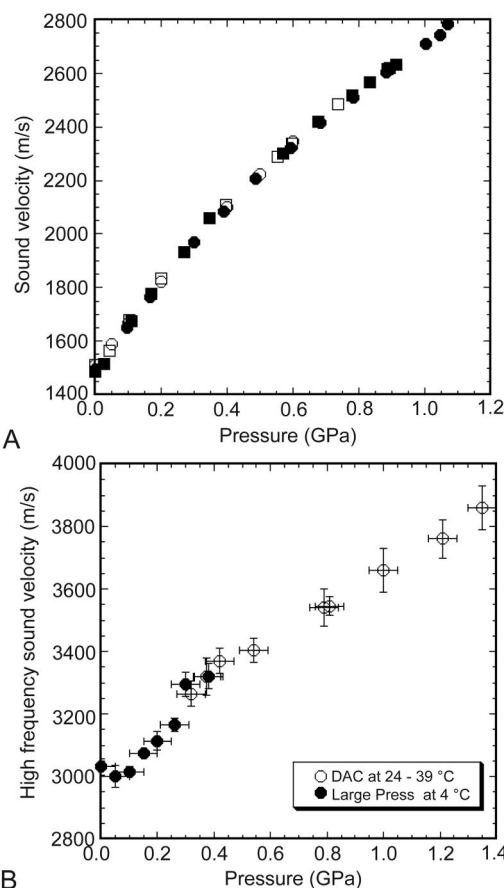


FIG. 4. Hydrodynamic ultrasonic velocity of liquid H_2O as a function of pressure. Data are after Holton (Ref. 27) (open circle), Smith and Lawson (Ref. 28) (open square), Hanayama *et al.* (Ref. 29) (solid circle), and Kimura *et al.* (Ref. 30) (solid square) (A). High-frequency sound velocity of liquid H_2O as a function of pressure (Ref. 31). Data were taken with two different high-pressure apparatus: Large volume cell (large press) and diamond anvil cell (DAC). The plotted data were provided by the courtesy of Dr. M. Krisch (B). See text for discussion.

change from sparse water to dense water at around 0.4 GPa (Fig. 3). However, there is no apparent change in the viscosity data as a function of pressure at room temperature up to 1 GPa (Ref. 33). Mirwald³⁴ suggested possible phase transitions based on subtle changes in compressibility, although the compressibility data seem to have larger uncertainties than the ultrasonic velocity data.

The present experimental data are limited to 300°C . However, structural change of hot water may occur at higher temperature conditions. In this case, the structural change should affect the chemical and physical properties of the aqueous fluid in the earth's subduction zones. Aqueous fluids influence most physicochemical characteristics of earth-forming materials: melting temperature, magma chemistry, density and viscosity, electrical conductivity, phase transition boundaries, element distribution, and so on.³⁵⁻⁴¹ For example, the Mg/Si ratios of silicate component dissolved into aqueous fluid are known to change drastically from SiO_2 rich to MgO rich at about $2-3\text{ GPa}$ and 1000°C (Refs. 41-43). Such changes may be explained by a structural change of water. The structure and polymorphism of aqueous solutions have so far been studied at low temperatures,^{44,45} but

should be investigated under high-pressure and -temperature conditions as well.

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