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Relaxation of Laser Induced Transient Plasmas in Liquids[1]

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With 2 Figures

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Transient plasma is induced in H_2O, D_2O, CS_2, optical glass, and Plexiglas by single pulses of a Q-switched neodymium laser in the power density range of 0.4 to 0.9 GW cm^{-2}. The relaxation times for the simple exponential decay of intensity of a white continuum emitted by all samples have been determined. Possible mechanisms of the formation and decay of the plasmas are discussed.

Introduction

The unique properties of laser radiation, namely a high degree of spatial and temporal coherence at high power densities, make it an outstanding tool for experimental investigation of the dynamics of changes of state in gaseous, liquid and solid systems.

In the present work we report on a series of experiments in which the high power level, and the short duration of a giant pulse from a Q-switched, solid state (Nd:glass) laser was utilized to perturb liquid systems. Under the experimental conditions, because of the high power density, plasma formation occurs that gives rise to transient luminosity. The radiative relaxation time was measured of laser flashed pure liquid water, D_2O and CS_2 as well as optical glass and Plexiglas, which are supercooled liquids. Possible mechanisms of the formation and the relaxation of the plasmas are presented below.

Experimental

The experimental setup is shown in Fig. 1. The Nd : glass laser (Apollo Lasers, Inc., Los Angeles) consists of an oscillator and two amplifier stages in tandem. With a Pockel's cell Q-switch, the maximum energy in a single

20 nsec duration 1.06 μm laser pulse is 40 joules. As the beam emerges from the second amplifier it has a diameter of 3 cm and is reduced through a glass lens to a final beam diameter of 0.4 cm at the focal point, 25 cm beyond the sample cell. The pumping flash of white light from the Xenon flash tubes is filtered out of the laser beam by four successive RG-780 Schott glass filters. The laser light then passes through a biconcave glass lens ($f = 0.5$ cm), and into the sample cell located 65 cm from the lens and 1.3 m from the exit end of the second laser amplifier. To eliminate backscattering and to reduce power density after passing the sample cell, the laser beam is expanded by a biconvex glass lens 50 cm beyond the focal point of the first lens. Then the beam is deflected by a front surface mirror and absorbed by a black felt light sink. The flat black, anodized aluminium, T-shaped sample cell is 10 cm across the top and 5 cm high with a 1 mm thick glass microscope slide glued at right angles over each of the three open cell ends using Varian Torr Seal. An RCA 1 P 28 photomultiplier tube is placed on the bottom of the T at a right angle to the laser beam, with a collecting lens between the tube and the cell. Using a 1.1 kΩ load, a Hewlett Packard 183 A oscilloscope, with an HP 1802 A dual channel vertical amplifier plugin, and HP 1840 A time base, the detection system has a response time τ_{det} of 60 nsec. Decay curves were photographed on the oscilloscope with an HP 195 A camera.

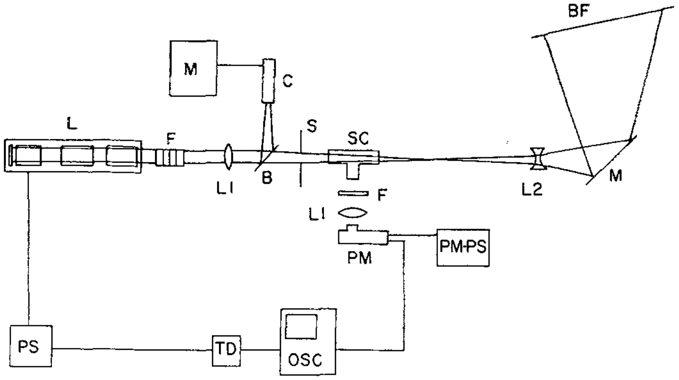

Fig. 1. Schematic diagram of experimental setup. L: laser; F: filters; B: beam splitters; S: stop; L 1: biconvex lenses; L 2: biconcave lenses; C: calorimeter; M: microvolt ammeter; SC: sample cell; M: front surface mirror; BF: black felt; PM: photomultiplier; PM-PS: photomultiplier power supply; PS: laser power supply and timing unit; TD: triggering delay

The integrated energy of each laser pulse was determined by reflecting a portion of the pulse into a Korad K-J calorimeter connected to a Keithley 150 B microvolt-ammeter.

The time integrated spectra of light emitted from the samples at right angle to the laser beam were recorded photographically with a spectrograph.

Spectroscopic grade D_2O and CS_2 (both from Merck), as well as doubly distilled demineralized water samples were filtered twice through a 250 Å

Millipore filter before laser irradiation at room temperature. In the experiments with optical glass and Plexiglas the sample cell was replaced by cubes of the respective glasses having optically flat surfaces.

Results and Discussion

Laser induced dielectric breakdown in gases[3] and liquids[4] has been observed previously. The breakdown usually occurs in the focal region of a focused Q-switch laser pulse, resulting in a transient plasma.

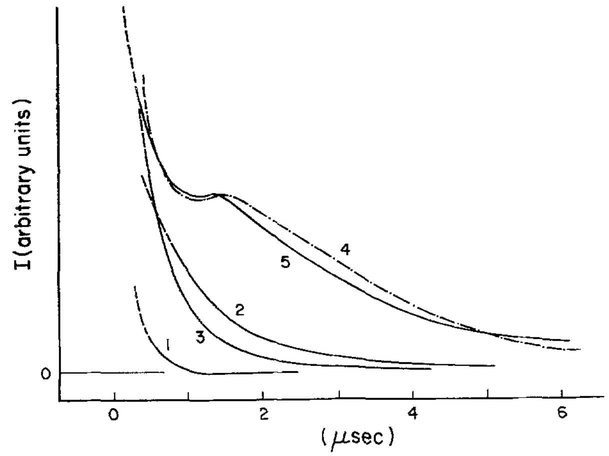

Fig. 2. Comparison of intensity of light emission vs. time in the first few μsec. Here $t = 0$ is the beginning of the emission. 1: H_2O, 2: D_2O, 3: CS_2, 4: optical glass, 5: Plexiglas. Power density of the laser pulse is 0.4 GW cm^{-2} in all cases

There is a power density threshold for breakdown of every material, and for gases certain pressure requirements also have to be met. In the experiments reported here using a Nd:glass laser in the power density range of 0.4 and 0.9 GW cm^{-2}, plasma formation already occurs several centimeters ahead of the focal point in pure water, D_2O and CS_2 as well as in optical glass and Plexiglass. No observable macroscopic change is caused by single 20 nsec pulses in the samples.

Fig. 2 shows typical wavelenght integrated intensity changes of white light emitted by the plasmas. The emission maximum occurs 10 ± 5 nsec after the peak intensity of the exciting laser pulse in all samples. Then, the intensity of the emission decreases non-exponentially, ending in a long lived tail that can be described as a single, or double exponential decay. Table 1 summarizes our results. Uncertainties associated with numerical values are given as average deviations from the mean. The radiative relaxation times, τ, listed in Table 1 represent true relaxation times since the observed values, τ_{obs}, were corrected for the finite response time of the detection system, τ_{det}, using

$$\tau = (\tau^2_{obs} - \tau^2_{det})^{1/2}. \tag{1}$$

τ_{obs} is defined by equation (2)

$$\dot{I} = \dot{I}_0 \exp(-t/\tau_{obs}), \tag{2}$$

where $\dot{I}$ is the wavelength integrated intensity of light (in arbitrary units) emitted at time t. $\dot{I}_0$ is the light intensity emitted at $t = 0$. The instant for $t = 0$ is chosen such that for $t > 0$, $\dot{I}(t)$ can be described by eq. (2). In the case of CS_2 and the glasses, two relaxation times are obtained ("fast" and "slow") from the plot of $\ln \dot{I}$ vs. time.

Table 1. *Radiative Relaxation Times for the Different Samples*

Substance		Radiative relaxation time τ
H_2O		220 ± 30 nsec
D_2O		1.6 ± 0.1 μsec
CS_2 fast		475 ± 25 nsec
CS_2 slow		2.67 ± 0.13 μsec
Optical glass	fast	1.3 ± 0.2 μsec
Optical glass	slow	2.9 ± 0.1 μsec
Plexiglas	fast	2.4 ± 0.5 μsec
Plexiglas	slow	30 ± 2 μsec

Laser produced plasma formation in various liquids has been attributed to dielectric breakdown at sites of particles suspended in the liquid. However, the presence of particles is not necessary for the phenomenon. Although careful filtering reduces the effect, it does not eliminate it[5]. At high energy densities (> 80 MW cm^{-2}), excitation, ionization, and plasma formation take place in most dust free liquids (as well as in gases depending on their pressure) even if the energy of the photons is smaller than the resonance, or the ionization energy.

The elementary processes involved in the formation and decay of the plasma are complex and numerous. For plasma formation it is necessary that a large number of free electrons be produced almost simultaneously at the beginning of the laser pulse. Possible mechanisms for this process are multiple photon absorption, autoionization through a tunnel effect in the radiation field[6], collision of virtually excited molecules, and quantum addition in collision complexes[7]. In the case of water, however, that has an absorbance of 0.067 cm^{-1} at the wave length of the Nd:glass laser ($\lambda = 1.06\ \mu m$), ionization through direct vibrational excitation can be the predominant mechanism of initiation. In the latter stages of the process ionizing collisions contribute to the multiplication of electrons.

After the first electrons have been produced by the leading edge of the pulse, they will be heated by electron-neutral and/or electron ion inverse "Bremsstrahlung". The conversion of linear momentum prohibits the high energy electrons from radiating. However, in the presence of another body, such as an ion or a molecule the electrons may suffer inelastic collisions, and the change in kinetic energy is emitted as a free-free continuous "Bremsstrahlung" spectrum. After the electrons have been slowed down sufficiently they will be captured into various excited states of the molecules and ions. The emission of a free-bound continuous "Bremsstrahlung" spectrum is the result of this process. This mechanism of decay is indicated by the emission spectra we observed in all samples with the possible exception of CS_2. The wavelength region of 380 to 900 nm we studied is free of any structure, and the time integrated spectra consist entirely of an intense continuum[8]. Selected wavelength ranges (obtained by placing Oriel 10 nm bandwidth interference filters between the cell and the photomultiplier) show the same time-behaviour as the wavelength integrated spectrum.

With the time resolution of our detection system, the observation of a free-free "Bremsstrahlung" emission from the microscopic, localized plasmas embedded in a condensed phase is highly unlikely, unless one considers the possibility of channeling[9] of the high energy electrons through open channels of a lattice. Due to this mechanism in the two glasses we studied, the free-free transition is apparently slow enough for observation on a longer time scale as a distinct process. This would correspond to the faster of the two relaxations measured for both glasses.

As it has been shown recently, the emission of a double exponentially decaying continuum can be explained in certain cases without the assumption of plasma formation. *Brus* has measured two exponential decays in N_2^+-laser ($\lambda = 337.1$ nm) excited CS_2 vapor, with 2.9 ± 0.3 and $17 \pm 2\ \mu$sec collision free lifetimes of two fluorescing states[10]. The fluorescence spectrum was observed in the range of 396 to 614 nm, where both components of the decay are apparently emitted as long, overlapping progressions throughout the visible. The phenomenon was explained by laser excitation of possibly several rotational levels of the unassigned U9 band. If the same explanation is applicable to our experiments in liquid CS_2, the two relaxation times we obtained can be interpreted as the lifetimes of fluorescing states. Our fast and slow relaxation times are 6.1 and 6.4 times, respectively, shorter than those obtained in the vapor phase in the pressure range of 3 to 200 mtorr. If the deexcitation is of a pseudo first order collision mechanism, we find an ≈ 6 times larger collision frequency of excited molecules under the conditions of the cooling plasma embedded in the liquid.

The radiative relaxation observed in D_2O is ≈ 7 times longer than in H_2O. In contrast to water, the absorbance of D_2O is negligible at 1.06 μm, thus direct vibrational excitation prior to electron multiplication can be excluded for this substance. Based on the scarce experimental results presently available on plasmas in liquids, one cannot decide whether a difference in state (temperature, composition, electron energy, electron density, etc.) or additionally a difference in the diffusion controlled rate of electron capture is the reason for the observed isotope effect.

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