

# TRACKING STILBENE EXCITED STATE EVOLUTION WITH FEMTOSECOND STIMULATED RAMAN SPECTROSCOPY

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Stilbene (1,2-diphenylethylene) exists at room temperature in *cis* and *trans* isomeric forms. The molecule has attracted attention in the past as a photoswitch because UV excitation enables the interconversion of the isomers.

Here femtosecond transient Raman spectroscopy has been applied to track the path of the excited stilbene molecules to the ground state. As a key device an optical parametric amplifier for the generation of tunable narrowband pulses was developed. Starting from the output of a Ti:Sa oscillator, 10 cm<sup>-1</sup> pulses were achieved and applied in a three-beam experiment. The stimulated Raman spectra were acquired with a peak accuracy of 1 cm<sup>-1</sup> and a temporal resolution of 120 fs, limited by the 290 nm pump pulses. Resonance enhancement due to the *cis* and *trans* excited state absorption was utilized by tuning the Raman beam to 580 and 620 nm respectively.

The S<sub>1</sub> excited state Raman spectrum of *cis*-stilbene is dominated by a 228 cm<sup>-1</sup> low frequency mode. During the risetime of the signal a significant bandshape change occurs. In contrast to previous impulsive Raman measurements in time domain<sup>[1]</sup> however, neither in *n*-hexane nor in acetonitrile a proceeding frequency shift of the corresponding band was observed. The deviant position of *trans*-stilbene on the excited state potential manifests in a clearly structured transient Raman spectrum. In *n*-hexane, intramolecular vibrational redistribution leads within 500 fs to an intensity decay of the Raman excited state spectra accompanied by an up-shift of the high-frequency bands, most prominently observed in the C=C stretching band around 1540 cm<sup>-1</sup>. On the 10 ps timescale vibrational cooling induces further up-shifts. In acetonitrile, on the other hand, solvation causes a downshift of the 1540 cm<sup>-1</sup> band.

## References

[1]. S. Takeuchi *et al*, Science **2008**, 322, 1073.

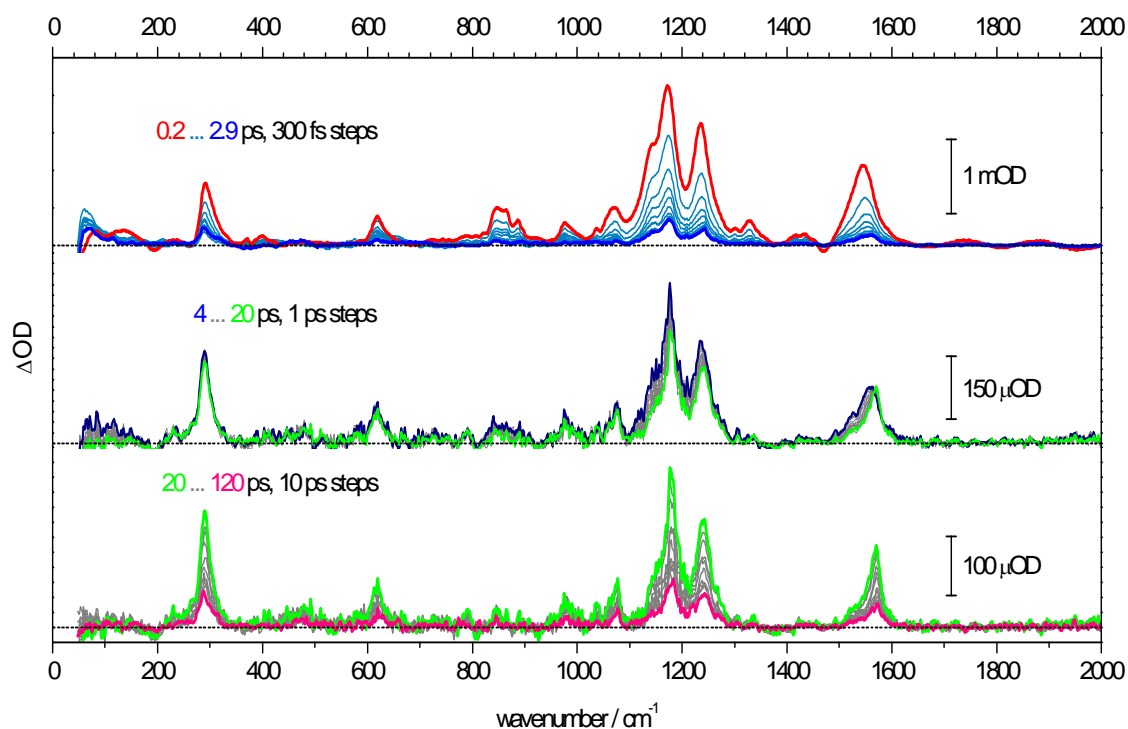


Figure 1: Time-resolved resonance Raman spectra of excited state *trans*-stilbene in *n*-hexane.