

III-F Photophysics and Photochemistry of Aromatic Molecules in the Condensed Phase

Excited aromatic compounds generally release energy by various pathways such as photophysical processes and photochemical reactions. Electronically excited molecules are relaxed into a stable or metastable state through radiative and/or nonradiative processes as photophysical processes. It is well known that photochemical reactions occurring from excited state are bond dissociation, cyclization, isomerization, hydrogen abstraction, electron transfer, and so on. In addition, there exist relaxation processes and their quantum yields characteristic to each compound. It is very important to investigate dynamics of photoexcited molecules.

Intermediates such as excited states and radicals, which can be generated with laser irradiation, have been detected by laser flash photolysis as described. The shorter pulse width of a light source becomes, the shorter-lived intermediates can be detected. Furthermore, the properties of intermediates would be clarified. These information should obtained photophysical and photochemical dynamics of the intermediate that are interested.

On the other hand, it becomes difficult to elucidate nonradiative processes, such as internal conversion and intersystem crossing from the excited state, by laser flash photolysis. Time-resolved photothermal techniques, however are powerful to study nonradiative processes because they can detect the released heat from excited molecules directly with high sensitivity. They should be described in detail. Combination of photoexcited and photothermal methods will give us detailed information on photophysical and photochemical dynamics of intermediates, as well as excited states.

III-F-1 Excited-State Dynamics of 4-Thiothymidine with UVA Light Irradiation

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Thionucleobases and thionucleosides have received renewed attention because of their distinct property, namely, high sensitivity to UVA light (320–400 nm) in which region normal DNA constituents are transparent. 4-Thiothymidine (4-TT), an analogue of the naturally occurring nucleoside thymidine, has strong absorption in the UVA region. Recently it was reported that 4-TT can be readily incorporated into cellular DNA and that low doses of UVA light can easily inflict lethal damage on the DNA containing 4-TT, causing cell death. The synergistic use of 4-TT and UVA light offers a novel approach to cancer treatment. Apparently, electronically excited state of 4-TT is at the initial and crucial stage of the UVA-induced cell killing, and thus photophysical and photochemical studies of 4-TT would be of great significance.

We have measured transient absorption spectrum of 4-TT in deaerated acetonitrile with the nanosecond 355 nm laser. Immediately after the laser shot, an intense bleaching at 335 nm and a broad absorption band at 380–600 nm (Abs. Max. 530 nm) were observed. The bleaching is ascribed to the depletion of the ground state molecules while the absorption band is assigned to the absorption of the lowest excited triplet (T_1) state of 4-TT (T–T absorption). The T–T absorption decayed with the rate constant of $1 \times 10^6 \text{ s}^{-1}$. In triplet quenching experiments by KI, the absorption intensity of the photoproducts decreased correspondingly to shortening of triplet lifetime of 4-TT. Our experimental results suggest that photochemical process would take place *via* the T_1 state of 4-TT and other several intermediate states. A good understanding of the photophysics and photochemistry of 4-TT could offer valuable insights to the mechanisms by which cancer cells are killed.

III-F-2 Photochemical Reaction Dynamics of *o*-Quinones

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Photoreaction dynamics of 9,10-phenanthrene-quinone (PQ) and 1,2-naphthoquinone (NQ) in solution has been studied by laser flash photolysis technique. The real-time transient absorption measurements found out; (1) by excitation at 355 nm in the presence of alcohol, absorption band characteristic to the quinone ketyl radical emerged as the triplet–triplet (T–T) absorption of the quinone submerged, (2) the rise of the absorption of the ketyl radical consisted of two components; the fast and slow ones, where the fast one had the rise rate constant corresponding to the decay rate of triplet quinone, while the slow one rose up much slowly. The experimental fact clearly revealed that the slow reaction should give rise to formation of the ketyl radical following the hydrogen abstraction of triplet PQ and NQ from alcohol, and should be attributed to the hydrogen atom transfer between the parent quinone in the ground state and counter α -hydroxyalkyl radical produced from alcoholic molecule. In this study, we carried out the real-time measurement and clarified the reaction mechanism between the α -hydroxyalkyl radicals and the ground state quinones.

Triplet PQ and NQ show remarkable high reactivity with benzene. The notable reactivity would result from their characteristic molecular conformation; namely, the existence of two adjacent carbonyl groups would cause the stabilized conformation in the transition state through doubly hydrogen bonding with the hydrogen donor.

III-F-3 Evidence of Phenoxyethyl Radical Formation in Laser Photolysis of Anisole in Solution

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Transient absorption spectrum of anisole in acetonitrile was observed by a 248-nm laser photolysis. In addition to the structured band observed at 400 nm, which was assigned to phenoxy radical, a broad absorption band appeared at around 440 nm. The lifetime of the unknown species was not affected by oxygen. By means of acetone photosensitization reaction, photolysis of 1,2-diphenoxyethane, and ESR measurements, the species was assigned to phenoxyethyl radical, produced with two-photon absorption through the S₁ state of anisole to form anisole cation and consecutive deprotonation of the cation.

III-F-4 Production and Excited State Dynamics of the Photorearranged Isomer of Benzyl Chloride and Its Methyl Derivatives Studied by Stepwise Two-Color Laser Excitation Techniques

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Production and photoexcited dynamics of reaction intermediates with photolyses of benzyl chloride (BzCl) and methyl-substituted benzyl chlorides (MeBzCls) were studied by using stepwise two-color laser excitation transient absorption (TC-TA) and two-color laser excitation time-resolved thermal lensing (TC-TRTL) measurements. With photoexcitation of BzCl the formation of transient photo-rearranged isomer was suggested in the previous paper.¹⁾ Such an isomer formation for MeBzCls was also observed in a 248 nm excitation. It was found that further photoexcitation of the isomers with the 308 nm light caused photodissociation to yield the corresponding benzyl radicals. The reaction quantum yield and the molar absorptivity of the photo-rearranged isomer of BzCl were estimated. The heat of reaction for the photodissociation of the isomer was successfully determined with the TC-TRTL measurement. These experimental results were consistent with MO calculations.

Reference

- 1) H. Hiratsuka, T. Okamoto, S. Kuroda, T. Okutsu, H. Maeoka, M. Taguchi and T. Yoshinaga, *Res. Chem. Intermed.* **27**, 137–153 (2001).

III-G Spectroscopy and Excited State Dynamics of Jet-Cooled Aromatic Molecules

The phenomena of energy relaxation in isolated molecules have been central in chemical kinetics over many decades. An extensive subject has been followed by the application of supersonic jet techniques, which enabled the study of well isolated ultra-cold molecules. The jet-cooled molecules are isolated in gas phase, thus, the experiments are not subjected to interactions between molecules and solvents or to vibrational relaxation in condensed phases.

The large transition energy is reserved in optically electronic excited molecules where the idea of temperature for molecular internal energy is replaced by the excess energy, by which photodissociation is induced. Investigation of nonradiative electronic relaxation processes, *i.e.* internal conversion (IC) or intersystem crossing (ISC) between two electronic states of the same or different electron spin multiplicity of photoexcited molecules, respectively, has long been interest of the photochemical dynamics because of the important role of these processes in photochemical reaction system.

A triplet state serves as an important intermediate in nonradiative processes of excited molecules. The dynamics of the triplet state generation, *i.e.* ISC, plays an important role in photochemical processes. For instance, chlorinated benzene derivatives in the first excited singlet (S₁) state have small values (10⁻²) of the fluorescence quantum yields, suggesting that the ISC process to excited triplet states takes place due to the large spin-orbit coupling induced by the heavy Cl atom effect. The excited triplet state molecules undergo the C–Cl dissociation whose quantum yield is almost unity. Accordingly, the investigation of the ISC process assists to understand the photochemical reactions.

The substituent of the CH₃ or OCH₃ group on the benzene ring should play an important role in their photoexcited states. When these molecules are excited to the singlet excited state, internal rotational bands of these groups are observed for lower frequency regions than 200 cm⁻¹ in the LIF excitation spectra. Measurements of these internal band intensities and their fluorescence lifetimes should give information on the relaxation dynamics of these molecules.

III-G-1 Spectroscopy and Relaxation Dynamics of Photoexcited Anisole and Anisole-d₃ Molecules in a Supersonic Jet

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The vibronic structures of the S₁–S₀ electronic transitions of jet-cooled anisole and anisole-d₃ molecules have been investigated in detail using the laser induced fluorescence and single vibrational level dispersed fluorescence (DF) spectroscopy. Normal mode frequencies of the ground and excited states including the methyl and methoxy internal rotations were determined by analyses of dispersed fluorescence spectra and molecular orbital calculations. Strong vibrational mixing in the S₁ state was observed in several DF spectra. Duschinsky rotation between 6a and 6b modes prominently appeared for both molecules and it was found that methyl deuteration depressed the second-order vibronic coupling of these modes. Another explicit Duschinsky rotation was found in 10b and 16a modes of both molecules. However, in the case of the deuterated molecule the mixing cannot be explained by only Duschinsky rotation. A Fermi resonance due to level proximity should be involved in the mixing scheme. Vibronic bands in the higher frequency regions exhibit broadened and structureless fluorescence due to intramolecular vibrational energy redistribution (IVR). The onset of the IVR process inferred from the DF spectra was found to be increased by methyl deuteration on the contrary to general propensity rule. The deuteration effect is characteristic of anisole molecules and indicates considerable decrease in the interaction with the dark bath modes. Fluorescence lifetime measurements suggest the enhancement of intersystem crossing in the levels with out-of-plane vibrational components. The observed broadening of DF spectra corresponded to nonradiative decay rates from levels with the in-plane vibrational modes. This suggests that the energy flow into out-of-plane bath modes through the IVR process should dominate nonradiative rates on initially excited in-plane vibrational levels. Our analysis clarified that the out-of-plane vibrations accompanying the methoxy motion make large contribution to the relaxation dynamics.

III-G-2 Internal Rotational Motion of the Chloromethyl Group of the Jet-Cooled Benzyl Chloride Molecule

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The mass-resolved resonance enhanced two-photon ionization spectra of jet-cooled benzyl chloride were measured. Some low-frequency vibronic bands around

the S₁–S₀ origin band were assigned to transitions of the internal rotational mode of the chloromethyl group. The internal rotational motion was analyzed by using the one-dimensional free rotor approximation. The conformation in the S₁ state was found to be that in which the C–Cl bond lies in orthogonal to the benzene plane. For the species with *m/e* 126, the transition energy of the internal rotational bands corresponded well to the potential energy values of $V_2 = 1900 \text{ cm}^{-1}$ and $V_4 = 30 \text{ cm}^{-1}$ in the S₁ state and the reduced rotational constant *B* values 0.50 and 0.47 cm^{-1} in the S₀ and S₁ states, respectively. The *B* values obtained for the chlorine isotopomer (*m/e* 128) were slightly different. The S₁ potential barrier height was found to be about 3 times larger than that for the S₀ state. Molecular orbital calculations suggest that the difference between energies of the HOMO and LUMO with respect to the rotation of the chloromethyl group correspond approximately to the potential energy curve obtained for the S₁ state.

III-G-3 Molecular Structure and Excited State Dynamics of Jet-Cooled *o*-, *m*- and *p*-Fluoroanisole

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Intramolecular isomerism plays a significant role in biologically relevant molecular systems such as the folding of proteins and molecular machines. In understanding the function of the complicated large biological molecules, it is important to know the conformational properties and excited state dynamics of their local units. In this point of view, the molecular structure and relaxation dynamics of anisole derivatives were studied. It is known that *meta*-substituted anisole has two stable *planar* conformers (*i.e.* *cis* and *trans*), which are raised from the orientation of the methoxy group with respect to the substituent. Our aim is to clarify fluorination effect against anisole on the electronic transitions, conformational structure, vibronic structure and relaxation dynamics of *o*-, *m*- and *p*-fluoroanisole (FA).

We measured the laser-induced fluorescence (LIF) excitation and single vibronic level (SVL) dispersed fluorescence spectra of jet-cooled *o*-, *m*- and *p*-FA. The SVL dispersed fluorescence spectra were also measured by pumping each vibronic band. The observed bands were assigned with the aid of the quantum chemical calculations. The SVL dispersed fluorescence spectra indicated that the vibrational band mixing should take place in the S₁ state, and the IVR process becomes more dominant with the higher excess energy. The vibrational band mixing and IVR process are characteristic for each isomer.

III-G-4 Evidence for a Non-Planar Conformer and Conformational Isomerization of *o*-Fluoroanisole in a Low-Temperature Ar Matrix

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FT-IR spectra of *o*-fluoroanisole were measured in a low-temperature Ar matrix with and without UV irradiation. The observed bands, without irradiation, were assigned to the *trans* conformer with the aid of the quantum chemical calculations at the B3LYP/cc-pVTZ level. By comparing the IR spectrum, after irradiation, with the calculated spectra, the formation of a *non-planar* conformer was established. The *non-planar* conformer gradually decayed by a unimolecular process under dark conditions at 16 K, while the *trans* conformer increased. The back-reaction rate was estimated, and the reaction dynamics between the *trans* and *non-planar* conformers was discussed.

III-G-5 Molecular Structure and Puckering Vibration of 1-Aminoindan in a Supersonic Jet

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The laser-induced fluorescence (LIF) and single vibronic level dispersed fluorescence spectra of 1-aminoindan (1-AI) were measured in a supersonic jet. Two prominent intense bands observed at 36934 and 37062 cm⁻¹ in the LIF spectrum were assigned to the 0⁰ bands of rotational isomers resulting from the orientation of the amino group. The low-frequency puckering vibration was compared with indan. The puckering frequency and transition intensity of 1-AI are the same as indan in the S₀ state and not in the S₁ state. The quantum chemical calculations suggest six possible isomers, however, only two stable rotational isomers were observed in the spectra. The intramolecular N–H···π hydrogen bond should play an important role in the stabilization of the rotational isomers.

III-H Photochemical Reactions in Microreactors

Many chemical synthesis has been so far conducted by temperature controlled chemical reactions using specific catalyst. Utilization of characteristic catalyst, however, is restricted to some enantioselective synthetic reactions. Light is a powerful tool to excite molecules into electronically excited states selectively to give rise to specific reaction channel. Our proposal is application of laser light to elucidate the mechanism of photo-induced chemical reactions taken place in micro-region reaction vessel. Laser light has a couple of advantages to investigate the reaction mechanism, such as high power, time-resolved analysis, and polarization character (linear or circular dichroism), that is specifically related to characteristic properties of the enantiomer. Another feature of the laser light is a small beam divergence, of which diameter still can be focused into much smaller area such as micrometer region. Taking into account of these considerations, we have set up the laser photochemical synthesis system and photocatalytic reaction system with immobilized titanium dioxide. Both the laser irradiation system and the product analysis section can be processed on the same site of the microreactor. The products generated by the laser irradiation can be analyzed at the downstream site of the reactor using a second laser irradiation. If the product emits the detectable fluorescence, the LIF measurement can be applicable. In case of non-emitting substance an opto-acoustic and/or photothermal spectroscopy, or Raman spectroscopy should be employed. We have investigated enantioselective reaction of cyclooctene derivatives as a model system, and photocatalytic degradation of endocrine disruptors with immobilized titanium dioxide.

III-H-1 Application of Microfabricated Reactors for Asymmetric Photoreaction

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We reinvestigated the asymmetric photoreaction of enantiodifferentiating *Z-E* photoisomerization of cyclooctene sensitized by aromatic esters in a microreactor. Effects of residence time, temperature, and laser power on the photoreaction were investigated. The results indicate that high ee value was obtained within the short residence time. In contrast, the longer residence time was required to achieve higher *E/Z* ratio. The higher

laser power and/or reputation rate becomes, the quicker the *E/Z* ratio should reach to the highest value. The ee value was quite sensitive to the temperature. The reaction mechanism will be discussed in terms of the conformational structure of excimer.

III-H-2 Photocatalytic Reaction in Microfabricated Reactors

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Photocatalytic reaction in microspace was investigated by using a microreactor with immobilized tita-

nium dioxide. Since a photocatalytic reaction takes place on an irradiated titanium dioxide surface, a micro-fabricated reactor which has a large surface-to-volume ratio must prove its advantages on the reaction.

Photodegradation of endocrine disruptors was examined as a model reaction. The microreactors made of quartz with a cross-section of 0.5 mm width and 0.1–0.5 mm depth were coated with a photocatalytic titanium dioxide layer of approximately 1 micron thickness. Aqueous solutions of 3-chlorophenol, monochlorobenzene, bisphenol A, and *N,N*-dimethylformamide were introduced to the microreactor with a syringe pump then irradiated with a UV light source. The following light sources were employed for the excitation of photocatalytic titanium dioxide: XeCl (308 nm) excimer laser, YAG (355 nm) laser and OPO laser (300–400 nm) excited with the YAG laser, and UV-emitting diodes (UV-LED, 365, 375 and 385 nm).

The variation profiles of the concentration of endocrine disruptors as a function of irradiation time were examined. Degradation increased with increasing the residence time and reaches 30% for 3-chlorophenol and 13% for bisphenol A at a irradiation time of 5 seconds in the case of 385 nm UV-LED excitation with a micro-reactor of 0.1 mm depth. Higher degradation was obtained for lower concentrations of endocrine disruptors and smaller thickness of microspace. Degradation kinetics and photonic efficiencies dependent on the nature of the light source are further discussed.

Feasibility of photocatalytic reaction in micro-reactors was thus proven and optimization of excitation wavelength and photon density, design of the micro-reactor, and flow rate and irradiation time are under progress for the establishment of the photocatalytic microreaction system.