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**Structural change during ultrafast photoisomerization of *cis*-stilbene monitored through nuclear wavepacket motion**



photo

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Stilbene is a prototypical molecule showing photoisomerization (Fig. 1). We recently carried out pump-probe measurements of *cis*-stilbene with 40-fs time-resolution and observed wavepacket motion (~220 cm-1) in the S1 state [1]. The dephasing time of the motion was much shorter than the isomerization time, implying that the ~220 cm-1motion is not directly correlated with the reaction coordinate.

To know more about the reactive potential energy surface (PES) of *cis*-stilbene, we carried out TR-ISRS experiments [2]. In this experiment, the S1 state is generated by the UV pump pulse, and the wavepacket motion is induced in the S1 state by the impulsive Raman process at a certain delay time (*T*). The resultant wavepacket motion is observed by the third pulse as the oscillation of the transient absorption intensity. We observed the ~220 cm-1 motion also in this experiment. Interestingly, Fourier analysis showed that the frequency of the wavepacket motion significantly changes with the delay time: 239 cm-1 (*T* =0.3 ps) → 224 cm-1 (1.2 ps) → 215 cm-1 (2 ps). The frequency of the wavepacket motion is determined by the curvature of the S1 PES along the corresponding coordinate. Therefore, the temporal frequency shift indicates that the relevant curvature of the S1 PES changes with time. We considered that it reflects a structural change occurring along another coordinate that is anharmonically coupled with the ~220 cm-1 mode.



**Fig. 1** Photoisomerization of *cis*-stilbene.

**References:**

[1] K. Wako, S. Niiza, and T. Riken, Chem. Phys. Lett. **398** (2004) 400.

[2] S. Niiza and T. Riken, Science **322** (2008) 1073