

Quantitative Characterization of the Wavepacket Motion in Cyanine Photoisomerization by Ultrafast Pump-Dump-Probe Spectroscopy

(Molecular Spectroscopy Laboratory, ASI, RIKEN)

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

【Introduction】

Ultrafast reactions are often associated with unrestricted continuous nuclear motions on an ultrashort time scale. The dynamics of such reactions can be described more suitably by motions of a nuclear wavepacket on a relevant potential energy surface (PES), rather than a kinetic population model with a constant rate. Although the wavepacket motion 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. In order to unveil the nature of ultrafast reactions, it is highly desirable to experimentally “visualize” the wavepacket motion over the whole PES. 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.

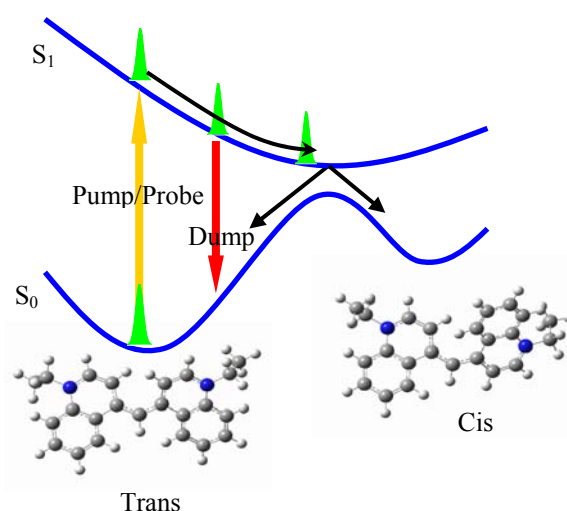


Fig. 1 Schematic illustration of the wavepacket motion on the S_1 PES monitored by pump-dump-probe experiments.

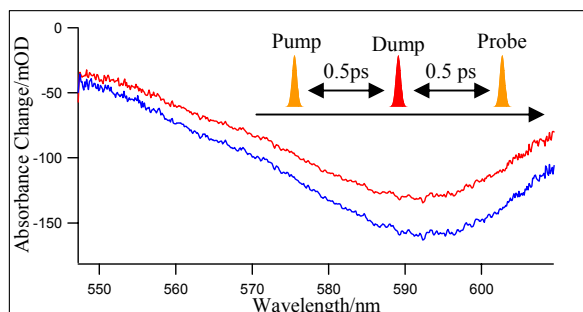


Fig. 2 The transient absorption spectra at 1 ps with and without the dump pulse (1 mM solution in ethylene glycol, pump/probe: 580 nm, dump: 950 nm).

【Results and discussion】

The cyanine dye (1144-C), which we selected, is well-known as a prototypical system showing ultrafast photoisomerization in a barrierless manner [1]. As shown in Figure 1, a wavepacket is created on the Franck-Condon region of the S_1 PES upon photoexcitation. Then, the wavepacket starts to migrate toward the energy minimum of S_1

PES, where the S_1 and S_0 PES get closer to each other. Reaching the minimum point, the wavepacket is transferred to the ground state by internal conversion, producing a cis-form or a trans-form. In Figure 2, the blue curve shows an ordinary pump-probe absorption spectrum of 1144-C at 1ps delay, which was dominated by the ground-state bleaching. To examine the wavepacket motion on the S_1 PES, we introduced a dump pulse (950 nm) that spectrally overlaps the $S_1 \rightarrow S_0$ stimulated emission band. As shown with red curve in Figure 2, the bleaching signal was decreased, 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 defined the dump efficiency as:

$$\text{dump efficiency} = 1 - \frac{\Delta \text{abs}(\text{dump} - \text{on})}{\Delta \text{abs}(\text{dump} - \text{off})},$$

and evaluated it at 15 ps after the dump pulse to eliminate the influence of dump induced additional processes. The dump efficiency is plotted as a function of the pump-dump delay in Figure 3b.

Interestingly, the dump efficiency does not grow up instantaneously but shows a ~ 330 fs rise time. 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 the dump pulse at 950 nm. We also changed the dump wavelength to fully track the wavepacket motion, and obtained the rise time of ~ 100 fs and ~ 390 fs for the 690 nm and 1200 nm dump wavelengths, respectively. In other words, the rise time gets longer for smaller dump photon energy. This is a clear experimental manifestation of the continuous wavepacket motion along the reaction coordinate. The dump efficiency also showed a long tail, which suggests a considerable broadening of the wavepacket itself. Thus, the present experiment provides quantitative characterization of the wavepacket motion as well as excited state PES.

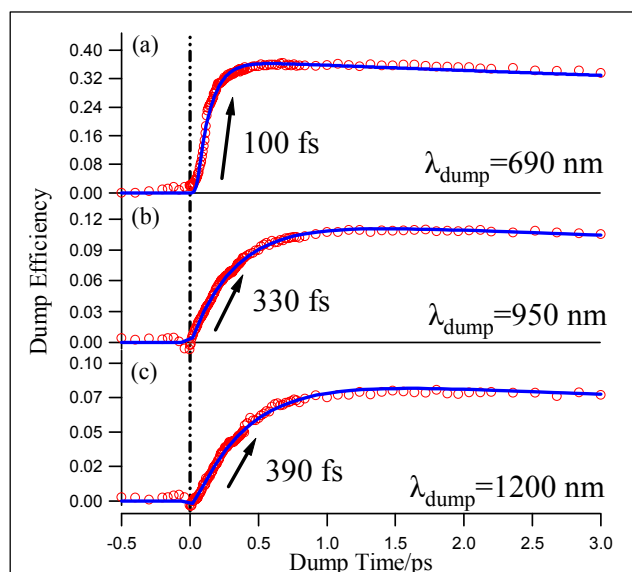


Fig. 3 Dump efficiency as a function of the dump time for the dump wavelengths of (a) 690 nm, (b) 950 nm and (c) 1200 nm.

【References】

- [1]. E. Åkesson, H. Bergström, V. Sundström, T. Gillbro, Chem. Phys. Lett. **126**, 385 (1986).