

Shock-front-stimulated optical scattering in water

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We have observed, for the first time, enhanced optical scattering off a picosecond laser pulse in water, under shock conditions. This enhancement is associated with the equilibration process characterizing the shock front. The observed signal from the shocked water samples qualitatively agrees with the calculated value based on the equilibration distance of the shock front.

I. INTRODUCTION

Shock waves can initiate chemical and physical changes in materials due to the increased pressure, temperature, and the large gradients associated with the shock front.¹ Shock waves are known to cause bond dissociation, phase changes, and the redistribution of energy among rotational, vibrational, and electronic states. Many of these phenomena are believed to take place or to be initiated in the shock front which can be on a picosecond time scale. The front of a mass-density shock wave, by virtue of its large area of constant large strain gradient, is capable of exhibiting local piezoelectric behavior due to the loss of inversion symmetry in the shock-front region.² That local piezoelectric behavior manifests itself as the "shock polarization" signals observed³ in diverse materials with impact loading experiments. The present theoretical understanding of the shock polarization signals for liquid water is described⁴ by a net statistical alignment of 1 in 10^4 water molecule electric dipole moments at 10 kbar (1 GPa) within a shock-front thickness of approximately 24 Å. Such a strong net alignment of dipole moments, although only within a thin sheet-like volume, can be viewed as highly correlated molecular polarization states. Such a situation gives rise to efficient laser scattering.⁵ Based upon the above shock-front picture, we have undertaken experiments designed to detect optical scattering from a mass-density shock front in water.

II. EXPERIMENTAL PROCEDURE

The shock waves were generated by focusing a 75-mJ, 30-psec, 1064-nm laser onto a 40- μ m-thick aluminum foil in contact with the water (see Fig. 1). The Al foil was bonded by a very thin layer of epoxy on a quartz plate. Separate measurements showed the epoxy layer to be essentially transparent at 1064 nm. A frequency-doubled 0.5-mJ, 25-psec, 532-nm laser pulse, focused by a 30-cm lens was used to probe the shock front. The probe beam was delayed approximately 30 nsec relative to the arrival of the 1064-nm beam (at the foil), so as to observe the water shock front after it emerges (~ 10 nsec) from the foil and before the shock amplitude decayed appreciably due to r^{-2} spreading (100 nsec). The shock duration (pulse width) is estimated⁶ to be of the order of 50 nsec. Parallel to the plane of in-

cidence optical polarization was employed throughout these experiments. Because of 1064-nm beam-induced damage to the aluminum foil, a different spot on the foil was employed each time that a shock was generated. The reflected and scattered light from the shock front was collected by a telescope and spectrally analyzed by a triple spectrograph. The first two stages of the spectrograph were zero dispersion $\frac{1}{4}$ -m (Spex) spectrometers which were used to eliminate the probe laser frequency. That was followed by an additional 1-m flat field spectrograph. The signal intensity was detected by an optical multichannel analyzer (OMA) II (Princeton Applied Research). The spectral range probed was from 50 to 500 cm^{-1} (on the Stokes side) from the laser probe frequency.

The experiments have demonstrated the existence of a shock-front enhanced intensity in the 50–500- cm^{-1} region. Based upon mechanical impedance matching and a knowledge of the shock pressures generated when the water is replaced by GaSe in a similar experimental configuration,⁶ we estimate that the shock pressures achieved were in the neighborhood of 5 kbar. A typical experimental spectral profile is displayed in Fig. 2. Each set of data was composed of a 1064-nm beam blocked event (the "no shock" curve of Fig. 2) followed by the 1064-nm unblocked shock enhanced signal. The salient difference between the two spectra, other than for the unshifted water shock-front-induced Fresnel reflectivity, is the increase in the light scattered by the shocked water sample. In addition the shocked spectra appear to have a broadband extending from 150 to 250 cm^{-1} . We consider that broadband to represent the ~ 175 cm^{-1} intermolecular hydrogen bond stretching mode of water.⁷

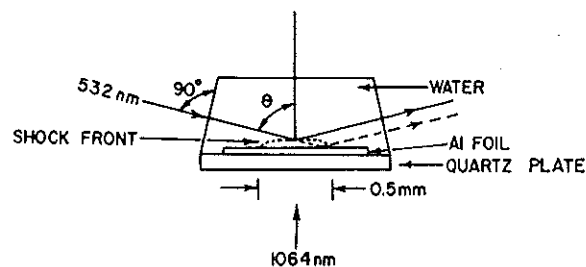


FIG. 1. Experimental arrangement for the generation of shock waves in water. The shock waves are generated by a 1064-nm laser pulse. The first harmonic 532 nm is used to probe the shock front.

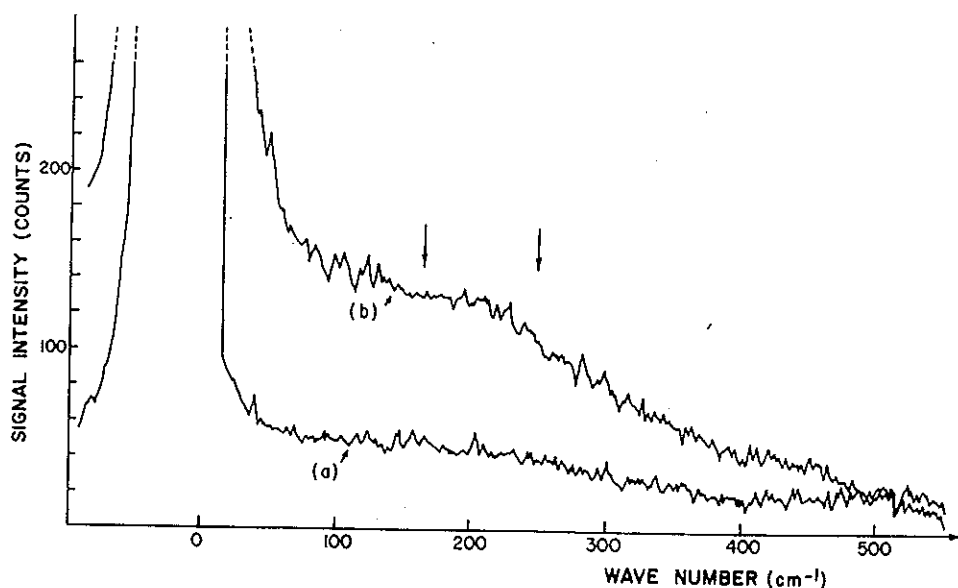


FIG. 2. Spectral profiles of the (a) unshocked and (b) shocked water samples, respectively. The two arrows denote the broadband around 200 cm^{-1} assigned to the intermolecular hydrogen bond stretching mode in water (see text).

III. DISCUSSION

It is possible to qualitatively understand the increase of the wing intensity in the presence of the shock front relative to the unshocked intensity through simple considerations. The ratio of the shocked to unshocked scattering intensities is given by⁵

$$\frac{I_s}{I_u} = \frac{V_s^*}{V_u^*} \frac{V_s}{V_u} \frac{\langle \Delta \epsilon_s^2 \rangle_{av}}{\langle \Delta \epsilon_u^2 \rangle_{av}} \quad (1)$$

where V is the scattering volume, V^* the fluctuation volume, $\Delta \epsilon$ the fluctuation amplitude of the permittivity, and the subscripts s and u denote shocked and unshocked, respectively. I_s is the intensity of the shock-front scattering process taken alone. For a probe beam diameter b and a total path length l in the water sample cell, $V_u = \pi b^2 l$. For a water shock-front thickness t and an optical angle of incidence θ (see Fig. 1) the shock-front-related scattering volume is given by $V_s = \pi b^2 t / \cos \theta$. The shock velocity at 5 kbar is $2.0 \times 10^5 \text{ cm/sec}$ so that the shock-front rise time⁴ of 1 psec gives $t = 20 \text{ \AA}$. Thus, for $\theta = 78^\circ$ and $l = 1 \text{ cm}$, $V_s/V_u = 9.5 \times 10^{-7}$. The shock front represents the equilibration distance for impressed strain. Within that distance the displacement of a molecule is directly influenced by the large strain-induced displacement of its neighboring molecules. Thus the fluctuation dimension within the shock front is 20 Å, and the fluctuation volume is $8 \times 10^3 \text{ \AA}^3$. In the unshocked sample the fluctuation dimension is expected to be of the order of the oxygen-oxygen separation or 2.7 Å. Thus, $V_s^*/V_u^* = 4.1 \times 10^2$.

Under shock conditions⁸ $\delta n \propto \delta \rho$ where ρ is the mass density. Because $\epsilon = n^2$, with n being the index of refraction $\langle \Delta \epsilon_s^2 \rangle_{av} / \langle \Delta \epsilon_u^2 \rangle_{av} \approx \eta_s^2 / \eta_u^2$ with η being the volume strain fluctuation. Let $\eta_u = (\delta x)_T / a$ where a is the oxygen to oxygen separation 2.7 Å and $(\delta x)_T$ is the thermally induced harmonic oscillator amplitude. For the reduced water molecule mass m (9 amu) at $\hbar\omega = 0.22 \text{ eV}$ (the $\sim 5 \text{ kcal/mol}$ hydrogen bond⁹ divided by Avogadro's number) $m\omega^2(\delta x)_T^2 = kT$ with $T = 300 \text{ K}$, yields $\eta_u = 5 \times 10^{-3}$. The

measured¹⁰ volume strain behind a 5-kbar shock front is 13%. Applying that value to the shock front, and assuming the shock front to be chaotic, results in $\eta_s = 0.13$. Consequently $\eta_s^2/\eta_u^2 = 5.4 \times 10^2$. Finally, Eq. (1) gives $I_s/I_u = 0.21$. The observed enhanced scattering in the shocked water cell includes scattering from the optical path available to the probe beam in the unshocked sample. Therefore, for a factor of 2 intensities $I_s + I_u = 2I_u$ or $I_s/I_u = 1$, which is to be compared with the derived value of 0.21. Insofar as I_s/I_u would be zero in the absence of shock-front-enhanced scattering we consider the agreement between theory and experiment to be good in light of the above simple considerations.

The experiments reported on here represent, as far as we know, the first time that nonclassical (e.g., distinct from Fresnel reflectivity) optical scattering signals have been associated with the equilibration process characterizing a shock front. The existence of such scattering enhancement should not be surprising; the $10^8 \text{ }^\circ\text{C/cm}$ temperature gradient characterizing a 5-kbar shock front in water^{4,10} is six orders of magnitude larger than those static gradients which result in observable¹¹ Brillouin scattering asymmetries. Further, in addition to the phonon flux associated with the temperature gradient, one expects the propagating mass-density (strain) gradient of the shock front to be an exceptionally strong source of an unbalanced phonon flux.¹² Such phonons are available for optical scattering.

There is a contribution to the total intensity at the spectrometer due to classical probe beam reflection from the shock.¹³ Such zero-frequency-shifted reflectivity signals do not affect the wing region and thus do not contribute to the effect under consideration here. Further, obtaining exactly the correct angle of incidence relative to the very small shock-front surface (for reflection into the spectrometer telescope) represents a very difficult probe beam focusing task. For that reason the shock-induced variation of the unshifted beam intensity, as well as the question of the total enhanced frequency integrated intensity, is not considered here.

The tail end of the shock pulse is still in the foil when the

probe beam interacts with the water shock front. It is thus necessary to rule out a possible aluminum foil contribution to the observed enhanced intensity. We have measured the wing of the reflectivity signal for the Al foil in air at 78° angle of incidence. The foil-air background signal is flat to within our signal-to-noise ratio, from 50 to 400 cm^{-1} and is estimated to be less than half of the normalized water-foil unshocked intensity background. The nonsignificance of a pressure-enhanced aluminum foil contribution is also supported by the experimental observation¹⁴ that away from the reflectivity versus wavelength minimum (800 nm for Al) pressure has negligible effect upon the total reflectivity. In addition, the compression in the foil at the water interface is less than 0.5% as compared to the 13% at the peak of the water shock front. The suggested identification of the near-200- cm^{-1} broadband as being associated with the 175- cm^{-1} intermolecular stretching mode of water is further evidence that the enhanced scattering is a property of the shock front in the water. Thus for all of the above reasons the conclusion is that the enhanced intensity signal is originating only in the water.

As previously mentioned a broadband near 200 cm^{-1} has been observed. Our current interpretation is that the total observed shock-enhanced wing is composed of a band at $\sim 60 \text{ cm}^{-1}$ (the hydrogen bond bending mode⁷) and $\sim 175 \text{ cm}^{-1}$ (the hydrogen band stretching mode⁷). Because of the inherent filtering of the triple spectrometer, which attenuated the observed OMA counts to approximately 100 cm^{-1} , the 60- cm^{-1} band is not observed. However, the presence of an intense broadband at 60 cm^{-1} would tend to push the apparent maximum of a 175- cm^{-1} band to the observed higher wave numbers (i.e., to be observed 200 cm^{-1}).

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