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RAMAN SPECTROSCOPY OF SHOCKED WATER

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Raman scattering has been used extensively to study the vibrational and rotational properties of molecules under a variety of conditions. Here our interest is in the behavior of water molecules shocked to high pressures and temperatures. Behind the shock front the water molecules undergo changes in bonding and the molecules may become ionized.¹ Raman spectroscopy can be used to determine the molecular species behind the shock front. In addition, changes in Raman spectra can yield information regarding inter- and intramolecular potentials and the temperature behind the shock front.

Raman scattering occurs as a result of the differential polarizability of molecules with respect to the inter-atomic separation. The effect is that light incident upon a molecule can excite molecular vibrations. For incident light at ν_i and a molecular vibrational frequency ν_0 , scattered light is observed at $\nu = \nu_i \pm \nu_0$. The process for which photons of frequency $\nu_i - \nu_0$ are emitted is termed Stokes scattering and anti-Stokes scattered photons have frequency $\nu_i + \nu_0$. For weak photon fields the effect is linear in intensity and very weak (cross-sections on the order of 10^{-29} cm² are typical) and is called spontaneous Raman scattering. When the incident intensity

is large the process is non-linear and stimulated Raman scattering occurs. Stimulated Raman backscattering experiments have been performed recently on shocked benzene.² Our interest is in spontaneous scattering. This is an inherently broadband technique which lends itself to study of the OH-stretch band in water which can be up to $\sim 1000\text{ cm}^{-1}$ wide. Also, spontaneous scattering does not significantly effect the vibrational thermal equilibrium, allowing it to be used for the determination of temperature.³

In our experiments we have observed the OH-stretch band in H_2O shocked to 7 GPa and a temperature of $\sim 370^\circ\text{C}$.^{4,5} The two-stage light-gas gun at LLNL was used to generate the shock wave in liquid water initially at 25°C and atmospheric pressure. A frequency-doubled Nd:glass laser at 532 nm was used to excite the shocked sample. Stokes radiation emitted at a 90° angle to the exciting laser beam was collected by an $f/2$ achromatic lens which imaged the sample volume onto the slit of an $f/3$ flat-field 0.25 m spectrograph. A micro-channel plate image intensifier was installed at the focal plane of the spectrograph to increase the brightness of the spectrum which was recorded on film. A spectrum is shown in Fig. 1. The broad peak above a continuum is the observed OH-stretch band in H_2O . The measured width is 690 cm^{-1} . The narrow line is the input laser radiation at 532 nm and the broad continuum, observed in all experiments, is believed to arise from radiation emitted by hot gas compressed on the baseplate of the target by projectile impact. The width of the band is significantly less than that observed in the same sample unshocked (904 cm^{-1}). The narrowing may be due to the breaking of weak hydrogen bonds between water molecules. These bonds are substantially responsible for the very wide OH-stretch band.⁶ We also observe a small ($+15\text{ cm}^{-1}$) increase in the Raman shift of shocked H_2O .

Fig. 1 Spontaneous Raman spectrum of water shocked to 7 GPa.

The experimental conditions for the spectrum shown were chosen for simplicity. That is, we wished to show feasibility of the technique and chose not to reach conditions of very high temperature and pressures for which anti-Stokes radiation or bands from ionized water molecules are expected. In future experiments we will investigate increasingly high shock pressures to attempt observations of these effects.

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