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Direct Raman Evidence for a Weak Continuous Phase Transition in Liquid Water

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This paper presents the Raman depolarization ratio of degassed ultrapure water as a function of temperature, in the range 303.4−314.4 K (30.2−41.2 °C). The pressure of the sample was the vapor pressure of water at the measurement temperature. The data provide a direct indication of the existence of a phase transition in the liquid at 307.7 K, 5.8 kPa (34.6 °C, 0.057 atm). The minimum in the heat capacity, C_p, of water occurs at 34.5 °C, 1.0 atm (*J. Res. Natl. Bur. Stand*. **1939**, *23*, 197[1]). The minimum in C_p is shallow, and the transition is a weak-continuous phase transition. The pressure coefficient of the viscosity of water changes sign as pressure increases for temperatures below 35 °C (*Nature* **1965**, *207*, 620[2]). The viscosity minimum tracks the liquid phase transition in the P, T plane where it connects with the minimum in the freezing point of pure water in the same plane (*Proc. Am. Acad. Arts Sci.* **1911−12**, *47*, 441[3]). Previously we argued (*J. Chem. Phys.* **1998**, *109*, 7379[4]) that the minimum in the pressure coefficient of viscosity signaled the elimination of three-dimensional connectivity in liquid water. These observations coupled with recent measurements of the coordination shell of water near 300 K (*Science* **2004**, *304*, 995[5]) suggest that the structural component that changes during the phase transition is tetrahedrally coordinated water. At temperatures above the transition, there is no tetrahedrally coordinated water in the liquid and locally planar water structures dominate the liquid structure. Water is a structured liquid with distinct local structures that vary with temperature. Furthermore, liquid water has a liquid−liquid phase transition near the middle of the normal liquid range.

1. Introduction

The structure of liquid water has generated considerable discussion but no consensus.[6−10] Models of liquid water with some level of local structural order[7,8] have appeared recently. Random network models represent one widely held view[9] of water. A mixture model with three-dimensional detail in the structure of each of the mixture components presents a quite different view of the same subject.[10]

Our approach to the underlying chemical structure of liquid water is based on three components. These are the following: (1) the packing density of the liquid structural components[4] as compared to the density of the liquid; (2) a dynamic equilibrium between these components as either temperature or pressure change; and (3) the heat capacity of the liquid,[1] C_p. The packing density approach was first used by Claussen[11a] and later adopted by Pauling and others.[11b,c] We extended the earlier packing density analysis[11a] to lower and higher temperatures.[4]

A weak continuous phase transition in water was located[12] using nuclear magnetic resonance (NMR) chemical shifts of cations and anions as a function of concentration in solutions of univalent electrolytes. The NMR evidence required extrapolation to zero ion concentration to give the transition in pure water.[12] A phase transition in liquid water at 307.6 K (34.5 °C), the minimum in the heat capacity of liquid water at 1 atm[1] requires the existence of local organized chemical structure in the liquid on both sides of the transition. This finding has broad implications for the study of chemical reactions in water. The electron delocalization that occurs through hydrogen bonds[13] organizes the liquid structure.

The NMR studies also have implications for the structure of solutions of univalent electrolytes.[14−16] The NMR experiments studied the chemical shift as a function of concentration. They found that in every case a plot of chemical shift against concentration showed a change in slope and intercept at the concentration where the specific heat minimum of the electrolyte solution corresponded to 298 K, the temperature of the experiment. The break in the chemical shift vs concentration plots is a signature for a phase transition occurring in the system at the corresponding temperature. The message for the structure of aqueous solutions is that water retains its structure in aqueous solutions of electrolytes. It does not become a devoted solvent shell structure for the ions dissolved in it.

Infrared[14] and Raman[15] spectroscopic studies of the structure of aqueous solutions have concluded that aqueous solutions of univalent electrolytes are composed of islands of pure water and islands of liquid crystalline electrolyte hydrates. This model is quite different from the Debye−Hückel model of aqueous solutions, which was founded on the mistaken use of kinetic data (conductivity based activity coefficients) in an equilibrium analysis (the equilibrium structure of dilute ionic solutions).[16] In the Debye−Hückel model, each addition of electrolyte disrupts the structure of water. In the model of aqueous solutions developed from vibrational spectroscopy, the structure of water remains intact, though its density changes[17] as does the position of the specific heat minimum.[12] This latter model is consistent with the observation of a weak continuous phase transition in aqueous solutions. This phase transition, extrapolated to zero electrolyte concentration, appears at 307.6 K (34.5 °C), 1 atm.

Cunningham and Lyons reported the Raman depolarization ratios for liquid water as a function of temperature in 1973.[18] The plotted values[18] are quantitatively different from the data below.

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The original report covered the temperature range 0−100 °C in 20 measurements.[18] With this coarse grain, it would not be possible to identify an isolated feature that is less than 0.2 K wide. The closest measurement of the depolarization ratio to the feature expected at 307.6 K was at 314.1 K[18] (41 °C), the original authors had no way to detect the transition.

A careful examination of the water depolarization ratio reported in 1973 shows significant differences with the data reported here for 41.1 °C (314.2 K). The largest difference is low values in the original report in the wavenumber range 3000−3200 cm^{-1}. We previously found this behavior in the depolarization ratio for water samples that were not thoroughly degassed. The same is true for the relatively low wavenumber cut off for the depolarization data (∼3100 cm^{-1} vs 3800 cm^{-1} for degassed samples).

In our experiments, we found it impossible to obtain reproducible results with samples that had the slightest connection to the atmosphere. Our original degassing procedure involved treatment at high power in an ultrasonic bath for 20 min, followed by capping the vial and temperature equilibrating the sample. The depolarization ratio, ρ ($\rho = I_{\perp}/I_{||}$), varied substantially when it was measured under conditions involving a degassed tube with stopper seal to the atmosphere. Similarly, in the temperature range near 307.6 K the depolarization ratio showed differences from the values at 307.6 ± 1 K, but not reproducible ones.

Raman spectroscopy is a powerful tool for the study of phase transitions.[19,20] In the liquid to glass phase transition in thin films of polystyrene, the intensity of the parallel-polarized scattering was greater than the intensity of the perpendicular-polarized scattering, just as for water (see below) and most other materials. The depolarization ratio for the transition in polystyrene showed a sharp trough feature at the transition. This is only one of many studies in the recent literature that have used Raman depolarization ratios to gather details on phase transitions.

2. Methods

We use a J. Y. Horiba Lab Ram HR 800 Raman spectrometer equipped with a Coherent I-308 Argon Ion laser operating at 488.0 nm and 250 mWatt. The spectrometer was configured for backscattering, which provided a 1 cm path length in the 1 cm Spectrosil cell. Optima, ultra-purified water, filled the cell. We flame sealed the cell, while pumping it with a mechanical vacuum pump protected by a liquid nitrogen trap. The sample had previously been ultrasonically degassed, and reduced in volume by ∼10%. Temperature control tubes surrounded the sample holder. A circulating thermostatic bath held temperature constant to less than ±0.1 °C. A thermocouple inserted in an external water-filled well below the water level in the cell measured the water temperature.

During the period when we were attempting to degas our samples with ultrasound, we recorded numerous scans of the depolarization ratio for water that were similar to the report of Cunningham and Lyons.[18] The reproducibility of the experiments was always below the standard that we expected from other work. As a result, we adopted the procedure described above. Dissolved gas in water is contained in a hydrophobic pocket lined with structured water. Some of the water molecules in these structures have two strong donor hydrogen bonds and contribute to the polarized Raman intensity in the region 3000−3600 cm^{-1}.

3. Results

The apparent sensitivity of the water Raman depolarization ratios to the presence of trace quantities of gases, presumably oxygen, provided a major stumbling block for collection of these data for pure water. Figure 1 presents the Raman depolarization ratio for water as a function of wavenumber and temperature. Figure 2 shows the unpolarized and polarized Raman intensities as a function of temperature, for the OH stretch region of the spectrum. The individual plots of $I_{\perp}$ and $I_{||}$ (Figure 2b,c) show the origins of the sharp feature in Figure 1.

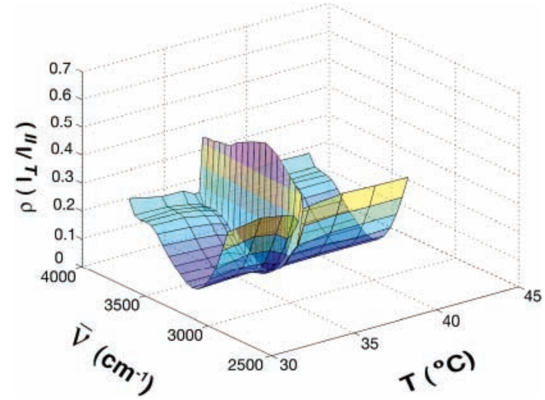

Figure 1. Raman depolarization ratio in the OH stretch region for pure water as a function of temperature and wavenumber. The spike at 34.6 °C indicates a phase transition in the liquid.

Figure 2a illustrates the change in Raman intensity with temperature. The intensity change with temperature tracks the change in the characteristic length associated with the phase transition.[21] The characteristic length of the phase increases when approaching the critical temperature from either higher or lower temperatures. The symmetric vibrations that give rise to the parallel-polarized intensity, probably involve only three water molecules, because X-ray spectroscopy shows only one strong donor hydrogen bond in the coordination shell of liquid water[5] at these temperatures. As the characteristic length increases from either low or high temperature, the change in polarizability of the symmetric vibration on vibrational activation decreases, and $I_{||}$ decreases. The nonsymmetric (perpendicular-polarization) vibration only requires one strong donor and one strong acceptor hydrogen bond per water molecule. The nonsymmetric intensity increases strongly with an increase in characteristic length from lower to higher temperatures. The same class of vibrations decreases in intensity, though not strongly, in proceeding toward the critical temperature from higher temperatures (Figure 2b.) Smaller organized water structures must be involved in the nonsymmetric vibration on the high temperature side of the transition than on the low temperature side. Previously we had suggested that these structures might include square arrangements of water.[4]

Figure 1 points to a phase transition that is sufficiently subtle that it has escaped notice until recently. The existence of this transition requires the existence of local chemical structure in liquid water that is different on both sides of the transition. The homeostatic temperature for mammals occurs curiously close to this transition (on the high side), as does the maximum in the sea surface temperature in the tropics (on the low side).

A relaxation time for the structure of liquid water must be associated with equilibrium establishment for the liquid structure on either side of this transition. These relaxation times have not been determined.

4. Discussion

One of the fascinating questions concerning the liquid−liquid phase transition for water reported here is, what are the structural features associated with this transition? It may be hard to believe

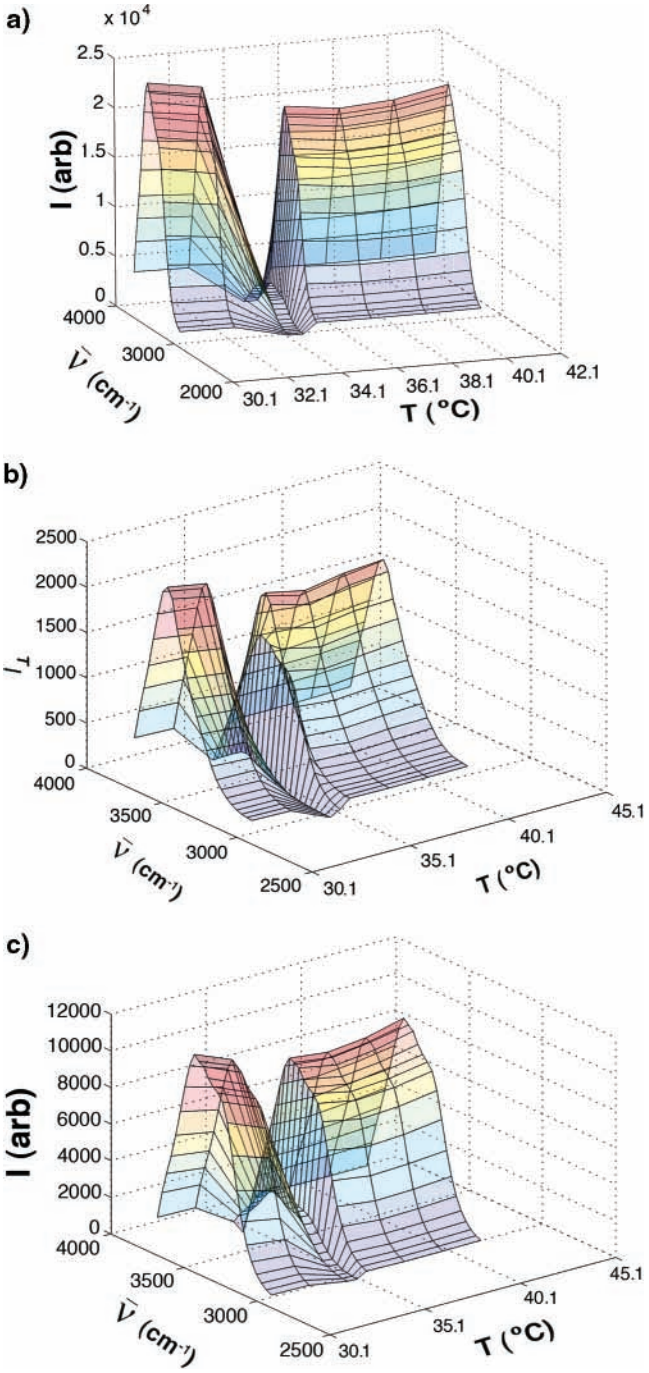

Figure 2. Raman intensities (arbitrary units) (a) unpolarized, (b) perpendicular, and (c) parallel for the OH stretch region of water, as a function of temperature and wavenumber. (b) and (c) are the underlying data for Figure 1.

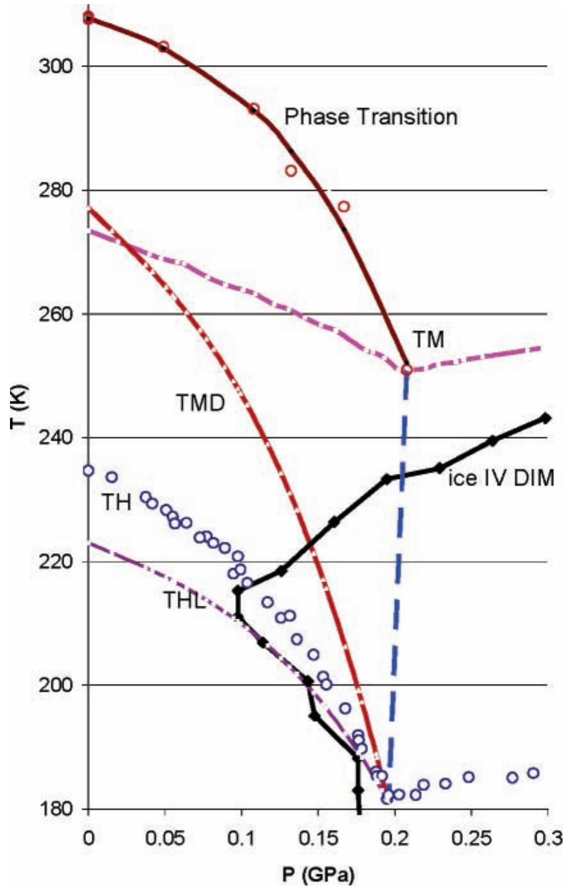

Figure 3. Pressure temperature properties of liquid water. Phase Transition: the line for the minimum in the pressure coefficient of viscosity,[2] data ~1 atm, this work. TM: melting temperature.[3] TMD: temperature of maximum density, extrapolated[24] from studies of D_2O.[25] TH: homogeneous nucleation temperature.[26] THL: theoretical limit for homogeneous nucleation based on the density of liquid disordered ice.[24] Ice IV DIM: Decompression induced melting curve for ice IV.[27]

that evidence of this transition was in the literature approximately forty years ago,[2] but not recognized as such. In 1965, Bett and Cappi reported observation of a negative pressure coefficient for the viscosity of water at temperatures below 33.5 °C, and a positive pressure coefficient for the viscosity at all temperatures from 50 °C up. The small discrepancy between their extrapolated value for the transition at 1 atm, 33.5 °C, and the minimum in C_p at the same pressure,[1] 34.5 °C, reflects extrapolation error. A change in the sign of a transport coefficient is a marker for a critical point.[23] The critical point in this case is the line of continuous (second-order) phase transitions in the liquid. Figure 3 illustrates a plot of the minima for the pressure coefficient of viscosity in the Bett and Cappi data,[2] along with a collection of other data that is relevant to the structure of liquid water as a function of temperature and pressure.

It is interesting that the weak-continuous phase transition in liquid water appears to connect with the minimum in the freezing temperature of the liquid as a function of pressure. If this conjecture is correct, the triple point for water, ice I_h, and ice III at 251 K, 0.207 GPa[3], is actually a quadruple point. Water exists in many distinct solid forms;[3] it should not be surprising that the presence of the solids correlates with different structures in the liquid.

The negative pressure coefficient of viscosity for water at temperatures below 307.6 K, 1 bar suggests that increasing pressure in effect removes a three-dimensional component from the liquid. That component is most likely tetracoordinated, tetrahedral water. At temperatures just below 307.6 K, X-ray evidence indicates that the number of tetrahedral water molecules in liquid water is small.[5] The change to a zero concentration above 307.6 K, 1 bar would account for both the variation in the pressure coefficient of viscosity and the weak continuous phase transition in the liquid.

Figure 4 illustrates the location of the liquid−liquid phase transition in water with reference to the *PVT* surface of the liquid. The precise relationship between the liquid−liquid transition line illustrated in Figures 3 and 4 and the corresponding solid−solid phase transition lines that underlie the liquid,[3] remain to be elucidated.

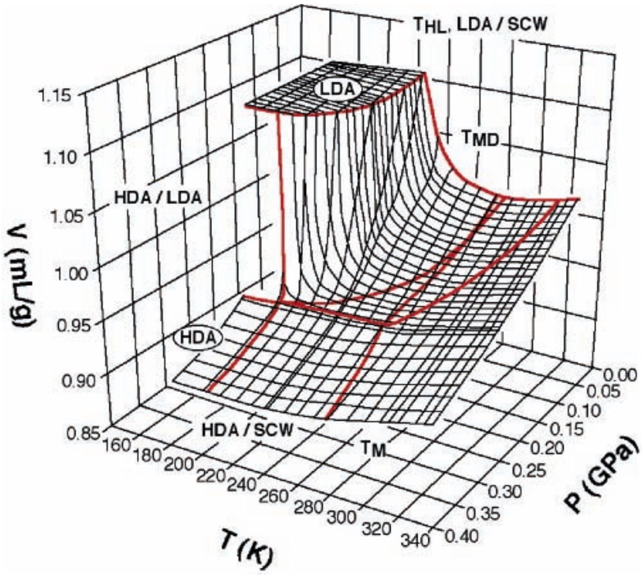

Figure 4. *PVT* surface for liquid water.[24] The curved red line at the highest temperature is the liquid−liquid phase transition. This line continues as a straight line from the minimum melting temperature to the predicted tricritical point at 0.195 GPa, 182 K.[24] Acronyms: LDA, low-density amorphous water (glass); HDA, high-density amorphous water (glass); TM, melting temperature; TMD, temperature of maximum density; SCW, supercooled water; T_{HL}, theoretical limit of the homogeneous nucleation temperature.

There should be a weak continuous phase transition in D_2O at ~100 °C, the minimum in C_p for D_2O.[11c] We expect that there will also be a weak phase transition near 256 K for supercooled liquid H_2O (~252 K, D_2O).[11c,22] At this temperature, the slope of the liquid H_2O heat capacity with temperature changes substantially. Below 256 K the slope is roughly −1.5 J/(mol K). At higher temperatures, below 273 K, the slope is roughly −0.15 J/(mol K).

Molecular dynamics and Monte Carlo models[7−9] probably will not be capable of demonstrating the structural features of liquid water that lead to this phase transition unless the molecular orbital potentials that are used can properly represent electron delocalization over approximately six or more water molecules.

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Supporting Information Available: The data used to prepare Figures 1 and 2 are available (PDF) free of charge via the Internet at http://pubs.acs.org.

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