Trial to Observe Wavepacket Motions near the Potential “Funnel” in Stilbene Photoisomerization by Pump-Dump-Probe Spectroscopy

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In ultrafast reactions, it is considered that the excited-state molecule relaxes rapidly to the ground state through a potential “funnel”, where the excited- and ground-state potential energy surfaces (PES) get close to each other. This potential region is expected to provide an efficient channel for rapid relaxation and to play a key role in ultrafast reactions. However, our knowledge is very limited on how the molecular structure (or nuclear wavepacket) evolves in this important potential region. Therefore, it is highly desirable to obtain quantitative information about the wavepacket motion near the funnel region. With this fundamental interest in mind, we tried to observe the wavepacket motion approaching the funnel region in a model system, photoisomerization of cis-stilbene, using pump-IR dump-probe spectroscopy.

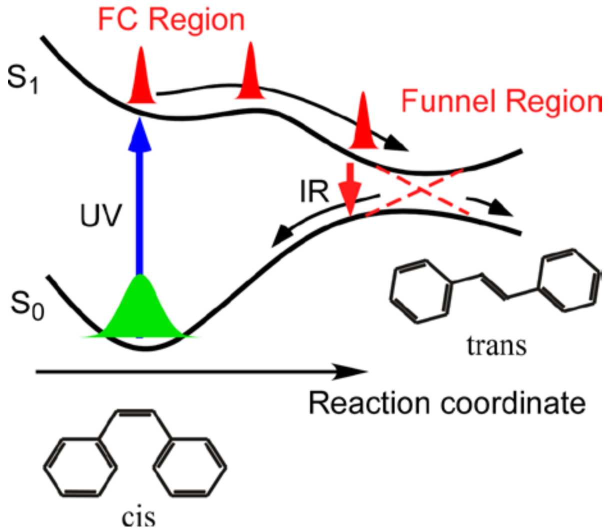

Fig. 1 Schematic illustration of the potential

The experiment was carried out based on a homemade pump-dump-probe setup. Briefly, the output of a Ti: sapphire amplifier was divided into three beams for generating the pump, dump and probe pulses. The pump pulse at 266 nm was produced through 3rd-harmonic generation of the 800-nm fundamental pulse. The dump pulse at various infrared wavelengths was generated by a commercial OPA system pumped by the 800-nm pulse. The white continuum probe pulse was obtained by focusing the fundamental pulse on a sapphire plate. The pump, dump, and probe pulses were focused together into a thin-film like jet stream of the sample solution (200 μm thickness) after timing adjustments by mechanical stages. The absorption change was monitored by a photodiode array detector.

As shown in Figure 1, it is suggested that the photogenerated S_1 state of cis-stilbene initially undergoes a twisting deformation and forms the relaxed S_1 state that corresponds to a shallow local minimum of the S_1 potential. This relaxed S_1 state, which exhibits a strong $S_n \leftarrow S_1$ absorption at 640 nm, is a precursor of the isomerization and is converted to the S_0 state (trans and cis) in a picosecond through the funnel region. To investigate the wavepacket motion

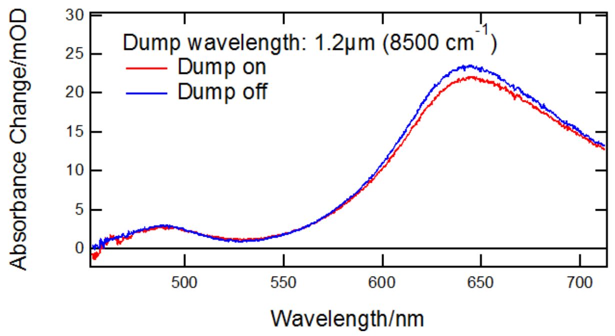

Fig. 2 The transient absorption spectrum of cis-stilbene with/without dump pulse (pump-probe delay time: 1 ps; pump-dump delay time: 0.5 ps).

that moves toward the funnel region, we introduced an infrared dump pulse at 0.5 ps after photoexcition and monitored the transient absorption by the probe at 1 ps. As shown in figure 2, the $S_n \leftarrow S_1$ transient absorption at 640 nm is decreased significantly by the dump pulse at 1.2 μm (8500 cm^{-1}). This result strongly indicates that the S_1 population is depleted by the dump pulse, implying that the S_1 population is resonantly driven back to the S_0 state by the stimulated emission dumping. We evaluated the following dump efficiency,

$$dump\ efficiency = 1 - \frac{\Delta Abs(dump-on)}{\Delta Abs(dump-off)} \quad , \tag{1}$$

and plotted it against the pump-dump delay. As shows in figure 3 (b), the dump efficiency shows almost instantaneous rise as short as 16 fs, which was evaluated by an analysis taking account of the instrumental response (FWHM=174 fs). The rise time of the dump efficiency corresponds to the time that the wavepacket needs to reach the potential region where the S_1-S_0 energy difference matches the 8500-cm^{-1} dump photon energy. To monitor the wavepacket motion at different PES regions, we carried out experiments with changing the dump photon energy, as shown in figure 3. It was found that the rise is almost identical in the range of 10-20 fs for the dump photon energy from 8500 cm^{-1} to 3374 cm^{-1}, while it is substantially longer (76 fs) for the 2570 cm^{-1} dump pulse (we note that the temporal response of the experiment does not change significantly with change of the dumping wavelengths).

The pump-dump-probe result clearly indicates the wavepacket motion toward the PES region, where the S_0 and S_1 potentials get as close to as 2570 cm^{-1}, and provides its quantitative characterization near the funnel region.

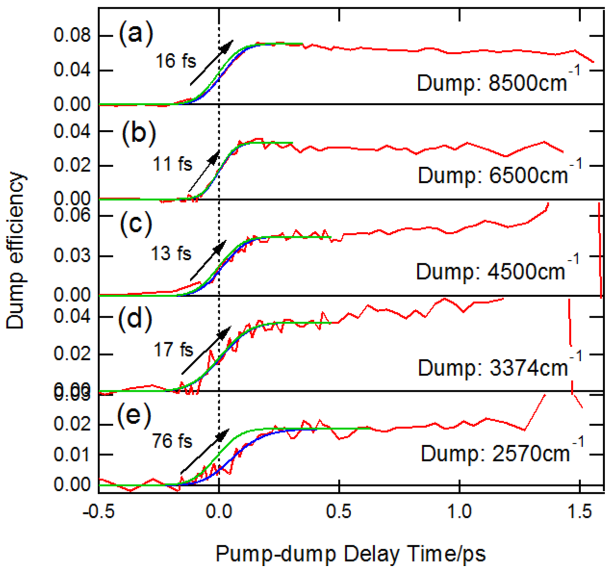

Fig. 3 Dump efficiencies as a function of pump-dump delay time for various dump photon energy.