III-H Spectroscopy and Photochemical Dynamics of the Methyl or the Methoxy Internal Rotation in Jet-Cooled Toluene Derivatives and Methylanisoles

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 in jets. 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 exited 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 (S_1) 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 CH_3 or OCH_3 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-H-1 Conformational Isomerism and Excited State Dynamics of Fluoroanisole in a Supersonic Jet

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It is known that substituted phenol and anisole derivatives have some stable conformers of internal rotation around the C(sp^2)–O bond both in the ground and excited states. In many cases, their stable structures corresponding to the energy minimum are *planar* conformers such as the *cis* and *trans* conformers. But recently, in addition to the existence of most stable *planar* conformer, it is suggested that the second stable *non-planar* conformer should exist for *o*-substituted anisole derivatives. However, a little information on such a *non-planar* conformer is reported so far. It is expected that the electronic excitation of the *non-planar* conformer should induce the geometrical change of the methoxy group related to the benzene ring, and alter the excited state dynamics compared to the *planar* conformer.

From these points of view, it is interesting to investigate how halogenation on the benzene ring of anisole affects on the excited state dynamics. In this study on *o*-, *m*- and *p*-fluoroanisole, in order to clarify the electronic transitions of rotational isomers, substituent effect on conformational structure and vibronic structure, and differences of excited state dynamics between the rotational isomers, the LIF excitation and SVL dispersed fluorescence spectra were measured in a supersonic jet. Figure 1 shows the LIF excitation spectra of *o*-, *m*- and *p*-fluoroanisole. The SVL dispersed fluorescence spectra were also measured by pumping each vibronic band observed in the LIF excitation spectra. The vibronic and vibrational bands observed in the spectra were assigned with the aid of quantum chemical calculations on the B3LYP/cc-pVTZ level. The SVL dispersed fluorescence spectra indicated that the vibronic mixing should take place in the S_1 state, and the IVR process becomes more dominant with the higher excess energy.

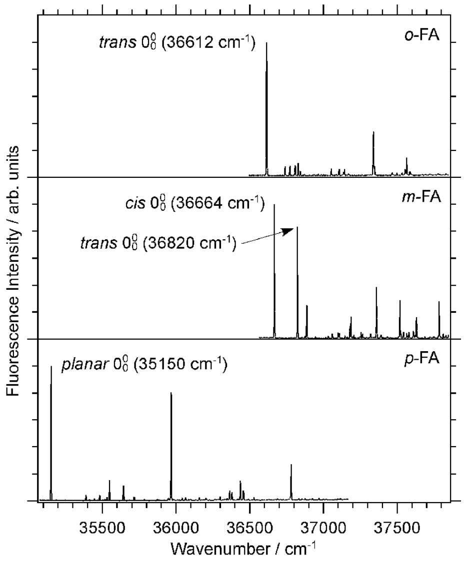

Figure 1. LIF excitation spectra of *o*-, *m*- and *p*-fluoroanisole.

III-H-2 Spectroscopy and Relaxation Dynamics of Photoexcited Anisole and Anisole-Methyl-d_3 Molecules in a Supersonic Jet

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In this work we measured the LIF and DF spectra of the S_1–S_0 electronic transition for jet-cooled anisole and anisole-methyl-d_3 molecules. This is the first time measurement of the fluorescence of the deuterated anisole species. The molecular orbital calculations on the molecular and vibrational structures on the electronic ground and excited state were also performed.

For anisole molecule, 3 vibrational modes in the S_0 state and 11 vibrational modes in the S_1 state were reassigned on the basis of experiments and calculations. For deuterated molecule, we assigned 13 and 12 vibrational modes in the S_0 and S_1 states, respectively. Dispersed fluorescence (DF) measurement clarified the anharmonic coupling between several vibrational modes. The Duschinsky rotation between the 10b and 16a, and 6a and 6b modes are significantly observed for both molecules.

In order to investigate the relaxation dynamics we measured fluorescence lifetimes of the single vibrational levels for the first time and calculated the nonradiative decay rate constant. Among the nonradiative processes, intersystem crossing to the triplet manifolds would be dominant for both species, as in the case of the condensed phase. It was found that the character of the SVL is deeply related to the ISC process; the excess energy dependence of the k_{nr} becomes larger for the out-of-plane bands than for the in-plane bands. Especially the methyl internal rotation in the anisole molecule and vibrational mode of 16a in the anisole-methyl-d_3 molecule exhibited fast nonradiative decay process, revealing accepting modes of the ISC processes. The IVR process was affected by the methyl deuteration but the results were against the expectation; the broadening of DF spectra below 940 cm^{-1} was depressed by deuteration. On the SVLs with in-plane component the broadening of DF spectra by the IVR and k_{nr} values are well correlated. Therefore we conclude the energy flow to the out-of-plane mode should be responsible for the nonradiative process.

III-I 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 photodynamics of excited 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 informations 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 sensibility. 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-I-1 Photochemical Dynamics of Phenoxy Alkanes

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Phenoxy radical is one of the fundamental chemical intermediates on the photochemistry. It is known to take an important role on combustion, lignin UV reaction in the plant, biochemical reactions, and so on. Photolysis of phenol and phenoxy alkanes is also known to produce phenoxy radical.1) In the gas phase phenoxy methane (anisole, methoxy benzene) was reported to produce phenoxy radical with the 193 nm laser excitation.2) We measured transient absorption spectra of several phenoxy-substituted alkanes in solution, however, not only phenoxy radical but also another transient were found. In this study, we made an assignment of the transient and discussed the reaction dynamics in detail. Furthermore, reaction pathway for excited methoxy-substituted toluenes (*o*-, *m*-, *p*-methylanisoles) was also discussed.

The transient absorption spectrum of phenol in solution obtained with the UV irradiation shows a structured band at around 400 nm. It is known as a typical absorption spectrum of phenoxy radical. However, the transient absorption spectrum of anisole was not the same spectrum of phenoxy radical; a broad absorption band appeared around 440 nm in addition to the structured band of phenoxy radical. The broad band was observed in the spectra of the polar and non-polar solutions. The lifetime of the transient was several μs. To make an assignment of the transient and to clarify the reaction mechanism, photosensitization experiment with acetone was carried out. The broad band appeared at around 440 nm, which is exactly the same one obtained with the photolysis of anisole. We could safely assign the new transient to a radical, which should be produced through hydrogen atom elimination by the UV irradiation.

References

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III-I-2 Relaxation Processes of Naphthalene in Highly Excited State in Condensed Phase

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Relaxation dynamics in highly excited singlet state of naphthalene (NP) in condensed phase is studied by time-resolved thermal lensing (TRTL) technique coupled with nanosecond laser photolysis. The results of TRTL measurements with the 248 nm excitation give heat conversion efficiency of NP, and lead to information on relaxation process, that is, rapid nonradiative process is found to take place from the highly excited singlet state (S_2) into the S_0 state, not through the S_1 (v = 0) state. The quantum yield is successfully estimated to be 0.31 ± 0.01. The occurrence of the rapid nonradiative process is also found in deuterated NP and 1-methylnaphthalene. The mechanism of the relaxation process from the highly excited state is discussed in detail.

III-I-3 Calorimetric Standards for Photothermal Methods at the 248 nm Excitation

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[*Chem. Phys. Lett.* **374**, 41–44 (2003)]

The time-resolved thermal lensing measurements were carried out on 2-hydroxybenzophenone, pyridazine and benzene in acetonitrile at the 248 nm excitation in order to investigate the feasibility for the calorimetric standards on photothermal methods. The heat conversion efficiency values of 2-hydroxybenzophenone and pyridazine were estimated to be unity compared with that of benzene, revealing that 2-hydroxybenzophenone and pyridazine should show no fluorescence and no photochemical reactions. Therefore, these molecules should be good calorimetric standards at the 248 nm excitation.

III-I-4 Production and Excited State Dynamics of Photo-Rearranged Isomer of Benzyl Chloride and Its Methyl Derivatives Studied by Transient Absorption and Time-Resolved Thermal Lensing Techniques

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[*J. Phys. Chem. A* submitted]

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 [*Res. Chem. Intermed.* **27**, 137 (2001)]. 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 excellently consistent with ab initio and DFT calculations.

III-J Excited State Dynamics of Organic Molecules in Cyclodextrin Nanocavities

III-J-1 The Cavity Size Effect on the Excited State Dynamics of Dimethylaniline Derivatives Complexed with Cyclodextrins

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[*Chem. Phys.* **286**, 399–407(2003)]
[*J. Phys. Chem. A* **108**, 7490–7495 (2004)]

The effect of cyclodextrin (CD) complexation on the excited state dynamics of some dimethylaniline derivatives, 4’-dimethylaminoacetophenone (DMAAP), methyl 4-(dimethylamino)benzoate (MDMAB), and ethyl 4-(dimethylamino)benzoate (EDMAB) in bulk solution was studied by means of steady state and time-resolved laser spectroscopy. The dimethylaniline derivatives complexed with CDs exhibited twisted intramolecular charge transfer (TICT) fluorescence whereas only the emission from the locally excited state was observed in aqueous solution without CD (Figure 1). In the case of α-CD complexes of MDMAB and EDMAB, dual TICT emission from different microenvironments was observed. The dependence of TICT emission intensity on pH and α-CD concentration suggested that the dual TICT emission can be attributed to the guest molecule in the 1:1 and 1:2 guest–α-CD complexes (Figure 2). Time-resolved emission spectra also indicate the formation of 1:2 complex with α-CD and faster backward electron transfer from TICT state for 1:1 complexes.

Though the effect of CD complexation on TICT photochemistry has been interpreted in terms of the restriction on molecular motion and the reduced polarity effect introduced by CD cavities, these effects tend to have opposite effects on the TICT emission yield. Thus the overall effect of CD encapsulation is probably complicated and the problem is still in controversy. Our results indicate that polarity effect introduced by the hydrophobic cavity is the dominant factor in the controlling the photochemistry of dimethylaniline derivatives in CD complexes.

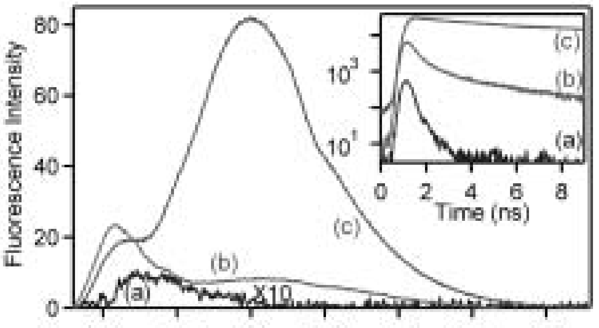

Figure 1. Dispersed emission spectra and emission decay profiles of MDMAB (2.5×10^{-5} M) in aqueous solutions (a) without CD, and in the presence of (b) 5.0×10^{-4} and (c) 5.0×10^{-2} M of α-CD excited at 315 nm.

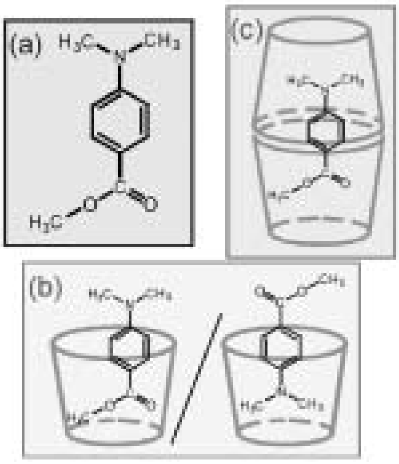

Figure 2. Possible structures of MDMAB–α-CD complex.