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著者	福村 裕史
journal or publication title	Applied Physics Letters
volume	64
number	20
page range	2745-2747
year	1994
URL	http://hdl.handle.net/10097/35095

doi: 10.1063/1.111461

Nanosecond imaging study on laser ablation of liquid benzene

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(Received 6 December 1993; accepted for publication 19 February 1994)

KrF excimer laser ablation of liquid benzene was studied by a nanosecond imaging technique. The ejection of a plume followed by remarkable transient morphological changes took place, which was directly observed over a wide range of the fluence. From imaging data, an ablation threshold was determined to be 100 mJ/cm^2 and ablation behavior induced by electronic excitation of liquid molecules is considered. A delay time prior to the plume ejection is about $40 \pm 20 \text{ ns}$, while the remarkable morphological change ranges from sub- μs to ms time regime.

Since the first report by Srinivasan *et al.*,¹ laser ablation has received much attention in the past decade because of its high potential in the fabrication of materials and in unique fundamental molecular processes.^{2,3} Ablation is a nonlinear photochemical behavior with respect to laser fluence, and has a threshold depending on photophysical properties of the absorbing molecules and thermal properties of the materials. The threshold is the most important parameter to elucidate the ablation mechanism, and in the case of polymers it has been determined from the etch profile, namely, etch depth brought about by one-shot excitation is measured by a depth profiler and plotted against the fluence. Below the threshold, usually no appreciable etching is observed.

For understanding the ablation mechanism, photophysical and photochemical studies by spectroscopic methods⁴⁻⁶ and theoretical modeling⁷ have been done by several groups. In the case of polymer ablation, bond breaking, intra- and intermolecular thermal energy dissipation, the ejection of the fragments with different masses are coupled with each other, so that the mechanism is complex and extremely difficult to analyze. From this viewpoint, molecular liquids will be one of the best systems for elucidating the ablation mechanism, since a liquid is deemed to be isotropic, all molecules in the liquid are equivalent, and no chemical bond is formed between the molecules. Nevertheless, the reports are limited.

Irradiation of a liquid or a solution with intense laser light often induces morphological changes, which are divided into the following two types. When the laser light excites the molecular vibrations of the liquid, vaporization by superheating resulting in a droplet rupture,⁸ drilling of a liquid surface,⁹ etc. take place, which are achieved by infrared (IR) laser irradiation. The second and well-known example of such case is laser cavitation¹⁰⁻¹² due to breakdown induced by the intense laser pulse irradiation. The morphological change can be brought about even if the liquid is transparent to the light. In both cases, the dynamics of morphological changes has been widely investigated by means of fast imaging techniques.

We consider that the morphological change of liquids can be brought about also by electronic excitation. This is just the ablation dynamics of a liquid. It will be interesting to compare the liquid ablation with the polymer ablation, the laser cavitation, and with related phenomena. However, no detailed information is available, particularly on the temporal evolution of the morphological changes induced by elec-

tronic excitation. For example, even a threshold value is difficult to determine because no permanent change can be identified. We consider a time-resolved imaging method is useful to determine the ablation threshold and to elucidate the related dynamics. In this work, nanosecond (ns) imaging of the ablation behavior of liquid benzene was conducted, and the transient morphological changes of the liquid ablation induced by electronic excitation were demonstrated here for the first time.

An experimental setup of a ns imaging system is schematically shown in Fig. 1. A KrF excimer laser pulse (Lambda Physik, EMG201MSC, 248 nm, FWHM 30 ns) was incident vertically on a liquid surface. Liquid benzene has a large absorbance ($\alpha=2100 \text{ cm}^{-1}$) at this wavelength, hence the ultraviolet (UV) pulse excites only the surface layer. For the fast imaging, a Nd^{3+} :YAG laser (JK Laser, HY750) and a CCD camera (Sony XC-77, 512 \times 512 pixels) were operated synchronously with the excimer laser. A dye solution (Rhodamine 101G in methanol) pumped by the second harmonic of the YAG laser provided a visible emission (duration 20 ns), which was used as back illumination. The delay time between the excimer laser and the YAG laser was adjusted employing a pulse generator (Stanford Research System, DG535). Two different types of vessels were prepared. Vessel I was a Pyrex test tube with 10 mm diameter and 35 mm depth which was completely filled with the liquid, so that the free surface swelled due to the surface tension. Vessel II was a quartz cell with 2 mm optical path length [2 mm (L) \times 10

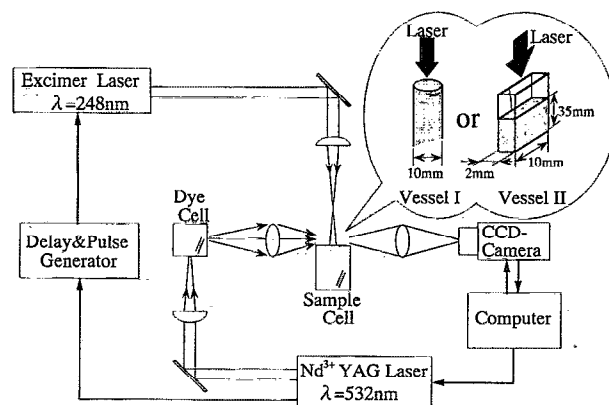


FIG. 1. A schematic diagram of the nanosecond imaging system.

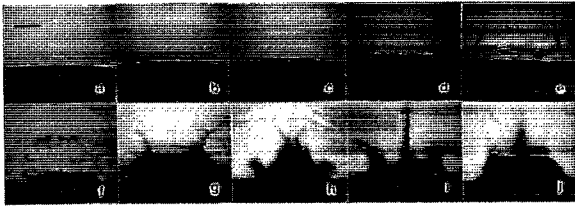


FIG. 2. Nanosecond images of the free surface of liquid benzene irradiated with the pulse of 1 J/cm^2 , which were taken using vessel I. The black area seen in the lower side of the photograph corresponds to the liquid surface which swells due to the surface tension. The size of the laser beam was $2.4 \text{ mm} \times 1.3 \text{ mm}$. The scale bar represents 1 mm . Delay times; (a) 0 ns , (b) 40 ns , (c) 100 ns , (d) 500 ns , (e) $1 \mu\text{s}$, (f) $2 \mu\text{s}$, (g) $5 \mu\text{s}$, (h) $10 \mu\text{s}$, (i) $20 \mu\text{s}$, and (j) $50 \mu\text{s}$.

mm (W) \times 50 mm (H)], which was filled to a depth of 35 mm with benzene. The former was used for observing a plume ejected from the surface, while the latter was suitable for monitoring a morphological change beneath the meniscus. Benzene (Nacalai Tesque, HPLC grade) was used without further purification. Benzene was bubbled with nitrogen gas and always flushed with the gas during irradiation.

We observed a remarkable morphological change of the liquid benzene surface accompanied with an impulse sound upon irradiation of the free surface with an intense pulse. As a representative example, Fig. 2 shows a series of images of the free surface of the liquid benzene irradiated at 1 J/cm^2 , which was examined with vessel I. As a plume grew from the irradiated area, a shock wave propagated hemispherically [Figs 2(d)–(f)] with an initial velocity of 1000 m/s . The shock wave velocity was confirmed to follow the t (time) $^{0.4}$ relationship.¹³ When the fluence was below 100 mJ/cm^2 , however, no appreciable change was observed above the liquid surface. This clearly indicates that the ablation of liquid benzene by the 248 nm pulse takes place with a distinct threshold of 100 mJ/cm^2 . At the threshold, the plume generation was detected at 500 ns after the exciting pulse. It was, however, observed at $40 \pm 20 \text{ ns}$ [Fig. 2(b)] when the fluence exceeded 200 mJ/cm^2 . It is worth noting here that the plume generation time scale is independent of the fluence above 200 mJ/cm^2 .

We now turn our attention to transient morphological changes beneath the meniscus in the vessel II. Again, nothing was observed at the fluence below 100 mJ/cm^2 , confirming that this value is the threshold as described above. In Fig. 3 the transient morphological changes at 1 J/cm^2 are given for the delay time up to 200 ms . At the early stages (0 – $1 \mu\text{s}$), a propagation of large amplitude stress wave inside the liquid phase was observed. The propagation velocity was estimated to be $1500 \pm 100 \text{ m/s}$, which is slightly above the sound velocity in liquid benzene (1280 m/s). An onset of the morphological change was clearly seen at about $5 \mu\text{s}$ after the irradiation as the “blackened area” just beneath the meniscus, and developed with time. Remarkable morphological changes were observed over sub-ms–ms time regime. As seen in Figs. 3(H)–(K), symmetrical and unique “blackened areas” were observed. Presumably, such shapes can be explained in terms of a hydrodynamic effect and/or an interaction between the liquid and the sample cell.^{11,12} In fact, when

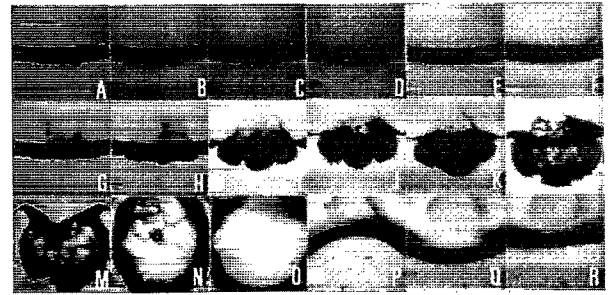


FIG. 3. Nanosecond images of morphological changes of liquid benzene beneath the meniscus irradiated with the pulse of 1 J/cm^2 , which were taken using vessel II. The horizontal black band corresponds to the meniscus, and its bending is due to the surface tension. The upper and lower sides of the meniscus correspond to gas phase and liquid phase, respectively. The size of the laser beam is $4 \text{ mm} \times 1.5 \text{ mm}$. The scale bar represents 3 mm . Delay time; (A) 0 ns , (B) 100 ns , (C) 500 ns , (D) $1 \mu\text{s}$, (E) $5 \mu\text{s}$, (F) $10 \mu\text{s}$, (G) $20 \mu\text{s}$, (H) $100 \mu\text{s}$, (I) $280 \mu\text{s}$, (J) $520 \mu\text{s}$, (K) $960 \mu\text{s}$, (L) 1.4 ms , (M) 3.0 ms , (N) 7.6 ms , (O) 20 ms , (P) 50 ms , (Q) 100 ms , and (R) 200 ms . In the images of (P)–(R), flowed benzene liquid is observed on the vessel wall.

we reduced the diameter of the focused laser beam ($2 \text{ mm} \times 1 \text{ mm}$) to decrease such effects, the unique shape was not observed.

In successive frames, the “blackened area” eventually grew to an apparent hollow of the liquid surface, or in other words, surface cavitation [Figs. 3(M)–(O)]. Based on the morphological behavior described above, we conclude that the observed “blackened area” corresponds to a profile (shadowgraph) of the actual hollow of the liquid surface, not to some optical effects such as thermal lensing. The time scale for growing of the hollow to its maximum was about 7 – 10 ms , which was almost invariant with the fluence. After the hollow reached to the maximum, the liquid surface commenced to oscillate with a period of about 100 ms , which was also independent of the fluence. This value is ascribed to an eigen period of the system for which the cell size and the amount as well as properties of the liquid such as viscosity are responsible. We observed the damped oscillation until 200 ms and the total morphological change was completed. Consequently, the surface returned to its initial state.

The present experimental results are compared with polymer ablation as well as cavitation behavior, and also with the ablation threshold published already. In the case of ablation of poly(methyl methacrylate), the delay time prior to an onset of the ablation involving the plume generation gets shorter as the fluence increases.^{14,15} The observed behavior different from that of the polymer ablation is of interest. Moreover, the time scale for growing of the hollow to the maximum was much longer compared to polymer ablation as well as laser cavitation. In polymer ablation, a total morphological change is generally completed within few tens of μs .^{15,16} In laser cavitation, where a bubble is generated by an abrupt rise of the temperature due to breakdown, the time scale for growth of the bubble is ranging from few tens of μs to few hundreds of μs .^{12,17} Probably, the drastic morphological changes observed over ms time regime were partly caused by the hydrodynamic effect due to the recoil momen-

tum generated by the supersonic plume ejection to the gas phase.

Concerning the ablation threshold, Srinivasan and Ghosh investigated ablative decomposition of liquid benzene irradiated with a Krf excimer laser by means of gaschromatography and a photoacoustic technique.¹⁸ Both data gave about 200 mJ/cm² as the threshold, however, even under this value the photoacoustic signals were not negligible and biphenyl and dimers were produced. It is noteworthy here that, according to their report, these dimers formation seemed to have a threshold of 100 mJ/cm², which corresponds to the ablation threshold value determined in our work. These results suggest that the precise definition of a liquid ablation threshold is extremely difficult, and their chemical and photoacoustic analyses are complementary to our morphological studies. On the other hand, the threshold value of polystyrene ablation by a 248 nm pulse was reported to be 250 mJ/cm² which was determined by a photoacoustic measurement.¹⁹ This value is larger than the threshold of liquid benzene ablation, although polystyrene has the same chromophore (phenyl group) as benzene. The larger threshold may be ascribed to scission of single bonds which are much stronger compared to weak intermolecular interactions of liquid benzene.

The authors are indebted to ANELVA Co. Ltd. for the use of the excimer laser. Y. T. acknowledges Dr. Hiroshi Miyasaka (Kyoto Institute of Technology) for his encourage-

ment. The present work was supported in part by the Grant-in-Aid from the Ministry of Education, Science, and Culture of Japan (63430003).

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