V-K Fast Bimolecular Reaction Kinetics in Solution

Since April 2000, we started a new research project for obtaining microscopic pictures of chemical reactions in a solution phase. 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. In particular, we try to detect time dependent transient absorption in the near-infrared region accompanying photoexcitation of reactant molecules and following photochemical reactions. A mode-locked Ti:sapphire laser system modified by Prof. Taira's Group, Laser Research Center for Molecular Science, will be used for this study.

V-K-1 Ultrafast Bimolecular Reaction Kinetics between S_1 *trans*-Stilbene and Carbon Tetrachloride Studied by Sub-Picosecond Time-Resolved Visible Absorption Spectroscopy

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Ultrafast bimolecular reaction kinetics between S_1 *trans*-stilbene and carbon tetrachloride is monitored by sub-picosecond time-resolved visible absorption spectroscopy. After the photoexcitation at 270 nm, the S_n–S_1 transition of *trans*-stilbene observed at 580 nm is quenched in a few picoseconds due to a bimolecular photochemical reaction between *trans*-stilbene and carbon tetrachloride. The observed reaction kinetics is well explained by assuming a time dependent bimolecular rate constant derived either from Smoluchowski's theory or from Collins-Kimball's theory of diffusion-controlled reactions. It is not obvious if diffusion is a suitable concept for describing a translational motion of molecules in a time period of a few picoseconds. The model of diffusion should be used for transportation phenomena, such as heat dissipation or molecular motion, in a macroscopic system. However, the experimental result suggests that the molecular motion in solution for a few picosecond time period is well described as a diffusion process for this molecular system.