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ARTICLES

Femtosecond Laser Ablation of Liquid Toluene: Molecular Mechanism Studied by Time-Resolved Absorption Spectroscopy

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A time-resolved absorption spectroscopic measurement of liquid toluene under femtosecond UV (300−500 fs, 248 nm) laser ablation conditions was carried out, and its molecular mechanism was studied. The lowest excited singlet state of toluene monomer and toluene excimer were clearly observed through the delay time by 19 ns, while benzyl radical was not detected unexpectedly under any condition no matter how high the laser fluence was. This indicates that the femtosecond laser ablation is based on a photothermal mechanism. A femtosecond double-pulse excitation, on the other hand, induced benzyl radical formation, which is consistent with the photochemical mechanism in the case of nanosecond laser ablation. The result that molecular mechanism is dependent on the excitation laser pulse width suggests a possible mechanism control of laser ablation.

Introduction

Studies on the interactions between intense laser pulses and condensed matters are becoming the main stream of laser science beyond the conventional photophysics and photochemistry at present. Laser ablation is one of the phenomena which can be induced commonly in solids and liquids as a result of such interactions. From this viewpoint, we have studied laser ablation dynamics and clarified its molecular mechanism as a representative of unconventional phenomena.

Since the first reports on nanosecond laser ablation on polymers by Namba et al.[1] and Srinivasan and Mayne-Banton,[2] there have been a lot of reports on nanosecond and picosecond laser ablation. As stable femtosecond laser systems prevail to scientific fields, the pulse width of excitation laser light is shifted to the shorter. A lot of papers on femtosecond laser ablation have been published since the first reports by Srinivasan et al.[3] and Küper and Stuke.[4] The number of papers on time-resolved measurements is, however, limited to several such as a reflectivity measurement by Shank et al.[5] Especially, no report on a time-resolved absorption measurement has been published so far except our report on liquid benzyl chloride,[6] even though such a measurement is indispensable to clarify the molecular mechanism directly.

We have adopted benzene derivatives such as benzyl chloride and toluene as samples to explore the laser ablation molecular mechanism since the first report by Tsuboi et al.,[7] because such liquids are so much more simply structured compared with spaghetti-like polymers that it is easier to elucidate their molecular mechanism. Further, those sample liquids are known as reactive species to UV light irradiation leading to benzyl radical formation as follows:

$$\phi\text{-CH}_2\text{X} + h\nu(\text{UV}) \rightarrow \phi\text{-CH}_2^{\bullet} + \text{X}^{\bullet}$$

In the case of nanosecond 248 nm laser ablation, the relation of ablation thresholds decided quantitatively by time-resolved shadowgraphy[7] and photoacoustic measurement[7] are correlated well to the relation of photochemical reactivity reported by Porter and Wright[8] but not to the relation of boiling points.[7] We have also detected the benzyl radical absorption band clearly and estimated quantitatively the concentration of benzyl radical to induce laser ablation by time-resolved absorption measurement.[9] It should be noticed that the benzyl radical formation results in the volume expansion when the radical concentration is extremely high under laser ablation condition, as the succeeding reactions produce gaseous molecules such as X_2, XH, and so on. On the basis of those results, we have concluded that nanosecond laser ablation is induced by instantaneous photochemical volume expansion. In the case of solutions of the benzene derivatives, it is demonstrated experimentally that the molecular mechanism changes from photochemical to photothermal as the solute concentration decreases.[10] This is one example of the mechanism control by changing the solute concentration of sample solutions.

Thus, we have constructed a high-power femtosecond Ti^{3+}:Al_2O_3/KrF laser system and applied it for the study of

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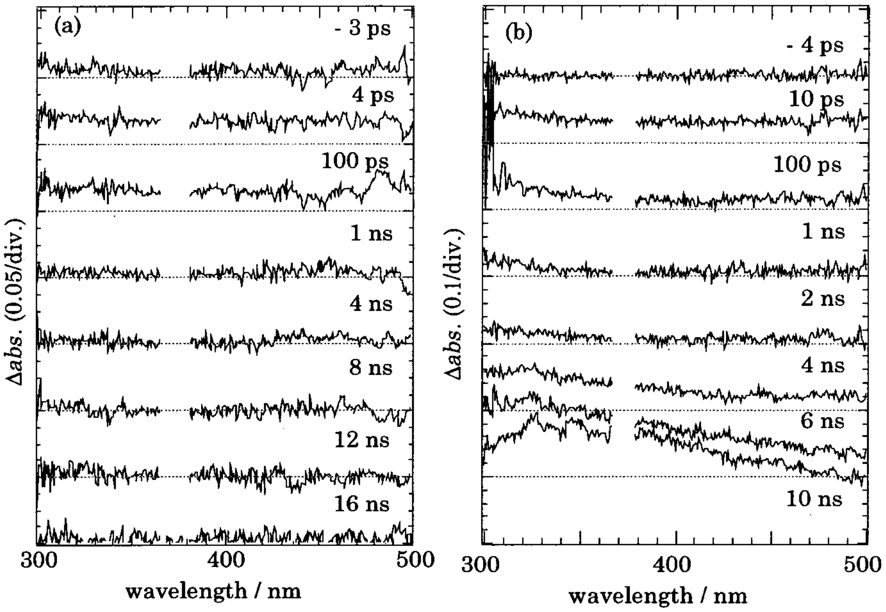


Figure 1. Time-resolved absorption spectra of liquid toluene in nanosecond time range. Laser fluences are (a) 15 mJ/cm^2 and (b) 60 mJ/cm^2, respectively. Times inserted in frames represent delay times.

femtosecond 248 nm laser ablation. For the observation of the sample surface first, in addition to the conventional shadowgraphy,[11] we have developed the picosecond time-resolved surface scattering imaging method and applied it to liquid benzyl chloride and liquid toluene under laser ablation condition.[12] This imaging method has clarified that the surface morphological changes begin to be induced at the delay time of 1−3 ns after excitation and the scattering evolution was analyzed in terms of surface roughness. It is interesting to see that its root-mean-square of surface roughness grows in the range of 10−300 nm. Further, in the case of liquid benzyl chloride, we have already measured molecular dynamics by the time-resolved absorption spectroscopy and clarified its femtosecond 248 nm laser ablation molecular mechanism.[6] An absorption band whose peak wavelength is 320 nm has been observed immediately after excitation and later, which indicates that benzyl radical is produced immediately after the excitation. Broadening of the bandwidth with the increase of laser fluence has not been observed dominantly, meaning little temperature elevation. We have concluded that the femtosecond laser ablation of liquid benzyl chloride is also induced by instantaneous photochemical volume expansion as the nanosecond laser ablation.

In this paper, we have adopted liquid toluene as a sample which is a representative of liquid alkyl benzene derivatives. In the liquid phase, the behavior of toluene in the femto−picosecond time range has not been clarified yet, and the molecular mechanism to produce benzyl radical is still not uncovered. By performing the time-resolved absorption measurement, we have clarified the photophysics and photochemistry of toluene in the femto−picosecond time range and explore its laser ablation molecular mechanism.

Experimental Section

Liquid toluene (Nacalai Tesque, 99%) was used as a sample after N_2 bubbling for several minutes. As an excitation light pulse, we used a third harmonic (wavelength = 248 nm, pulse width = 300−500 fs) from a 10 Hz high-power femtosecond Ti^{3+}:Al_2O_3/KrF laser system.[6] The excitation light pulse irradiated a sample liquid free surface vertically downward after being focused by a lens ($f = 30$ cm), where the spot size on the surface was about 1 × 1 mm^2. The sample liquid was stirred after every shot to avoid exciting photoproducts.

The details of our time-resolved absorption spectroscopic measurement system under laser ablation condition have been already introduced before.[6] Here we describe its outline. A white light continuum from D_2O irradiated by a second harmonic (372 nm, 150 fs) from the laser system was divided into two by a beam splitter and then used as a probe light pulse and a reference for compensating fluctuations of intensity and spectral shape. The probe interrogated the excited spot ($\phi < 1$ mm) on the sample free surface being focused by a lens ($f = 15$ cm). The transmitted probe light pulse through the sample and the reference were introduced respectively into polychromators with multichannel photodiode arrays (Otsuka Electronics Co. Ltd., MCPD110-A), then absorption spectra were calculated by a personal computer. The correction for a time dispersion effect induced by an optical chirp of the white light continuum was also done in the similar manner described elsewhere.[13] Spectra around the wavelength of 372 nm were eliminated because we could not calculate them correctly due to the saturation of white light continuum intensity. Measurements were performed at room temperature (21 °C) at atmospheric pressure under N_2 atmosphere.

Results and Discussion

Scattering of Probe Light Pulse in the Nanosecond Time Range. Figure 1 shows sequential time-resolved absorption spectra of liquid toluene in the time range earlier than 16 ns. When the laser fluence was relatively low (15 mJ/cm^2, Figure 1a), a broad spectrum was observed immediately after the excitation over the observing wavelength range (300−500 nm). Subsequently, its absorbance decayed with time, then there was no significant absorption detected after 1 ns. Candidates for this absorption are excited singlet (S_1) and triplet (T_1) states of toluene monomer, toluene excimer, and so on. The T_1 absorption of benzene in solution is on the wavelength shorter than 300 nm (the peak is at 235 nm),[14] which is thought to be the similar case to liquid toluene. As a result, T_1 of toluene monomer is not the main origin for the absorption observed in the wave-

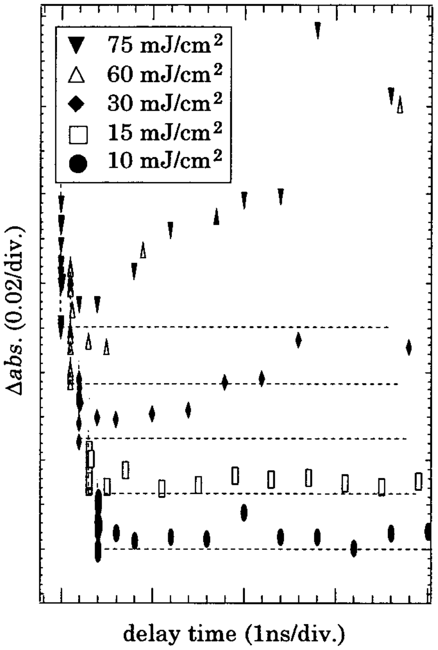


Figure 2. Rise and decay time profiles of absorbance at the wavelength of 320 nm in the nanosecond time range. The laser fluences are given in the inset. Vertical and horizontal dotted lines represent the origins to the two axes, respectively. Each profile is shifted by 1 ns horizontally in the delay time axis and by 1.25 vertically in the Δabs. axis, respectively.

length range here. The detailed discussion on the other transient species will be described in the next section.

When the laser fluence was relatively high (60 mJ/cm^2, Figure 1b), the same broad spectrum was observed until 1 ns as described above. In addition to the transient species discussed for 15 mJ/cm^2 excitation, ions such as toluene radical cation were possibly observed if two-photon absorption (10 eV) occurred efficiently because the ionization energy of toluene in the liquid phase was reported to be 6.9 eV.[15] Contrary to the case when the laser fluence was low (Figure 1a), after the absorbance almost decayed once by 2 ns, another broad spectrum tailing to the longer wavelength was observed again in the late time range after 4 ns. Further, its absorbance increased over the absorbance saturation point of our measurement system (0.7) with time. Figure 2 shows rise and decay time profiles ($<$19 ns) of absorbance at the wavelength of 320 nm as a function of laser fluence. When the laser fluence is relatively low (10 and 15 mJ/cm^2), the absorbance was continuously decaying and kept a constant small value in the nanosecond time range. When the laser fluence was relatively high ($\geq$30 mJ/cm^2), on the other hand, absorption which decayed completely once became to be observed again in the nanosecond time range.

This unconventional time-dependent absorbance behavior was characteristically observed when the laser fluence was higher than 30 mJ/cm^2 so that the behavior could be due to the scattering of probe light pulse induced by some morphological changes such as roughness on the sample liquid surface and bubbles produced under the liquid surface. Indeed, in the picosecond time-resolved surface scattering imaging carried out in advance,[12] it was directly confirmed that it takes about 1−3 ns for the surface roughness on the order of tens of nanometers to be induced and the roughness grew to a few hundred nanometers by the delay time of 19 ns. In addition, the femtosecond 248 nm laser ablation threshold value of liquid toluene has been already estimated to be 25 mJ/cm^2 by the nanosecond time-resolved shadowgraphy.[11] These experimental results lead us to the conclusion that the probe light pulse scattering induced by the surface roughness as the ablation initial stage is the origin of the unconventional absorbance behavior.

Similar behaviors in the nanosecond time range were also observed in the spectroscopy[6] and the scattering imaging[12] when the sample was liquid benzyl chloride under the ablation condition, where the ablation molecular mechanism has been already clarified to be photochemical.[6] The femtosecond 248 nm laser ablation threshold value of liquid benzyl chloride has been estimated to be 30 mJ/cm^2, which is higher than that of liquid toluene. In the cases of *nanosecond* laser ablation, on the other hand, the threshold of liquid toluene (35 mJ/cm^2) is higher than that of liquid benzyl chloride (30 mJ/cm^2) and this relation between the thresholds is clearly correlated to the photochemical reactivities as described in the Introduction. Further, the observations of benzyl radical in the *nanosecond* time-resolved absorption spectroscopy led us to the conclusion that the nanosecond 248 nm laser ablation molecular mechanism of liquid benzene derivatives such as benzyl chloride and toluene was photochemical; volume expansion model.[16] The knowledge suggests strongly that the femtosecond 248 nm laser ablation molecular mechanism of liquid toluene be different from that of liquid benzyl chloride and the nanosecond 248 nm laser ablation molecular mechanism of liquid benzene derivatives, because we did not observe benzyl radical here and the ablation threshold value of femtosecond laser ablation is lower than that of nanosecond laser ablation. To clarify the ablation molecular mechanism directly, we focused on the spectral behavior by the delay time earlier than 1 ns when the initial stage of laser ablation occurred, which will be described in the following section.

Ablation Molecular Mechanism in the Picosecond Time Range. Figure 3 shows time-resolved absorption spectra of liquid toluene in the time range earlier than 1 ns when the laser fluences were (a) 10, (b) 25, and (c) 80 mJ/cm^2, which correspond to the spectra obtained below, at, and above, the ablation threshold, respectively. As described above, similar broad spectra over the wavelength range of 300−500 nm were observed all through the time range $\leq$ 1 ns no matter how high the laser fluence was. In the shorter wavelength range ($<$400 nm), there has been no report on spectra so far. Figure 4 shows the absorbance at the wavelength of 320 nm as a function of laser fluence. It can be concluded by considering the signal to noise ratio of the data that the slope is almost unity, which means that the transient species inducing the shorter wavelength absorption is produced via a one-photon process. Figure 5 shows rise and decay time profiles of the absorbance at the wavelength of 320 nm (closed circle) and 480 nm (open circle). The absorbance at 320 nm rose immediately after the excitation and began to decay in a few tens of picoseconds. These experimental data indicate that the origin for the absorption in the shorter wavelength range is mainly S_1 of toluene when we take into consideration that the absorption band of benzene monomer has a tail to this wavelength range,[14] while T_1 of toluene is unlikely to be the candidate in this time region because the intersystem crossing time constant is ~6 ns. As for the longer wavelength range ($>$400 nm), we have assigned the band to the superimposed absorption of the S_1 and toluene excimer because their wavelength range is in accordance with references.[17−20] As shown in Figure 5, the absorbance at 480 nm rose immediately after the excitation and kept rising even after 10 ps where the rise time was about 20 ps. This implies that excimer formation under femtosecond 248 nm laser irradiation condition is occurred

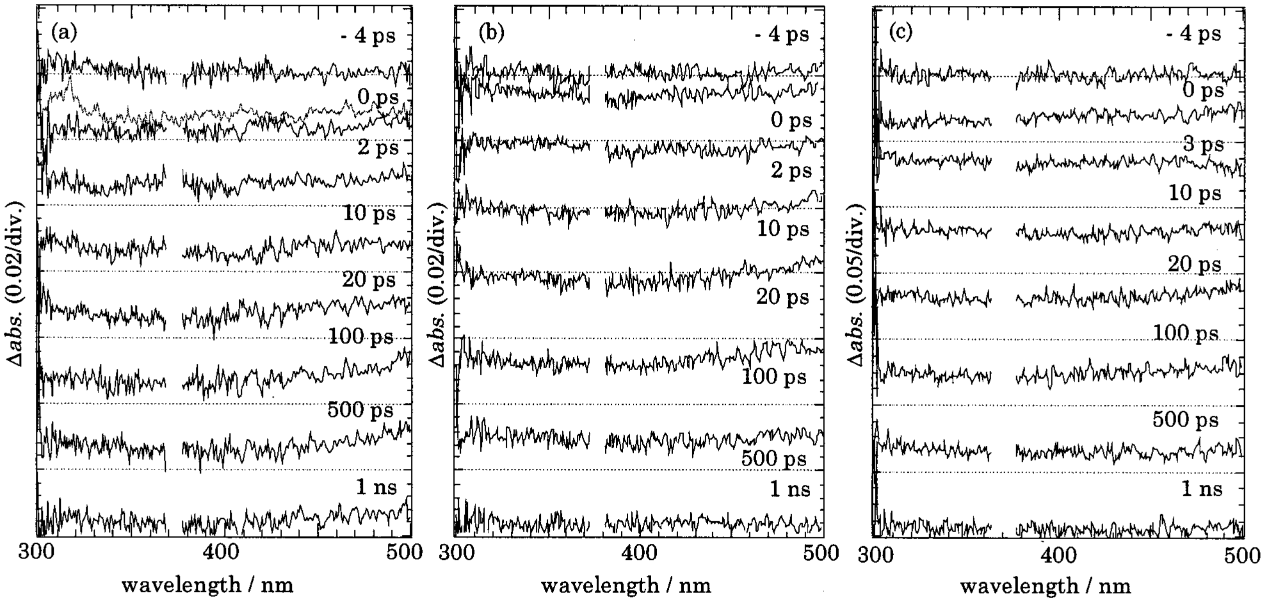


Figure 3. Time-resolved absorption spectra of liquid toluene in the picosecond time range. Laser fluences are (a) 10, (b) 25, and (c) 80 mJ/cm^2, respectively. Times inserted in frames represent delay times. The dotted spectrum at 0 ps in (a) is the spectrum obtained under the condition of nanosecond laser ablation of liquid toluene at the laser fluence of the ablation threshold.[9] A horizontal dotted line represents a baseline for each set of profiles.

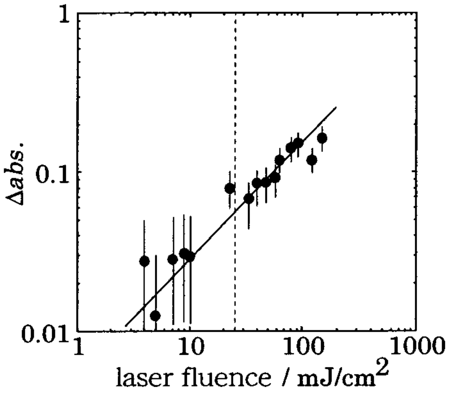


Figure 4. Absorbance at the wavelength of 320 nm as a function of laser fluence. The vertical dotted line represents the ablation threshold (25 mJ/cm^2). The diagonal line is a guide for readers. The vertical lines represent error bars.

in 20 ps by rotational relaxation, diffusion, and collisions after S_1 formation.

There is no dominant spectral shape change at <1 ns even though there is a possibility that ions such as toluene radical cation can be produced as described above. The spectrum of toluene radical cation is reported to be broad around the wavelength of 500 nm,[21] which cannot be distinguished easily from those of S_1 and excimer, indeed. From the viewpoint of laser ablation molecular mechanism, however, laser ablation is not induced by phenomena related to ions such as Coulomb explosion,[22] because we do not observe any significant absorption at the delay time of 1 ns when laser ablation occurred.

On the basis of the discussions above, we have concluded that the main transient species under femtosecond laser ablation condition are S_1 and toluene excimer. From the viewpoint of laser ablation molecular mechanism, these photophysical transient species should have key roles. Further, absorbance at the wavelength of 320 nm (Figure 5, closed circle) corresponding to the concentration of S_1 decayed with the lifetime of a few hundred of picoseconds, while the usual lifetime of S_1 is reported to be 34 ns.[23] This difference indicates that interactions between excited states such as $S_1{-}S_1$ annihilation are dominated under laser ablation condition and enhance nonradiative relaxation resulting eventually in much heat generation. Even though we cannot deduce quantitative temperature elevation directly from the broad spectra, the temperature elevation velocity can be estimated from laser fluence, heat capacity of liquid toluene, and so on to be 4.3×10^{10} to 4.3×10^{13} K/s on the assumption that all the excitation laser energy absorbed by molecules is converted into heat in the time range of 1 ps to 1 ns. This value is reasonable for laser ablation when we take it into account that Dlott et al.[24] reported that the temperature elevation velocity, what they called "temperature jump", was on the order of 10^{12} K/s under the picosecond laser ablation of poly(methyl methacrylate) doped with IR-165 dye whose absorption spectrum is sensitive to temperature. Above estimation here, we have come to the conclusion that femtosecond laser ablation of liquid toluene is induced by instantaneous heat generation resulting from the interaction between excited species such as S_1 and the excimer of toluene (photothermal mechanism).

Ablation Molecular Mechanism Dependent on Benzyl Radical Formation Process. The most striking feature of time-resolved absorption spectra of liquid toluene is that we do not observe any peak around the wavelength of 320 nm originating from benzyl radical under any condition; no matter how high the laser fluence was and no matter how late the observing time was. This result is definitely contrary to many reports which have been published so far since Porter's first report.[8] It has been believed that benzyl radical is produced from toluene and other benzene derivatives such as benzyl chloride under UV light irradiation condition. Indeed, we clearly observed a peak at the wavelength of 320 nm in the time-resolved absorption spectroscopic measurement under nanosecond 248 nm laser ablation condition of liquid benzene derivatives including toluene as shown in Figure 3.[9] We have assigned the band to benzyl radical absorption because the spectrum was in good agreement with a reference.[25] We have also estimated the amount of benzyl radical to induce morphological changes about 0.05 M.[9] Further, even in the case of femtosecond 248 nm laser ablation, we observed the similar absorption spectra when the sample was benzyl chloride.[6] Contrary to these cases, we

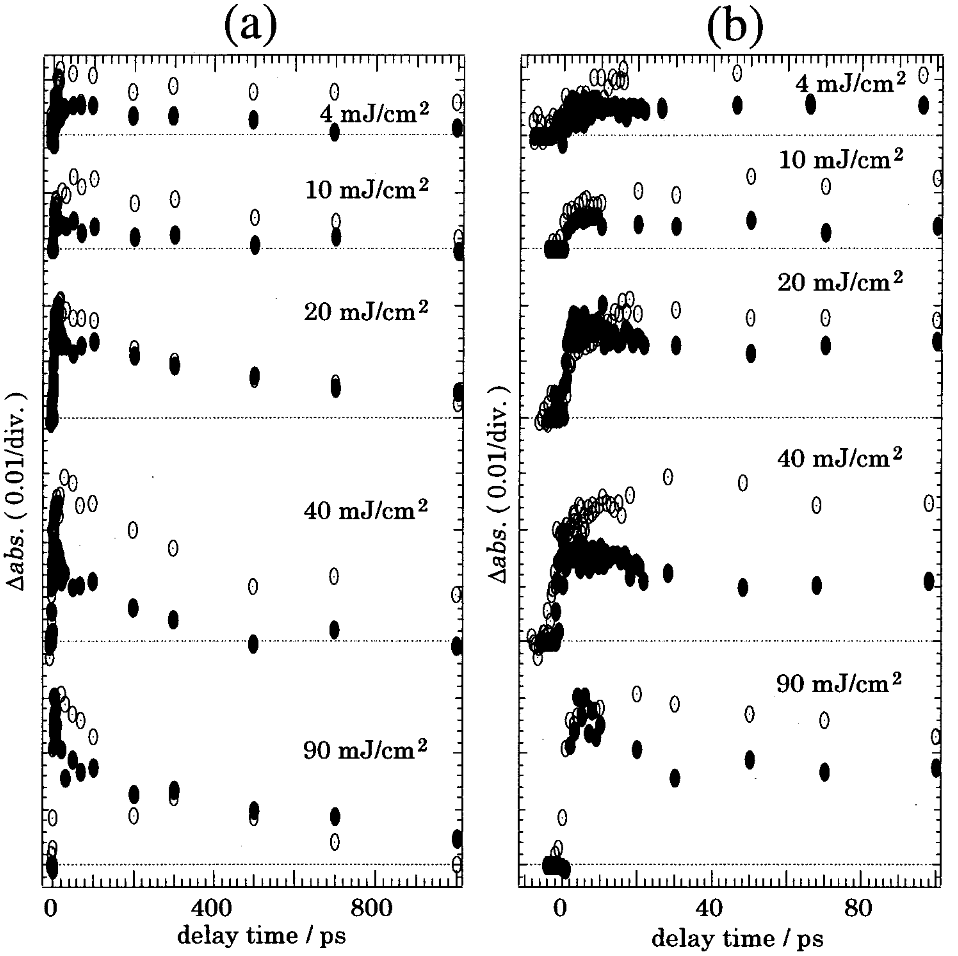


Figure 5. Rise and decay time profiles of absorbance in picosecond time domain: (a) <1 ns; (b) <100 ps. The laser fluence is given in each frame. Closed and open circles represent absorbances at the wavelength of 320 and 480 nm, respectively. A horizontal dotted line represents a baseline for each set of profiles.

observed here only a broad spectrum over the wavelength range of 300−500 nm all through the time earlier than 19 ns after the excitation.

The benzyl radical formation process from toluene in the liquid phase has been still uncovered directly until now. The most remarkable difference between the nanosecond laser ablation and the femtosecond one is the pulse width, naturally, which strongly indicates that benzyl radical is produced via one transient species whose formation time constant is on the order of picoseconds to nanoseconds. As for such benzyl radical formation, a nanosecond pulse can be equivalent to a sequential femtosecond pulses. On the basis of this consideration, we carried out femtosecond double-pulse excitation. Figure 6 shows two transient absorption spectra, one is measured under single pulse excitation condition (thin line. excitation 1 ← 19 ns → probe) and another is measured under double-pulse excitation condition (thick line, excitation 1 ← 9 ns → excitation 2 ← 10 ns → probe). In the former case, no significant spectrum was observed as also shown in Figure 1. On the other hand, in the latter case, we observed an absorption band whose peak wavelength was about 320 nm. This band originates from benzyl radical without any doubt because the spectrum is in good agreement with a reference.[25]

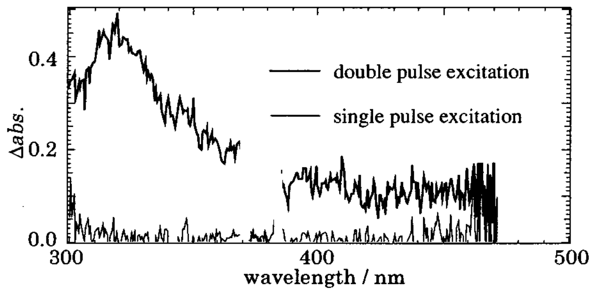
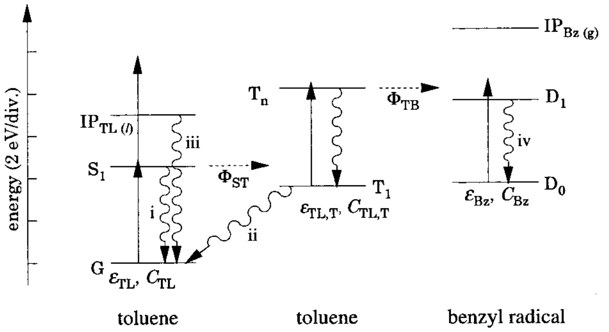


Figure 6. Absorption spectra measured under the conditions of single pulse excitation and double pulse excitation. The thin solid spectrum was measured under the single pulse excitation condition; excitation 1 ← 19 ns → probe. The thick solid spectrum was measured under the double pulse excitation condition; excitation 1 ← 9 ns → excitation 2 ← 10 ns → probe. Laser fluences of excitations 1 and 2 are 10 and 40 mJ/cm^2, respectively.

A lot of reports on the benzyl radical formation process in gas phase have been published. For instance, Nakashima et al.[26] reported the process under the nanosecond 193 nm laser pulse excitations condition. Troe et al. also reported the process under the shock wave pulse excitation condition[27] and other conditions.[28,29] Those reports suggested “hot molecular mechanism”[30] as a benzyl radical formation process, where benzyl radical is thought to be produced via a highly vibrationally excited state of the electronically ground state. In the liquid phase as in this case, however, collisions between molecules are dominated so much in picosecond time domain that hot molecular mechanism is unlikely as a candidate for the benzyl radical formation process. In fact, benzyl radical absorption was not observed in our experiments under the condition that such a highly vibrationally excited state could be produced, that is, when the laser intensity was much higher. On the other hand, Koyanagi and

SCHEME 1: Jablonski Diagram of Toluene in the Liquid Phase[a]



[a] G, ground state; S_1, the lowest excited singlet state; $IP_{TL(l)}$, ionic state in the liquid phase; T_1, the lowest excited triplet state; T_n, excited triplet state; D_0, ground state of benzyl radical; D_1, the lowest excited doublet state; $IP_{Bz(g)}$, ionic state of benzyl radical in the gas phase; Φ_{ST}, intersystem crossing quantum yield from S_1 to T_1; Φ_{TB}, dissociation quantum yield from toluene to benzyl radical. Upward arrows represent energy of one photon excitation (248 nm, 5 eV). Downward waves represent nonradiative relaxation.

Uejoh[31] reported that toluene in a benzene matrix at 77 and 4.4 K dissociated into benzyl radical from a higher excited triplet state. Thus, it is suggested that benzyl radical can be produced via triplet state (T_1) from toluene in the liquid phase. Normally, the intersystem crossing time constant is about 6 ns from the lowest excited singlet state (S_1) of toluene to the lowest excited triplet state (T_1), and the time can be shorter under laser ablation conditions because of S_1-S_1 annihilation. This means that there is no time for T_1 to absorb photons when an excitation light pulse width is on the order of femtosecond as this case. This is the reason we do not observe the absorption band of benzyl radical under single pulse excitation conditions.

Now we go back and summarize the femtosecond laser ablation molecular mechanism of liquid toluene and compare it with the mechanisms in nanosecond laser ablation of the liquids and its diluted solutions. Scheme 1 shows a Jablonski diagram of toluene in the liquid phase. Under femtosecond laser pulse excitation conditions, light absorption induces S_1 formation followed by nonradiative relaxation (i) and T_1 formation via intersystem crossing. Such produced T_1 of toluene, however, cannot absorb further photons because the excitation pulse width is too short compared with the intersystem crossing time constant. As a result, T_1 also decays via nonradiative relaxation (ii). Further, when the laser intensity is relatively high, toluene radical cation could be produced. Even though the amount of such ionic species is thought to be small, it also decays by recombination followed by nonradiative relaxation (iii). All the nonradiative relaxations are in principle enhanced under the condition of laser ablation because of the interactions between such condensely produced transient species. Those nonradiative relaxations effectively produce heat to induce morphological changes (photothermal mechanism).

In the case of nanosecond ablation of liquid toluene[7] and a relatively more highly concentrated solution,[10] on the other hand, such produced T_1 can also absorb another photon followed by a higher excited triplet state (T_n), then benzyl radical is formed. Under laser ablation conditions, benzyl radical and its geminate radical, hydrogen atom in the case of toluene, are produced densely on the sample surface layer, which leads to a formation of gaseous products, such as hydrogen gas, inducing surface morphological changes (photochemical mechanism).

In the case of nanosecond laser ablation of relatively lower concentration solution,[10] the amount of benzyl radical is comparative to that of toluene in the ground state. As a result, such produced benzyl radical can further absorb another photon. The lifetime of the excited state of benzyl radical in solution at room temperature is reported to be 770 ps[25] so that the cyclic multiphotonic absorption process[32] proposed by Fukumura and Masuhara occurs between the two states; a formed excited state benzyl radical relaxes to its ground state rapidly and reabsorbs another photon during the nanosecond laser pulse width. This process enhances heat generation (iv) repeatedly and results in explosive boiling (photothermal mechanism).

This scheme shows that we can control the molecular mechanism of laser ablation not only by changing the solute concentrations as reported before[10] but also by changing the excitation laser pulse width or by using a double-pulse excitation method.

Summary

In this paper, we have carried out time-resolved absorption spectroscopy of liquid toluene under femtosecond 248 nm laser ablation conditions, studied the laser ablation molecular mechanism, and explored the possibility of controlling the molecular mechanism. We have detected excited singlet state of toluene monomer and toluene excimer directly, not benzyl radical at all unexpectedly. The estimated temperature elevation velocity is consistent with the reported value. These experimental data strongly indicate that the femtosecond laser ablation of liquid toluene is induced photothermally. Further, the benzyl radical formation process of toluene in the liquid phase is clarified by a femtosecond double-pulse excitation method to be via triplet states. This inversely indicates the possibility to be able to control the ablation mechanism by femtosecond pulses.

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