III-F Spectroscopy of Jet-Cooled Aromatic Molecules and Photochemical Reaction of Aza- and Thio-Substituted Nucleobases

The phenomena of energy relaxation in isolated molecules have been essential issue in chemical dynamics over many decades. The laser spectroscopy coupled with the jet expansion gives us much information on molecular structure and relaxation processes. The substituent of the -NH_2 or -SCH_3 group should play an important role for the structure and the relaxation processes in their excited states.

Transient molecules such as excited states and chemical intermediates, which can be generated with laser irradiation, have been detected by laser flash photolysis. Time-resolved photothermal techniques are powerful to study nonradiative processes because they can detect the released heat from excited molecules directly with high sensitivity. 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 Conformation of 2-Aminoindan in a Supersonic Jet: The Role of N–H···π Hydrogen Bonding

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Weak intramolecular hydrogen bonding has attracted considerable attention of many researchers because it would govern chemical and physical properties of flexible molecules. Previously, we studied 1-aminoindan in a supersonic jet expansion, and two rotational isomers stabilized by an intramolecular N–H···π hydrogen bonding were observed. To further understand the interaction we investigate the effect of the position of the substitution. We measured laser-induced fluorescence (LIF) and dispersed fluorescence spectra of 2-aminoindan (2-AI). Three series of bands in the LIF spectrum were observed, and were assigned to the corresponding conformational isomers with the aid of *ab initio* calculation at the MP2/6-311+G(d,p). A hydrogen atom of the amino group in the most stable conformer points toward the benzene ring, suggesting the contribution of an intramolecular hydrogen bonding between the hydrogen atom and the π-electron of the benzene ring. The contribution of the extremely weak intramolecular hydrogen bonding to the molecular structure of 2-AI was elucidated. The strength of the hydrogen bonding of 2-AI was discussed in detail.

III-F-2 Conformation of Thioanisole in a Supersonic Jet

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It is suggested that thioanisole has a planar and perpendicular conformers with respect to the rotation of methylthio group around the C(sp^2)–S bond. Despite of many experimental and theoretical attempts, the most stable conformer and potential energy curves are still of subject because the experimental and theoretical results are not consistent each other. In this study, to elucidate the molecular structure of thioanisole in S_0 and S_1 states we measured the laser-induced fluorescence (LIF) and dispersed fluorescence (DF) spectra of thioanisole in a supersonic jet. We can firmly conclude that the most stable conformer in the S_0 and S_1 states is the planer conformer. In the LIF spectrum, low-frequency out-of-plane torsional mode, which is only allowed if their quantum numbers change by an even number, was observed relatively intensive. It is suggested that in the S_1 state structure of thioanisole is slightly twisted outside the benzene ring.

III-F-3 Excited-State Dynamics of 6-Azauracil with UVA Light Irradiation

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Analogues of nucleobases have been paid much attention because of distinct properties to originals. Aza-nucleobase, incuding a N atom into the skeleton of the nucleobase molecule, is one of the well-known analogues for anti-neoplastic and fungistatic properties. For the wide application, it is important to obtain information on relaxation and reaction mechanism of photoexcited nucleobase analogues.

We have measured transient absorption spectrum of 6-Azauracil (6-AU) in deaerated acetonitrile with the nanosecond 248 nm laser. Immediately after the laser shot, an absorption band peak at 320 nm and a broad absorption band at 500–700 nm were observed. The absorption bands are assigned to the lowest excited triplet (T_1) state of 6-AU (T–T absorption). The T–T absorption decayed with the rate constant of 5.0×10^6 s^{-1}. With the time-resolved thermal lensing experimant, it was found that the triplet 6-AU produces singlet oxygen ($^1\Delta_g$) efficiently.

III-F-4 Ultrafast Excited-State Dynamics of 4-Thiothymidine in Aqueous Solution

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Thionucleobases and thionucleosides have received renewed attention because of high sensitivity to UVA light (320–400 nm) in which region normal DNA constituents are transparent. 4-Thiothymidine (s^4-TdR), an analogue of the naturally occurring nucleoside thymidine, has strong absorption in the UVA region. Recently it was reported that s^4-TdR can be readily incorporated into cellular DNA and that low doses of UVA light can easily inflict lethal damage on the DNA containing s^4-TdR, causing cell death. The synergistic use of s^4-TdR and UVA light offers a novel approach to cancer treatment. Apparently, electronically excited state of s^4-TdR is at the initial and crucial stage of the UVA-induced cell killing, and thus photophysical and photochemical studies of s^4-TdR would be of great significance. Recently, we elucidated that the major process of deactivation of photoexcited s^4-TdR is intersystem crossing (ISC) to triplet manifolds, and the quantum yield for ISC of s^4-TdR to be unity. In this study, ultrafast transient absorption measurement was performed with the pump-probe technique in order to obtain more detailed information on the S → T ISC process.

We have measured a time profile of the transient absorption of s^4-TdR in aqueous solution (pH 7.4) monitored at 570 nm obtained by 263 nm femtosecond laser excitation. The transient absorption emerged within the instrumental response time (< 0.50 ps) and decayed with the decay time of 10 ps. We have also measured a time profile of the transient absorption of thymidine (TdR) under the same experimental condition for s^4-TdR. The transient absorption emerged by the excitation decayed immediately to the initiate level, and it was found the transient should decay with time constant of equal or faster than 0.50 ps. For both cases of s^4-TdR and TdR, the observed transients should be assigned to be their excited singlet states, and the decay rate constants of the transient absorption should be regarded as the lifetime of the excited singlet states. It was clarified that s^4-TdR decays much slowly (10 ps) compared with TdR (0.5 ps), and the S → T ISC process of s^4-TdR should take place with time of approximately 10 ps.

III-G Photochemical Reactions in Microreactors

In the last decade, microreaction system has developed using the features unique to microspace such as short molecular diffusion distance, excellent heat transfer characteristics, laminar flow, and large surface-to-volume ratio. Although microreaction systems are successfully examined in a wide range of applications of analytical and organic chemistry, there are only several reports on photoreactions in microreactors as described in the following section. We can expect microreactors to exhibit higher spatial illumination homogeneity and better light penetration through the entire reactor depth in comparison to large-scale reactors. Thus, we are investigating applications of microreactors on organic photoreactions.

III-G-1 Application of Microreactors for Photoreactions

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[*Photoreactions*, in *Microchemical Engineering in Practice*, T. R. Dietrich, Ed., Blackwell Publishing (2006)]

We investigated effects of residence time, reaction temperature, laser power, and excitation wavelength on photosensitized enantio- and diastereo-differentiating reactions in microreactors. Photonic efficiencies of model reactions were considerably larger than those in conventional batch reactors. Further, the yield of photosensitized diastereodifferentiating addition of methanol to terpenes was greatly improved in the microreactor.

Photocatalytic oxidation of endocrine disruptors, reduction of organic compounds, and amine alkylation processes were investigated in a microreactor with immobilized photocatalytic TiO_2 layer. Apparent reaction rates in microreactors were much larger than those in conventional batch reactors. A photocatalytic process of N-alkylation of benzylamine in alcohol media was successfully observed by using microreactors with immobilized Pt-free TiO_2 as well as Pt-loaded TiO_2, while it has been reported that the N-alkylation didn't occur by the irradiation of Pt-free TiO_2 in conventional batch reactors. The study on the oxidation process of olefins by using a multiphase-photocatalytic microreactor was also reported.

III-G-2 Photocatalytic Reduction in Microreactors

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Photocatalytic reduction of benzaldehyde and nitrotoluene in microspace was investigated by using a microreactor with immobilized titanium dioxide. Since a photocatalytic reaction takes place on an irradiated titanium dioxide surface, a microfabricated reactor which has a large surface-to-volume ratio must prove its advantages on the reaction.

Photoreduction was carried out with a microreactor made of quartz which has a microchannel of 500 μm width, 100 μm depth, and 40 mm length. The bottom and side walls of the microchannel were coated with a photocatalytic TiO_2 layer. To appear the advantages of the miniaturized reaction vessel, a light source of minimal space and lower photon cost is suitable for the microreaction system. We employed UV light emitting diodes (UV-LEDs) for the excitation light source of photocatalyst. Alcohol solutions of benzaldehyde or nitrotoluene saturated with nitrogen were introduced to the microreactor with a syringe pump and irradiated with UV-LEDs. The reactions proceeded within 60 s to yield 10.7% of benzylalcohol from benzaldehyde and 45.7% of *p*-toluidine from *p*-nitrotoluene by the excitation of 365 nm UV-LED. The results suggest the possibilities of a catalytic microreaction system on organic photoreactions.