

## PS-TR<sup>3</sup> SPECTROSCOPY OF S<sub>1</sub> CIS-STILBENE IN SOLUTION

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Picosecond time-resolved resonance Raman (TR<sup>3</sup>) spectrum with ~1 ps lifetime has been observed when probing under intense transient S<sub>1</sub> *cis*-stilbene absorption band at 630 nm and photoexciting at 267 nm. The spectrum, ascribed to S<sub>1</sub> *cis*-stilbene, is notable for high intensity of low-frequency bands (243, 475 and 742 cm<sup>-1</sup>).

**Keywords:** *Cis*-stilbene; resonance Raman; time-resolved; picosecond; photoexcited

Stilbene plays an important role as a model system for isomerisation dynamics. Its two isomers, *trans* and *cis*, undergo fast isomerisation in solution following photoexcitation to the first excited electronic state. For S<sub>1</sub> *trans*-stilbene, the process is hindered by a barrier and occurs on ~100 ps timescale. In contrast, S<sub>1</sub> *cis*-stilbene isomerisation is near barrierless and occurs on ~1 ps timescale competing with vibrational relaxation process. Successful modelling of reaction dynamics require a detailed knowledge of the molecular structure of the S<sub>1</sub> state. Unlike *trans*-stilbene, there has been no TR<sup>3</sup> investigation of S<sub>1</sub> *cis*-stilbene. Our new concept OPA TR<sup>3</sup> system offering independently tunable and

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synchronised ( $\sim 1$  ps) pump and probe pulses has been used in this study. The apparatus is described in detail elsewhere in these proceedings. Pump and probe pulse energies at the sample were 0.4–2  $\mu$ J and beams with parallel polarisation were focused to approximately 100  $\mu$ m diameter spot size. *Cis*-stilbene (97% purity) was obtained from Aldrich and used without further purification. Solution was prepared at concentration  $1 \times 10^{-3}$  mol·dm $^{-3}$  in spectroscopic grade solvents. TR $^3$  signal was collected in 90° geometry. The apparatus detection range was  $> 200$  cm $^{-1}$ .

Picosecond time-resolved resonance Raman (TR $^3$ ) spectrum ascribed to S $_1$  *cis*-stilbene with  $\sim 1$  ps lifetime has been observed when probing under intense transient S $_1$  *cis*-stilbene absorption band at 630 nm and photoexciting at 267 nm (see Fig. 1). The spectrum is notable for high intensity of low-frequency vibrations at 243, 475 and 742 cm $^{-1}$ . A similar spectrum has been obtained at longer pump wavelengths (273 and 305 nm), longer probe wavelength (670 nm) and other solvents (cyclohexane and acetonitrile). The lifetime was shorter in acetonitrile and longer in cyclohexane relative to *n*-hexane which is consistent with previously published data on the lifetime of the S $_1$  state [1].

The high intensity of observed low-frequency bands is attributed to larger displacements. The position of the observed bands strongly suggests that the spectrum contains high overtones of 243 cm $^{-1}$ . This would be consistent with fast evolution of the wavefunction in the resonant S $_n$  state. Enhanced activity in low-frequency region of S $_0$  *cis*-stilbene relative to the S $_0$  *trans*-stilbene has been reported earlier by Myers and co-workers [2]. Hochstrasser and co-workers [3] have recently observed a similar a strong low frequency activity in S $_1$  *cis*-stilbene in solution using transient absorption spectroscopy. Though the observed wavepacket motion frequency (associated with phenyl torsion mode) was lower ( $\sim 100$ –125 cm $^{-1}$ ). The mode dephasing time was estimated to be  $\sim 100$  fs which is in agreement with Raman bandwidths observed in our study.

It is hoped that the TR $^3$  spectra of S $_1$  *cis*-stilbene will provide structural information to further our understanding of reaction dynamics [3, 4].

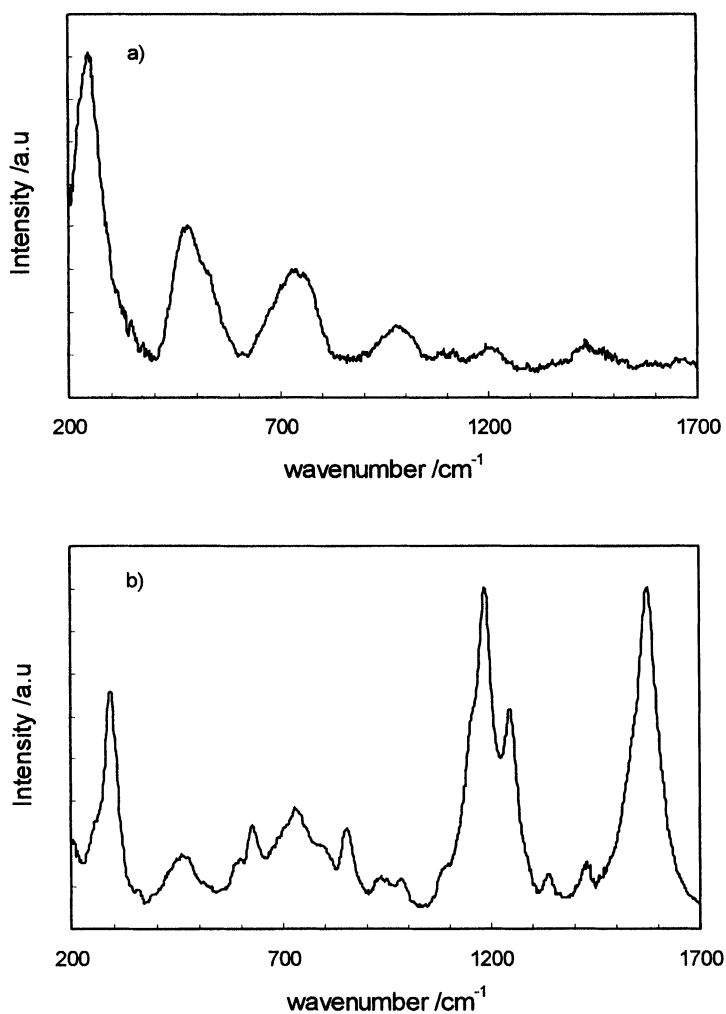


FIGURE 1 (a) ps-TR<sup>3</sup> spectrum of S<sub>1</sub> *cis*-stilbene in *n*-hexane (1 mM) obtained at time delay 0 ps and pump and probe wavelengths 267 and 630 nm, respectively; (b) ps-TR<sup>3</sup> spectrum of S<sub>1</sub> *trans*-stilbene in *n*-hexane obtained under the same conditions at time delay 20 ps is shown below for comparison. Solvent spectra and in the case of *cis*-stilbene weak *trans*-stilbene spectrum were subtracted.

### References

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