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FEATURE ARTICLE

Role of Hot Molecules Formed by Internal Conversion in UV Single-Photon and Multiphoton Chemistry

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The UV photochemistry of benzenes, alkylbenzenes, and olefins in the gas phase is described from a new point of view: the hot-molecule mechanism. After UV excitation the hot molecule (denoted as S_0**) is formed by internal conversion from an excited singlet state to a highly vibrationally excited ground electronic state. The S_0** thus produced has a very high equivalent temperature and a narrow initial energy distribution. Therefore, it is intriguing to study the reactions, collisional relaxation, absorption line shape, formation process etc. of S_0**. The reactions can be discussed as a specific reaction driven by thermal energy. We have measured dissociation rates via the hot molecule for more than 60 molecules. It has been demonstrated that the hot molecule mechanism is one rather general reaction route of unsaturated hydrocarbons. Observation of the formation process of S_0** gives a new direct method of studying radiationless transitions, namely, internal conversion. For the first time, it has been found that the hot molecule has another role. It can be an intermediate in UV multiphoton dissociation. S_0** shows a strong absorption in the UV region and hence efficiently absorbs a second photon which causes dissociation. Radical fragmentations are the major reaction of this new multiphoton chemistry.

I. Introduction

In this paper we demonstrate that vibrationally highly excited molecules can be one of the intermediates in UV single-photon and multiphoton decomposition in the gas phase. Such species (denoted as S_0**, or stated as hot molecules) treated in this article are formed by optical excitation, followed by internal conversion (IC) to the ground electronic state. Hot molecules carry a high vibrational energy, which is nearly equal to the photon energy absorbed. Consequently the equivalent temperatures of S_0** are very high, 2000–4000 K for the benzenes, alkylbenzenes, and olefins treated in this paper. In fact, these molecules dissociate with rate constants expected for reactions driven by thermal energy. We have been successful in directly measuring the decomposition rates of olefins and alkylbenzenes and the rate constants can be interpreted in terms of the hot molecule mechanism.[1,2]

The first example of the hot-molecule mechanism for single-photon photochemistry was proposed in 1962 for large polyatomic molecules. The reaction considered was isomerization of cycloheptatriene to toluene followed by dissociation to the benzyl radical.[3,4] This reaction has been studied extensively by Troe and his co-workers, and direct evidence for the involvement of the hot molecule has been obtained by means of the laser flash photolysis technique.[5] A few other examples had already been proposed in the 1960s, namely the isomerization of benzene[6] and the dissociation of olefins.[7] However, the hot molecule mechanism has been disregarded or considered to be a minor reaction channel for a long time. It should now be considered as a major pathway for UV–vacuum UV photochemistry of unsaturated hydrocarbons, because many convincing examples have recently been established. Several are described in section III. The hot-molecule mechanism in the photochemistry of some carbonyl compounds, most notably formaldehyde, has also been studied,[8] although we do not treat them in this paper.

S_0** itself is a subject worthy to study. It has a narrow thermal energy distribution under collision-free conditions. Collisional relaxation, reaction rate constants, and absorption line shape of S_0** have been studied and are briefly described in sections III and IV.

We have recently found that hot molecules have another role in UV laser photochemistry as one of the intermediates in UV multiphoton dissociation.[9] Decomposition of toluene with ArF laser light (193.2 nm) is a typical example. Hot toluene shows a strong absorption in the UV region and hence readily absorbs a second photon. The second photon dissociates S_0** into a benzyl radical. We believe that a third photon decomposes the benzyl radical. This mechanism is also operative in the ArF laser photolysis of alkylbenzenes. This is the first observation of UV multiphoton decomposition via a hot molecule. Most recently multiphoton isomerization via a hot molecule has been proposed for the isomerization of azulene to naphthalene.[10]

The UV multiphoton chemistry via the hot molecule has a different aspect from that via excited singlets or the lowest triplet state. In the case of UV multiphoton absorption via electronically excited states, the second photon often ionizes the parent molecule and the subsequent photons induce ion fragmentation reactions.

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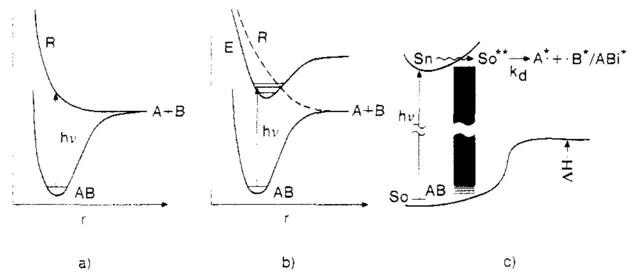

Figure 1. Three dissociation mechanisms: (a) direct dissociation, (b) predissociation, and (c) hot-molecule mechanism. In (c) after irradiation with UV–vacuum UV light, rapid internal conversion occurs to the ground state. Intramolecular vibrational redistribution is very rapid and is completed before dissociation. The hot molecule, S_0**, dissociates to A^{**} + R^{**} and/or isomerizes to AR^*_i with a rate constant much slower than the other two cases.

This picture is called the ladder switching model.[11] On the other hand, in the case of the hot molecule mechanism the second absorbed photon does not ionize the hot molecule, because the energy of the first photon has rapidly been distributed in the different vibrational modes. It should be noted that neutral rather than ion fragmentation takes place. This subject is discussed in section V.

II. Experimental Methods

Interesting observations are absorption spectra and reaction rate constants of S_0** under collision-free conditions. One of the powerful experimental methods and the one employed here is laser flash photolysis. Other methods could be applied. Laser-induced fluorescence might be detectable from S_0**, but a very vague spectrum would be expected. It has been shown that S_0** is a dark species in multiphoton ionization (MPI) spectroscopy.[12] IR emission spectroscopy has also been applied.[13]

Much information has been obtained by laser flash photolysis, as described in this paper. The irradiation light sources used here are an excimer laser and a picosecond UV laser. With these excitation sources it is not difficult to observe absorption spectra of S_0** and its reaction rates. Typical irradiation light in the nanosecond time range is from an ArF excimer laser (193.2 nm) with a pulse width of 10–20 ns (fwhm), and an irradiation energy of 5 mJ/cm^2. To measure rate constants under collision-free conditions, sample pressures were 10–50 mTorr in a 50- or 100-cm cell. Picosecond time resolution allowed us to study the fast radiationless formation of S_0**, namely, the internal conversion.[14] In that experiment a tunable picosecond laser and a laser-driven Xe flash lamp were used as pump-and-probe sources. Other details are described elsewhere.[1,9,14]

III. Photodissociation via S_0**

A. Direct Dissociation and Predissociation. Two well-known dissociation mechanisms are illustrated in Figure 1, a and b. When a molecule is excited to a repulsive potential, *R*, it directly dissociates within a very short time, comparable to a few periods of the vibration (Figure 1a)). Direct measurements have been made by femtosecond spectroscopy. Zewail et al. showed that the dissociation time of the ICN molecule is less than 300 fs.[15] Figure 1b indicates predissociation. A molecule AB is excited to a stable upper level, E. When this level is crossed by the repulsive potential, *R*, the molecule predissociates into A + B by a radiationless transition to the repulsive state R.

B. Hot-Molecule Mechanism. Figure 1c shows the hot-molecule mechanism. A radiationless transition occurs to the ground electronic state directly or via excited states which are lower than the originally excited state. Actually this is the initial step of dissociation for many unsaturated hydrocarbons on irradiation with UV–vacuum UV light. For a polyatomic molecule intramolecular vibrational energy redistribution (IVR) will occur very rapidly before the dissociation from the initially prepared (by IC) highly vibrationally excited state. Even if the incident energy is much larger than the bond dissociation energy, the molecule does not decompose immediately. After IVR is completed, the vibrational energy distribution is expected to become microcanonical. The equivalent vibrational temperatures are 2000–4000 K; therefore, the reactions will be close to those expected as the specific reaction with a fixed internal energy in thermal reaction. In fact dissociation rates are very much slower than those observed in the other two dissociation mechanisms. The rate constants determined for the hot-molecule reaction can be explained quite well by RRKM statistical reaction theory. The above three mechanisms may be operational simultaneously depending upon experimental conditions.

Three different energy redistributions are involved in the dissociation reaction by the hot-molecule mechanism.

(i) The specific energy distribution in vibrational energy is expected in the ground electronic state immediately after internal conversion. The vibrational energy is distributed in accepting modes in the electronic ground state. The modes are presumably the overtone of CH stretch vibration. If the initially prepared state had a lifetime long enough to be detected, we could expect a structured spectrum, for instance, for the hot benzene formed by internal conversion at 193-nm excitation.[16] But there has been no report on a structured spectrum of the initially prepared state by internal conversion for benzenes and olefins. We believe that the lifetime of that state is too short to be detected. Berry and his co-workers have measured overtone spectra up to the ninth CH (23276 cm^{-1}) mode of benzene.[17] They estimated the lifetimes for intramolecular rate processes on the basis of the homogeneous bandwidths. The lifetimes are of the order of 50 fs. When the initially prepared state has an internal energy of 50000 cm^{-1} in total, the lifetime is presumably shorter than 50 fs.

(ii) The intramolecular vibrational redistribution takes place very rapidly. IVR is completed before we detect absorption spectra of hot molecules and/or measure dissociation rate constants. The complete state indicates that the molecule is in the microcanonical state. In fact, the observed spectra and the dissociation rate constants can well be explained on the basis of microcanonical energy distribution as described below. The time to reach the final state under collision-free conditions is presumably much shorter than 1 ns. It should be noted that we could explain the dissociation time of a few nanoseconds in an olefin by the RRKM theory. This energy is presumably redistributed in all of the modes in a time that is much shorter than the dissociation time. The equivalent temperature in this paper defined as the vibrational temperature of molecules whose internal energy is distributed microcanonically.

(iii) After many collisions the initial incident energy should be redistributed and reach a new equilibrium. If the hot molecule does not react, but is collisionally deactivated by foreign molecules and/or cold molecules of the same kind, the sample temperature rises. This temperature rise of the entire system has been measured spectroscopically and used to determine an yield of nonradiative transition of benzene.[18] We can define an equilibrium distribution function, assuming that the internal energy of molecules is exchanged freely with translational energy. The distribution of the internal energy can be calculated by using the vibrational modes.[19] The distribution function in the intermediate stage of the collisional deactivation is not simple. The initial distribution, immediately after optical excitation under collision-free conditions, is calculated by using the equilibrium distribution function at room temperature. The width (fwhm) of this function for benzene is calculated to

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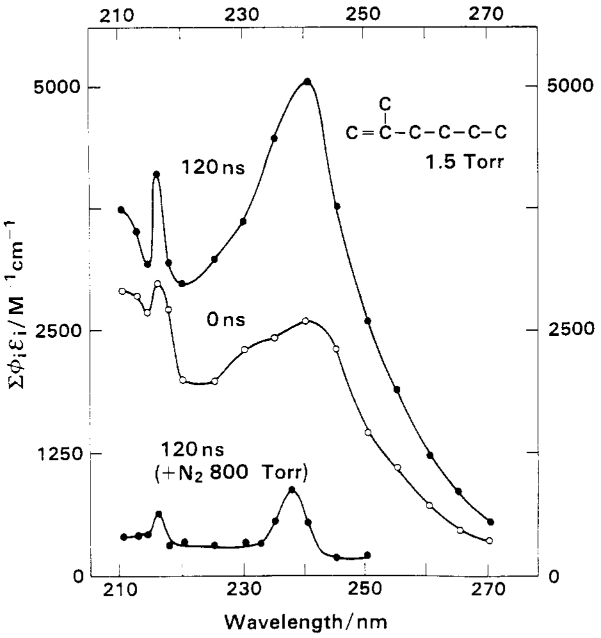
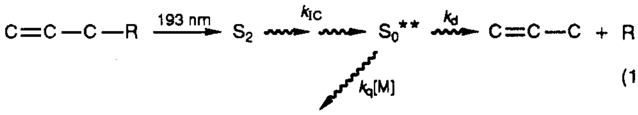


Figure 2. Transient absorption spectra of 2-methyl-1-hexene The peak at 240 nm is due to the methallyl radical and the peak at 216 nm to the methyl radical. Absorption intensities increased with time at a pressure of 1.5 Torr of olefin. The yields of radicals were depressed by addition of 800 Torr of a foreign gas (nitrogen in the present case).

be 430 cm^{-1} at room temperature.

C. Dissociation of Olefins. In the photochemistry of olefins, it is well established that the C–C single bond dissociates at the position β to the double bond under near-vacuum-UV irradiation. This dissociation reaction can be explained in terms of the hot-molecule mechanism. Chesick[7] proposed that the C–C bond ruptured via highly excited vibrational states in the ground electronic state, i.e., by the hot-molecule mechanism.

The dissociation pathway of olefins is shown by the following scheme:



$$C{=}C{-}C{-}R \xrightarrow{193\ \mathrm{nm}} S_2 \xrightarrow{k_{IC}} S_0^{**} \xrightarrow{k_d} C{=}C{-}C + R$$
$$S_0^{**} \xrightarrow{k_q[M]}$$

(1)

The rate constant k_{IC} is for the nonradiative transition, k_d is the dissociation rate constant, and k_q[M] is the rate of a competing deactivation process, induced by a foreign gas. For the first time, we have succeeded in measuring directly the formation rate constants of allylic radicals.[1] More than 50 olefins have been investigated, including cyclic olefins and dienes. The observed rate constant, k_d, corresponds to the specific rate constant of a unimolecular dissociation reaction.

Absorption spectra assignable to β-methallyl (240 nm) and methyl (216 nm) radicals appear in the transient spectra of 2-methyl-1-olefin systems, as shown in Figure 2. The major photodissociation is expected to occur at the position β to the double bond. Formation of the methyl radical indicates that one of the minor reaction pathways is C–C bond dissociation at the α-position. It is clear that the absorption intensity of the methallyl radical increases with time and that the intensity is considerably decreased by adding 800 Torr of nitrogen. As will be shown later, these observations indicate that the reaction mainly proceeds via the hot molecule.

D. Formation Process of Products under Collision-Free Conditions. Figure 3 shows rise curves of the β-methallyl radical generated from 2-methyl-1-olefins. In order to analyze the rise curves, an impulse response function, $D(t)$, was assumed as follows:

$$D(t) = (1 + C_1) - \exp(-k_d t) \qquad (2)$$

The factor C_1 represents contributions from absorption of photoproducts which are formed much faster than the excitation pulse width. These products could be those formed via predissociation (hot methallyl radical, hot vinyl radical, etc.) and those formed via multiphoton absorption if any. The factor C_1 is also a function of absorption of the hot olefin and hot methallyl radical.[1] The rise curves fitted well the curve generated by convolution of the laser pulse with the function $D(t)$. The best-fitted curves are shown as solid lines in Figure 3.

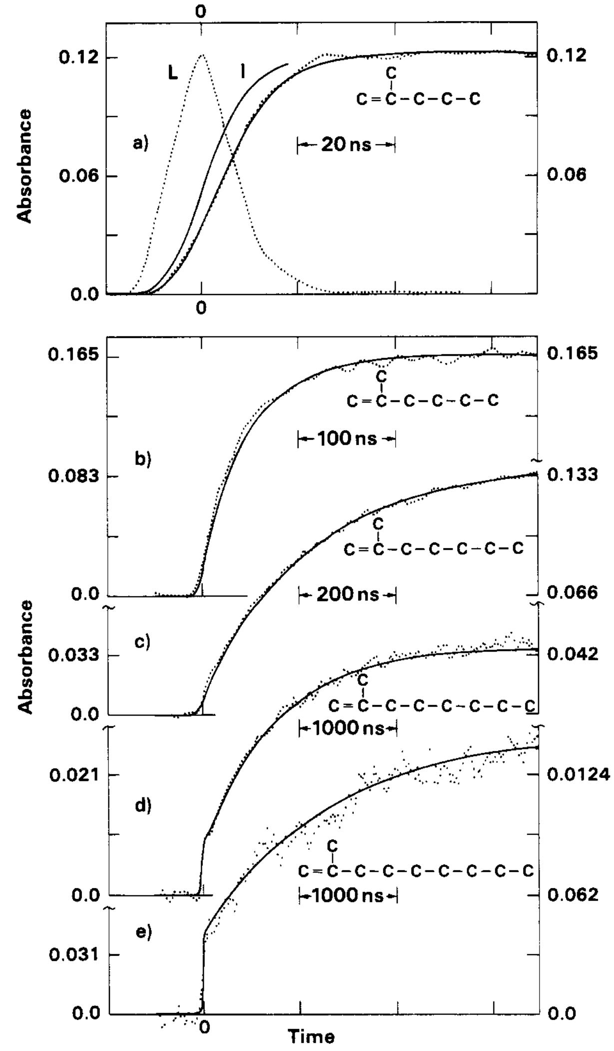


Figure 3. Direct measurements of rise curves of methallyl radicals formed by photolysis of 2-methyl-1-olefins. These curves were measured at 240 nm. L is the shape of the irradiating laser pulse. I is the integrated curve of L. Olefins of smaller size exhibit faster rise curves.[1]

E. Comparison with RRKM Rate Constants. If the hot-molecule mechanism is appropriate, the dissociation rate constants should be explicable in terms of the statistical theory for thermal reactions.[20] The observed rate constants are compared with these calculated by the RRKM theory. These are in fair agreement as can be seen from Figure 4.

In calculating these rate constants, the results of previous studies of the thermal reactions of olefins have proved to be very useful. The method of chemical activation has been applied extensively to the dissociation reactions of the β bond in 1-olefins. Dorer and Rabinovitch have determined these rate constants[21] and have reproduced them successfully by means of the RRKM theory in which an activated complex model was employed. A rather tight structure was found to be a good model for 1-olefins (called "semiloose activated complex model I").[21] We have applied model I to 2-methyl-1-olefins. The discrepancies between the measured and calculated rate constants are not very large for this kind of calculation. The calculated constants strongly support the view

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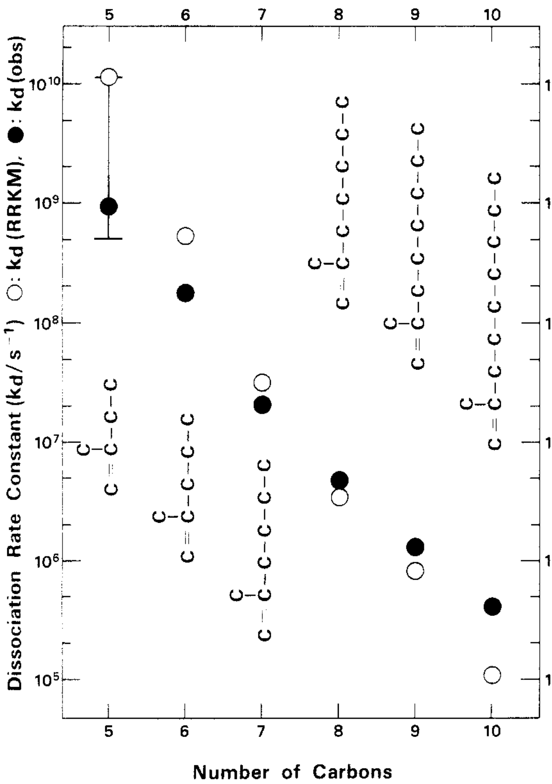


Figure 4. Observed (closed circles) and calculated (open circles) dissociation rate constants for 2-methyl-1-olefins.[1] Calculations are based on RRKM theory (see text).

that the precursor of the slow reactions is a hot molecule and that the activated complex is similar in structure to the activated complex in thermal reactions.

We can conclude that an RRKM-type dissociation from S_1 and T_n is neglected unless the C–C bond energy dramatically weakened in the electronically excited state. Vibrational energy (ca. 100 kJ/mol) in the S_1 state cannot exceed the bond dissociation energy (ca. 290 kJ/mol). The twisted triplet state[22] may give the maximum available energy (ca. 350 kJ/mol). However, the RRKM-type calculation predicts a bond dissociation rate constant more than several orders of magnitude smaller compared to the observed ones if the C–C bond dissociation energy is the same as that in the S_0.

It is worth noting the reliability and precision of the RRKM-type calculations. The present calculations for a series of olefins are in agreement within a factor of 5. Troe and his co-workers measured and calculated the reaction rate constants for cycloheptatrienes and obtained only 2–2.5 times difference between them.[5,23]

F. Alkylbenzenes. The major product in the UV photolysis of *n*-alkylbenzenes is the benzyl radical. The dissociation mechanism has been postulated to be predissociation. However, we have shown that the hot-molecule mechanism is operative in the photodissociation. A rise curve of benzyl radical upon excitation of toluene is shown in Figure 5. The dissociation rate constants of 14 compounds are listed in Table I. Slower rates are observed for alkylbenzenes with longer methylene chains. This trend is in accordance with the rate constants of olefins. Smaller dissociation rate constants are seen for more highly deuterated alkylbenzenes, and this observation is also expected on the basis of reactions driven by thermal energy. Perfluorinated toluene has a 2.6 times smaller rate constant than toluene.

For the dissociation of toluene, three independent experimental values are available. On irradiation of cycloheptatriene (CHT) with the KrF laser light (248 nm), the excited state turns to S_0^{**} and then isomerizes to hot toluene. The hot toluene formed by this route has 623 kJ/mol of internal energy. This energy is very close to that (627 kJ/mol) of S_0^{**} produced by internal conversion of toluene by the 193-nm (ArF laser) irradiation. The strain energy of CHT happens to nearly coincide with the energy difference of the KrF and ArF laser photon energy. The dissociation rate constant for the CHT route was measured by Hippler et al.[23] and confirmed with a different experimental technique by Tsukiyama et al.[24] These values are in the range $(2.6–3) \times 10^6$ s^{-1} and are in fairly good agreement with the present value of 2.0×10^6 s^{-1} listed in Table I.

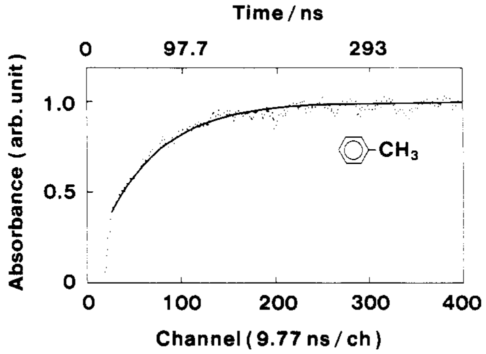
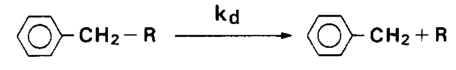


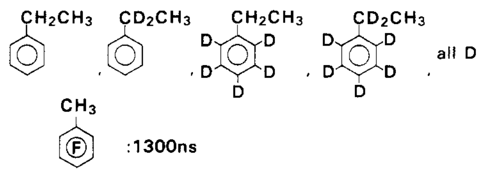
Figure 5. Benzyl radical formation upon excitation of toluene at 20 mTorr observed at 260 nm. The initial fast rise was followed by a slow formation process.

TABLE I: Formation Time (k_d^{-1}/ns) of the Benzyl Radicals



	no. of deuteriums				
	0	2 or 3	5	7 or 8	9 or 10
toluene	500	750	830	990	
ethylbenzene[a]	36	43	50	69	89
propylbenzene	130				
butylbenzene	620	830			1100

[a]



G. Applicability of Hot-Molecule Mechanism to Single-Photon Dissociation. As explained above, olefins and alkylbenzenes dissociate by the hot-molecule mechanism. We believe that the formation of S_0^{**} and its subsequent reactions are not exceptional but rather common phenomena for the vacuum UV–UV irradiation of hydrocarbons. The first example is isomerization of CHT.[3,4] This system has been studied extensively by Troe and his co-workers.[5,23] Also isomerization reactions of benzene and hexafluorobenzene have also been shown to occur via S_0^{**}.[25,26] Some of the decomposition reactions of carbonyl compounds can be explained in terms of the hot-molecule mechanism.[8] Recently Ichimura has suggested that halobenzenes dissociate via S_0^{**} to some extent.[27] Pyridine and related aza compounds also show transient absorption spectra of S_0^{**} by 193-nm laser irradiation. All of these compounds have very weak fluorescence quantum yields in the wavelength region of 200 nm. Acetylenes and dienes also have very weak fluorescence quantum yields and we have actually detected in these molecules slow rise curves of photo-

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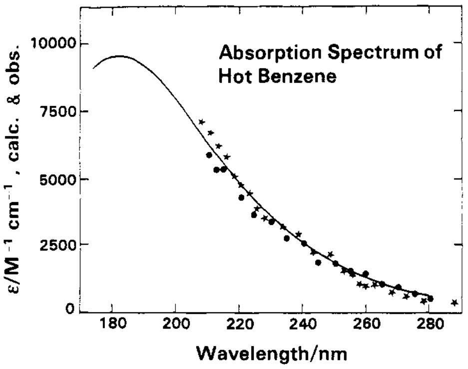

Figure 6. Absorption spectrum of S_0^{**} of benzene formed by internal conversion on irradiation with an ArF laser. The solid line is a simulation spectrum on the basis of a modified Sulzer–Wieland model at 3389 K. Transient absorbance was obtained immediately after excitation of 2 Torr of benzene (closed circles) and 2 Torr benzene in the presence of 800 Torr of nitrogen (stars).

products. However, not all hydrocarbons dissociate by the hot-molecule mechanism. For instance, although saturated hydrocarbons have a fluorescence quantum yield of 0.001, it is well-known that this small yield is mainly caused by decomposition reactions.

We expected to observe hot molecules in the photolysis of phenol and anisole. For these systems the formation rates of the phenoxy radical were too fast to be detected by our apparatus.[28] From the observation that the rise curve of the phenoxy radical can be reproduced by the integrated excitation pulse we concluded that the rate constant was greater than 10^9 s^{-1}. On the basis of the rate constants for alkylbenzene dissociation, the formation rate constants for the phenoxy radical is expected to be slower than 10^9 s^{-1} and should be observable, if the hot-molecule mechanism was operative. Therefore, the formation of phenoxy radical is not explicable in terms of the hot-molecule mechanism, and predissociation is the preferred pathway. We suggest that these molecules predissociate via the (π,π^*) states.

IV. Formation of S_0^{**}, Collisional Relaxation, and Direct Measurements of Internal Conversion

A. Observation of Hot Benzene. Before discussing multiphoton chemistry via S_0^{**}, we will describe briefly the absorption spectra of hot molecules in the nanosecond time-resolved spectra. We detected absorption spectra of S_0^{**} formed by internal conversion from the initially prepared states of S_1 as well as S_2,[18,25] the quantum yield of hot-molecule formation being estimated to be unity from S_2.[25] Figure 6 shows the absorption spectrum of S_0^{**} of benzene.[25] The energy of absorbed photon (193 nm) is distributed among all the vibrational modes, and the estimated equivalent vibrational temperature becomes 3390 K. This line shape can be interpreted as a result of an extraordinarily broadened spectrum due to the high temperature. Astholtz et al. were successful in applying a modified Sulzer–Wieland model to hot alkylbenzenes.[29] This model was originally developed for describing the absorption line shape of diatomic molecules at higher temperatures. Benzene has an allowed transition, $^1E_{1u} \leftarrow {}^1A_{1g}$, in the wavelength region of 180 nm. The strong and structureless absorption in the deep UV region (>200 nm) due to the hot molecule becomes a wing of the allowed transition. This method for spectral simulation of hot molecules is not perfect. Further improvement in the spectral simulation method is required. Recently some more elaborate theoretical analyses were performed.[16,30]

The collisional relaxation of the hot molecule is a very interesting subject. The initial energy distribution of S_0^{**} is very narrow; for example, it is less than 0.1 eV (430 cm^{-1} from the equilibrium distribution function at room temperature plus ca. 260 cm^{-1} from the bandwidth of ArF laser) when benzene S_0^{**} is formed by 193-nm (corresponding 6.42 eV) irradiation (see section IIIB). Therefore we can study energy transfer at highly vibrationally excited states, where thermal reactions might occur. One point is whether or not the transferring energy $\langle \Delta E \rangle$ per collision is constant or depends on the internal energy of the hot molecule. Some systems can be explained on the basis of $\langle \Delta E \rangle$ = constant.[31,46] However, we obtained results for benzene which can be explained in terms of an energy-dependent model.[25] Recently, the hot molecule in solution has been studied and a relaxation time of 40 ps has been obtained.[32]

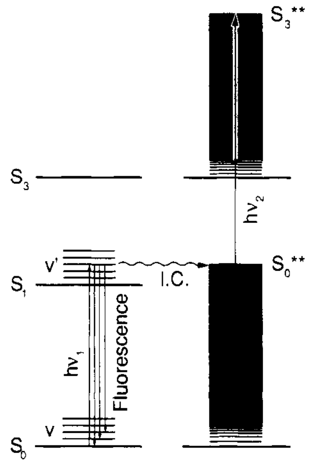

Figure 7. Energy diagram and scheme for the observation of the rate of internal conversion by the flash photolysis method. The pump source is a deep-UV tunable picosecond laser which excites vibronic levels. The probe source is a laser-triggered Xe flash lamp.

The second interest is direct observation of the formation rate constants of S_0^{**}. In the early stage of these studies the multiphoton ionization technique was applied to benzene.[12] The rate constant for the radiationless process was estimated to be ca. 20 ps on the basis of the integrated MPI signals.

B. Picosecond Observation of Internal Conversion Rates. Under collision-free conditions, observation of the formation process of S_0^{**} followed by optical excitation

$$S_0 \xrightarrow{h\nu} S_n \overset{\mathrm{IC}}{\rightsquigarrow} S_0^{**}$$

gives a direct measurement of the internal conversion rate (Figure 7).

Several vibronic states of S_1 benzene were pumped by a picosecond tunable laser, which uses sum-frequency mixing of Stokes–Raman shifted fourth-harmonic radiation with optical parametric radiation. The time evolution of S_0^{**} was observed by probing $S_3^{**}(E_{1u}) \leftarrow S_0^{**}(A_{1g})$ absorption by a Xe flash lamp triggered by the YAG fundamental pulse. Three vibronic bands ($6^1 10^2 1^1$, 245.7 nm; 7^1, 242.8 nm; and $6^1 1^3$, 241.7 nm) were chosen and the formation of S_0^{**} was observed. In all cases the rise times corresponded to fluorescence lifetimes upon excitation of each single vibronic level, namely 27 ns for $6^1 10^1 1^1$, dual lifetimes of 4 and 18 ns for 7^1, and 250 ps and 2.9 ns for $6^1 1^3$ (ref 33). This is the first observation of the formation process of such a hot state, namely, the internal conversion process in real time.[14]

There are many studies on direct observation of radiationless transitions. Laser flash photolysis has been applied to the studies of internal conversion[18,25] and intersystem crossing.[34] Multiphoton

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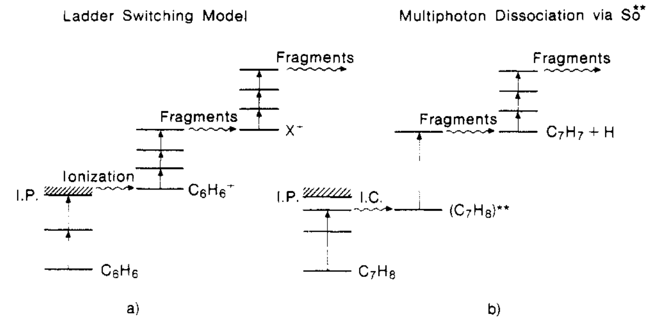

Figure 8. Two mechanisms of UV multiphoton dissociation. (a) Ladder switching model. For instance, benzene can be ionized by two-photon absorption; thereafter, the ion absorbs photons and dissociates to secondary ions. (b) Hot-molecule mechanism. For instance, ArF laser light (193.2 nm) pumps the S_3 state of toluene. Internal conversion finally leading to $S_0{}^{**}$ takes place. The second photon excites $S_0{}^{**}$ and the excitation leads to toluene dissociation into a benzyl radical. The benzyl radical is assumed to disappear on absorption of a third photon. Neutral fragmentation is the major reaction.

ionization[12,35-37] and photoelectron spectroscopy[38] has also been applied. The present picosecond measurement presents a new alternative and direct method of studying internal conversion.

V. UV Multiphoton Dissociation via Hot Molecule

A. Ionic Dissociation and Neutral Fragmentation. Extensive studies have been made on UV multiphoton dissociation of molecules at low pressures.[39-41] Gedanken et al. classified the mechanisms of multiphoton dissociation into three types. A molecule absorbs one or more photons and ionizes. The parent ion thus produced further absorbs photons and dissociates (class A, ladder switching model[11]). One- or multiple-photon excited state dissociates to neutral fragments. These fragments absorb more photons and further dissociate (class B). The coherent absorption of many photons instantaneously populates a very high super excited state. This state either autoionizes or fragments to neutrals (class C). We found a new intermediate of multiphoton dissociation as shown in Figure 8b.[9] This mechanism is compared with the ladder switching mode[11] shown in Figure 8a. In the latter case, when benzene is irradiated at 266.8 nm, for example, it is ionized by two-photon absorption and the cation is formed in $v = 0$. The cation is photodissociated to acetylene, $C_4H_4{}^+$, etc. The nonradiative transition has been known to occur very efficiently in the cation. We may call this path of photodissociation as dissociation by a "hot ion mechanism". In fact, photodissociation rate constants of the benzene cation have been measured and analyzed in terms of the RRKM-type reaction theory.[42] It should be noted that ion fragmentation is the major reaction in this multiphoton dissociation.

In the new model the first photon excites molecules to a level below the ionization potential. The efficient nonradiative transition is the key process. The subsequent photons absorb, which brings the molecule into an electronically excited state with highly vibrational energy. Efficient nonradiative transition occurs again to the ground electronic state. A hot molecule with an energy of double photons is formed. This very hot molecule efficiently decomposes. The equivalent temperature of the hot molecule of the last step must be several thousand degrees. It should be noted that neutral fragmentation is the major reaction in this mechanism. Among the ion and neutral mechanisms, the importance of the neutral mechanism was emphasized recently,[41,43] because the neutral channel was almost completely ignored in the previous studies. The first example of multiphoton dissociation via hot molecule has been found for toluene and will be described in the next section. Most recently it was found that acetylene was formed from benzene by a multiphoton process via the hot molecule.[44]

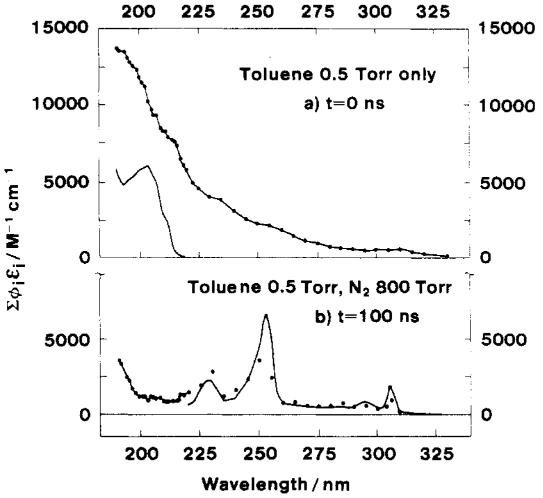

Figure 9. (a) Transient absorption spectra of toluene in the absence of a foreign gas and at $t = 0$ ns. (b) Observed at $t = 400$ ns. The solid line in the wavelength region longer than 220 nm is the absorption spectrum of the benzyl radical, with molar extinction coefficients multiplied by 0.24. Observed data in (a) and (b) were corrected for the ground-state depletion of toluene. Laser fluence was 11–12 mJ/cm^2. The absorption spectrum of toluene is depicted in the left side of (a) as a solid line.

B. Multiphoton Dissociation via Hot Molecule. The following scheme explains the mechanism of benzyl radical formation by multiphoton excitation of toluene.

$$S_0 \xrightarrow{h\nu} S_3 \tag{3}$$

$$S_3 \rightsquigarrow\!\rightarrow\!\rightsquigarrow S_0{}^{**} \tag{4}$$

$$S_0{}^{**} \rightsquigarrow B^{**} + H, \quad k_3 = 2.0 \times 10^6 \text{ s}^{-1} \tag{5}$$

$$S_0{}^{**} \overset{[M]}{\rightsquigarrow} S_0 \tag{6}$$

$$S_0{}^{**} \xrightarrow{h\nu} B^{**} + H \tag{7}$$

$$S_3 \rightsquigarrow B^{**} + H \tag{8}$$

$$B^{**} \xrightarrow{h\nu} X + Y \tag{9}$$

$$B^{**} \overset{[M]}{\rightsquigarrow} B \tag{10}$$

The ArF laser (193 nm) pumps the valley between the S_2 and S_3 states in process 3. We label the pumped level the S_3 state in this paper. Internal conversion has been shown to be the major deactivation processes in the case of S_2 and S_3 excitation.[45] The final dissociation products of $S_0{}^{**}$ have been detected directly.[2] The fluorescence quantum yield at 184.9 nm is as low as 10^{-5} and the yield of the lowest triplet state has been estimated to be of the order of 0.01 (ref 45). The rate constant of process 4 is presumably higher than 10^{11} s^{-1}, since internal conversion to $S_0{}^{**}$ competes with relaxation from S_3 to the fluorescence state (S_1). Gregory et al. suggested a rate constant of 10^{14} s^{-1} (ref 45).

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Process 5 is a slow dissociation process from S_0^{**}, where B_0^{**} indicates benzyl radical with vibrationally and translationally excited state. Three independent experimental values are now available, as discussed above (section IIIF). The collisional relaxation processes 6 by the foreign gas (M) have been studied in detail. Helium atoms with pressures as low as 20 Torr completely suppress formation of the benzyl radical.[5] The collisional deactivation efficiency of nitrogen is 1.4 times as great as that of helium.[46] Therefore, when the benzyl radical is detected in the presence of 800 Torr of nitrogen, it can be stated with certainty that this is not a result of process 5. The formation of the radical in the presence of high pressures of foreign gases will be explained in terms of the photodissociation of S_0^{**}, as shown by process 7. The quantum yield of the predissociation process 8 was lower than our detection limit (0.02). The benzyl radical is assumed to decompose photochemically on absorption of a third photon as indicated by process 9. Process 10 is collisional deactivation of the hot benzyl radical.

Figure 9 clearly shows formation of the benzyl radical under 800 Torr of nitrogen. The solid line in Figure 9b shows the absorption spectrum of the benzyl radical, measured by the photolysis of benzyl chloride.[47] The closed circles were obtained by the photolysis of toluene. The closed circles are in good agreement with the solid line over the wavelength range longer than 225 nm. It can be concluded that the major absorbing species is the benzyl radical. The molar extinction coefficient at the strongest peak (253 nm, $4^2B_2 \leftarrow {}^2A_2$ transition) has been determined to be 28 000 M^{-1} cm^{-1} (ref 47). The solid line can be normalized to the observed data by a factor of 0.24 times the molar extinction coefficients. Therefore, the apparent quantum yield of the benzyl radical, φ_B, is 0.24 under a laser fluence of 11.5 mJ/cm^2.

The spectrum at $t = 0$ (the solid line in Figure 9a) is considered to be the overlapping spectra of S_0^{**} and the benzyl radical. The largest component in the spectra at $t = 0$ ns in Figure 9 is assignable to the absorption of S_0^{**}. The spectrum in the wavelength region longer than 215 nm can be compared with that of Hippler et al.[30] They measured the absorption spectrum of S_0^{**} produced by photoisomerization of cycloheptatriene. This hot toluene has an internal energy of 623 kJ/mol close to that (627 kJ/mol) resulting from the internal conversion of toluene. The spectral shape is similar to that obtained by Hippler et al.[30]

These hot species relax within 80 ns in the presence of 800 Torr of nitrogen. The relaxation time of the hot benzyl radical is about 15 ns[47] when produced by photolysis of benzyl chloride. It is expected to be 19 ns for S_0^{**}.[46] Therefore, the spectra observed at $t = 100$ ns in Figure 9b can be regarded as those of the relaxed species. The spectra (closed circles) in the wavelength region shorter than 210 nm were due to a depletion of the ground-state toluene molecules.

C. Laser Power Dependence of the Concentration of Benzyl Radical. Figure 10 shows the absorbance of the benzyl radical vs the laser fluence along with a simulation curve. The benzyl radical concentration was measured at $t = 100$ ns in the presence of 800 Torr of nitrogen. It was found that the absorbance was proportional to the square of the laser fluence in the region lower than several mJ/cm^2. We did not observe any indication of the existence of a single-photon process until the lowest laser fluence (0.6 mJ/cm^2). In the region higher than 10 mJ/cm^2 a saturation effect was seen. No strong absorption was detected other than that of the benzyl radical around the peak (253 nm) at a laser fluence of 11.5 mJ/cm^2 (Figure 9b). Therefore, the absorbance can be directly related to the concentration of the benzyl radical by using its molar extinction coefficient ($\epsilon_B = 28\,000$ M^{-1} cm^{-1}). This allowed the apparent yield of benzyl radical to be determined. It increased from 0.02 at 0.6 mJ/cm^2 to 0.24 at 11.5 mJ/cm^2, and finally to 0.25 at 25 mJ/cm^2.

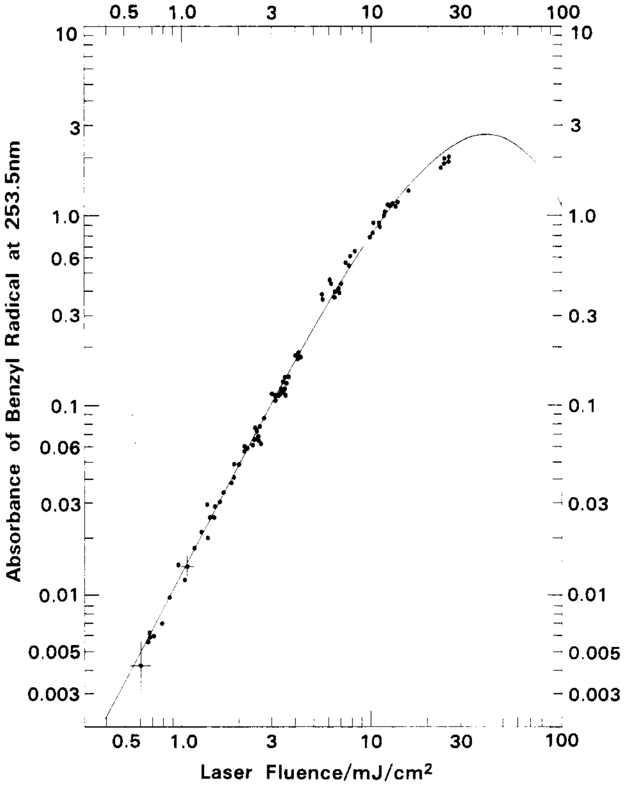

Figure 10. Laser fluence dependence of absorption intensity of the benzyl radical. The absorption was observed at 100 ns delay time and at 253.5 nm. Toluene pressures were 0.5–8 Torr in the presence of 800 Torr of nitrogen. The solid line is a simulation curve calculated by using the molar extinction coefficient of S_0^{**} at the same wavelength of the first photon absorbed. Excitation pulse function in time is also taken into account for simulation.

D. Power Dependence of Multiphoton Dissociation. We have found reasonable parameters which reproduce the relationship between the benzyl radical absorbance and the laser fluence. The fitting curves in Figure 10 were calculated on the basis of a model of UV multiphoton decomposition via hot toluene. The schematic diagram is shown in Figure 8b and the elementary reaction processes are described in the previous scheme, i.e., process 3–10. This model assumes that the second photon dissociates hot toluene into a benzyl radical and that a third photon decomposes the benzyl radical. The later part of the exciting laser pulse will be absorbed more efficiently by higher concentrations of hot toluene and benzyl radical, which will have been produced by the earlier part of the laser pulse. There are two variable parameters. One of them accounts for absorption of the second photon as described in process 7. The absorbance can be written by $\varphi_d\epsilon_h$, where φ_d is the dissociation yield of benzyl radical by irradiation of S_0^{**}, and ϵ_h is the molar extinction coefficient of hot toluene at 193.2 nm. The other variable parameter accounts for the third photon as indicated in process 9 and is, in fact, ϵ_B, the molar extinction coefficient of the benzyl radical at 193.2 nm. We assumed that the benzyl radical decomposes with a yield of 1.0 at 193.2 nm. The best fit parameters were as follows:

$$\varphi_d\epsilon_h = 20000\ M^{-1}\ cm^{-1} \tag{11}$$

$$\epsilon_B = 22500\ M^{-1}\ cm^{-1} \tag{12}$$

We could measure the molar extinction coefficient, ϵ_h, in eq 11 and found it to be $1.9 \times 10^4 < \epsilon_h < 2.7 \times 10^4$ M^{-1} cm^{-1}. Therefore, φ_d is close to 1.0. When $\varphi_d\epsilon_h$ is changed to 25 000 M^{-1} cm^{-1}, the calculated curve undergoes a nearly parallel shift of 1.24 times the best fit curve. When $\varphi_d\epsilon_h = 15000$ M^{-1} cm^{-1}, it shifts in the opposite direction by a factor of 0.75. To explain the saturation behavior, the decomposition process of the benzyl radical was introduced, and a best fit curve was obtained for $\epsilon_B = 22\,500$ M^{-1} cm^{-1}, when all of the deviation was assumed to be caused by the decomposition.

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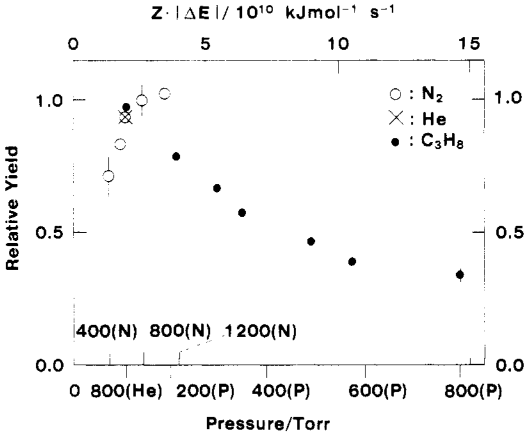

Figure 11. Pressure dependence of the relative yield of benzyl radical. Open circles are for nitrogen, crosses for helium, and black circles for propane. The horizontal scale was normalized to a collision parameter.

In fact, we have found that the benzyl radical is easily decomposed by UV irradiation.[9] Possible decomposition products are as follows:

$$C_6H_7 \rightsquigarrow C_2H_2 + C_5H_5 \quad \text{or} \quad C_4H_4 + C_3H_3 \qquad (13)$$

These reactions are observed under thermal reaction conditions.[48]

E. Pressure Dependence of Yield of the Benzyl Radical. The relative yield decreased by 30%, when the nitrogen pressure was changed from 800 to 400 Torr as shown in Figure 11. It decreased by about one-third on increasing the pressure of C_3H_8. The yields are plotted against the collisional parameter, $Z\langle\Delta E\rangle$, where Z is collision number and $\langle\Delta E\rangle$ is the energy transferring per collision obtained from the literature.[46]

These observations can be explained in terms of the pressure dependence of the value of $\varphi_d\epsilon_h$. In the low-pressure region, ϵ_h became small, because collisional relaxation of the hot molecule is in the early stage and so the molar extinction coefficient does not reach its maximum value. There are two possible reasons for the decrease of the yield in the high-pressure region of C_3H_8. The dissociation yield, φ_d, decreases and/or the molar extinction coefficient, ϵ_h, decreases due to collisions. These findings for the pressure dependence also support the assignment of the intermediate in the UV multiphoton dissociation as hot toluene.

Figure 12 shows that S_0^{**} has a long lifetime in the presence of a high pressure of nitrogen, enough to be excited by the next photons in the 15-ns pulse. We can also predict time profiles of S_0^{**} as shown in Figure 12c. This calculation is based on a modified Sulzer–Wieland model and on an energy-transfer model, where energy transferring per collision is constant. Therefore, it is possible to predict how S_0^{**} absorbs laser light under specific conditions.

F. Ladder Switching Model vs Hot-Molecule Mechanism. Principally both processes are possible under any conditions. Several parameters affect the formation yield of ions and neutral radicals. They are the lifetimes of the initially excited state, in other words, the rate of internal conversion, molar extinction coefficients of the excited states, the laser fluence, and the laser pulse shape. It can be noted that the long lifetime of the initially excited state, the large molar extinction coefficient, and the short pulse induce preferentially the ladder switching model.

Our simulation code for the multiphoton ionization, which includes all parameters given above, predicted an yield of ca. 0.0026 of toluene cation at a laser fluence of 11 mJ/cm². We assumed that the intermediate S_3 has a lifetime of 0.2 ns with $\epsilon = 20\,000$ M⁻¹ cm⁻¹ at 193 nm and that every photon absorbed by the S_3 state yields a toluene cation. The S_3 state shows a very weak fluorescence (its yield is of the order of 10^{-5} (ref 45)), indicating that the lifetime is much shorter than 1 ns. Therefore, it can be concluded that the yield of toluene cation is much smaller than that of the benzyl radical.

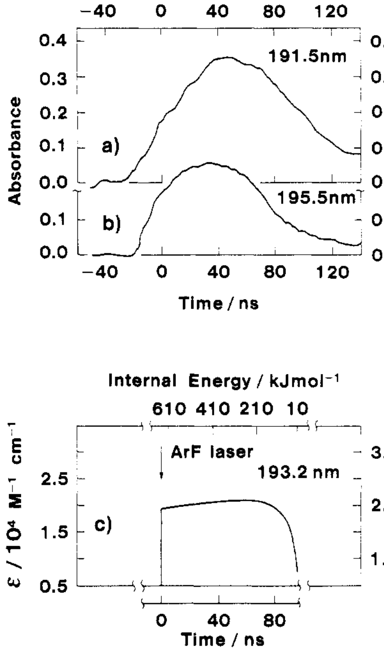

Figure 12. (a and b) Time profiles of absorption of hot molecule in the presence of 100 Torr of nitrogen at 191.5 and 195.5 nm, respectively. (c) A simulation curve calculated by using a transfer energy $\langle\Delta E\rangle$ = constant and a modified Sulzer–Wieland model.

We tried to detect the toluene cation, which will be produced by multiphoton absorption. But the yield of the cation formation was actually lower than our detection limit and estimated to be less than 0.1 (ref 9).

G. Characteristics of UV Multiphoton Dissociation via S_0^{**}. In this section we describe various characteristics of the hot-molecule mechanism of UV multiphoton dissociation observed with toluene.

(i) As Figure 5 shows, the rise curve of the benzyl radical has fast (instrument limited) and slow components under low-pressure conditions. It has been shown clearly (see above) that the fast component includes a two-photon process via hot toluene (process 7). The slow process (process 5) has already been studied[2,23,24] and is known to be a dissociation process of the hot toluene. The dissociation rate constant, k_d, is 2×10^6 s⁻¹.

(ii) Detectable benzyl radical concentrations in the presence of 800 Torr of nitrogen result from the fast process and are formed by photodissociation of hot toluene (process 7).

$$\begin{tikzcd} S_0^{**} \arrow[r, "h\nu"] \arrow[rr, bend right, squiggly, "k_d"'] & S_3^{**} \arrow[r, "k_d^{**}"] & B^{**} + H \end{tikzcd} \qquad (14)$$

Internal conversion from S_3^{**} could take place to the ground state. Such a ground-state molecule will have very high internal energy and its dissociation rate constant, k_d^{**}, could well be faster than the rate of collisional relaxation induced by nitrogen.

(iii) UV multiphoton chemistry via the hot molecule differs in one respect from that via excited singlets or the lowest triplet state. In the case of UV multiphoton absorption via electronically excited states, the second photon often ionizes the parent molecule and the subsequent photons induce ion fragmentation reactions (ladder switching model described in section IV.A).[11] On the other hand, in the case of the hot-molecule mechanism the second absorbed photon does not ionize the hot molecule, because the energy of the first photon has been distributed among the vibrational modes. Therefore neutral fragmentation takes place rather than ion fragmentation.

(iv) We did not detect any single-photon predissociation of toluene (process 8) at 193 nm. This means that the yield is less than 0.02. This is similar to the C–H bond dissociation of benzene, where predissociation on irradiation with light of 193 nm scarcely

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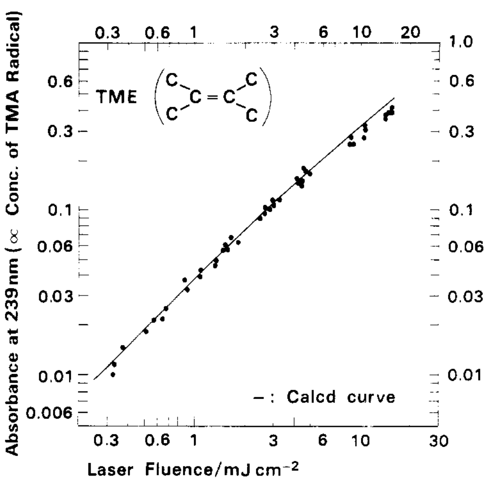

Figure 13. Laser fluence vs absorption intensities of the trimethylallyl (TMA) radical and methyl radicals formed upon excitation of tetramethylethylene (TME). Absorbances of TMA were measured at 239 nm and at a delay time of 50 ns in the presence of 800 Torr of nitrogen. The solid curve was calculated by assuming a single-photon process without any inner filter effect (see also ref 1b and 9).

occurs.[18] However, this is not commonly found for electronic excitation at 193 nm. In olefins the yield of predissociation of C–C or C–H is 0.1 (ref 1), whilst phenol and its derivatives predissociate with high quantum yields.[28]

(v) A linear relation between the absorption intensity of the trimethylallyl (TMA) radical and the laser fluence was observed upon excitation of tetramethylethylene (TME), indicating that the radical is formed by a single-photon process. In the presence of 800 Torr of nitrogen, the absorption intensity of the TMA radical increased almost linearly with the irradiation energy (Figure 13). The absorbance was measured at the peak of the TMA radical (239 nm) and at 50 ns delay time, when collisional relaxation is complete. The solid curve in Figure 13 was calculated by assuming that the TMA radical is produced by a single-photon process. It is concluded that the TMA radical is formed via a one-photon process upon excitation of TME. Multiphoton dissociation of TME was not detectable. The difference between this system and the toluene system is presumably due to a low molar extinction coefficient of the intermediate, the hot TME for multiphoton absorption. In other words, the molar extinction coefficient of S_0^{**} is expected to be weak during the laser pulse, when collisional relaxation occurs. On the other hand hot toluene has a large molar extinction coefficient during collisional relaxation, as shown in Figure 12.

VI. Conclusion: Characteristics of Hot Molecules Formed by Internal Conversion

Investigations of a large number of molecules, including benzenes, alkylbenzenes, carbonyls, olefins, and ring olefins, indicate that the hot-molecule mechanism will be quite common in UV–vacuum UV photochemistry. More molecules will be found to dissociate according to the hot-molecule mechanism. A new role for the hot molecule has been found as an intermediate step of multiphoton dissociation. This mechanism is especially important for neutral radical formation. In addition the direct observation of the S_0^{**} formation process provides an alternative method for investigating radiationless transitions.

Although the hot molecule is in a highly excited vibrational state and electronically in the ground state, its chemistry may not necessarily be determined by the lowest barrier of thermal reaction. The internal energy of hot molecule will be greater than the minimum energies of many reaction routes. The reaction rate will be determined by the state densities above the minimum potential energy surfaces. The hot molecule may have many possible reaction routes because it has rich internal energy.

Collisional cooling of products is another important factor in determining final reaction products. For example, excitation of benzene with 193-nm light produces a valence isomer of fulvene. High-temperature thermal reaction produces a thermally stable molecule of acetylene. In this case a general rule of photochemistry, which sometimes gives thermally unstable molecules as reaction products, is retained. Collisional cooling process is effective to stabilize products.

It is very intriguing to study the characteristics of the hot molecule itself. We can get information on elementary processes of a reaction at a given fixed internal energy. Among different methods of creating vibrationally highly excited molecules,[49] namely, (a) chemical activation, (b) overtone excitation, (c) stimulated emission pumping, (d) infrared multiphoton excitation, and (e) optical excitation of an electronic excited state followed by internal conversion, only the last method gives high excitation energy and narrow thermal energy distribution simultaneously. For the above reasons, the hot molecule, which is created by the last method, has been extensively studied on collisional relaxation, specific rate constants, $k(E)$, and the absorption line shape. Until very recently, it has been known that only a few systems could create hot molecules. We have shown in this paper that a variety of molecules can be converted to hot molecules. If we know $k(E)$ values, they can be converted to their rate constants at high temperatures, which are not easily measurable directly. Very importantly, the photon energy for an ArF laser (620 kJ/mol) exceeds that of most chemical-bond energies.

The width of the initial distribution is determined by thermal energy at the ambient temperature and the exciting laser bandwidth. Taking the example of exciting benzene with an ArF (193 nm) laser, the width (ΔE) is estimated to be less than 0.1 eV at room temperature, and excitation energy (E) is 6.42 eV. The ratio of $\Delta E/E$ is on the order of 0.01. The observed rate constant is very close to the specific rate constant, $k(E)$, which is defined as the reaction rate with fixed internal energy. The ΔE value can be significantly improved by using narrow-band lasers and supersonic-jet molecular beams.

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Registry No. Toluene, 108-88-3; ethylbenzene, 100-41-4; propylbenzene, 103-65-1; butylbenzene, 104-51-8; 2-methyl-1-butene, 563-46-2; 2-methyl-1-pentene, 763-29-1; 2-methyl-1-hexene, 6094-02-6; 2-methyl-1-heptene, 15870-10-7; 2-methyl-1-octene, 4588-18-5; 2-methyl-1-nonene, 2980-71-4; benzyl, 2154-56-5.

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