V-G Probing Time-Dependent Processes in Solution with Time-Resolved Spectroscopic Methods

A solute molecule surrounded by solvent molecules is exposed to dynamic environments of rapidly changing energy, polarity, or relative distance and orientation with adjacent molecules. The effects of these fluctuations, which are caused by the room temperature solvent molecules, are clearly demonstrated when the solute molecule experiences a chemical reaction. Intermolecular energy transfer and rotational or translational diffusion determine the fate of the chemical reaction.

Time-resolved spectroscopy is quite effective for studying time-dependent events occurring in solution. We use various types of time-resolved spectroscopy for observing dynamical processes. In this Annual Review, we report on five research projects, in which we use femtosecond time-resolved fluorescence spectroscopy with single channel detection, picosecond time-resolved fluorescence spectroscopy with multi-channel detection, picosecond time-resolved Raman spectroscopy, and nanosecond time-resolved infrared spectroscopy. We discuss (i) fast internal conversion of biphenyl, (ii) disagreement between Stokes- and anti-Stokes scattering frequencies observed under strong pump or probe light field, (iii) photoinduced Cl transfer reaction between biphenyl and carbon tetrachloride that results in the generation of the trichloromethyl (CCl_3) radical, (iv) solvent- and temperature-dependent Raman spectral changes of S_1 *trans*-stilbene and the mechanism of the *trans* to *cis* isomerization, and (v) picosecond dynamics of stepwise double proton-transfer reaction in the excited state of the 2-aminopyridine/acetic acid system.

V-G-1 Femtosecond Time-Resolved Anisotropy Measurement of Biphenyl Fluorescence

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The fluorescence intensity and its anisotropy decay of biphenyl were observed in the hexane solution. Biphenyl in hexane was photoexcited with a linearly polarized femtosecond light pulse at 260 nm. Time dependence of the fluorescence intensity as well as its anisotropy was measured with the up-conversion method. The observed fluorescence decay curve showed a fast decay component of 0.4 ps, in addition to a slow component that corresponds to the reported fluorescence decay time of 16 ns. The fluorescence anisotropy was approximately 0.4 at time 0, indicating that the direction of the fluorescence transition dipole at time 0 is same as the S_2–S_0 absorption transition at 270 nm. The observed decay curve of the anisotropy was well fitted by a superposition of two exponential decay functions, with the time constants of 0.3 ps and 9 ps. The S_2–S_1 internal conversion rate of biphenyl is thus estimated to be 0.3 ps.
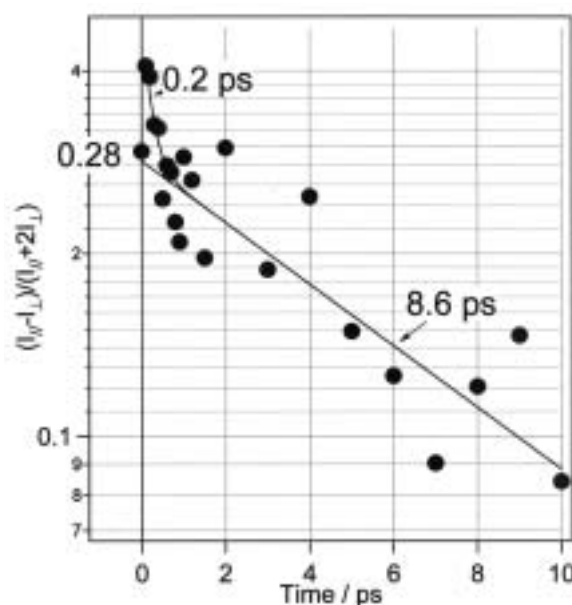

Figure 1. Observed curve of fluorescence anisotropy decay of biphenyl in hexane.

V-G-2 Effect of Pump and Probe Light Field on Picosecond Time-Resolved Resonance Raman Spectra of S_1 *trans*-Stilbene. Disagreement between Stokes- and Anti-Stokes Scattering Frequencies

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Picosecond time-resolved spontaneous resonance Raman spectra of the first excited singlet (S_1) state of *trans*-stilbene were measured with various power densities of pump or probe light, for both the Stokes and anti-Stokes scattering regions. Careful calibration of the peak positions of the 285 cm^{-1} Raman bands reveals that the Stokes scattering band and the anti-Stokes

scattering band shift to the same direction in absolute wavenumber, or to the opposite directions in Raman shift, when the pump or probe power density is increased. The direction of the wavenumber shift caused by the pump light field is opposite to that caused by the probe. Because of these apparent peak shifts, the Stokes Raman band and the anti-Stokes Raman band are recorded at different Raman shifts. The intrinsic change of the vibrational level spacing and the apparent peak shift caused by the pump or probe light field can be clearly separated by calculating the "symmetric" and "anti-symmetric" components from the Stokes and anti-Stokes peak positions. The experimental results are not explained by the optical Stark effect in its simplest form. Possible mechanisms to account for the results are discussed.
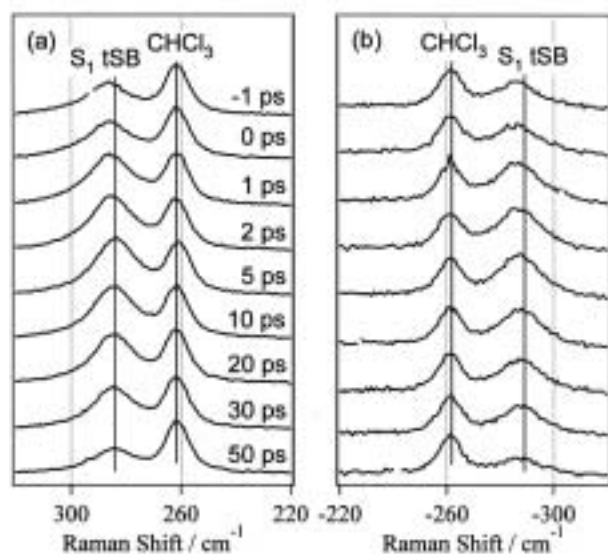

Figure 1. Time-resolved Raman spectra of S_1 *trans*-stilbene in chloroform. Stokes scattering bands (a) and Anti-Stokes scattering bands (b). Raman bands from S_1 *trans*-stilbene and solvent chloroform as well as time delay for each spectrum is indicated in the figure.

V-G-3 Photoinduced Cl Transfer Reaction between Biphenyl and Carbon Tetrachloride Studied by Nanosecond Time-Resolved Infrared Spectroscopy and Picosecond Time-Resolved Fluorescence Spectroscopy

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Photochemical reaction between biphenyl and carbon tetrachloride is studied with nanosecond time-resolved infrared spectroscopy and picosecond time-resolved fluorescence spectroscopy. Fluorescence lifetime of biphenyl in carbon tetrachloride solutions is measured with a picosecond time-resolved fluorescence spectrometer. The recorded lifetime is 3.8 ps, shorter than fluorescence lifetime in cyclohexane by a factor of four thousands. After the photoexcitation of biphenyl in carbon tetrachloride, the trichloromethyl (CCl$_3$) radical is formed as a reaction intermediate, which is confirmed by the detection of the radical's 896 cm^{-1} infrared band with nanosecond time-resolved infrared spectroscopy. One of the Cl atoms in solvent carbon tetrachloride is transferred to biphenyl to form the CCl$_3$ radical and a biphenyl-Cl adduct. Together with the already reported spectroscopic detection of the CCl$_3$ radical as an intermediate in photochemical reactions of *trans*-stilbene or anthracene with carbon tetrachloride, it is likely that this series of reactions are common for aromatic molecules.
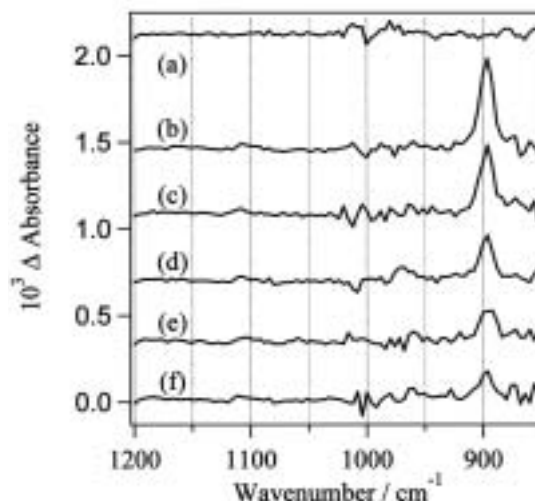

Figure 1. Time-resolved infrared difference spectra of biphenyl after photoexcitation in a carbon tetrachloride solution. Averaged spectrum for (a) –5 to 0 μs, (b) 0 to 5 μs, (c) 10 to 15 μs, (d) 20 to 25 μs, (e) 30 to 35 μs, and (f) 40 to 45 μs. Transient absorption band from the trichloromethyl (CCl$_3$) radical is observed at 896 cm^{-1}.

V-G-4 Analysis of the Solvent- and Temperature-Dependent Raman Spectral Changes of S_1 *trans*-Stilbene and the Mechanism of the *Trans* to *Cis* Isomerization: Dynamic Polarization Model of Vibrational Dephasing and the C=C Double-Bond Rotation

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Solvent- and temperature-dependent band shape changes of the olefinic C=C stretch Raman band of S_1 *trans*-stilbene have been analyzed on the basis of the dynamic polarization model. The analysis has shown that the solvent-induced dynamic polarization gives rise to the dephasing of the C=C stretch vibration and, concomitantly, triggers and facilitates the rotation around the C=C bond leading to the *trans* to *perpendicular* (and eventually to *cis*) isomerization. Picosecond time-resolved Raman spectra have been measured in three alkane solvents, hexane, octane, and decane at a number of different temperatures ranging from 268 K to 338 K and a total of 40 peak positions and the bandwidths have been determined for the C=C stretch band. The correlation plot of the bandwidth against peak position shows a clear linear relationship that is predicted by the dynamic polarization model.

Picosecond time-resolved fluorescence measurements have been performed in the same three alkane solvents at five different temperatures from 283 K to 313 K and 15 rates of the *trans* to *perpendicular* isomerization have been determined. The plot of the peak position against the rate of isomerization indicates another linear relationship between these two quantities which have no obvious reason to be correlated with each other. The dynamic polarization model accounts very well for this linear relationship and yields a new formula that relates the rate of isomerization to the frequency of the solvent-induced dynamic polarization. This formula seems to possess certain generality because it shows an excellent numerical agreement with the Arrhenius formula. The new formula derived from the dynamic polarization model gives the molecular-level details of the reaction process as to how the reaction is triggered and in what time scale the reaction actually proceeds. A new view of the photoisomerization of *trans*-stilbene has thus been obtained.

V-G-5　Picosecond Dynamics of Stepwise Double Proton-Transfer Reaction in the Excited State of the 2-Aminopyridine/Acetic Acid System

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The dynamics of the amino-imino double proton-transfer tautomerism reaction of the 2-aminopyridine (2AP)/acetic acid system in hexane have been investigated with steady-state absorption, steady-state fluorescence, and picosecond time-resolved fluorescence spectroscopies. It has been confirmed that the double proton transfer reaction takes place in the excited state of the double hydrogen-bonded complex of 2AP with acetic acid. The imino tautomer fluorescence shows a rise behavior with a 5 ps time constant at 480 nm, while a decay with a 5 ps time constant has been observed at 360 nm. The rate of this kinetics is reduced to 7 ps with deuterium substitution. From the comparison with the steady-state fluorescence spectra of proton-transferred model compounds, the 5 ps decaying species has been identified as the intermediate in which one proton is transferred from acetic acid to 2AP. It is thus concluded that the 5 ps time constant represents the second proton-transfer process which follows the first proton transfer that is too fast to be detected in the present experiment. The photoexcited double hydrogen-bonded complex of 2AP and acetic acid undergoes a stepwise double proton-transfer reaction within 5 ps in the excited state.