Spontaneous Raman Scattering from Shocked Water

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The OH-stretch Raman band of liquid water has been observed for the first time at high pressures and temperatures. A new single-pulse spontaneous Raman technique was used to obtain spectra from H_2O shocked up to 26 GPa and 1700 K. Band-shape changes over the range 7.5–26 GPa are fitted well by a two-component mixture model. Intermolecular hydrogen bonding, dominant at 12 GPa, is nearly absent at 26 GPa. The spectra indicate that transport of H^+ and OH^- ions is most probably the mechanism for the electrical conductivity of shocked water.

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Water continues to be one of the most extensively studied molecular systems at high pressures because of its multiplicity of structures due to intermolecular hydrogen bonds. Ice X, the symmetric ice structure, was detected recently at 44 GPa in a diamond-anvil cell by Brillouin scattering.[1] Amorphous ice was recently synthesized by means of pressurizing ice I at 77 K to its extrapolated melting point at 1 GPa, which is below the glass transition temperature.[2] Strong shock waves produce both high pressures and high temperatures, allowing the study of H_2O in its liquid state at high pressure. Previously, only bulk properties of shocked water have been measured; see Mitchell and Nellis,[3] and references therein. The development of spectroscopic probes of shocked materials means that the nature of condensed matter at high dynamic pressures can now be investigated on a molecular level. Recently, stimulated Raman scattering was used to measure the frequency shift of the ν_1 symmetric-stretch mode of benzene shocked to 1.2 GPa.[4] We have developed a fast, single-shot, broad-band spectrographic system to obtain spontaneous Raman spectra of liquids shocked to pressures limited only by the optical transparency of the shocked specimen, which for water is over 30 GPa.[5]

Our goals were to determine the chemical species present in H_2O at extreme conditions of pressure and temperature and the mechanism responsible for the high electrical conductivity of shocked water. Between 3 and 30 GPa the electrical conductivity of shocked H_2O increases by more than five orders of magnitude,[6,7] saturating at about 20 $(\Omega\text{-cm})^{-1}$ between 30 and 60 GPa.[3] Hamann and Linton proposed that water becomes fully ionized to H_3O^+ and OH^- at 15–20-GPa shock pressure[8] and that transport of these ions would account for the observed conductivity. This is the same mechanism as in liquid water at ambient conditions[9] but much enhanced by the high temperatures and densities. To test this hypothesis, we chose to observe the OH-stretch vibration using spontaneous Raman scattering because of its high inherent bandwidth and because almost all Raman spectroscopic studies of H_2O have used spontaneous scattering. Thus the results can be more easily compared to the available literature. The presence of H_3O^+ and OH^- ions has been unambiguously determined under ambient conditions in observations of the OH-stretch region in strong acids and bases by both Raman[10] and infrared techniques.[11]

Strong shock waves were generated by planar impactors accelerated to 2.1–3.2 km/s by a two-stage light-gas gun.[12,13] Water specimens initially at 20 °C and atmospheric pressure were contained in Al holders. Target and impactor dimensions were chosen to allow uniform, steady shock waves to propagate through the entire specimen free of shock-wave attenuation and edge-rarefaction effects. Since the duration of these experiments is about 10^{-6} s, a fast, single-shot spectrographic system was required.

An unpolarized KrF laser [248 nm, 0.2 J, 10-ns pulse width (FWHM)] was used to excite the Raman spectrum. The laser beam was aligned collinearly with the axis of the specimen holder and the impactor, and entered the water cell through a *z*-cut, α-quartz window with no detectable fluorescence. Raman-scattered light, exiting from the cell through the quartz window, was collected at 45° to this axis with a fused-silica lens. The lens was focused to form an image, on the slit of an $f/4$ 0.3-m–focal-length flat-field spectrograph, of a region 3.5 mm behind the shock front with a volume of about 10^{-4} cm^3. Trigger pins installed in the target provided timing signals for the laser and data recording system. The spectra were recorded with a 1024-element gated and intensified linear-diode-array detector. Spectral resolution was 15–20 cm^{-1}, limited mainly by the KrF-laser bandwidth.

TABLE I. Experimental conditions for five spontaneous-Raman experiments in shocked H_2O. Shock pressures and densities were calculated with use of shock impedance matching. Calculated temperatures are from Ref. 17.

Shot No.	Impactor	Impactor velocity (km/s)	Pressure (GPa)	Density (g/cm^3)	Calculated temperature (K)
Raman 8	Al	2.1	7.5	1.56	640
Raman 9	Al	2.88	11.7	1.71	840
Raman 11	Ta	2.90	21.9	1.94	1480
Raman 12	Ta	2.86	21.4	1.93	1460
Raman 13	Ta	3.23	25.7	2.00	1710

Shock pressures in the experiments were obtained by shock impedance matching,[14] with use of the equations of state for impactor, base plate (Al), and water.[3,15,16] Data for five experiments are summarized in Table I along with calculated shock temperatures.[17] In all cases the water was in the liquid state according to the ice-VII melting curve.[18]

The OH-stretch spectrum of H_2O shocked to 7.5 GPa and 640 K is compared in Fig. 1 to unshocked water at ambient conditions and to the data of Lindner[19] for statically compressed and heated water at 0.4 GPa and 670 K. The shocked-water spectrum differs from the static data in the low-frequency region, and scattering is dramatically enhanced in this region compared to Lindner's spectrum, at nearly the same temperature. Lindner proposed that his data provided evidence for the destruction of intermolecular hydrogen bonds, consistent with the work of Walrafen.[20] This interpretation is based on a mixture model of liquid H_2O, which postulates that the wide OH-stretch band arises from the superposition of scattering from spectroscopically distinguishable classes of molecules. One class is strongly hydrogen bonded in tetrahedral clusters of C_{2v} symmetry through linear O–H$\cdot\cdot\cdot$O bonds. The strong intermolecular coupling results in a lowering of the OH-stretch frequency for those molecules. The second class is thought to be weakly bonded[21] or essentially free, monomeric water.[20] These molecules have a slightly higher OH-stretch frequency. Studies of ice VII indicate an inverse correlation between the O-O distance and the intramolecular O-H distance.[22] As the O-O distance decreases with compression, the frequency of the components is expected to decrease as the O-H length increases and the force constant between them weakens.

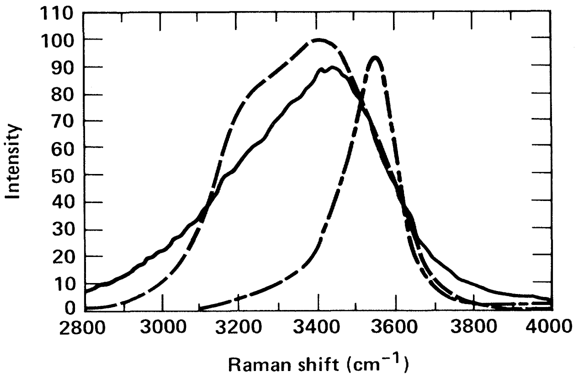

FIG. 1. Comparison of spontaneous Raman spectra of OH-stretch band of liquid H_2O for static and shock conditions. Dashed curve is spectrum for water at ambient conditions. Long-dashed–short-dashed curve is a static spectrum from Lindner (Ref. 19) at 0.4 GPa and 670 K. Solid curve is the spectrum of shocked water at 7.5 GPa and 640 K.

Since the broadening mechanisms for the vibrational spectra of water molecules lead to inhomogeneous broadening, we used a least-squares technique[23] to decompose the Raman spectra into Gaussian components. A two-component fit is found to agree very well with all of the shocked H_2O spectra. The quality of the fits is shown in Fig. 2 and summarized for five experiments in Table II. We interpret the lower-frequency component to be from strongly hydrogen-bonded H_2O and the higher-frequency component to be from monomeric water. The fraction of the total scattering in the lower-frequency component is plotted versus pressure in Fig. 3. In the figure, we see that strong hydrogen bonding persists to 12 GPa, and then diminishes to zero at about 26 GPa. At the highest pressure the band consists almost entirely of a single Gaussian component of width 415 cm^{-1}. This width is explained by a distribution in bond lengths and angles under shock conditions and by collisional effects.[24] The frequency is about 200 cm^{-1} lower than for monomer water under ambient conditions. This shift is due to surrounding water molecules, but interacting through electrostatic forces on the asymmetric H_2O molecule, rather than through the partially covalent linear hydrogen bonds. These electrostatic forces act on all water molecules and at high compression can produce a large shift in the average frequency of the OH-stretch vibration. The complex structure near the peak of the OH-stretch spectrum observed at

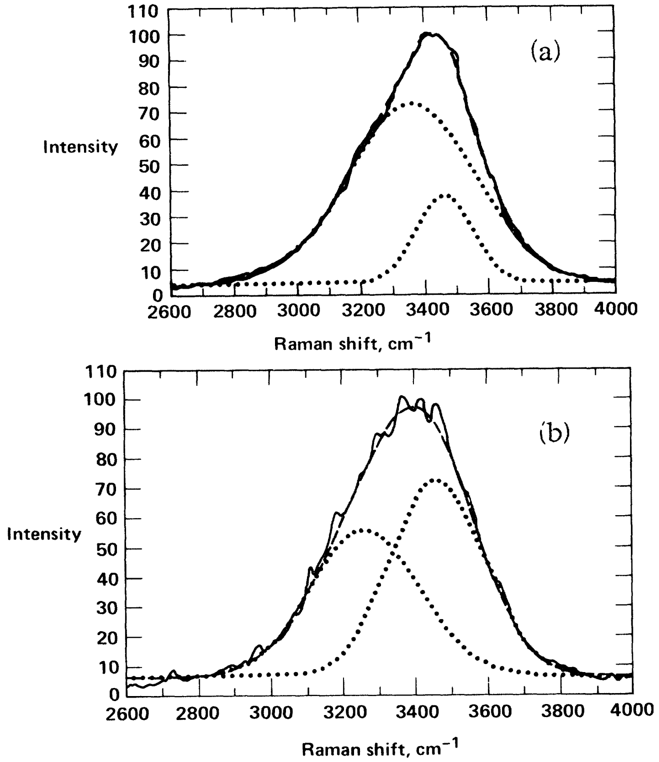

FIG. 2. Spectra for experiments at (a) 11.7 and (b) 21.9 GPa are compared with two-component Gaussian fits. The solid line is the experimental data, the dotted curves are components, and the dashed curve is their sum.

or near ambient conditions, which has been attributed to Fermi resonance effects,[21] is not observed in our shock data. We cannot distinguish separate contributions from H_2O molecules and OH^- ions. Intermolecular forces may perturb the OH^--stretch frequency enough to cause it to overlap the H_2O spectrum, or a change in the character of the O-H bond under strong compression to a more ionic character in a way similar to that proposed for symmetric ice VII[22] or for ice X[1] may be responsible.

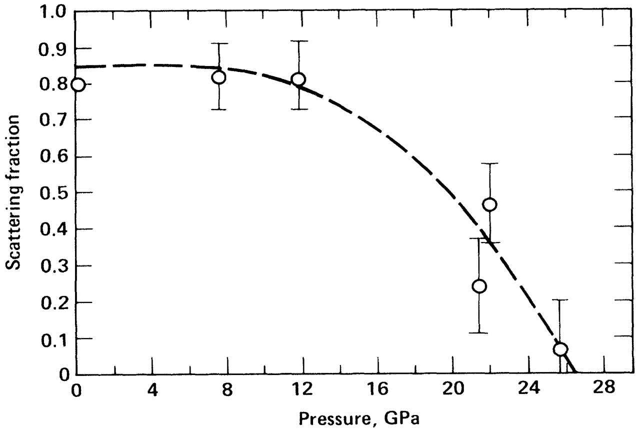

FIG. 3. Variation in integrated scattering fraction in lower-frequency component vs pressure.

The prevailing view of the conductivity of H_2O is that conduction occurs by the rapid transfer of charge through molecular complexes of the form $H_9O_4^+$ and $H_7O_4^-$,[9] or more simply through the motion of the "transient" ionic species H_3O^+ and OH^-. This model accounts very well for water at or near ambient conditions. At high shock pressures where conductivity is highest, however, the hydrogen-bonded structures contributing to the conductivity are absent, so that this process is unlikely to be important. If H_3O^+ existed in significant concentrations in our experiments, as might be expected from extrapolations of ionic-product data,[25] we would expect a strong, broad band centered at 2900–3000 cm^{-1}.[10,11] No conclusive evidence for such a band is found in our data. The alternative is that the conductivity proceeds through the transport of H^+ and OH^- ions. The mobility of protons is very high, even at elevated temperatures,[26] and at high concentrations could account for the measured conductivity. Electronic contributions to the conductivity of shocked H_2O can be ruled out on the basis of our observations of strong Raman-scattering signals for pressures of 21 GPa. With use of the measured electrical conductivity of shocked H_2O at 21 GPa, the electronic

TABLE II. Results of two-component Gaussian decompositions for OH-stretch spectra of shocked H_2O. Spectra were scaled to maximum value of 1.0; center frequencies and widths (FWHM) for each component are given by ν and $\Delta\nu$, respectively.

	Component 1			Component 2			
Shot No.	I	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	I	$\Delta\nu$ (cm^{-1})	ν (cm^{-1})	rms fit error (%)
Raman 8	0.62	490	3345	0.43	208	3479	1.1
Raman 9	0.68	466	3358	0.33	208	3461	1.2
Raman 11	0.49	353	3260	0.66	300	3462	2.1
Raman 12	0.36	240	3185	0.84	325	3423	1.8
Raman 13	0.14	166	3241	0.72	415	3426	3.7

skin depth at 284 nm is roughly 0.3 μm, far too short to account for Raman-scattered light observed from 3.5 mm behind the shock front.

In conclusion, we have observed the behavior of the OH-stretch vibrational band in liquid water up to 26-GPa shock pressure and 1700 K by spontaneous Raman scattering behind the shock front. The spectra show that the OH vibration persists to 26 GPa. Compelling evidence is found that strong intermolecular hydrogen bonds persist to 12 GPa; these bonds diminish above that pressure and are essentially absent at 26 GPa. The excellent agreement of two-component fits to the spectra at all shock pressures confirms the validity of a two-component mixture model of liquid H_2O at high pressures and temperatures. No evidence for the hydrated proton H_3O^+ was observed. On the basis of these data, we conclude that the mechanism most probably responsible for the high electrical conductivity of shocked water is the dissociation of water into H^+ and OH^- ions.

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