Pressure- and temperature-dependent structural change in liquid water

Benefits at a glance
- Non-contact analysis of a system at elevated temperature and pressure in a diamond anvil cell
- Monitoring of a phase transition in a liquid

Introduction

Despite being arguably the most important chemical compound in the universe as a result of its vital role in biology and ecology, much about water is still not completely understood. In particular, the structural forms of liquid and solid water are still being elucidated. As of this writing, 18 polymorphs of ice are known, including the hexagonal form normally found at ambient temperatures and pressures, and a cubic form found at extremely low temperatures. In addition to these, liquid water, including its glass forms, also exhibits polymorphism. Neutron-diffraction studies have shown that a polymorph known as low-density water (LDW) changes gradually to a second polymorph called high-density water (HDW) with increasing pressure. However, these studies were carried out at low temperature and pressure (−5 °C and 0.02 to 0.4 GPa). Classical molecular dynamics simulations indicate that this phase transition may take place at temperatures up to 127 °C. This note describes the use of Raman spectroscopy to follow a structural change in liquid water under high temperature and pressure.[1]

Experimental

Milli-Q water was placed in an externally heated diamond anvil cell with a rhenium gasket and continuously compressed in a gearbox. Pressure was monitored by measuring fluorescence from small ruby chips placed in the gasket with the water resulting in a precision better than 0.1 GPa. Temperature was controlled with thermocouples attached to the diamonds. Raman spectra of the water were acquired using a Raman analyzer with 532 nm excitation radiation at an exposure time of 15 seconds. The Raman bands corresponding to the O–H stretching of water were analyzed by subtracting a linear baseline between 2800 and 3800 cm^{-1} and fitting the remaining feature to two Gaussian curves, optimized for height and position by a least-squares method.

Results

Of the two bands isolated by the curve fitting, the lower-frequency band is assigned to hydrogen-bonded H_2O molecules of an undetermined configuration and the higher-frequency band is assigned to less associated molecules. At constant temperature, the Raman intensity of the lower-frequency band increases with increasing pressure, indicating that as pressure increases, so does hydrogen bonding (Figure 1).
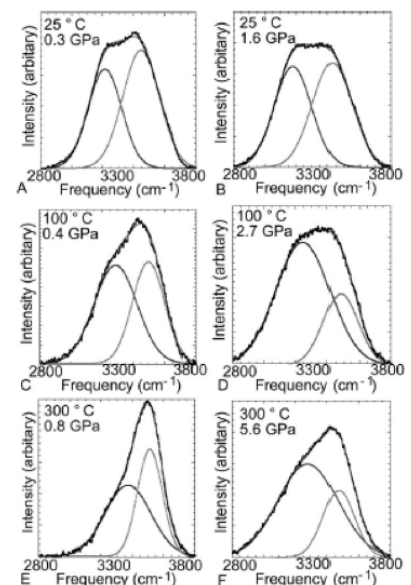

Figure 1: Band analysis of Raman spectra of water. *(Reprinted with permission from Ref. 1. Copyright © 2004 American Institute of Physics.)*

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

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The frequencies of the peaks also vary, increasing with increasing temperature and decreasing with increasing pressure. This indicates that the strength of the hydrogen bonding increases with increasing pressure and decreases with increasing temperature, which correlates well with the results and interpretation of the Raman intensity data described above. Significantly, there are discontinuities in plots of the Raman frequency versus pressure and Raman frequency versus density (Figure 2). These discontinuities may be interpreted as a structural change in the water from what can be referred to as "sparse water" at higher temperatures and lower pressures and "dense water" at lower temperatures and higher pressures. Another possible explanation is that this change could result from Fermi resonance between the stretching vibrational mode and
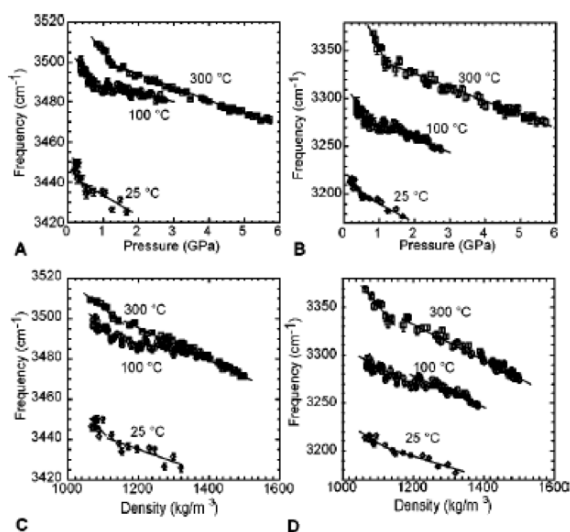

Figure 3: Phase diagram for water showing the boundary between sparse water and dense water. *(Reprinted with permission from Ref. 1. Copyright © 2004 American Institute of Physics.)*

Figure 2: Pressure- and density-dependence of the frequencies of the O–H vibration Raman bands in water. *(Reprinted with permission from Ref. 1. Copyright © 2004 American Institute of Physics.)*

the bending overtone without a structural change. Since the bands move further away from each other in the frequency domain as pressure increases, this explanation seems unlikely. Hydrodynamic ultrasonic velocity data also support the structural change explanation.[1]
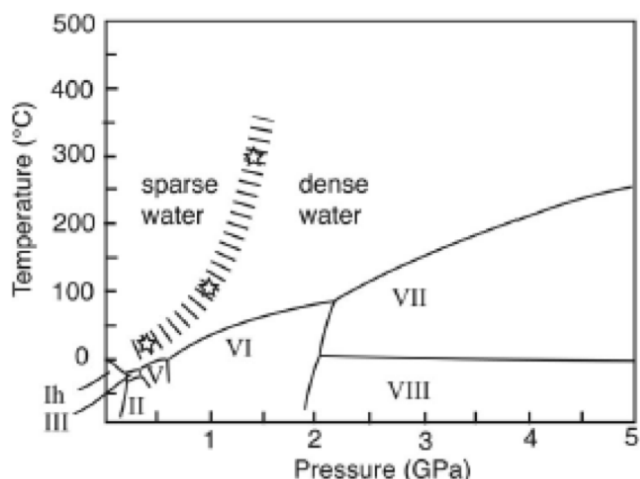
The phase change appears to occur gradually, so the boundary between sparse water and dense water in the phase diagram is not sharp, as are the boundaries between the different polymorphs of ice, but is less defined (Figure 3).

Conclusion
Raman is often lauded for it's avoidance of interference by water in aqueous solutions. Raman has a very weak cross-section across much of the useful spectral range. However, the O–H stretching bands, which lie near the high-wavenumber extreme in Raman spectra, are rich in information about the structure of water. The ratios of the two bands in the $2800–3800 \text{ cm}^{-1}$ region can be used to determine the extent of hydrogen bonding in the system. Because Raman spectroscopy can be used in a non-contact mode, data can be acquired easily on a pressurized system in a diamond anvil cell.

Reference
1. Kawamoto, T., Ochiai, S., and Hiroyuki, K. "Changes in the structure of water deduced from the pressure dependence of the Raman OH frequency." *Journal of Chemical Physics*, Vol. 120, No. 13, **2004**, 5867.

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