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STUDY OF LASER ABLATION IN LIQUIDS USING PULSED PHOTOACOUSTIC TECHNIQUE

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Laser ablation processes in liquid benzene, toluene and carbon disulphide have been investigated by pulsed photoacoustic technique using 532 nm radiation from a frequency doubled Q-switched Nd:YAG laser. The nature of variation of photoacoustic signal amplitude with laser energy clearly indicates that different phenomena are involved in the generation of photoacoustic effect and these are discussed in detail. Our results suggest multiphoton induced photofragmentation as the most plausible interaction process occurring during laser ablation in these liquids.

1. Introduction

Interaction of laser radiation with matter in different phases has been studied by various workers.[1–5] Laser ablation in liquids is one among such interesting processes.[6] The direct photodissociation of chemical bonds and the photothermal decomposition following the rapid conversion of the light energy into heat are the major processes which are crucial in the context of laser ablation in liquids. Ablation is a nonlinear photochemical behavior in terms of laser energy and it has a threshold which depends on photophysical properties of the absorbing molecules and the thermal properties of the material. The two important processes occurring during the laser ablation of liquids in the presence of an incident laser pulse are the formation of shock waves and the gas dynamic sputtering of the ablation products with supersonic velocities.

Molecular liquids are considered as ideal systems for studying photochemical ablation mechanisms mainly because the liquid is expected to give a rather simple relation between ablation behavior and photochemical reactions due to its homogeneity, isotropic structure and absence of chemical bonds between the molecules. There are very few reports based on laser ablation in liquids and most of them pertain to excimer laser as the excitation source.

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The present letter deals with the study of laser ablation processes in liquid benzene, toluene and carbon disulphide using pulsed photoacoustic (PA) technique. The PA effect is a phenomenon where acoustic waves originate from the nonradiative part of the energy released in the decay of a molecule from an excited state induced by the laser pulses. The PA effect has been utilized to investigate multiphoton processes in organic molecules where efficient nonradiative relaxations $S_n \rightarrow S_1$ release a significant amount of thermal energy into the medium.[7,8]

2. Experimental

The schematic diagram of the experimental set up and the details of the PA cell are given elsewhere.[8,9] The PA cell is made of stainless steel and is provided with glass windows for the entry and exit of the laser beam. The acoustic transducer that detects the laser induced PA signals consists of a lead-zirconate-titanate (PZT) disc firmly mounted in a stainless steel chamber which is screwed onto the side of the cell. A lead disc followed by a copper disc forms the backing of the PZT, which is spring loaded within the chamber. Spurious electrical pick-up is negligible, and signal ringing is reduced to a tolerable level.

The second harmonic output beam (532 nm) from a Q-switched Nd:YAG laser is focused by a convex lens (focal length 5 cm) into the PA cell. The lens position is adjusted so that the beam focus is at the center of the cell (spot size $\sim$200 μm). The laser pulse width (FWHM) is $\simeq$9 ns and the pulse repetition frequency is 10 Hz. The pump laser pulse energy is measured using a laser energy meter. The transducer output is observed on a 200 MHz digital storage oscilloscope. The averaged amplitude of the first pulse in the PA signal trace is monitored as a function of the laser energy.

3. Results and Discussion

It is well known that the PA signal $q \propto I^n$ where I is the incident photon energy. Log–log plot of q versus I will give the slope n corresponding to the number of photons taking part in the multiphoton process.[10] The log–log plot of photoacoustic signal against laser energy for benzene, toluene and carbon disulphide are given in Figs. 1, 2 and 3 respectively. All the liquids show somewhat similar behavior. Two separate break points are distinctly observed in the log–log plots. From the nature of these log–log plots, the role of many photon processes in the generation of PA signal in the sample becomes clearly evident. It is obvious that the various photophysical and photochemical processes involved are distinctly different for various ranges of incident pulse energies. The PA signal increases moderately at low laser energies and rises abruptly at the first break point. Tsuboi *et al.*[6] attributed the sudden change in the first break point to the recoil of the supersonic plume ejection. The threshold laser energy density for the process is found to be different for toluene (3.2 J/cm^2), benzene (0.4 J/cm^2) and carbon disulphide (1.5 J/cm^2). We have observed that the threshold for benzene is lower than that for toluene while reverse in the case reported by Tsuboi *et al.*[6] This is because two photon absorption cross

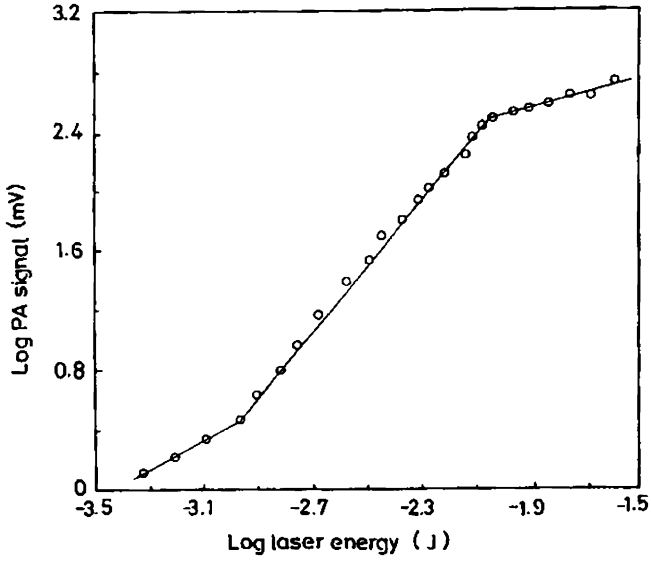

Fig. 1. Log–log plots of photoacoustic signal strength against laser energy for toluene.

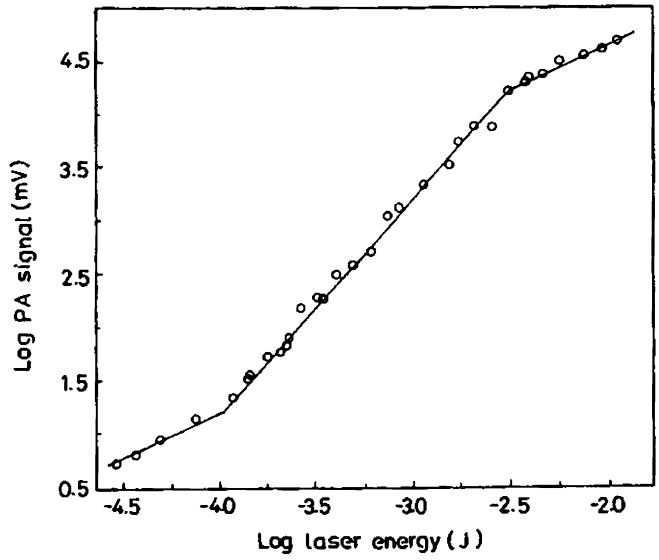

Fig. 2. Log–log plots of photoacoustic signal strength against laser energy for benzene.

section for benzene is larger than that for toluene at 532 nm, while reverse is the case for one photon process at 248 nm. The slope of the log–log plot of the PA signal versus pulse energy after the first break point is found to be $\simeq 2$ for toluene

and benzene and ≃4.5 for carbon disulphide and this shows the involvement of multiphoton processes in the media. The second break point after which the PA signal increase gradually is found in the case of polymer ablation by Zweig *et al.*[11] and they ascribed this to plasma generation.

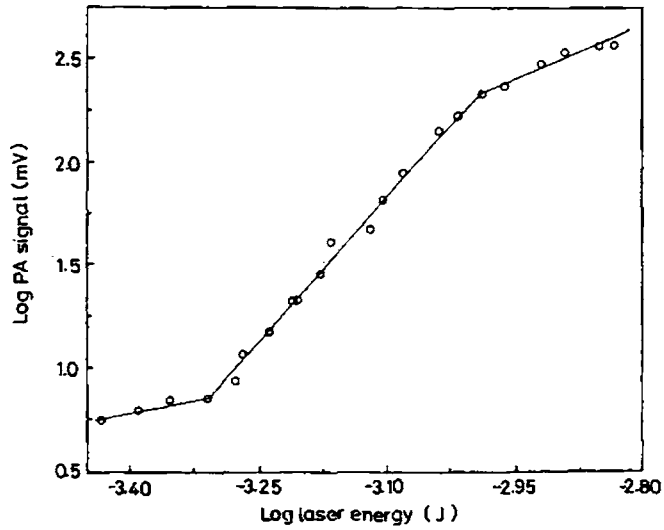

Fig. 3. Log-log plots of photoacoustic signal strength against laser energy for carbon disulphide.

The two possible mechanisms for the laser ablation in liquid are explosive boiling and Coulomb explosion. The necessary condition for explosive boiling is that molecules in the irradiated volume should be overheated to a metastable state within a time interval shorter than that required for heat to diffuse from this volume. In this case the temperature of the molecules rises high enough for an intense formation of gas-phase bubbles in a fluctuating manner. Visually we do observe gas-phase bubble formation at the onset of the first break point and it can be detected easily by monitoring the scattering of a weak probe laser beam passing through the irradiation region. In Coulomb explosion, strong repulsive interaction between molecular cations, which are formed due to the electron ejection from the liquid surface by light radiation, takes place. Tsuboi *et al.*[6] found that Coulomb explosion is not a likely processes to explain the phenomena observed above. They, however found that photofragmentation of the organic molecules as the plausible cause for the second break point. Fukumura *et al.*[12] have proposed cyclic multiphoton absorption for laser ablation in polymer films doped with aromatic molecules. If such a process is involved, fragmentation from the hot molecule[13] may also play a role in the liquid ablation phenomenon.

The present PA measurements clearly show that beyond the first break point (i.e. beyond a fluence of 3.2 J/cm^2 for toluene and 0.4 J/cm^2 for benzene) two photon absorption at 532 nm occurs in both benzene and toluene. The dissociation

energies for benzene and toluene are 4.7 eV and 3.8 eV respectively[14] which matches with two photon energy of 532 nm radiation. The observation of slope having $\simeq$4.5 for carbon disulphide after the first break point indicates both four photon and/or five photon absorption phenomenon which corresponds to the photodissociation process in the molecule.[8] By absorbing four photons at 532 nm, CS_2 molecules are excited to 3*d* Rydberg states $^1\Delta_u^7$ which photodissociates giving sulphur atoms in the $^9P_2$ state and CS in the excited state ($a^9\pi$). At higher incident laser energies CS^+ can be produced by ionizing CS by absorbing five photons which corresponds to an energy of 11.3 eV.

In conclusion, pulsed photoacoustic measurements have been successfully used to study laser ablation in liquids. The results of present PA measurements strongly suggest multiphoton induced photofragmentation as the major cause for the occurrence of these processes.

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