

New views through old holes: looking for the perpendicular “phantom” state of photoisomerizing stilbene

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In the photoisomerization path of stilbene, a perpendicular state P on the S_1 potential energy surface is expected just before internal conversion through a conical intersection S_1/S_0 . The situation is depicted schematically in Fig. 1. For decades the observation of P was thwarted by a short lifetime τ_P in combination with slow population flow over a barrier (A_1 or B_1 in the figure). But these limitations can be overcome by ethylenic substitution. Comparing stilbene and 1,2-dimethyl-stilbene with precision transient absorption spectroscopy in the range 250-800 nm, we determine the electronic properties of P.^[1,2]

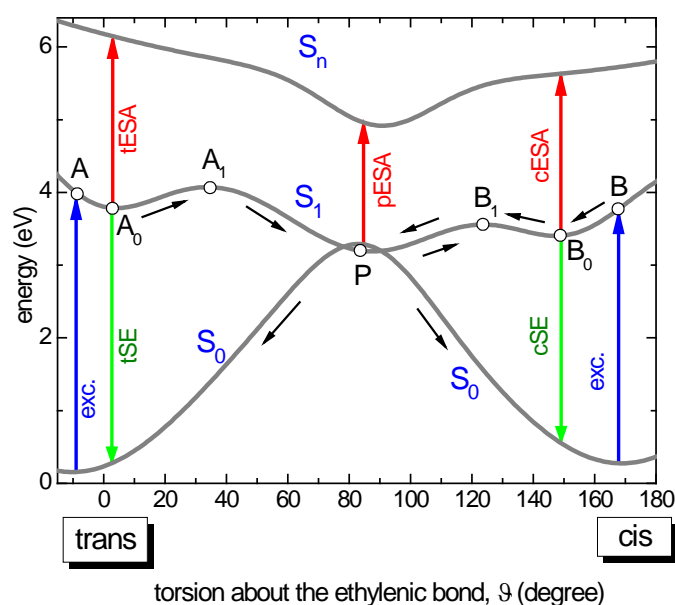


Figure 1. Stilbene PES in n-hexane. When starting from A (trans), a fraction of excited population has enough energy to overcome A_1 ($E_{A1} \approx 1250 \text{ cm}^{-1}$) and reach the cis conformation. The rearrangement takes 0.2-0.3 ps as seen from transient absorption spectra. The cis population relaxes back to P over barrier B_1 ($E_{B1} \approx 300 \text{ cm}^{-1}$) and then to the ground state. The major trans population equilibrates around A_0 and thermally decays to P with $\tau = 84 \text{ ps}$. When starting from B (cis) a part of population overcomes B_1 within 0.2-0.3 ps; the rest equilibrates around B_0 and decays to P by thermal activation with 0.9 ps, in agreement with experimentally observed biexponential behavior in solution.

By substitutions the excited *trans*, *cis*, and *perpendicular* forms can be stabilized on a >10 ps timescale. Their excited-state absorption bands (ESA in the figure) are used for resonance in fs stimulated Raman spectroscopy.^[3] We find:

- *trans* stilbene upon $S_0 \rightarrow S_1$ excitation is cooled by 45°K.^[4] This partly explains the “stilbene enigma”, *i.e.* a reduced isomerization rate compared to RRKM predictions.
- Raman spectra of different rotamers in the excited *trans* state can be obtained, for example, when an *ortho* hydrogen atom in each phenyl group is substituted by a fluorine atom.
- Excited *cis* stilbene does not show a low-frequency spectator mode (as had been reported) to the isomerization process.^[3,5]
- It is possible to observe Raman-active vibrations in the excited electronic *trans* or *cis* state directly from the electronic ground state.^[6]
- For the *perpendicular* state of 1,1'-dicyano-stilbene, the first few Raman lines are seen.^[7]

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