1P041 **Study of the Wavepacket Motion in Photoisomerization of Cyanine Dye by Ultrafast Pump-Dump-Probe Technique**

(Molecular Spectroscopy Laboratory, ASI, RIKEN)

○Zhengrong Wei, Takumi Nakamura, Satoshi Takeuchi, Tahei Tahara

【**Introduction**】

The dynamics of chemical reactions is usually described by the rate of population transfer between two states corresponding to the local minima on the potential energy surface (PES). In ultrafast reactions, however, we can see the dynamics that is regarded as a fast and continuous change within a relevant excited-state PES. Figure 1 depicts continuous motions of a wavepacket, a superposition of states having different energies, on a monotonously-sloping barrierless S_1 PES along the simplified reaction coordinate. Although this wavepacket provides an intuitive picture of the dynamics of ultrafast reactions, in reality, we only have very limited knowledge on how the wavepacket evolves on the PES. Therefore, it is highly desirable to experimentally examine and "visualize" the motion of the wavepacket, thereby unveiling the nature of the ultrafast reaction. In this presentation, we show our pump-dump-probe spectroscopic study of the excited-state wavepacket motion in ultrafast photoisomerization of a cyanine dye molecule.
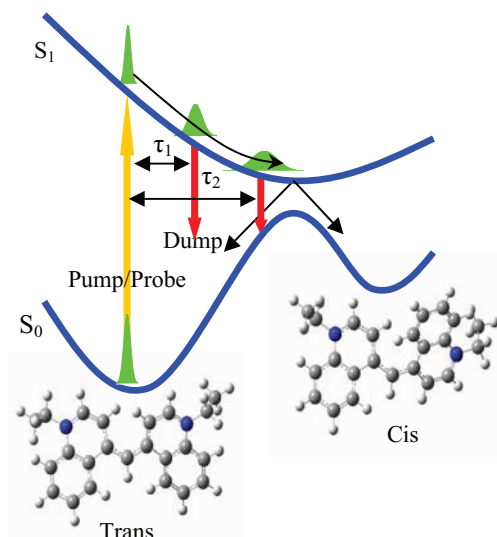

Fig. 1 Schematic illustration of the S_0 and S_1 PES as well as the wavepacket motion monitored by pump-dump-probe experiments.

【**Results and discussion**】

The cyanine dye (1144-C), which we selected as a sample, is known as a representative molecule showing ultrafast photoisomerization [1]. As shown in Figure 1, it has been suggested that the wavepacket generated by the pump pulse (580 nm) moves rapidly on the S_1 PES from the Franck-Condon state toward a sink region, where the wavepacket goes back to the ground state with a time constant of ~9 ps. This recovery of the ground-state bleaching is readily seen by ordinary pump-probe measurements (Figure 2 black curve).

To examine the wavepacket motion on the S_1 PES, we introduced a dump pulse (λ_{dump}=690 nm) that spectrally overlaps the stimulated emission band. As shown in Figure 2, the bleaching signal decreased instantaneously at each dump time, indicating that a substantial fraction of the S_1 molecules was driven back to the ground state through the stimulated emission transition by the dump pulse. We evaluated the dump efficiency which was defined as,
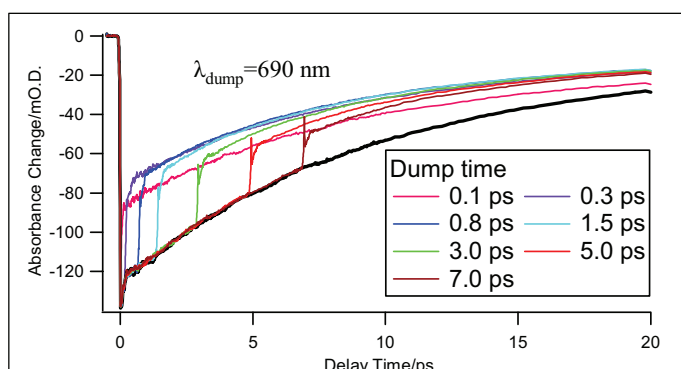

Fig. 2 Time-resolved pump-dump-probe signals obtained with and without the dump pulse for various pump-dump delays (1 mM solution in ethylene glycol, pump/probe: 580 nm, dump: 690 nm).
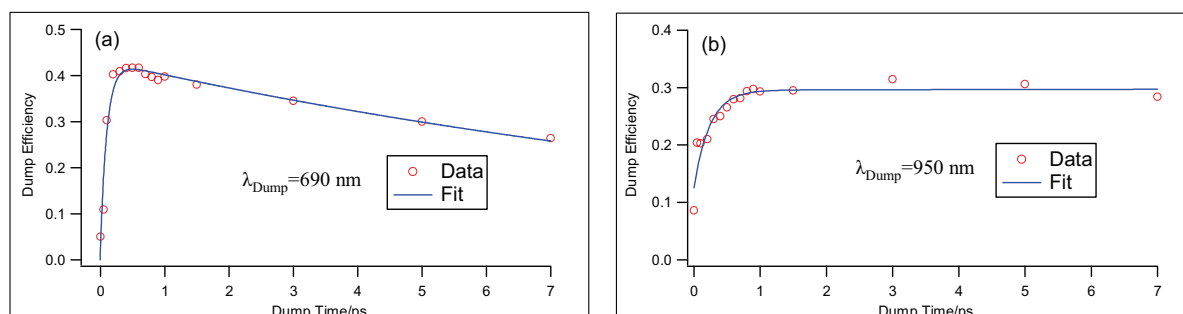
$$Dump\ efficiency = 1 - \frac{\Delta abs(dump\ on)}{\Delta abs(dump\ off)}$$

, for every dump time, and plotted it in Fig. 3a. Interestingly, the dump efficiency showed a rise time with ~100 fs time constant. This result clearly indicates that the wavepacket needs this finite time to reach the potential region, where the S_1-S_0 energy difference matches the photon energy of dump pulse at 690 nm. Furthermore, when the photon energy of the dump pulse was lowered (λ_{dump}=950 nm), the corresponding time

Fig. 3 Dump efficiency as a function of the dump time for the dump wavelength of (a) 690 nm and (b) 950 nm.

became substantially longer (~240 fs). This corresponds to the change of the potential region where the dump process occurs: the 950 nm pulse dumps the S_1 state in the vicinity of the sink where the S_1 and S_0 energies come closer to each other (Figure 3b). The present observation provides a quantitative representation of the wavepacket motion as well as a relative shape of the S_0 and S_1 PES along the reaction coordinate.

【References】

[1]. E. Akesson, H. Bergstrom, V. Sundstrom, T. Gillbro, Chem. Phys. Lett. **126**, 385 (1986).