

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

Typical molecules in solutions experience several "collisions" in 1 ps. Therefore, many time-dependent processes in solution reach the stationary states in a picosecond time scale. Time-resolved spectroscopic techniques that can record rapidly changing phenomena with a picosecond ( $10^{-12}$  s) to sub-picosecond ( $10^{-13}$  s) temporal window are effective for probing the time-dependent processes. By using picosecond or femtosecond time-resolved spectroscopic methods, we study the rapidly changing events in solutions. In particular, we try to observe the relative translational motions and the process of intermolecular energy transfer. These processes are deeply involved in the mechanism of a chemical reaction and can determine the fate of the reactant molecules.

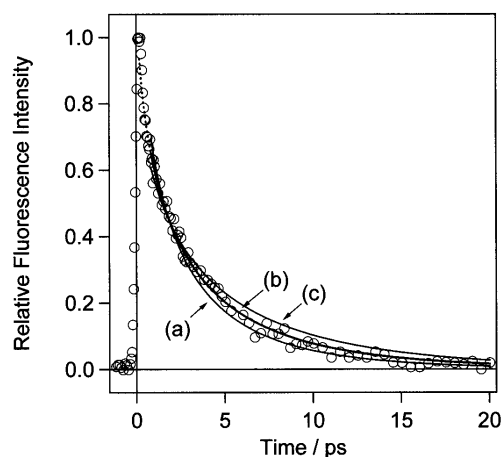
We started a new research project for studying the dynamic processes accompanying chemical reactions in solutions with experimental methods. For this purpose, we construct a new time-resolved spectrometer that can trace reaction kinetics in solution with a time resolution of a few hundreds of femtoseconds. With this apparatus, we try to detect time dependent transient absorption associated with electron- or charge-transfer processes, in the near-infrared region. A mode-locked Ti:sapphire laser system modified by Prof. Taira's Group, Laser Research Center for Molecular Science, is used for this study. We also study ultrafast bimolecular reaction kinetics in collaboration with Prof. Tahara's Group. Their femtosecond time-resolved fluorescence spectrometer is successfully applied for tracing ultrafast photochemical reaction between biphenyl and carbon tetrachloride.

### V-G-1 Photochemical Bimolecular Reaction between Biphenyl and Carbon Tetrachloride: Observed Ultrafast Kinetics and Diffusion-Controlled Reaction Model

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Reaction kinetics of an ultrafast bimolecular reaction is successfully interpreted by theories of diffusion-controlled reactions. When biphenyl is photoexcited to the first excited singlet ( $S_1$ ) state in carbon tetrachloride solutions, it reacts with the solvent carbon tetrachloride in a few picoseconds. We observe this fluorescence quenching kinetics by using a fluorescence up-conversion technique with a cross correlation time of 320 fs. The obtained decay kinetics is well explained by a model function derived from Smoluchowski's theory of diffusion-controlled reactions when the fitting parameter  $R$ , distance between the reactants for the reaction, is 0.39 nm (Figure 1). A modified kinetic theory by Collins and Kimball also gives a satisfactory fit, when  $R$  is 0.40 nm and the bimolecular reaction rate constant  $k_{\text{act}}$  is  $3.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . It is suggested that molecular motions in solution for a time period of a few picoseconds is well described by a concept of diffusion.



**Figure 1.** Fluorescence decay curves of biphenyl in carbon tetrachloride simulated by Smoluchowski's theory with the fitting parameter  $R = 0.43$  nm (curve (a)),  $R = 0.39$  nm (curve (b), best fit), and  $R = 0.35$  nm (curve (c)). Observed fluorescence decay curve is also shown with open circles.

### V-G-2 Construction of Femtosecond Time-resolved Near-infrared Absorption Apparatus for Tracing Chemical Reaction Dynamics

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It has been known that some molecular systems show strong electronic transitions associated with electron- or charge-transfer processes in the near-infrared region. Combination or overtone transitions of vibrational levels in general are also located in this spectral region. Therefore, ultrafast time-resolved near-infrared spectroscopy will be quite effective for studying kinetic processes in solution. It provides us with information, on time-dependent phenomena, that is not accessible by other spectroscopic methods. To the best of our knowledge, however, ultrafast time-resolved

near-infrared spectroscopy has been rarely used for studying chemical systems.

We are constructing a femtosecond time-resolved near-infrared absorption apparatus. The apparatus adopts a basic pump-probe scheme. Output light from a mode-locked Ti:sapphire laser (wavelength, 1030 nm; pulse width, 100 fs) is used as “probe” while its second harmonic (515 nm) is used as “pump.” The probe light after the sample is detected with an electrically cooled InGaAs photodiode. Time delay between the pump and probe is controlled by an optical delay unit. We are planning to use the apparatus for tracing kinetics of electron- or charge-transfer reactions.