Accounts

VUV Laser Chemistry—Formation of Hot Molecules and Their Reactions in the Gas Phase—

Tomoyuki Yatsuhashi* and Nobuaki Nakashima

Department of Chemistry, Graduate School of Science, Osaka City University,
3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585

(Received August 15, 2000)

The hot molecule (S_0**) is in a highly vibrationally excited state formed by rapid internal conversion from initially prepared electronic excited states. The importance and predominance of the S_0** mechanism in VUV gas phase photochemistry has been demonstrated. In this account, the fundamental physicochemical properties of S_0** are discussed in order to understand the characteristic features of S_0** reactions, and VUV laser chemistry is reviewed from the following two points of view: 1) The generalization and classification of VUV chemistry for a variety of molecules, including the hot molecule mechanism and other competitive mechanisms; 2) A new strategy of multiphoton chemistry that employs hot molecule as an intermediate. Internal conversion is a dominant deactivation process for many molecules in the VUV region. Aromatic hydrocarbons and olefins are the representative examples of S_0** reactions. However, fluorescence and intersystem crossing are major deactivation processes in some cases such as large condensed aromatic hydrocarbons. The reactions of chlorinated compounds and phenols are explained by other reaction mechanisms such as direct dissociation and predissociation. Carbonyl compounds and some amines are classified into the intermediate cases. Due to the large molar extinction coefficient and relatively long lifetime of S_0**, the multiphoton absorption process can be induced by a single nanosecond laser pulse. As a result of fast internal conversion and intramolecular energy redistribution, the second photon and further photons will not be absorbed by the molecule in the electronic excited state but by that in the S_0**, and the photon energy of the multiphoton is accumulated as vibrational energy. Therefore, ionization is minor process in the case of the multiphoton reaction of S_0**. The neutral radical formation is predominant in the dissociation reaction, and the rate constant increases because the internal energy is multiplied by the multiphoton absorption process. The applications of these findings lie in the following: 1) Large molecules of which the single-photon hot molecule reaction rate is small; 2) Molecules which have been deemed to be photoinert.

Molecules in highly vibrationally excited states are one of the intermediates in VUV laser chemistry. After VUV laser excitation, such species are formed by internal conversion, finally leading to the electronic ground state. Intramolecular vibrational redistribution in polyatomic molecules is complete within a period much shorter than 1 ns. The molecule is populated in highly excited vibrational states with the internal energy of the incidental photon energy plus the energy associated with room temperature. We call this a hot molecule and denote it as S_0**. The equivalent temperature of S_0** can reach more than a few thousand Kelvin, then S_0** dissociates and/or isomerizes. This type of pathway in photochemistry is called the hot molecule mechanism.[1]

We will review VUV laser chemistry from two points of view. The first asks, how widely operative is the hot molecule mechanism? The second asks, are there cases of two or three photon chemistry in the hot molecule mechanism: photochemistry of S_0** which is produced by successive excitation.

The reaction mechanism for large molecules was first proposed for isomerization of cycloheptatriene to toluene in 1962 by Srinivasan and by Thrush and Zwolenik.[2] Troe and his coworkers studied this process extensively as a model system of S_0**.[3,4] Nakashima and Yoshihara studied hot molecule mechanism of benzene, a typical aromatic molecule, by UV-VUV laser excitation.[5] Toluene was found to dissociate to a benzyl radical by hot molecule mechanism in a sub-microsecond range in 1985 and since then has been treated as a model system of dissociation from S_0**.[6–10] As shown in Table 1, olefin, cycloheptatriene, and formaldehyde[11] had already been discussed on the basis of hot molecule mechanism; however, many types of molecules have remained untested or have not been thoroughly discussed in terms of the hot molecule mechanism. VUV laser excitation is very effective to study hot molecule mechanism because the available internal energy is sufficiently large to induce a chemical reaction in a short time if a non-radiative transition takes place, which leads to the question: Do any molecules become hot and react? Answering this question is one of the targets of this account. We have exam-

Table 1. VUV Laser Chemistry[a)]

		WL	Reaction	Mechanism	MP?
Hydrocarbons					
Aromatics	Benzene[5,27]	193, 158	Iso, Dis	Hot	Yes[b)]
	Toluene[12]	193	Dis	Hot	Yes
	Azulene[13]	308	Iso	Hot	Yes
	[2.2]Paracyclophane[74]	193	Dis	Hot	Yes
	Naphthalene[58]	193	Iso	Hot	Yes
	Anthracene[46]	193	T, F	—	—
Alkane	Methane[c)]	121	Dis	Hot, T	No
	Cyclohexane[d)e)]	158[d)]	Dis	Hot, PD	No
Alkene	Tetramethylethylene[38]	193	Dis	Hot	No
	Cycloheptatriene[3]	193	Iso	Hot	Yes
	1,4-Cyclohexadiene[f)]	193	Dis	Hot	—
Alkyne	Acetylene[68]	193	Dis	S, T	No
	Diphenylacetylene[46]	193	T	—	—
Others					
Oxygen	Formaldehyde[11]	UV	Dis	Hot	No
	Phthalic anhydride[34]	193	Dis	Hot	No
	Coumarin[49]	193	Dis	Hot	Yes
	Benzyl alcohol[67]	193	Dis	Hot	No
	Phenol[66]	193	Dis	PD	—
	1-Benzofuran[49]	193	Dis	Hot	No
	9-Fluorenone[46]	193	Dis, T	—	—
Nitrogen	Pyrazine[57]	248, 266	Dis	Hot	Yes
	Acetonitrile[59]	121	Dis	Hot	No
	Acrylonitrile[g)]	193	Dis	Hot	No
Halogen	Chlolobenzene[60]	193	Dis	Hot?	No
	Hexafluorobenzene[62]	193	Iso	Hot	—
	Fluoroethylene[63]	158	Dis	Hot, DD	No
	Vinyl chloride[65]	193	Dis	DD, Hot	No
Sulfur	Thiophene[h)]	193	Dis	Hot	No
	Dimethyl sulfoxide[i)]	193	Dis	Hot, DD	No

a) Abbreviation: WL, Laser wavelength (nm) used in the experiments; MP?, Multiphoton hot molecule process?; Iso, Isomerization; Dis, Dissociation; T, Triplet excited state; F, Fluorescence; S, Singlet excited state; Hot, Hot molecule mechanism; DD, Direct dissociation; PD, Predissociation.

b) We have found two-photon reactions of benzene by 193 nm laser irradiation, details will be published in a separate paper.

c) J-H. Wang and K. Liu, *J. Chem. Phys.*, **109**, 7105 (1998). A dissociation reaction channel on the triplet surface has also been investigated.

d) T. Shimada, Thesis, Osaka University (1993). The rise of product ($7\pm2\times10^6$ s^{-1}) has been observed at 225 nm. The rise component was diminished by the addition of helium.

e) F. P. Schwarz, D. Smith, S. G. Lias, and P. Ausloos, *J. Chem. Phys.*, **75**, 3800 (1981).

f) A. Kumar, P. D. Naik, R. D. Saini, and J. P. Mittal, *Chem. Phys. Lett.*, **309**, 191 (1999); X. Zhao, R. E. Continetti, A. Yokoyama, E. J. Hintsa, and Y. T. Lee, *J. Chem. Phys.*, **91**, 4118 (1989).

g) D. A. Blank, A. G. Suits, Y. T. Lee, S. W. North, and G. E. Hall, *J. Chem. Phys.*, **108**, 5784 (1998).

h) F. Qi, O. Sorkhabi, A. H. Rizvi, and A. G. Suits, *J. Phys. Chem. A*, **103**, 8351 (1999).

i) D. A. Blank, S. W. North, D. Stanges, A. G. Suits, and Y. T. Lee, *J. Chem. Phys.*, **106**, 539 (1997). The contribution of hot molecule mechanism on the promary fragmentation has been estimated to be 83% for DMSO-h_6 and 73% for DMSO-d_6 respectively.

ined several types of molecules using VUV lasers, aiming to extend further the hot molecule reactions.

A second photon is easily absorbed by S_0**, because S_0** often has a high molar absorption coefficient at the laser wavelength. The absorption line shape of S_0** is interesting because of its high temperature with a narrow energy distribution. The excited state resulting from the second photon will be converted again to S_0**. In this case, the internal energy becomes about twice that of the S_0** produced by the first photon. The multiply excited species dissociates and/or isomerizes very fast. These types of reactions were first demonstrated in 1987 with the toluene dissociation reaction to benzyl radical[12] and azulene isomerization to naphthalene.[13] Even CW laser excitation can induce multiphoton chemistry of azulene.[14] How widely does this type of multiphoton reaction occur? Three photons and more are conceivable, as discussed in the original papers. C_{60} reactions[15] by nanosecond laser excitation can be classified as this sort of mechanism. We have tried to find some other examples and this is the second topic of this account.

Three factors about the physical chemistry of the hot molecule mechanism are important and will be discussed briefly. The first point is the fast and highly efficient non-radiative transition, the nature of which was discussed in the 1980s. The one major target at that time was the third channel of benzene.[16,17] Recently the study of non-radiative transition entered a new stage. VUV ultrafast spectroscopy has clearly shown that an internal conversion occurs on the order of femtoseconds and picoseconds for molecules such as benzene and toluene,[18] benzene dimer,[19] benzene-ammonium complex,[20] pyrazine,[21] ethylene, and vinyl chloride.[22] As a result of recent theoretical work, the internal conversion process is explained in terms of a conical intersection between the initial and final states.[23] Unfortunately, the theoretical calculation for the non-radiative transition from the highly electronic excited state to the electronic ground state is difficult due to the complexity; however, such an internal conversion process has been demonstrated well experimentally.

Since S_0^{**} has interesting characteristics, including high temperature with a narrow energy distribution and the ability to be instantly prepared, it is a good object for studying direct measurements of a reaction rate constant compared with the statistical theory. Agreement between observation and theory is excellent, and this is the second point. Collisional energy transfer is the third point. Many papers concerning this subject have been published. We utilize these results to explain reactions of the hot molecule mechanism by single as well as multiple excitation.

In the first section we briefly describe our experimental technique. The second section contains a review of some of the fundamental aspects of the absorption profiles of S_0^{**} of benzene, examples of dissociation rate constants of alkylbenzene, and one comment on a yield of photoproducts affected by collisional relaxation. An understanding of these concepts is necessary so that the reader can interpret individual experimental results. In the later sections, examples of the hot molecule mechanisms are described.

1. Experiments

Before describing the details of hot molecule reactions, we will explain the experiments briefly. The molecules that have sufficient vapor pressure at ambient temperature can be examined under any experimental conditions, such as the collision-free conditions to obtain a reaction rate constant or high-density conditions to achieve multiphoton reactions. For our experiments, samples were gasified at a suitable temperature. Small molecules such as benzene can be examined under these different conditions well; however, nonvolatile samples require special handling. For that reason, the large molecules, which have a low vapor pressure at room temperature, were left unexplored. The molecules could be prepared for the photolysis by elevating the experimental temperature for efficient vaporization and for sufficient absorbance at the laser wavelength. A typical suprasil gas cell was placed in a homemade hot cell; the temperature was controlled by a thermocouple-heater combination. The reaction cell was kept for over 30 minutes at the experimental temperature to ensure complete vaporization and complete mixing with the foreign gas. The transient absorption measurements were performed by a flash lamp-photomultiplier tube combination with an ArF excimer laser (193.3 nm, 200 mJ/pulse, fwhm 14 ns). Zero s was defined as the time where the transient absorption has a sharp hump in the plenty amount of nitrogen as shown in Fig. 4. The details of the each definition of zero s have been noted in the original paper. The sample and cell were renewed at every laser shot in order to avoid effects due to the accumulation of photoproducts. Sometimes a surprising difference was found between the first and second laser shots by VUV laser excitation due to the photoproducts.

2. Physicochemical Properties of S_0^{**}

2-1. Absorption Spectrum of S_0^{**}. We will describe briefly the absorption spectra of hot molecules. Fig. 1 shows the absorption spectra of benzene at room temperature and its S_0^{**} formed by internal conversion on irradiation with an ArF laser as an example.[5] The energy of an absorbed photon (193 nm) is distributed among all of the vibrational modes (ν_i). The equivalent vibrational temperature can be calculated to be 3389 K according to Eq. 1, under the assumption of harmonic oscillation of the vibrational modes.

$$E_0 = \sum_{i=1}^{n} \frac{h\nu_i}{\exp\left(\dfrac{h\nu_i}{kT}\right)-1} = h\nu(193nm) + E_{RoomTemp}, \qquad (1)$$

where E_0 is the total internal energy, $E_{\mathrm{Room\ Temp}}$ is the average

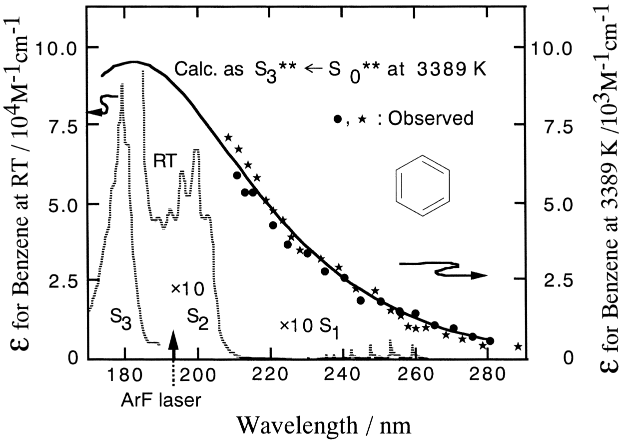


Fig. 1. Absorption spectrum of S_0^{**} of benzene formed by internal conversion on irradiation with an ArF laser. The solid line is a simulation spectrum on the basis of a modified Sulzer–Wieland model at 3389 K. Stars and closed circles are observed values of transient absorbance immediately after excitation of 2 Torr benzene (circles) and 2 Torr of benzene in the presence of 800 Torr of nitrogen (stars). The dotted line is the absorption spectrum of benzene at room temperature. The vertical scale on the left side is for the dotted line and for the solid line is on the right side.

thermal internal energy at room temperature, h is Planck's constant, k is Boltzmann's constant, and T is the vibrational temperature, respectively.

The absorption line shape, molar extinction coefficient (ε) can be estimated using a modified Sulzer–Wieland model, which was originally developed to explain the absorption spectra of halogen molecules at high temperatures.

$$\varepsilon(T,\nu) = \varepsilon_{\max}\frac{\nu}{\nu_0}\sqrt{A}\exp(-AB^2), \qquad (2)$$

where ν is the observing wavelength and ν_0 is the absorption maximum at 0 K. A and B are parameters based on the spectrum at low and the high vibrational temperatures.[24] The spectral line profile has a Gaussian shape, as can be seen in Eq. 2 and Fig. 1. Fair agreement between the observation and calculation is seen within experimental errors, indicating formation of S_0** with the quantum yield of close to unity for the internal conversion to S_0**. The absorption spectrum can be interpreted as a broadened spectrum of the allowed transition of $S_3 \leftarrow S_0(^1E_{1u} \leftarrow {}^1A_{1g})$ due to the high vibrational temperature. An interesting result in the spectrum is that a hot molecule has strong molar absorption coefficients in the wavelength region on both sides of an allowed transition. This is a key parameter when inducing VUV-multiphoton chemistry.

2-2. Specific Rate Constant. A hot molecule produced by VUV excitation has enough internal energy to induce reactions. Such a hot molecule is in a microcanonical state with a small width of energy distribution, which means the reaction will give a specific rate constant and can be explained in terms of the statistical reaction theory. The most rigorous comparison between experiments and theory has been done for alkylbenzene. The first measurement of the rate constant was done by Troe's group for the system of hot toluene formed by isomerization of excited cycloheptariene by a KrF (248 nm) laser in 1981.[4] Ikeda et al. found that hot toluene can be produced by internal conversion of toluene excited directly by an ArF (193 nm) laser, and the dissociation rate constant to the benzyl radical was measured in 1985.[6] A number of commercially available molecules allowed the study of hot molecules to expand. The major techniques were transient UV absorption of radicals by nano-microsecond laser photolysis,[4,6,9,10] time-resolved laser-induced fluorescence of dissociated hydrogen,[25] and molecular beam measurements by varying the flight distance.[26] An F_2 laser (158 nm) was employed to increase the internal energy of hot molecules.[10,27]

It is important to note here that observations are in good agreement with a statistical reaction theory, as shown in Fig. 2. The dissociation rate constant $k_{E,J}$ at an energy E and angular momentum quantum number J is given by Eq. 3, where $N_{E,J}$ is the number of quantum routes and $\rho_{E,J}$ is the density of state of the parent molecule.

$$k_{E,J} = \frac{N_{E,J}}{h\rho_{E,J}} \qquad (3)$$

The observed values are plotted in Fig. 2 with calculated curves. The specific rate constants are calculated by Brand et al.[9] and Fröchtenight et al.[26] for C–H bond dissociation of methyl-substituted alkylbenzenes. Reported values that were scattered more than one order of magnitude between research groups in the early stage of the measurements, have converged to reasonable values. In Fig. 2, only the central values without error bars are plotted. Many other alkylbenzenes have been measured, including deuterated compounds.[8,9,26] For the case of olefins, measurements are in fair agreement with calculations by the RRKM statistical theory.[1,28]

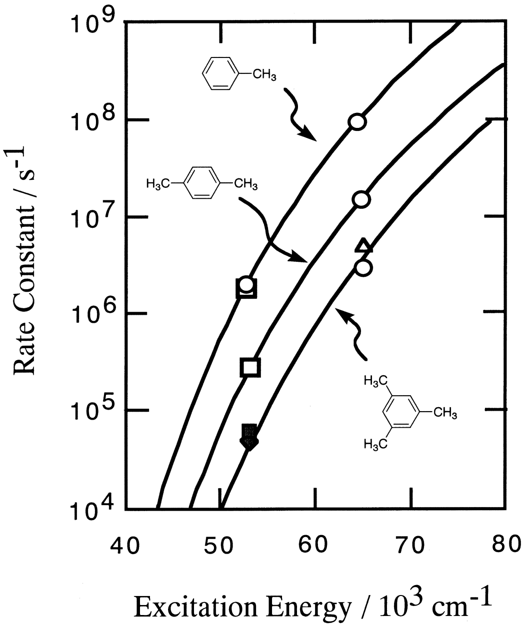
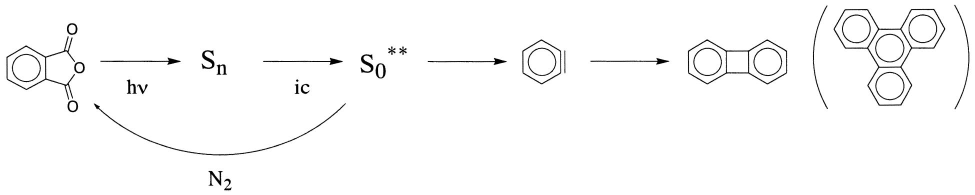


Fig. 2. Specific rate constants for C–H bond dissociation of toluene (upper curve), p-xylene (middle curve), and mesitylene (lower curve). The curves are re-plotted from Ref. 9 for toluene and *p*-xylene, and from Ref. 26. Detailed prameters for SACM calculation and correction factors can be found in the Refs. The measured points are from Ref. 9 (□), Ref. 26 (■, ◆), Ref. 25 (△), and Ref. 8, 10 (○). Only central values without error bars are plotted.

2-3. Depression of Reaction Yield by Collisional Relaxation. Hot molecules are collisionally deactivated by foreign gases. The collisional energy transfer has been a good subject to study, because of the narrow energy distribution in the initially prepared S_0** state (ca. 0.1 eV in the case of benzene). Many systems have been studied and reviewed, including results from the use of other methods.[29] The collisional cooling process of S_0** in gas phase and even in supercritical fluids[30] is one of the central topics of physical chemistry. Many experiments and molecular dynamics simulations have been performed for small molecules[31] such as benzene[32] as well as for large molecules.[33] In the relation to chemical reaction from S_0** with the internal energy of single and/or multiphoton energy, the pressure dependence of the yield should be discussed. The dissociation rate constant of toluene is 2×10^6 s^{-1} at 193 nm excitation, and the single-photon reaction is completely depressed in the presence of several tens Torr (1 Torr = 133.322 Pa) of nitrogen. In the case of two-photon chemistry, the initially prepared hot toluene is still active within the pulse width of an ArF laser. The relative yield decreased to about 35% of the peak when the pressure of propane increased from 100 to 800 Torr.[1]

One of our recent observations is shown in Fig. 3. The for-



Scheme 1.

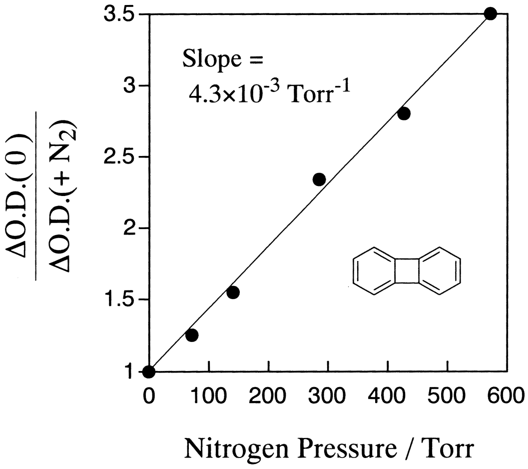


Fig. 3. Pressure dependence of the relative yield of biphenylene formed by dimerization of benzyne which is derived from the vibrationally hot phthalic anhydride. Absorbance are measured at 355 nm observed at 400 ns after the laser pulse (423 K).

mation of biphenylene by an ArF irradiation to gaseous phthalic anhydride was significantly suppressed by the addition of nitrogen, and a fairly linear correlation was obtained. The dimerization of benzyne would not be affected by foreign gas, however, the formation of benzyne will be strongly quenched if the precursor of benzyne is derived from vibrationally hot species. Assuming the collisional frequency is 5×10^7 Torr s^{-1}, hot molecule collides every 35 ps in the presence of 570 Torr of nitrogen. This is an important observation that supports the conclusion that biphenylene is formed by Scheme 1, including hot phthalic anhydride:[34]

More discussion of this system is included in this account.

3. UV-VUV Gas Phase Photochemistry: Hot Molecule Formation and Reactions

In the early stage of studies of hot molecule chemistry, aromatic hydrocarbons and olefins have been spotlighted. In particular, the dissociation reactions of alkylbenzenes and olefins are good target reactions because the produced radicals are easily detectable and identifiable. The molecules other than hydrocarbons have not been discussed well in terms of the hot molecule mechanism. Recently, we have started to examine several types of molecules using VUV lasers with the goal of making generalized statements about hot molecule reactions. VUV photochemistry of various molecules has been widely studied by other researchers too, especially Y. T. Lee group has recently developed a photofragment translational spectroscopy which is an effective method to discern a contribution of S_0**. It is impossible to list all of the many and detailed experimental and theoretical results; selected examples of VUV photochemistry are listed in Table 1.

What is a hot molecule? How can we identify hot molecules? We have mentioned benzene as the most typical example of a hot molecule and discussed it briefly in section 2. The agreement of the theoretical and experimental absorption spectra is strong evidence of a hot molecule formation (2-1). How can we say whether the reaction occurred as a result of the hot molecule mechanism? The success of the reaction rate calculation by the statistical rate theory provides the answer (2-2). The quenching of the product yield by a foreign gas is strong evidence of the hot molecule mechanism (2-3).

Are there any examples of hot molecules other than hydrocarbons? Though studies of the reaction of hot molecules other than hydrocarbons are ongoing, some examples of carbonyl compounds and ethers will be shown to examine whether the reaction is explained well by the hot molecule mechanism or not (3-2). Other examples of which hot molecule mechanism are not operative, including works by other researchers, will be mentioned (3-3). In the next paragraph first we will mention some examples of hydrocarbons only briefly (3-1) because the detailed results have already been described elsewhere.[1] We will also describe the results of the photolysis of condensed aromatic hydrocarbons.

3-1. Hydrocarbons as Typical Examples of Hot Molecule Chemistry. Benzene has been regarded as a good target molecule for long time by chemists and physicists since the first discovery. The photophysical and photochemical properties are still under study by theoretical calculations and new experimental methods.[35] Benzene is also an important and interesting molecule in hot molecule chemistry. The fundamental photophysical properties of hot benzene have been discussed as a model case. Another important feature for photochemists is that thermally unstable and different products than that obtained in an ordinary thermolysis would be expected because the intermediate and the products can be cooled down by collisional relaxation in the case of hot molecule chemistry. A rapid cooling process for S_0** is a distinctly different point from the thermal reactions at the corresponding temperature. In the case of benzene, fulvene is derived from S_0** and acetylene (biphenyl) from ordinary thermolysis as a major product. In the latter case, the most thermally stable product was produced after the frequent collisional heatings. The continuous UV-VUV photoirradiation to liquid aromatic hydrocarbons results in the formation of soot.[36]

These characteristic features of S_0** chemistry are significant in the case of olefins. Olefins have been examined well under various conditions. Collin published a detailed review in 1988 that covered the hot molecule chemistry of over 25 years.[37] Dissociation rate constants have been measured.[1,28,38] Olefins are regarded as good examples of S_0^{**} chemistry in which the product distribution can be controlled by several factors such as excitation wavelength and reactant pressure.[39] The simplest olefin, ethylene, has now attracted attention again, and the photodissociation[40] via S_0^{**} was reinvestigated by both ultrafast spectroscopy and theoretical calculations.[41] An ultrafast internal conversion of ethylene (30 fs) was measured in real time.[22]

Condensed Aromatic Hydrocarbons. Benzene is one of the most important model molecule that has been studied well in terms of S_0^{**} chemistry. And so a simple question may arise: Can we see S_0^{**} in even larger aromatic molecules? The important data are the correlation between the fluorescence quantum yield (lifetime) and the excitation wavelength. Experiments have been done for many molecules such as benzene[17] and naphthalene.[42] As the exciting wavelength becomes shorter, the fluorescence yield (lifetime) drops suddenly. This feature has been discussed in terms of the third decay channel. In the case of naphthalene, the threshold energy is estimated to be 10000 cm^{-1} above the lowest excited singlet state, whereas that of tetracene is 25000 cm^{-1}.[43] We have succeeded in observing hot naphthalene using an ArF laser irradiation,[44] which, at room temperature, did not produce triplet state, cation radical, nor emission. We can safely say that the internal conversion channel is operative for naphthalene by exciting it with an ArF laser. The transient spectrum during the laser pulse is well simulated by the modified Sulzer–Wieland model for S_0^{**}. Through the examination of foreign gas effects and laser fluence dependencies, we have found that the consumption of naphthalene is suppressed by nitrogen and the product is formed by a two-photon process. We have assumed azulene as a plausible product from the energy diagrams and the results of azulene photolysis.[45] However, identification of products is necessary for drawing the whole reaction scheme, because we can suggest an isomerization reaction as another possible reaction of hot naphthalene.

We have examined other large aromatic hydrocarbons such as anthracene, phenanthrene, and triphenylene.[46] A significant emission was observed for these large aromatic molecules even by an ArF laser light excitation in the gas phase. Figure 4 shows the time-resolved absorption spectra of anthracene obtained at 473 K. A strong emission as shown in the inset of Fig. 4 was observed during the laser pulse and therefore the spectrum at 0 ns was not shown in the wavelength region between 330 and 440 nm. The absorbances of the stable product observed at 260 and 400 nm were proportional to the laser fluence. The species which has peaks at 380 and 400 nm is assigned to be the triplet state of anthracene.[47] No other product was found in the transient spectra but we can see the evidence of collisional relaxation of hot species in the decay profile, as shown in the inset of Fig. 4. We can assign it to be anthracene in a vibrationally excited state; however, the multiplicity is unknown. In conclusion, it is clear that the internal conversion is not a main deactivation pathway of highly electronic excited anthracene, phenanthrene and triphenylene. The experimental results showed that naphthalene is only in large condensed aromatic molecule safely assignable as an S_0^{**} after an ArF laser irradiation.

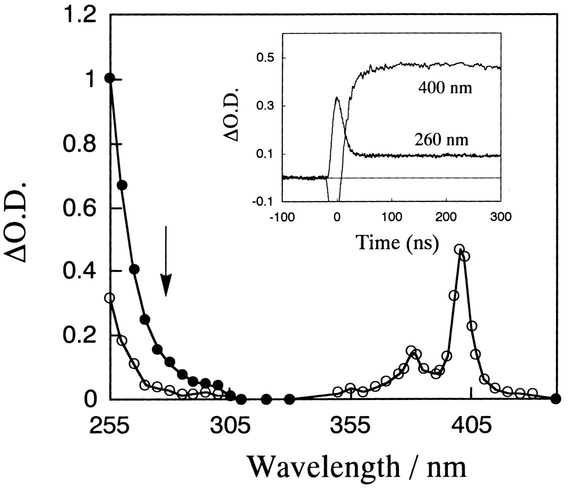


Fig. 4. Transient absorption spectra of anthracene at 0 ns (●) and 200 ns (○) after 193 nm laser irradiation in the presence of 690 Torr of nitrogen at 473 K, and the inset shows the transient time profiles at 260 and 400 nm.

3-2. Hot Molecule and a Variety of Deactivation Mechanisms Found in Carbonyl Compounds and Ethers. Formaldehyde[11] and its fluorinated derivatives[48] are known to be the typical examples of hot molecule chemistry of carbonyl compounds. Except for these compounds, hot molecule has not been sufficiently investigated in the carbonyl compounds. On the other hand, strong emission from S_1 was observed in the case of dibenzofuran (ether). These results clearly show that internal conversion ($S_0^{**} \leftarrow S_n$) is not a dominant deactivation pathway, even though molecules were excited to a higher electronic state. The competition with another photophysical process such as the internal conversion to the S_1 state ($S_1 \leftarrow S_n$) or intersystem crossing ($T_n \leftarrow S_n$) should be considered in these cases.

We would like to show the one-photon benzyne formation from phthalic anhydride and the two-photon decarbonylation of coumarin via S_0^{**}. The details of coumarin photolysis will be described later (4-2).

Phthalic Anhydride (Internal Conversion).[34] Phthalic anhydride (PA) is an important reactant as a source of benzyne. The study of benzyne has been performed by flash vacuum pyrolysis or photolysis, and it has been isolated in a cold matrix for direct spectroscopic observations. Many steady-state spectroscopic methods have been used successfully to characterize benzyne; however, time-resolved spectroscopy was reported only in the 1960s. The observation of benzyne and its dimerization process was successful in the microsecond region, but flash photolysis in the nanosecond region was not achieved.

The photolysis of PA by VUV light is a good example to compare the hot molecule mechanism with thermolysis such as flash vacuum pyrolysis because of the simplicity of the decomposition reaction. One can expect an easily detectable final product, biphenylene, which has characteristic absorption peaks and large molar extinction coefficients. The transient absorption spectra of PA irradiated by an ArF laser are shown

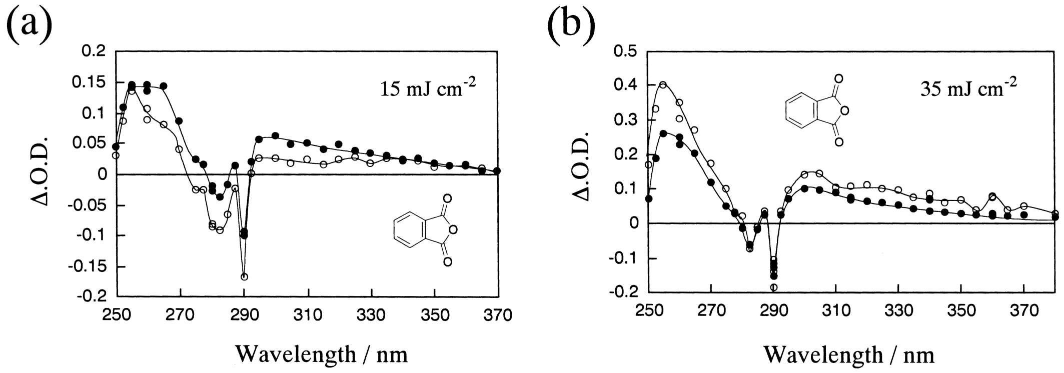


Fig. 5. Transient absorption spectra of phthalic anhydride at 0 ns (●) and 400 ns (○) after the laser excitation in the presence of 570 Torr of nitrogen (423 K). (a) Low-laser fluence condition (15.0±0.6 mJ cm^{-2}). (b) High-laser fluence condition (36.1±1.5 mJ cm^{-2}).

in Fig. 5. The spectra exhibited strong bleaching between 270 and 300 nm, which corresponded to the depletion of the ground state PA. The absorbance at 0 ns monotonically decreased with increasing wavelength, and no vibrational structure was observed in the region of 300–370 nm, where the ground state PA did not have significant absorption. The monotonic spectra were understood to be those of a hot molecule. It is reasonable to conclude that the hot PA which is instantaneously formed with a laser pulse and a dominant absorber at 0 ns.

The characteristic absorption peaks of biphenylene are clearly seen at 355 nm in the high laser fluence condition (Fig. 5b). It is possible to quantify biphenylene, although the intermediates such as hot PA and benzyne have a broad and structureless spectrum. Examining the wavelength of 355 nm, where biphenylene would be the only observable product at 400 ns after the laser pulse, one can easily obtain the effects of laser fluence and foreign gas on the final product yield. Figure 6 shows the effects of laser fluence on the biphenylene formation. Two important conclusions can be drawn from the data in Figs. 3 and 6. First, the biphenylene formation is suppressed by the addition of foreign gas, indicating the inclusion of S_0^{**} as an intermediate. Second, the biphenylene formation requires two photons, indicating that the formation of benzyne is a one-photon process. We can then safely say that biphenylene is formed by the dimerization of benzyne, which is derived from the vibrationally hot PA.

An interesting finding indicates that a successive reaction after the complete cooling of hot molecule. The transient time profile at 260 nm, measured at a relatively high laser fluence (35 mJ cm^{-2}), has a slow rise component even in the presence of nitrogen. This behavior should not originate in the collisional cooling processes nor reaction of hot molecule but the intermolecular reactions because the hot molecule was almost completely de-energized by the collision with nitrogen. The most likely species to appear at the high laser fluence conditions would be triphenylene, which has a strong absorption at 260 nm. The formation of triphenylene would contribute to the transient absorption at 260 nm, and the slope of the plot (open circle, 260 nm) in Fig. 6 is greater than 1 in the high fluence region (> 10 mJ cm^{-2}).

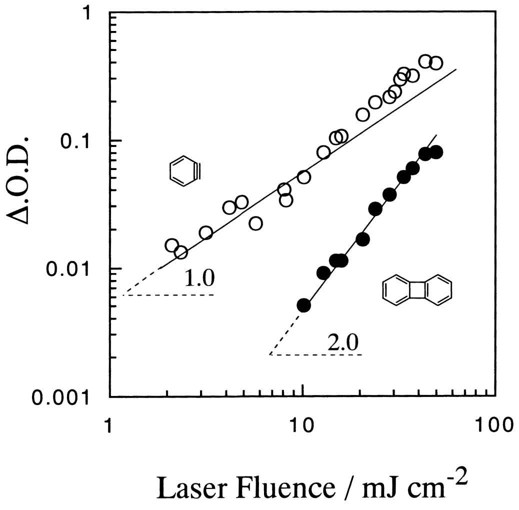


Fig. 6. Laser fluence dependency of the transient absorption of phthalic anhydride at 400 ns after the laser irradiation in the presence of 570 Torr of nitrogen observed at 260 nm (○) and 355 nm (●). The solid line has a slope of 1.0 (○) and 2.0 (●), respectively.

1-Benzofuran (Internal Conversion).[49] We examined 1-benzofuran (BF), which does not have favorable leaving groups (CO, CO_2) as PA has. No absorption corresponding to the cation radical and triplet state were found in the transient absorption spectra, but BF emits very weakly. The foreign gas efficiently suppresses the yield of the product which is formed by the single-photon process. All the results indicate that the hot BF would mainly be formed as an intermediate by 193 nm laser irradiation. The decomposition reaction of BF occurrs via S_0^{**}; however, the steady-state absorption spectrum of residuals after the laser irradiation gives no clear indication about the product. The product may be complicated mixtures of the fragmented BF.

It should be noted that Sorkhabi et al. have recently found the contribution of S_0^{**} in the decomposition reaction of furan excited at 193 nm.[50]

9-Fluorenone (Intersystem Crossing) and Dibenzofuran (Fluorescence).[46] The decarbonylation of gaseous fluorenone occurrs on irradiation with a 193 nm laser. The formation of biphenylene has been clearly observed in the absorption

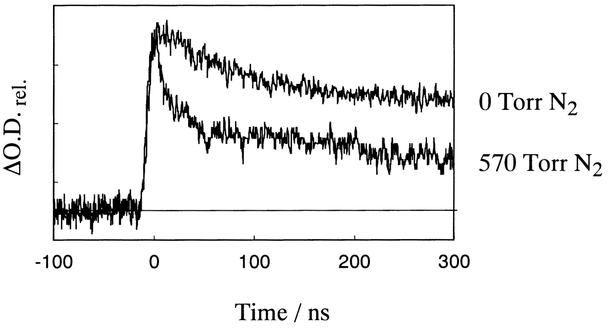


Fig. 7. Normalized transient time profiles of fluorenone at 290 nm in the absence and presence of 570 Torr of nitrogen at 420 K.

spectrum of photolysate. The normalized transient time profiles of fluorenone in the absence and presence of 570 Torr of nitrogen are shown in Fig. 7. The transient profile at 290 nm consists of two decay components. The fast component is affected by the nitrogen, while the effect of nitrogen is not observed in the slow component. The transient absorption spectrum is similar in shape to that of triplet fluorenone. The spectrum obtained within a laser pulse was slightly red-shifted compared with that obtained at 100 ns after the laser pulse. From these results, we conclude that the very fast hot triplet formation and cooling process contribute to the decay profiles. The deactivation to T_1 from an initially prepared highly excited state presumably complets within a instrumental response time period. A similar decarbonylation reaction of fluorenone, including the formation of biphenylene as well as biphenyl and fluorene, has been observed in the pyrolysis at 1100 K.[51] The decarbonylation reaction of fluorenone, which was rarely observed in the condensed phase photolysis, is interesting in view of photochemistry, although the contribution of S_0** is uncertain. In the case of dibenzofuran, the transient species appearing at 255 nm was almost completely diminished with 580 Torr of nitrogen. The suppression of the transient indicates the existence of S_0**; however, an internal conversion is probably not the only deactivation pathway from an electronic excited state, because a strong S_1 emission is observed.

3-3. Comments on Other Molecules of Which Hot Molecule Mechanism Are Not Operative. We have examined various types of molecules by transient absorption spectroscopy to find a clue to distinguish which molecules become S_0** and which do not. Some examples not described in this section are also listed in Table 1.

Amine and Related Compounds. Aliphatic and aromatic amines have rarely been examined by transient absorption spectroscopy in the gas phase, perhaps due to the difficulty in distinguishing an S_0** reaction from an electronic excited one. Diphenylamine, which has an internal conversion yield of 0.6 in the condensed phase,[52] was examined by an ArF laser in the gas phase. The transient time profiles were not so much affected by a foreign gas. It is difficult to discern the existence of hot diphenylamine. The direct dissociation of the N–H bond would be induced by exciting a n-σ* transition of diphenylamine at around 200 nm. However, recent VUV photolysis studies on ammonia[53] and methylamine[54] have shown the significant contribution of S_0** by photofragment translational spectroscopy. These results may indicate the limitation of transient absorption spectroscopy to explore these types of molecules.

Diazabenzenes (diazines) are interesting examples because the predominance of internal conversion process has been discussed in terms of third decay channel.[55] Recently, the internal conversion of pyrazine has been shown to be fast enough (20 ps)[21] to compete with the other reactions. Both the single[56] and multiphoton S_0** reactions of pyrazine have been investigated.[57] Such fast internal conversions and multiphoton reaction have been observed for pyridazine and pyrimidine,[58] too, which shows a high internal conversion yield of 0.93 and 0.88, respectively.[52]

As listed in Table 1, Moriyama et al. have found H atom elimination from vibrationally hot acetonitrile formed by fast internal conversion from a primary photoexcited state prepared by a 121.6 nm laser.[59]

Halogenated Compounds. Many halogenated compounds have been employed in laser photolysis studies. The most important point in the case of halogenated compounds is the identification of the reaction mechanism. A direct dissociation and predissociation mechanism are possible in the VUV photolysis, especially in the chlorinated compounds. Chlorobenzene[60] and benzyl chloride[61] have been examined as a source of phenyl radical and benzyl radical. In both cases, the hot radicals have formed within the laser pulse. Researchers still do not agree on whether the dissociation reaction mechanism is a direct dissociation mechanism or an S_0** reaction. In either case, the studies have contributed important information about radicals in the vibrationally excited state. The details of the relaxation process and the molar extinction coefficients of radicals have been determined. On the other hand, hexafluorobenzene[62] showed similar behavior toward benzene. The formation of S_0** is dominant, and the transient spectrum is well simulated theoretically as a hot molecule. Unlike chlorinated benzene, dissociation of both C–F and C–C bonds of hexafluorobenzene excited by a 193 nm light is too slow to be measured. Lin et al. have examined a series of fluorinated ethylenes using a 158 nm laser and concluded that the major photodissociation reactions, C=C bond breaking and HF elimination, occurrs on the ground electronic potential surface through internal conversion from the initially excited electronic state.[63] Brownsword et al. investigated the direct C–Cl bond dissociation of CH_3CF_2Cl as a primary reaction after photoexcitation at 193 nm.[64] In the case of vinyl chloride, five dissociating channels have been found.[65] A major reaction channel has originated in a direct dissociating surface (πσ*), and the other four channels originated in the S_0**. From these facts, we can conclude that it is impossible to avoid the direct dissociation channel as long as a molecule, which contains chlorine, is excited by 193 nm laser.

Phenol and Alcohol. Phenol and anisole are isovalent molecules of alkylbenzenes; however, the formation of phenoxyl radical by a 193 nm laser irradiation in the gas phase has been explained by the predissociation mechanism.[66] On the other hand, Chowdhury reported that a 193 nm laser excitation induced the dissociation of the C–O bond of benzyl alcohol via the ground electronic state.[67] The hot molecule mechanism is well supported by the agreement of the observed fragments

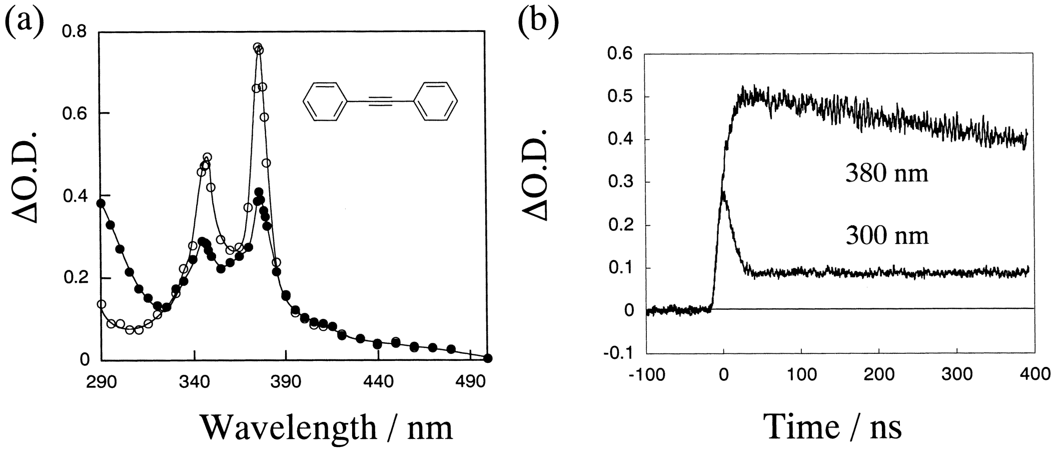


Fig. 8. (a) Transient absorption spectra of diphenylacetylene in the presence of 430 Torr of nitrogen at 403 K observed at 0 ns (●) and 100 ns (○) after the laser pulse. (b) Transient time profiles of diphenylacetylene at 300 and 380 nm observed at 403 K in the presence of 430 Torr of nitrogen.

rise time and calculated data on the basis of statistical unimolecular rate theory. It can be said that the internal conversion channel is opened for aromatic alcohols but closed for phenols by a 193 nm light.

Alkynes. 1,3-Butadiyne is formed from acetylene by VUV laser via two different pathways, the singlet and the triplet pathways.[68] The contribution of the S_0** mechanism has not been found in acetylene photolysis. On the other hand, diphenylacetylene, whose internal conversion yield is nearly unity (0.96) in the condensed phase,[69] is thought to be S_0** at first glance. However, preliminary measurements showed the clear appearance of a triplet state in the transient absorption. Figure 8a shows the transient absorption spectra of diphenylacetylene in the presence of 410 Torr of nitrogen at 403 K. Two characteristic absorption peaks can be seen at 347 and 376 nm. The spectra are similar in shape to that of the triplet state observed in the condensed phase.[70] The typical decay profiles are shown in Fig. 8b. Two types of decay behavior are observed. The absorbance between 330 and 470 nm was slightly decayed, while decay profiles below 320 nm included a sharp hump, which is understood to be the collisional deactivation of hot molecule. The absorbances observed at 300 and 380 nm are proportional to the laser fluence. From these results, the transient absorption has been assigned to be that of the triplet state. The spectral feature looks like that of a cation radical; however, a single photon's energy is not enough to eject an electron from diphenylacetylene.[71] Contrary to the expectation, there is a strong contribution of intersystem crossing in the diphenylacetylene photoprocess. The tale of the hot species was obvious in the wavelength region below 320 nm, which overlapped with the ground state absorption of diphenylacetylene, however, it is difficult to determine whether the hot species is S_0** or T_n**. If the examinations are expanded to the overlapped wavelength region and the whole spectrum can be obtained, the contribution of intersystem crossing and internal conversion may become clear.

4. Hot Molecule as an Intermediate in Multiphoton Reactions

The hot molecule reaction has been studied both by steady-state lamps and by pulsed lasers. An important advantage of a laser as a light source is the high photon density during a short period. Therefore, an accumulation of internal energy by successive photon absorption by an intermediate is possible in laser photochemistry. Multiphoton reactions of S_0** occur for toluene[12] and azulene.[13] As we have already stated, S_0** is a suitable intermediate in multiphoton reactions for the following reasons: (1) S_0** is formed instantaneously with a laser excitation; (2) S_0** has relatively long lifetimes compared with the initially formed electronic excited state;[72] (3) S_0** has large molar extinction coefficients at the laser wavelength. In the condensed phase, vibrational relaxation takes place within several tens of picosecond. The second photon from a nanosecond laser will be absorbed by either (1) the lowest electronic excited state and then ionized, or (2) the vibrationally relaxed states electronically in the ground state. Photon energy will not be accumulated. We suggest three important features in multiphoton hot molecule reactions. The first feature is that because a hot molecule reaction is a reaction of vibrationally excited species, as the size of molecule becomes larger, the reaction rate constant becomes smaller. If the reaction rate is below the collisional deactivation rate, only the formation and deactivation of S_0** will be observed. An accumulation of energy by a successive second photon absorption enables the molecule to have an increased reaction rate higher than the collisional relaxation rates. The second feature is that a different chemical reaction is expected due to the high internal energy. An inert molecule by an one-photon process can be converted to a labile by the multiphoton process. One of several examples we have found is multiphoton reactions of biphenylene.[73] Furthermore the reaction pathways can be different from the ordinary thermal reactions, because the rate constant is determined by the state density. The third feature is that the products are cooled down by collisional relaxation for the case of an S_0** reaction. It should be noted that the collisional deactivation rate is controllable by adjusting the foreign gas pressure. On the other hand, it is difficult to obtain thermally unstable product in the case of thermolysis because the subsequent heating by collision finally produces thermally stable products.

It should be emphasized again that such internal conversion is not a useless process, but a very interesting pathway for forming an intermediate in multiphoton chemistry. In this section, we would like to introduce some examples of multiphoton reaction of $\mathrm{S_0}^{**}$.

4-1. Alkylarenes as Typical Examples of Multiphoton Hot Molecule Chemistry. The most simple alkylarene is toluene, which decomposed to benzyl radical. The formation rate of benzyl radical from hot toluene is $2\times10^6\ \mathrm{s}^{-1}$ (one-photon process).[6] This process is completely suppressed by several tens of Torr of foreign gas; however, we have found the two-photon reaction of toluene as our first example of multiphoton $\mathrm{S_0}^{**}$ reactions.[12] The suitable target for the second step of the multiphoton $\mathrm{S_0}^{**}$ chemistry is alkylarenes because we can easily predict the chemical reactions, and the sufficient spectroscopic data for the related radicals are available. In addition, the effect of molecular size, strain energy, and deuterium substitution as well as the differences among structural isomers, are interesting problems that can be discussed in terms of the $\mathrm{S_0}^{**}$ mechanism. The multiphoton hot molecule reaction of alkylarenes will be discussed here in view of these factors.

[2.2] Paracyclophane (2PC) and its methyl-substituted derivatives have been examined using an ArF laser,[74] for examining the effects of strain energy on the reaction rates. The cleavage of cyclophanes into *p*-quinodimethane has been found to be a two-photon process in all the cyclophanes examined. The appearance of quinodimethane from 2PC was within the excitation pulse width. The specific rate was calculated on the basis of RRKM theory taking account of strain energy and the rate was ca. $10^{10}\ \mathrm{s}^{-1}$ at the two-photon energy. This rate is fast enough to overcome the collisional quenching by several hundreds Torr of nitrogen. The assumption of the amount of strain energy, which contributes to the activation energy, is a key factor in the case of strained molecules. The observations of the product formation rise times of cyclophane derivatives under the collision-free conditions and the calculations of rate constants have been successful.[75]

A large cyclophane, [2.2.2] paracyclophane (3PC), was examined.[76] Figure 9a shows the transient absorption spectra of 3PC in the absence and presence of nitrogen observed 100 ns after the laser pulse. The characteristic absorption of *p*-quinodimethane was clearly observed; however, the spectrum measured without nitrogen included unknown products. Figure 9b shows the transient time profiles of 3PC at 290 nm in the absence (II) and presence (III) of 640 Torr of nitrogen. The collisional cooling of hot *p*-quinodimethane was observed in profile III at 290 nm. While an increase of the absorbance was observed in profile II at 290 nm, the slow rise probably originated in the formation of a product, which was diminished in the presence of a sufficient amount of nitrogen. The equivalent vibrational temperature and dissociation rates were calculated to be 2520 K, $10^{11}\ \mathrm{s}^{-1}$ (2PC, $2h\nu$); 1900 K, $5.7\times10^7\ \mathrm{s}^{-1}$ (3PC, $2h\nu$); and 2480 K, $8.8\times10^{10}\ \mathrm{s}^{-1}$ (3PC, $3h\nu$), respectively. The RRKM calculation indicates that at least three photons are necessary to overcome the collisional deactivation by 640 Torr of nitrogen and to form *p*-quinodimethane from 3PC. The rate of the slow rise in the absence of nitrogen observed in Fig. 9b was evaluated to be $1.9\times10^7\ \mathrm{s}^{-1}$, which is in fair agreement with the calculated value. The observed rise in the absence of nitrogen can be assigned to the two-photon process. Unfortunately, the vapor pressure of 3PC is not great enough to allow us to examine the effect of laser fluence, even at 473 K (7×10^{-6} mol dm^{-3}, 0.2 Torr) and the product formation would be saturated due to the depletion of the ground state.

We have demonstrated some examples of two-photon reactions of $\mathrm{S_0}^{**}$, which led us to another simple question: How many photons can be absorbed by a hot molecule? We then examined α,ω'-diphenylalkanes[77] to investigate the three-photon $\mathrm{S_0}^{**}$ reaction. However, the examined diphenylalkanes, which have methylene chain lengths of 1 to 3, were decomposed by the two-photon process via hot molecules. Figure 10 shows the correlation between the transient absorbance of 1,3-diphenylpropane (DPP) and laser fluence. The initial transient (●) is formed by one photon, which is ascribed to be hot DPP, and the appearance of radicals (○) is proportional to the square of the laser fluence. The change from a two-photon process to a three-photon process was not observed, even when the methylene chain length was expanded to 3. From the results of a se-

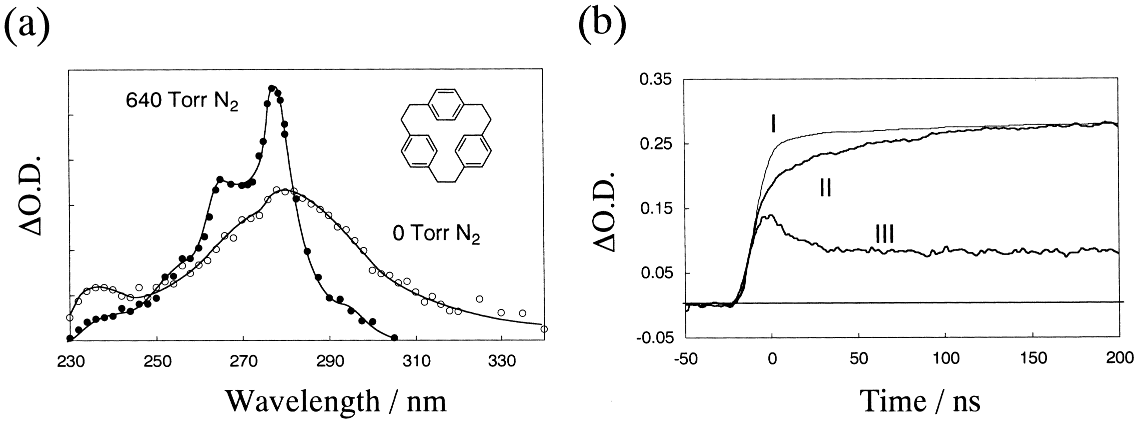


Fig. 9. (a) Transient absorption spectra of [2.2.2]paracyclophane in the absence (○) and presence of 640 Torr of nitrogen (●) at 473 K observed 100 ns after the laser pulse. (b) Time evolution of [2.2.2]paracyclophane transient absorbance at 290 nm in the absence (II) and presence (III) of 640 Torr of nitrogen. The line I is an integrated profile of the laser pulse.

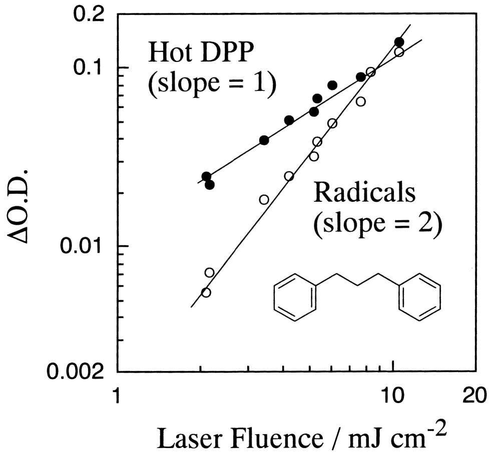


Fig. 10. The correlation between the transient absorbance of 1,3-diphenylpropane (DPP, 230nm, 403 K) and the laser fluence. Absorbances are indicated at 0 ns (●) and 300 ns (○) after the laser pulse.

ries of diphenylalkanes, we have concluded that the hot diphenylalkanes at 193 nm excitation do not need the help of a second photon to cleave the C–C bond in the benzyl position. This conclusion is also supported by the RRKM rate calculation. In order to observe three-photon processes, it is necessary to increase in the number of vibrational modes for lowering the equivalent vibrational temperature by substituting with more bulky substituents.

According to these results, we examined the C–H bond dissociation of triphenylmethane (TPM).[78] TPM is a bulky and distorted molecule with an internal conversion yield of 0.81 in the condensed phase.[79] Generally, whether the second and additional photons can be absorbed depends on the lifetime and molar extinction coefficient of the S_0**. In principle, the reactions of the first, second, and third photon could be observed concurrently although the reaction rates are very different. The suppression of slow reaction components can easily be achieved either by adding a foreign gas or by increasing the concentration of the reactant itself to deactivate S_0** collisionally. We can diminish the one- and two-photon processes of S_0** by adjusting the pressure of a foreign gas.

Figure 11a shows the transient absorption spectra of TPM in the absence (●) and presence of 585 Torr of nitrogen (○) observed at 400 ns after the laser excitation. The fully relaxed spectrum (○) is identified as TPM radical by an analogy with the condensed phase result. The unrelaxed spectrum (●) is originated in hot TPM and hot TPM radical. The spectra corresponding to the triplet state and cation radical as well as fluorescence were not observed in the wavelength region up to 700 nm. Based on the experimental results, we have concluded that the dominant deactivation pathway of TPM from an electronic excited state is an internal conversion, and that TPM radical was derived from vibrationally hot TPM. Figure 11b shows the correlation between the absorbance of TPM radical and laser fluence. The experiment clearly demonstrats that the formation of TPM radical is a three-photon process via S_0**. The saturation of TPM radical due to both the photodecomposition by the additional photon and the depletion of the ground state TPM was observed in the laser fluence region above 20 mJ cm^{-2}.

The multiphoton chemistry of TPM has also been studied in the condensed phase;[80] however, the reaction mechanism in the condensed phase is very different from that in the gas phase. In the condensed phase, TPM radical is formed by the deprotonation of a cation radical, which is formed by the two-photon ionization. Although the multiphoton reaction is one of the most distinctive advantages of laser-induced reactions,[81] ionization is the most probable process in the condensed phase. The multiphoton reaction via a S_0** is a special case, and is important in multiphoton laser chemistry because not a cation radical but a neutral radical is obtained even though a multiphoton reaction takes place. A simple summation of photon energy exceeds the ionization potential; however, the energy is distributed over the whole vibrational modes (99 in the case of TPM) in a very short time. If the photon energy is distributed equally to each vibrational mode, the energy is only 6.9 kJ mol^{-1} per vibrational mode. Therefore, the absorption of sec-

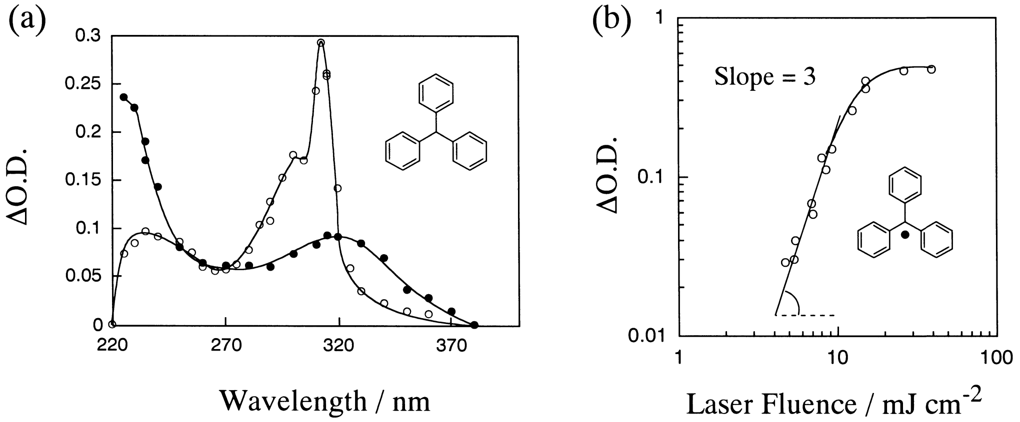


Fig. 11. (a) Transient absorption spectra of TPM in the absence (●) and presence of 585 Torr of nitrogen (○) measure at 433 K observed 400 ns after the laser pulse. (b) The correlation between the absorbance of TPM radical and laser fluence. TPM radical (315 nm) was observed at 400 ns after the laser pulse in the presence of 600 Torr of nitrogen at 443 K. The solid line has a slope of 3.0.

ond photon is not enough to ionize the molecule. Ionization does not occur but the reaction rate of hot molecule increases due to the accumulation of vibrational energy as a result of photoexcitation–internal conversion sequences.

4-2. Multiphoton Hot Molecule Reaction Found in Heterocyclic Compounds. Several examples of multiphoton S_0** reaction of hydrocarbons have been found. However, studies of the multiphoton hot molecule reactions have been limited to a small variety of molecules. To our knowledge, the decarbonylation of coumarin and HCN fragmentation of pyrazine[57] are only examples of multiphoton hot molecule reactions other than those with hydrocarbons. The further investigation is necessary to expand the multiphoton hot molecule chemistry. Here, the reaction of coumarin will be introduced as a typical example.

Decarbonylation of Coumarin.[49] We found the two-photon decarbonylation of coumarin as the first example. Coumarin derivatives are one of the famous laser dyes, while unsubstituted coumarin emits little fluorescence. The photochemical reaction of coumarin, for example its dimerization, has been well studied; however, the unimolecular reaction of coumarin has not been well studied. The formation of hot coumarin is strongly expected due to its low fluorescence and triplet yield even in the condensed phase.[52] Coumarin is a favorable molecule to use to compare the hot molecule mechanism with the thermal decarbonylation reaction, which was observed by the flash vacuum pyrolysis.[82]

The vibrational structure of the 1-benzofuran (BF) absorption has been clearly observed around 240 and 280 nm after the photolysis of coumarin. No other products were observed in the absorption spectra. The results show that ArF excimer laser irradiation of the gaseous coumarin results in the formation of BF. The time evolutions of the transient absorption of coumarin in the absence and presence of 570 Torr of nitrogen are shown in Fig. 12a. In the absence of nitrogen, the fast and slow rises at 230 nm and the fast and slow decay at 310 nm can be seen. The slow components are understood to be the collisional deactivation of the hot product with the ground state of coumarin. In the presence of 570 Torr of nitrogen, the transient time profile consisted of a sharp hump, which is understood to be the collisional deactivation of hot coumarin, and a long-lived stable absorption (profile 2 in Fig. 12a). The transient absorption spectra of coumarin are shown in Fig. 12b. In the transient spectra, there is no cation radical, no triplet state, and no emission, so the internal conversion should be the dominant deactivation pathway. The characteristic product spectrum (○) is clearly seen at around 240 nm, which can be assigned to BF. The spectrum at 0 ns (●), which is monotonically decreased with increasing wavelength in the region longer than 340 nm where the ground state of coumarin does not have a significant absorption, is understood to be that of hot coumarin. The best corrected transient absorption spectrum (•) with that of ground state coumarin is shown in Fig. 12b. The solid line on the corrected spectrum in Fig. 12b was the theoretical simulation curve of the S_0** spectrum by the modified Sulzer–Wieland model.[24] A discrepancy between the best simulated spectrum and the corrected spectrum is seen at around 240 nm. The difference can be attributed to the influence of BF even at 0 ns due to the large molar extinction coefficient and fast formation of BF. The correlation between the transient absorbance of coumarin at 230 nm, where BF is the dominant species at 300 ns after the laser pulse, and the laser fluence is on a line with a slope of 2.0, indicating that the formation of BF is a two-photon process. From the facts described above, we have concluded that BF is derived from the vibrationally hot coumarin as an intermediate in a two-photon reaction.

5. Concluding Remarks

Laser flash photolysis studies in the VUV region for various molecules in the gas phase have shown the predominance of the hot molecule (S_0**) mechanism as summerized in Table 1. The generalization and classification of hot molecule reactions are important subjects in photochemistry, with the goals of 1)

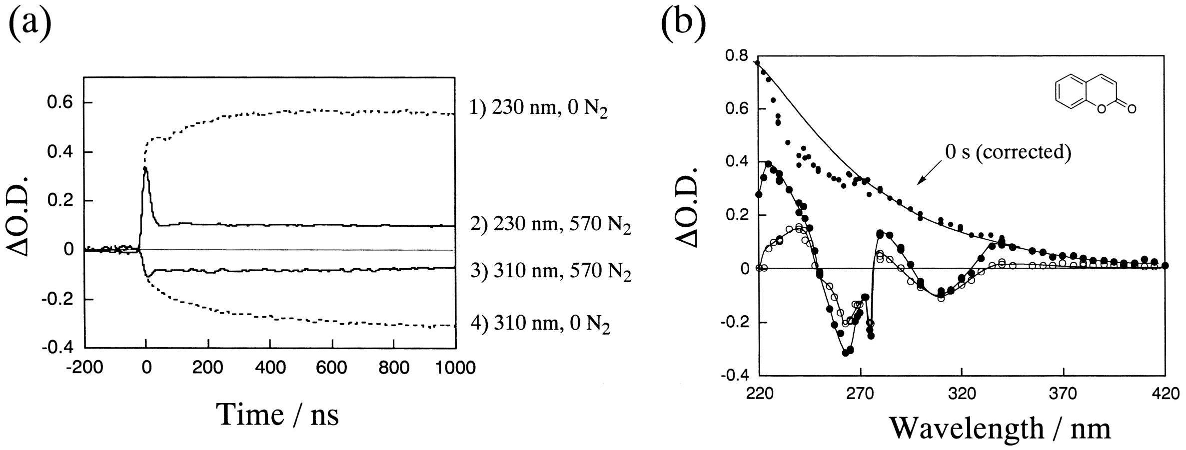


Fig. 12. (a) Transient time profiles of coumarin (1, 230 nm, 0 Torr of nitrogen; 2, 230 nm, 570 Torr of nitrogen; 3, 310 nm, 0 Torr of nitrogen; 4. 310 nm, 570 Torr of nitrogen). (b) Transient absorption spectra of coumarin in the presence of 570 Torr of nitrogen were observed at 0 ns (●) and 300 ns (○) after the laser pulse. The corrected transient spectrum at 0 ns with the absorption spectrum of ground-state coumarin (•). The solid line on the corrected spectrum is the simulated spectrum of hot coumarin by modified Sulzer–Wieland model. The details are described in the text.

showing the similarity and difference between the thermolysis and S_0** mechanism; 2) finding new chemical reaction pathways via S_0** as an intermediate in the multiphoton process; 3) studying the photochemistry of radicals that can be produced by the S_0** mechanism without interfering with surroundings in the gas phase; and 4) finding the factors that determine the efficient internal conversion.

The further detailed investigation of the S_0** formation mechanism will be fulfilled both by ultrafast VUV laser spectroscopy and by theoretical consideration. The conical intersection mechanism has come to occupy an important position in nonradiative transition theory.[23] The real-time investigation of ultrafast internal conversion process has been excellently demonstrated by Radloff et al.[19–22] The factors such as internal energy (excitation wavelength), structural distortion, and electronic excited state character will be examined using various molecules.

A nanosecond laser photolysis is important to achieve multiphoton chemistry especially a sequential multiphoton process, with a single nanosecond laser pulse. The hot molecule reaction is important in multiphoton laser chemistry because not a cation radical but a neutral radical is obtained even though a multiphoton reaction takes place.[61,83] The multiphoton S_0** reactions have also been applied to the molecules that have been deemed to be photoinert, such as biphenylene.[73] It should be reiterated that an internal conversion is not an ineffective photophysical process, but a very interesting pathway for forming an important intermediate in multiphoton chemistry.

Hot molecules exist even in the condensed phase, but the collisions with the surrounding solvent are very frequent, so the lifetime of S_0** is within 1 ns. In spite of this brevity, S_0** is observable in the condensed phase with the help of ultrafast spectroscopy.[84] The hot molecule reaction was thought to be difficult in the condensed phase, but it is a very interesting problem in S_0** chemistry. Recently, interesting examples have appeared in the hydrogen bonding system.[85] The internal conversion rate of aminoanthraquinone[86] and aminofluorenone[87] derivatives, having an intramolecular charge transfer nature, is accelerated by forming hydrogen bonds with alcohols. The promotion of internal conversion by forming a specific interaction in such a system would be one of the special and important cases of S_0** formation processes in the condensed phase.

The authors thank collaborators of our group at Osaka City University for their contributions to this work. The present research was partially supported by a Grant-in-aid (No. 11750720) from the Ministry of Education, Science, Sports and Culture.

References

1 N. Nakashima and K. Yoshihara, *J. Phys. Chem.*, **93**, 7763 (1989).

2 R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 3432,4141(1962); B. A. Thrush and J. J. Zwolenik, *Bull. Soc. Chim. Belg.,* **71**, 642 (1962).

3 H. Hippler, Ch. Riehn, J. Troe, and K.-M. Weitzel, *J. Phys. Chem.*, **94**, 6321 (1990); H.G. Löhmannsröben, and K. Luther, *Z. Phys. Chem.*, **149**, 129 (1986); H. Hippler, J. Troe, and J. Wendelken, *J. Chem. Phys.*, **78**, 6709 (1983).

4 H. Hippler, V. Schubert, H. J. Wendelken, and J. Troe, *Chem. Phys. Lett.*, **84**, 253 (1981); H. Hippler, J. Troe, and H. J. Wendelken, *J. Chem. Phys.*, **78**, 5351 (1983).

5 N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **79**, 2727 (1983); N. Nakashima and K. Yoshihara, *J. Chem. Phys.*, **77**, 6040 (1982).

6 N. Ikeda, N. Nakashima, and K. Yoshihara, *J. Chem. Phys.*, **82**, 5285 (1985).

7 K. Tsukiyama and R. Bersohn, *J.Chem.Phys,.* **86**, 745 (1987).

8 Y. Kajii, K. Obi, I. Tanaka, N. Ikeda, N. Nakashima, and K. Yoshihara, *J. Chem. Phys.*, **86**, 6115 (1987).

9 U. Brand, H. Hippler, L. Lindemann, and J. Troe, *J. Chem. Phys.*, **84**, 6305 (1990).

10 T. Shimada, Y. Ojima, N. Nakashima, Y. Izawa, and C. Yamanaka, *J .Phys. Chem.*, **96**, 6298 (1992).

11 C. B. Moore and J. C. Weishhaar, *Annu. Rev. Phys. Chem.*, **34**, 525 (1983); W. H. Green, Jr., C. B. Moore, and W. F. Polik, *Annu. Rev. Phys. Chem.,* **43**, 591 (1992).

12 N. Nakashima, N. Ikeda, and K. Yoshihara, *J. Phys. Chem.*, **92**, 4389 (1988).

13 M. Damm, H. Hippler, and J. Troe, *J. Chem. Phys.*, **88**, 3564 (1988).

14 S. Hassoon, D. L. Snavely, and I. Olef, *J .Chem. Phys.*, **97**, 9081 (1992).

15 M. Tchaplyguine, K. Hoffmann, O. Dühr, H. Hohmann, G. Korn, H. Rottke, M. Wittmann, I. V. Hertel, and E. E. B. Campbell, *J. Chem. Phys.,* **112**, 2781 (2000); R. Lykke and P. Wurz, *J. Chem. Phys.*, **96**, 3191 (1992).

16 E. Riedle, Th. Weber, U. Schubert, H. J. Neusser, and E.W. Schlag, *J. Chem. Phys.*, **93**, 967 (1990).

17 M. Sumitani, D. V. O'Connor, Y. Takagi, N. Nakashima, K. Kamogawa, Y. Udagawa, and K. Yoshihara, *Chem. Phys.*, **93**, 359 (1985); M. Sumitani, D. O'Connor, Y. Takagi, N. Nakashima, K. Kamogawa, Y. Udagawa, and K. Yoshihara, *Chem. Phys. Lett.*, **97**, 508 (1983).

18 P. Farmanara, O. Steinkellner, M. T. Wick, M. Wittmann, G. Korn, V. Stert, and W. Radloff, *J. Chem. Phys.*, **111**, 6264 (1999).

19 W. Radloff, T. Freudenberg, H. –H. Ritze, V. Stert, F. Noack, and I. V. Hertel, *Chem. Phys. Lett.*, **261**, 301 (1996); W. Radloff, V. Stert, T. Freudenberg, I. V. Hertel, C. Jouvet, C. Dedonder-Lardeux, and D. Solgadi, *Chem. Phys. Lett.*, **281**, 20 (1997).

20 W. Radloff, T. Freudenberg, H.-H. Ritze, V. Stert, K. Weyers, and F. Noack, *Chem. Phys. Lett.*, **245**, 400 (1995); W. Radloff, T. Freudenberg, V. Stert, H.-H. Ritze, K. Weyers, and F. Noack, *Chem. Phys. Lett.,* **258**, 507 (1996).

21 V. Stert, P. Farmanara, and W. Radloff, *J. Chem. Phys.*, **112**, 4460 (2000).

22 P. Farmanara, V. Stert, and W. Radloff, *Chem. Phys. Lett.*, **288**, 518 (1998).

23 F. Barnardi, M. Olivucci, and M. A. Robb, *Chem. Soc. Rev.*, **25**, 321 (1996); W. Fuβ, S. Lochbrunner, A. M. Müller, T. Schikarski, W. E. Schmid, and S. A. Trushin, *Chem. Phys. Lett.*, **232**, 161 (1998).

24 P. Sulzer and K. Wieland, *Helv. Phys. Acta*, **25**, 653 (1952); D. C. Astholz, L. Brouwer, and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **85**, 559 (1981).

25 J. Park, R. Bersohn, and I. Oref, *J. Chem. Phys*. **93**, 5700 (1990).

26 R. Fröchtenight and J. P. Toennies, *J. Photochem. Photobiol. A. Chem*., **80**, 67 (1994).

27 T. Shimada, N. Nakashima, Y. Izawa, and C. Yamanaka, *J. Chem. Phys*., **98**, 9218 (1993).

28 N. Nakashima, T. Shimada, Y. Izawa, and C. Yamanaka, *Nuclear Instru. Methods Phys. Res*., **A331**, 253 (1993). The rate constant of C_{10} olefin at 158 nm should be 0.7×10^6 s^{-1} instead of 1.7×10^6 s^{-1} in Table I.

29 I. Oref and D. C. Tardy, *Chem. Rev*., **90**, 1407 (1990).

30 D. Schwarzer, J. Troe, and M. Zerezke, *J. Chem. Phys*., **102**, 4207 (1998).

31 S. Y. Bae, In-Ja. Lee, and J. Park, *Chem. Phys*., **255**, 103 (2000); M. Fraelich, M. S. Elioff, and A. S. Mullin, *J. Phys. Chem*., **102**, 9761 (1998); M. C. Wall and A. S. Mullin, *J. Chem. Phys*., **108**, 9658 (1998).

32 J. R. Barker and B. M. Toselli, *Int. Rev. Phys. Chem*., **12**, 305 (1993).

33 C. Heidelbach, I. I. Fedchenia, D. Schwarzer, and J. Schroeder, *J. Chem. Phys*., 108, 10152 (1998); J. D. Pitts and J. L. Knee, *J. Chem. Phys*., **108**, 9632 (1998).

34 T. Yatsuhashi and N. Nakashima, *J. Phys. Chem. A*, **104**, 203 (2000).

35 S-T. Tsusai, C-K. Lin, Y. T. Lee, and C-K. Ni, *J. Chem. Phys*., **113**, 67 (2000).

36 J. Pola, M. Urbanová, Z. Bastl, Z. Plzák, J. Subrt, V. Vorlícek, I. Gregora, C. Crowley, and R. Taylor, *Carbon*, **5**, 605 (1997).

37 G. J. Collin, *Adv. Photochem*., **14**, 135 (1988).

38 N. Nakashima, N. Shimo, N. Ikeda, and K. Yoshihara, *J. Chem. Phys*., **81**, 3738 (1984); N. Nakashima, N. Ikeda, N. Shimo, and K. Yoshihara, *J .Chem. Phys*., **87**, 3471 (1987).

39 W. J. Leigh and B. H. O. Cook, *J. Org. Chem*., **64**, 5256 (1999); Y. Inoue, S. Takamuku, and H. Sakurai, *J. Chem. Soc., Perkin Trans*., **2**, 1635 (1977).

40 B. A. Balko, J. Zhang, and Y. T. Lee, *J. Chem. Phys*., **97**, 935 (1992).

41 M. Hayashi, A. M. Mebel, K. K. Liang, and S. H. Lin, *J. Chem. Phys*., **108**, 2044 (1998); M. Ben-Nun and T. J. Martínez, *Chem. Phys. Lett*., **298**, 57 (1998).

42 E. C. Lim and C. S. Huang, *J. Chem. Phys*., **58**, 1247 (1973); J. C. Hsieh, C. S. Huang, and E. C. Lim, *J Chem. Phys*., **60**, 4345 (1974).

43 M. Jacon, C. Lardeux, R. Lopez-delgado, and A. Tramer, *Chem. Phys*., **24**, 145 (1977).

44 T. Suzuki, T. Ichimura, M. Kusaba, and N. Nakashima, *Chem. Phys. Lett*., **263**, 197 (1996).

45 M. Damm, F. Dechert, H.Hippler, and J. Troe, *J. Phys. Chem*., **95**, 2005 (1991).

46 T. Yatsuhashi and N. Nakashima, unpublished results.

47 M. B. Ledger and G. A. Salmon, *J. Chem. Soc., Faraday Trans*., **2**, 883 (1976).

48 Y. S. Choi and C. B. Moore, *J. Chem. Phys*., **103**, 9981 (1995).

49 T. Yatsuhashi and N. Nakashima, *J. Phys. Chem. A*, **104**, 1095 (2000).

50 O. Sorkhabi, F. Q. Abbas, H. Rizvi, and A. G. Suits, *J. Chem. Phys*., **111**, 100 (1999).

51 R. F. C. Brown and R. K. Solly, *Aust. J. Chem*., **19**, 1045 (1966).

52 S. L. Murov, I. Carmichael, G. L. Hug, "Handbook of Photochemistry," 2nd ed, Marcel Dekker, New York (1993).

53 D. H. Mordaunt, R. N. Dixon, and M. N. R. Ashfold, *J. Chem. Phys*., **104**, 6472 (1996).

54 C. L. Reed, M. Kono, and M. N. R. Ashfold, *J. Chem. Soc., Faraday Trans*., **92**, 4897 (1996).

55 I. Yamazaki, T. Murao, T. Yamanaka, and K. Yoshihara, *Faraday Discuss. Chem. Soc*., **75**, 395 (1983).

56 G. W. Johonston, J. Park, S. Satyapal, N. Shafer, K. Tsukiyama, R. Bersohn, and B. Katz, *Acc. Chem. Res*., **23**, 232 (1990).

57 E. T. Sevy, M. A. Muyskens, S. M. Rubin, G. W. Flynn, and J. T. Muckerman, *J. Chem. Phys*., **112**, 5829 (2000).

58 T. Suzuki, T. Ichimura, M. Kusaba, and N. Nakashima, Abstract of Papers, Bunsikouzou Sougou Touronkai, Osaka Japan (1999), p. 114.

59 M. Moriyama, Y. Tsutsui, and K. Honma, *J. Chem. Phys*., **108**, 6215 (1998).

60 N. Ikeda, N. Nakashima, and K. Yoshihara, *J. Am. Chem. Soc*., **107**, 3381 (1985).

61 N. Ikeda, N. Nakashima, and K. Yoshihara, *J. Phys. Chem*., **88**, 5803 (1984).

62 T. Ichimura, Y. Mori, N. Nakashima, and K. Yoshihara, *J. Chem. Phys*., **83**, 117 (1985); J. R. Gascooke, Z. T. Alwahabi, K. D. King, and W. D. Lawrance, *J. Chem. Phys*., **109**, 3868 (1998).

63 J. J. Lin, S. M. Wu, D. W. Hwang, Y. T. Lee, and X. Yang, *J. Chem. Phys*., **109**, 10838 (1998); J. J. Lin, T. C. Hsu, D. W. Hwang, Y. T. Lee, and X. Yang, *J. Chem. Phys*., **109**, 10719 (1998).

64 R. A. Brownsword, P. Schmiechen, H-R. Volpp, H. P. Upadhyaya, Y. J. Jung, and K-H. Jung, *J. Chem. Phys*., **110**, 11823 (1999).

65 D. A. Blank, W. Sun, A. G. Suits, Y. T. Lee, S. W. North, and G. E. Hall, *J. Chem. Phys*., **108**, 5414 (1998).

66 Y. Kajii, K. Obi, N. Nakashima, and K. Yoshihara, *J. Chem. Phys*., **87**, 5059 (1987).

67 P. K. Chowdhury, *J. Phys. Chem*., **98**, 13112 (1994).

68 K. Seki, N. Nakashima, N. Nishi, and K. Yoshihara, *J. Chem. Phys*., **85**, 274 (1986).

69 R. C. Henson, J. L. W. Jones, and E. D. Owen, *J. Chem. Soc. A*, **1967**, 116.

70 Y. Hirata, T. Okada, N. Mataga, and T. Nomoto, *J. Phys. Chem*., **96**, 6559 (1992); K. Ota and K. Murofushi, *Tetrahedron Lett*., **15**, 1431 (1974).

71 S. Erbel, K. Lienert, A. Krebs, and H. Dieck, *Liebigs Ann. Chem*., **1981**, 1785.

72 S. Y. Bae, In-Ja. Lee, and J. Park, *Chem. Phys. Lett*., **255**, 103 (2000); J. R. Barker and B. M. Toselli, *Int. Rev. Phys. Chem*., **12**, 305 (1993).

73 T. Yatsuhashi, T. Akiho, S. Shimizu and N. Nakashima, Abstracts of Papers, Asian-Pacific Forum on Science and Technology, Kanazawa Japan (1998), p. 58.

74 S. Shimizu, N. Nakashima, and Y. Sakata, *Chem. Phys. Lett*., **284**, 396 (1998).

75 Y. Hosoi, T. Yatsuhashi, S. Shimizu, N. Nakashima, and Y. Sakata, Abstract of Papers, Hikarikagaku Touronkai, Hokkaido Japan (2000), p. 11.

76 T. Yatsuhashi, K. Ohtakeyama, Y. Hosoi, S. Shimizu, N. Nakashima, and Y. Sakata, Abstract of Papers, Bunsikouzou Sougou Touronkai, Osaka Japan (1999), p. 634.

77 T. Yatsuhashi and N. Nakashima, Abstract of Papers, Hikarikagaku Touronkai, Okayama Japan (1999), p. 75.

78 T. Yatsuhashi and N. Nakashima, *J. Phys. Chem. A*, **104**,

10645 (2000).

79 F. H. Watson and M. A. El-Bayoumi, *J. Chem. Phys.*, **55**, 5464 (1971); H. G. Lewis and E. D. Owen, *J. Chem. Soc. B*, **1967**, 422.

80 J. L. Faria and S. Steenken, *J. Am. Chem. Soc.*, **112**, 1277 (1990).

81 N. Nakashima, S. Nakamura, S. Sakabe, H. Schilinger, Y. Hamanaka, C. Yamanaka, M. Kusaba, N. Ishihara, and Y. Izawa, *J. Phys. Chem. A*, **103**, 3910 (1999).

82 W. Reichen, *Helv. Chim. Acta.*, **20**, 186 (1977).

83 M. Damm, F. Deckert, H. Hippler, and G. Rink, *Phys. Chem. Chem. Phys.*, **1**, 81 (1999).

84 A. Hertwig, H. Hippler, H. Schmid, and A-N. Unterreiner, *Phys. Chem. Chem. Phys.*, **1**, 5129 (1999); L. Nikowa, D. Schwarzer, and J. Troe, *Chem. Phys. Lett.*, **233**, 303 (1995).

85 T. Yatsuhashi and H. Inoue, *J. Phys. Chem. A*, **101**, 8166 (1997); T. Yatsuhashi, Y. Nakajima, T. Shimada, and H. Inoue, *J. Phys. Chem. A*, **102**, 8657 (1998).

86 H. Inoue, M. Hida, N. Nakashima, and K. Yoshihara, *J. Phys. Chem.*, **86**, 3184 (1982).

87 T. Yatsuhashi, Y. Nakajima, T. Shimada, and H. Inoue, *J. Phys. Chem. A*, **102**, 3018 (1998).

Tomoyuki Yatsuhashi was born in Yokohama, Japan in 1969. He was graduated, and received his D. Eng. from Tokyo Metropolitan University under the guidance of Prof. Haruo Inoue in 1998. He has been a research associate of chemistry, Graduate School of Science, Osaka City University since 1998. His current research interests are photophysics and photochemistry of organic and inorganic compounds.

Nobuaki Nakashima is a Professor of Chemistry at Osaka City University. He received his Doctor's degree from Osaka University in 1974. He worked as a research associate of Institute for Molecular Science, as an associate professor of Institute of Laser Engineering, Osaka University, and has joined the present faculty since 1996. He constructed a picosecond flash photolysis system in 1974 and studied benzene photophysics in the eighties. He is interested in hot molecule reactions and high-intensity laser chemistry.