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Phase diagrams and isotopic effects of normal and deuterated water studied via x-ray diffraction up to 4.5 GPa and 500 K

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We present synchrotron x-ray measurements in a diamond anvil cell of the molecular structure factor of H_2O and D_2O fluids up to 4.5 GPa and 500 K. We observe large changes in the structure factor and a dramatic increase in the oxygen coordination number over a 2 GPa pressure range. A P-T diagram of the nearest-neighbor oxygen coordination number, n_{OO}, is disclosed. Also, a counterintuitive isotopic shift of the variation of n_{OO} with pressure is observed.

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The knowledge of the structural properties of water under pressure is of great current interest. It is important to understand better how water is fine tuned for life,[1] what are the possibilities for exotic chemical reactivity in dense water[2] or how water influences some planetary interiors.[3] Yet, the phase diagram of water is still largely unknown. We focus here on the transition from the biological molecular fluid with low coordination number to the normal molecular fluid. The structural evolution of water under pressure has already been investigated by many studies. In the pressure range covered here, first principles molecular dynamics simulations have predicted that the structure of water should be substantially altered from that at ambient conditions, with a large increase of the coordination of the oxygen atoms.[4] A result that conclusively determines the pressure evolution of the structure of water is the neutron diffraction measurements of Soper and Ricci up to 0.4 GPa.[5] The modeling of these neutron data implies a continuous transformation with increasing pressure from a low-density form of water (LDW), with an open hydrogen-bonded tetrahedral structure, to a high density form of water (HDW), with non-tetrahedral O-O-O angles and a collapse of the second coordination shell. The neutron measurements have recently been extended up to 6.5 GPa, showing that with increasing density water approaches a local structure common to simple liquids.[6] But, in the neutron scattering measurements, the oxygen-oxygen structure factor contributes only to 9% of the overall signal. Consequently, the extraction of the oxygen coordination from the overall signal is dependent on structural modeling. On the other hand, the x-ray scattering signal essentially contains information about the O-O correlations (making of 80% of the overall signal). Hence, the evolution with pressure of the isotropic arrangement of the oxygen atoms can be directly extracted from the x-ray data. The present measurements, using a diamond anvil cell (DAC) and the ESRF synchrotron radiation, significantly extends the P-T domain and the accuracy of a previous x-ray study of water under pressure, limited to below 0.7 GPa at 300 K.[7] The oxygen coordination number, n_{OO}, is here chosen as the metric of the water structural evolution to a compact fluid. Also, we report here an isotopic effect of the evolution of n_{OO} with pressure. A counterintuitive shift is observed, at odds with most predictions. Since near ambient pressure, nuclear quantum effects significantly impact the behavior of water,[8,9] this observation could have dramatic implications for the accuracy of calculations of water.

Water samples were confined in an externally heated diamond anvil cell with a large x-ray aperture (±37°). To prevent possible chemical reaction between water and the rhenium gasket, the sample was isolated from the gasket by a 10 μm thick ring of gold. The pressure was measured with the ruby luminescence gauge[10] for the ambient temperature run and with the x-ray data of gold[11]otherwise. Temperatures were measured by a thermocouple in contact with the diamond. Accuracy of the pressure-temperature measurements was checked by comparing the melting points obtained in the course of the experiment with a previous determination.[12] The x-ray diffraction data of water were collected along isotherms. The x-ray diffraction experiments were performed on the ID30 and ID09 beamlines at the ESRF. We used a doubly focused monochromatic beam of diameter 30 μm and energy $E=33$ keV or $E=29.5$ keV. The scattered photons were collected by an image-plate MAR345 detector. The diffraction patterns were integrated with the FIT2D computer code[13] after having carefully masked the diamond Bragg peaks. Since the diamond anvils are many times thicker than the sample, Compton background scattering from anvils constitutes the major contribution to the x-ray diffraction signal. Therefore, excessive care must be taken in the background subtraction. The quality of the diffraction data depends on the relative contribution of the sample to the total signal which is related to the thickness ratio between the sample and the diamond anvils. This was maximized for the ambient temperature run by using 500-μm-thick anvils and a 100-μm-thick sample. Under the most extreme conditions of the present experiment, 2.5-mm-thick anvils and a 30-μm-thick sample were used. Data were collected on eight different samples. The present experimental determination has three primary sources of errors: random error that is estimated from the dispersion of the large number of data points of the present study; systematic errors due to the limited Q range of the x-ray signal that is quantified by varying Q on the experimental data and noise error due to the weak signal to background ratio.

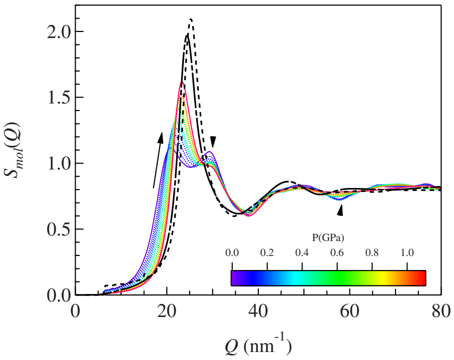

FIG. 1. (Color online) Molecular structure factor of water at different pressures. The color lines, the black line and the black dash-line represent the data at T=300 K with the associated color pressure scale, at 2.5 GPa and 365 K and at 4.1 GPa at 500 K, respectively.

Also, experimental data are compared to calculations essentially to quantify the systematic uncertainty in the data analysis. Monte Carlo simulations of water have been performed using the well-known TIP4P water model.[14] This force field describes reasonably well the properties of water under ambient conditions and also it allows us to reproduce the density of the liquid phase at high pressure.[15] Isothermal-isobaric simulations have been performed using a primitive box containing 256 water molecules.

A self-contained analysis has been described in detail previously to measure the structure factor of low-Z liquids in a DAC (Ref. 16) when the diffuse scattering of the sample is dominated by the background scattering from the diamond anvils. It has been validated with fluid argon and water near ambient pressure. Recently, it has been applied to fluid O_2 over an extended P-T range.[17] The molecular structure factor determined from x-ray diffraction data can be written as

$$S_{mol}(Q) = \frac{I^{coh}(Q)}{NZ_{tot}^2 f_e^2(Q)} = \frac{\Sigma K_p^2}{Z_{tot}^2} + \rho \int_0^\infty [g_{mol}(r) - 1]\frac{\sin Qr}{Qr} 4\pi r^2 dr, \quad (1)$$

with ρ, the liquid density; Z_{tot}, the total atomic number of the molecular unit; K_p, an effective atomic number and $f_e(Q)$ as an effective electronic form factor. Our definition of $f_e(Q)$ ignores the effect of charge transfer and covalent bonding. Using the modified atomic scattering factor, given by Sorenson[18] to reproduce the change of electron density upon the formation of water molecules from isolated oxygen and hydrogen atoms, does not change appreciably the analysis. Our self-consistent procedure also optimizes $f_e(Q)$ and so compensates partially for this charge transfer effect.

As observed in Fig. 1, the main feature effecting the structure factor is the continuous evolution below 40 nm^{-1} from a doublet to a singlet peak evidenced by a strong increase of the intensity of the first peak while the second peak progressively disappears. Hence, the molecular structure factor tends toward that of a simple fluid. Previous diffraction studies of water under pressure have already revealed similar distinct changes in $S(Q)$,[7,5] but they are more clearly observed here and extended over a large P-T range.

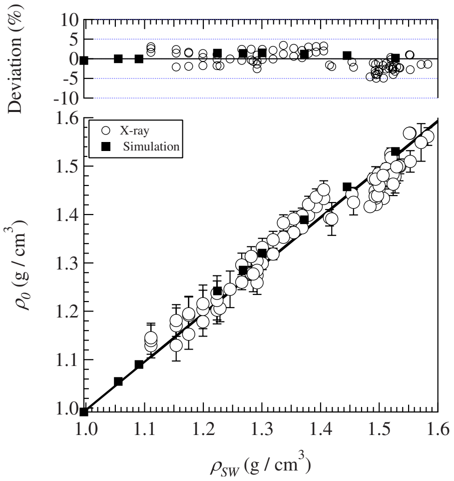

FIG. 2. (Color online) Comparison between the measured density and the Saul and Wagner equation of state (Ref. 19). The experimental points are represented as open symbols. The full squares are the data from the TiP4P calculation.

The self-consistent corrective procedure allows us also to determine the density, ρ. The error bars on the density have been obtained by varying Q between 65 and 90 nm^{-1}, following the methodology described in our previous paper.[16] Also, the analysis was done by using either the solid sample reference or the empty cell reference, yielding two ρ data points for each measurements. The present ρ data set is plotted in Fig. 2. All the data points agree within 4%, up to 1.6 g/cc, with the most used equation of state (EOS) of water under pressure, namely that of Saul and Wagner (SW) EOS.[19] It has been recently shown that in this pressure range the S&W equation of state is accurate enough.[20] In Fig. 2, it is seen that the TIP4P calculation and the SW EOS are in very good agreement.

The molecular pair distribution function, $g_{mol}(r)$, is obtained by the Fourier transform of Eq. (1). In fact, our x-ray analysis is based on a procedure that applies the Fourier transformation between $S_{mol}(Q)$ and $g_{mol}(r)$ iteratively to converge to a unique well-defined minimum in the figure of merit of the optimization.[16] In our methodology paper, the $g_{mol}(r)$ at ambient pressure has been compared to previous x-ray and neutron determinations which are also in very good agreement with the TIP4P calculation. The dominant peak (at 0.28 nm) is principally due to the O-O contribution and this peak is broader and smaller in our determination. This is due to the limitation of the Q range below 90 nm^{-1} in our measurements. Much of the information on the first peak in $g_{mol}(r)$ resides in the tail of $S(Q)$ at large values of Q. A limited Q range has two effects: to decrease the height of the first peak and also to widen it. Interestingly, these two effects almost compensate in the calculation of the coordination number. It should be noted that the structure factors measured in two simple fluids, Ar (Ref. 16) and O_2,[17] in the DAC over the same Q range give $g(r)$ in very good agreement with simulations. So, upon increasing pressure, as water is

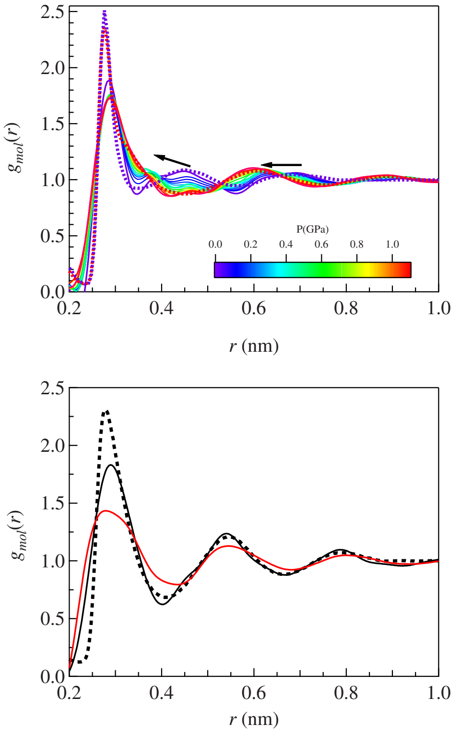

FIG. 3. (Color online) Pressure evolution of $g_{mol}(r)$. Upper panel: Evolution from near ambient pressure to 1 GPa, as full lines with pressure given by the color scale. Two TiP4P calculations, at ambient pressure and at 1 GPa are plotted as dash-lines. Lower panel: $g_{mol}(r)$ at 4.1 GPa and 500 K, as full black line, compared to TiP4P calculation under same thermodynamical conditions as dash-line and the $g_{o\text{-}o}(r)$ of fluid O2 at 7 GPa and 352 K (Ref. 17), as red line.

becoming a simple fluid, the determination of $g_{mol}(r)$ should become more accurate. The evolution of $g_{mol}(r)$ with pressure is reported in Fig. 3. The changes in the radial distribution function are particularly strong up to 1 GPa. That is in very good agreement with the previous x-ray determination up to 0.7 GPa (Ref. 7) and with the g_{OO} refined from the neutron data.[5,6] The arrows highlight the change of the second and third peaks with pressure. A dramatic negative shift of the position of the second peak at 0.45 nm is observed. Yet, the first peak is almost unaffected by the pressure change. This has been interpreted as a collapse of the second shell of water molecules into the first shell.[5,6] At 1 GPa, the first peak of $g_{mol}(r)$ at 0.28 nm has a shoulder at 0.36 nm corresponding to the second shell of water molecules. The evolution of $g_{mol}(r)$ to a symmetric first peak shape would only occur above 2 GPa. At all pressures, the height of the experimental first peak is smaller than the calculated one. Yet, there is a relative decrease of the height of the first peak under pressure, as expected if water is evolving to a compact fluid, which is consistent between experiment and calculation. But, because of the uncertainty due to the limited Q-range of the measurements, it is impossible to exploit further the comparison between calculation and experiment. In Fig. 3 (lower panel), the $g_{mol}(r)$ under the most extreme conditions of our experiment, i.e 500 K and 4.1 GPa, is also compared to the $g_{OO}(r)$ recently measured in fluid O_2 at 7 GPa and 350 K in a DAC over the same Q range.[17] In fluid O_2, the first peak is widened by molecular disorder compared to the radial distribution function of the center of mass of the molecules. Hence, under similar thermodynamical conditions, the oxygen seems more structured in fluid H_2O than in fluid O_2.

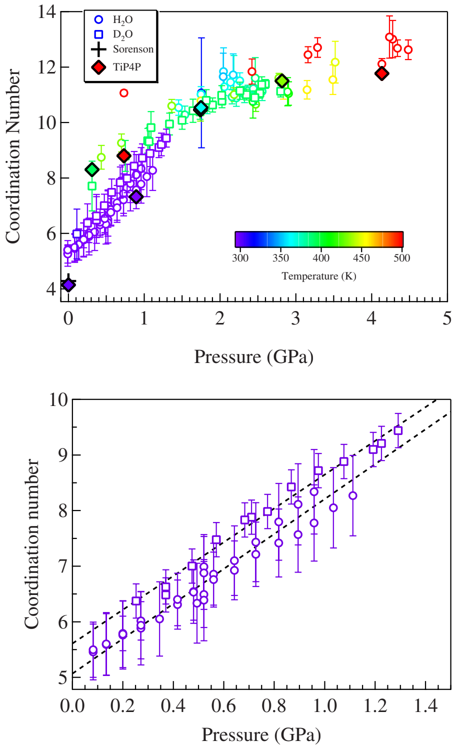

FIG. 4. (Color online) Evolution of the oxygen coordination number with pressure. The dots, squares, thick diamonds and the cross represent respectively experimental data on H_2O, data on D_2O, the TIP4P calculation and the data of Sorenson. The temperature is given by the color scale. Lower panel: enlarged view of the isotopic difference in the pressure evolution of oxygen coordination number at ambient temperature.

The evolution of the packing of the fluid can be directly quantified with the oxygen coordination number. The coordination number is defined as the value $n_{OO} = 4\pi\rho\int_0^{R_1} r^2 g_{OO}(r)dr$, with the R_1 value limiting the first peak in $g(r)$. We have defined R_1 as corresponding to the first minimum in $r^2 g_{OO}(r)$. Instead of the true g_{OO} we use $g_{mol}(r)$ in the integral (with the TIP4P calculation, we confirmed that this approximation has a negligible effect). The error bar on n_{OO} has been estimated by propagating the 4% uncertainty in ρ and the uncertainty in the location of R_1. Near ambient conditions, the coordination obtained is approximately 4, reflecting well the tetrahedral geometry of the first neighbors (part of the uncertainty should be ascribed to the pressure effect since our first data point is near 0.1 GPa). Certainly a different criteria to define the contribution of the first peak could slightly change the absolute value of n_{OO} but the variation of n_{OO} is a more robust quantity. The evolution with pressure and temperature of n_{OO} is plotted in Fig. 4. The coordination number drastically increases with pressure up to 2 GPa to reach, above this pressure, a plateau corresponding to the 12 nearest neighbors characteristic of a compact liquid. n_{OO} is also increasing with temperature. The values of n_{OO} obtained with the TIP4P calculation are also reported in Fig. 4. A good agreement between experiment and calculation is obtained.

Experiments have been performed using exactly the same DAC configuration for H_2O and D_2O to detect any isotopic effect. The isotopic shift is quite straightforwardly obtained since the x-ray intensity is not weighted by the H/D substitution. Molecular dynamic simulations with quantum nuclei and a recent full *ab initio* quantum calculation have shown that the quantum fluctuations soften the structure of liquid water.[8] Quantum effects in water should then affect the structure in a similar way as temperature. An ambient pressure x-ray study seems to validate this interpretation.[21] On the other hand, another quantum *ab initio* calculation has reached the opposite counterintuitive conclusion that nuclear quantum effects harden the structure of the liquid water.[9] As shown in Fig. 4 (lower panel), the n_{OO} of D_2O is slightly greater than the n_{OO} of H_2O at a given P-T condition in the domain where the coordination number is strongly changing. Although this shift is smaller than the absolute uncertainty of the determination, it is significant in the relative difference between the two isotopes measured under exactly the same experimental conditions. The isotopic shift in the coordination number thus seems opposite to the one expected if one associates quantum effects with effective temperature effects. This isotopic comparison is thus quite surprising and invites a more definitive study.

The present x-ray data are certainly insufficient to give a full microscopic description of the structural evolution of water or to question the disappearance of the H bonding. However, n_{OO} measured for various P-T conditions is a direct experimental structural information that we can plot in Fig. 5 to visualize the phase diagram of liquid water. The data points are scattered over the whole phase diagram. A two-dimensional quadratic fit enables us to continuously interpolate between the data and a smooth evolution of n_{OO} is clearly observed. On the other hand, two spectroscopic studies: a Brillouin[22] and a Raman measurement,[23] have interpreted breaks in the evolution with density, of the sound velocity and of the Raman OH frequency respectively, as evidence of an abrupt transition from LDW to HDW, as guided by a theoretical calculation.[24] These pseudotransition lines are plotted in Fig. 4. The Brillouin transition line almost agrees with the limit of the domain where n_{OO} is smaller than 6. The Raman transition line does not seem to be correlated with any trend in n_{OO}, which could reflect the ambiguous interpretation of the Raman spectra.

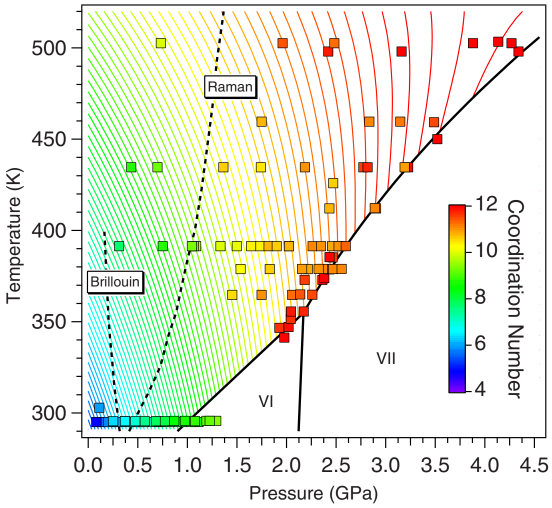

FIG. 5. (Color online) Phase diagram of water. n_{OO} is given by the color scale. The squares are the data points. The continuous and dashed lines indicate respectively the melting curve and a pseudo LDW to HDW transition line as measured by Brillouin (Ref. 22) and Raman spectroscopies (Ref. 23).

The x-ray structural measurements of water have been performed to cover the P-T domain of the change of water from a tetrahedral coordinated fluid to a compact fluid. The oxygen coordination number n_{OO} is directly obtained from x-ray data. Plotted as a third dimension in the phase diagram of water, it shows that the structural evolution of water is continuous, with the oxygen coordination number going from 4 to 12 over a fairly small density range, hence not associated to a first order transition from the LDW form to the HDW form of water. The quantum difference on $n_{OO}(P)$ between H_2O and D_2O is observed opposite to the thermal effect, contrary to most predictions. Extending these structural measurements to probe the transition from the normal molecular liquid, with a coordination number near 12, to the conducting astrophysical fluid, associated with dissociation and ionization effects, should now probably be within the reach of a similar synchrotron/DAC approach.

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