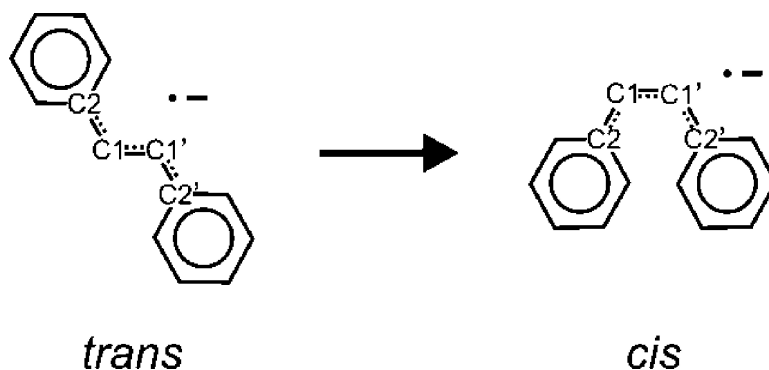


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Direct Observation of the Primary Bond-Twisting Dynamics of Stilbene Anion Radical

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The isomerization of neutral stilbene, a model system for conformational twisting in chemical and biological chromophores, has been studied extensively in the past, both experimentally^{1,2} and theoretically.³ The central bond (vibrational) twisting and barrier crossing occur on the femtosecond to picosecond time scale in the isolated molecule^{4–6} and in the condensed phase.⁷ In contrast, for the anions (and cations) of stilbene, the results are very scarce and only available from studies in solid matrices^{8,9} and in solution using pulsed radiolysis methods.^{10–12} This is because the ions are more difficult to study in the gas phase and, because of the very low density, the dynamics of twisting becomes even more challenging to probe.

In this communication, we report real-time femtosecond (fs) observation of the primary bond-twisting dynamics of *trans*- and *cis*-stilbene anion radicals made by electron attachment in a molecular beam and selected using mass spectrometry. Following the selection, a pulse of 110 fs intersected the anion beam to excite (400 nm) it into the D_2 state, and a second pulse was delayed to photodetach an electron whose kinetic energy was resolved and monitored as a function of time.¹³ Besides being the first study of the anion in the isolated collisionless phase, the results reported here provide the dynamics of the *cis*- (and *trans*-) configuration giving the time constant of ~ 650 fs for the primary step, with a coherent vibrational motion (~ 42 cm^{-1}) during the twisting along the multidimensional reaction coordinate. This is vastly different from the time constant of 10 ns reported in the solution phase study.¹²

Figure 1 depicts the energetics and the relevant experimental scheme. The steady-state and transient photoelectron spectra (PES) of both *trans*- and *cis*-stilbene anion radicals taken at 400 and 800 nm are shown in Figure 2. The vertical detachment energy (VDE) obtained from both of these spectra is ~ 0.6 eV. Using density functional theory (DFT), we calculated¹⁵ energies of 0.61 (*trans*) and 0.59 eV (*cis*), which are in good agreement with the experimental value. The most noticeable difference in the PES of the isomers is the structure observed for 400 and 800 nm excitation of the *trans*-isomer and the peak at ~ 1.5 eV.¹⁶ The importance of these differences is in ruling out the possibility of a major contamination caused by the thermal isomerization channel during the sample delivery and ionization processes.

Transient difference PES at -0.9 ps and zero time delay, relative to that at 8 ps, are shown in the bottom panels of Figure 2. Three energy windows centered at 1.2, 2.3, and 3.6 eV (3.9 eV for *cis*-isomer) have been investigated, and the corresponding transients are shown in Figure 3 for both *trans*- and *cis*-stilbene anions. For the *trans*-isomer, the peak at ~ 1.5 eV eKE changes in concert with the major peak at ~ 2.5 eV eKE, again consistent of being for the

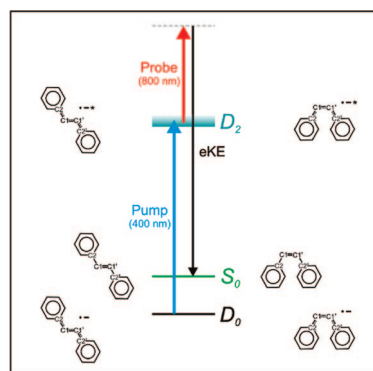


Figure 1. The energetics and probing scheme are illustrated. The pump pulse (blue arrow) at 400 nm promotes the population from D_0 to D_2 of the anion. The delayed probe-pulse (red arrow) at 800 nm then photodetaches the electron and yields the electron with kinetic energy shown as a black arrow. The neutral S_0 is displayed and located at 0.6 eV above D_0 as obtained here from both the experiments and DFT calculations.

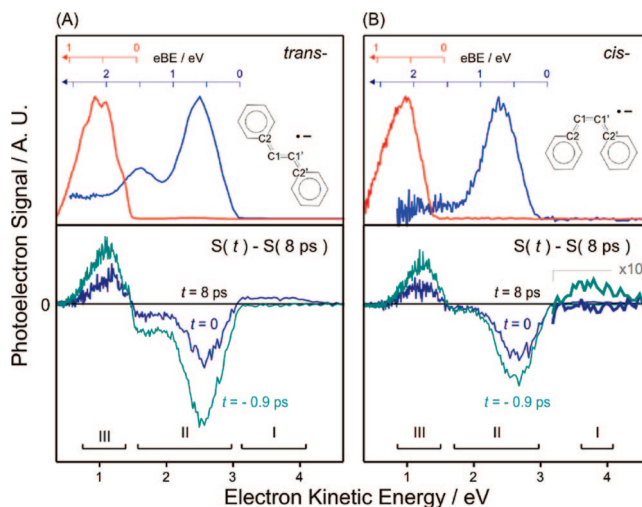


Figure 2. Transient and steady-state photoelectron spectra (PES) of the radical anions of *trans*- (A) and *cis*- (B) stilbene. Top panels: steady-state PES taken at 400 nm (blue) and 800 nm (red). Bottom panels: transient PES shown at two time delays. The difference was referenced to the spectra taken at 8 ps, when no further changes were observed (steady state). The brackets at the bottom denote the energy windows of interest, labeled as I, II, and III and centered at 3.6 (3.9 for *cis*), 2.3, and 1.2 eV, respectively.

same anion species. Despite the difference in steady-state PES, the measured transients in all three windows are similar in shape for both isomers.

The enhancement of PES in window I only appears at a time delay close to zero, and thus, the transients obtained in this window (left panel of Figure 3) represent the initially excited state (D_2)

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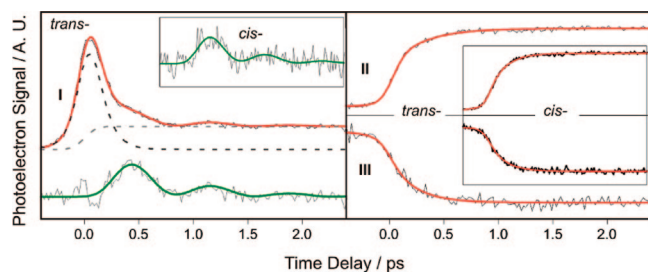


Figure 3. Transient PES for *trans*- and *cis*- (insets) stilbene radical anions. Panels show the transients obtained by integrating the PES at the energy windows **I**, **II**, and **III** indicated (see Figure 2). The red solid lines are the best fit to the experimental transients (black). The dashed lines give the different components contributing to the transients. The oscillatory behavior is shown in the residual signals (gray and green). Note that the plateau remains constant up to 80 ps; for window **I**, it is of the same origin as window **II** but for two-photon (400 nm) probing.

dynamics, as evidenced from the energetics and the temporal behavior. The energies of windows **II** and **III** overlap with those of the pump or probe PES at steady state (see Figure 2). In these two regions, the signal arises from the depopulation of the ground state by the pump or probe photons, which arrive prior to the detaching pulse (probe or pump, respectively). The fitted rise (decay) is on the time scale of the transient observed in window **I**, which is consistent with the dynamics of the initially excited D_2 state,¹⁷ as described below. Similarly, the behavior in window **III**.

The transients in window **I** clearly show an ultrafast decay and a coherent oscillatory behavior. The fs initial decay component reflects the initial wave packet motion away from the Franck–Condon (FC) region of D_2 , which leads at longer time to the actual twisting along the reaction coordinate. Given this initial decay, the damped oscillation was described by a molecular response function, $M(t)$, which takes into account the build up/decay of the population, together with the oscillatory behavior:

$$M(t) = \frac{k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) \cos(\omega t + \varphi) \quad (1)$$

where ω and φ are the frequency and phase of the oscillation, respectively. From the analysis, we obtained an initial wave packet motion on the time scale of $k_1^{-1} \sim 100$ fs, but with the oscillatory behavior being on a much longer time scale (see Figure 3): $T = 2\pi\omega^{-1} \sim 800$ fs (42 cm^{-1}) and $k_2^{-1} \sim 650$ fs.

Several points can now be made regarding the dynamics. First, both the *cis*- and *trans*-isomers of the anion exhibit similar behavior, and this is a very different situation from that of neutral *cis/trans* isomerization. For the neutral (S_1) *trans*, there exists a barrier of 3.4 kcal/mol, while for the *cis*, the potential is barrierless.^{4,5} For the anion (D_2), the twisting process originates on a potential surface of similar forces for both isomers, perhaps because of the antibonding character acquired with the additional electron. Second, the difference in time scales reported here with that of neutral *cis*-stilbene ($k_2^{-1} = 307$ fs, $T = 360$ fs)⁴ is also consistent with the force field being weaker. The 42 cm^{-1} could be the reaction coordinate, but we must consider other motions involving the phenyl rings.⁴ Third, and finally, these results are at variance with previous experimental data from pulse radiolysis–flash photolysis experiments in the condensed phase.¹² The study in the solution phase suggests that only *cis* is capable of twisting, and with a time constant of ~ 10 ns (5 ns for lifetime) for the same D_2 state. This would indicate 4 orders of magnitude change in rate due to solvent interactions, a situation that was not the case of neutral stilbenes.

This disparity suggests a major solvent (friction and polarity) retardation, either in the barrier^{18,19} or conical intersection³ region.

In conclusion, the contribution made here indicates the significance of studying these anion dynamics in the isolated molecule, revealing the actual time scales in primary dynamics involved and the coherent vibration motion involved. The observed behavior for twisting is vastly different from that reported in the solution phase.

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Supporting Information Available: Complete ref 15. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) The peak of the *trans*-isomer at ~ 1.5 eV eKE is 0.9 eV higher in electron binding energy (eBE) when compared to the major peak at 0.6 eV eKE. However, the energy gap of S_1-S_0 or T_1-S_0 is higher than 0.9 eV. Thus, it is not due to the photodetachment of the electronically excited neutral states (S_1 or T_1). However, it is possible that autodetachment through the hot D_1 or D_0 state will produce this peak whose position and intensity are determined by the Franck–Condon overlap between the hot anion (D_1 or D_0) and neutral (S_0) state.
- (17) The observed transient behavior in windows **II** and **III** represents both the fs response of the D_2 state, which should match the decay in window **I** (see text), and the prompt photodetachment (for window **II**), as expected.⁶ For the window **III**, since it is at the probe region, the transient should be dominated by the photodetachment. However, the additional decay can be understood given the fact that the energy difference between windows **I** and **III** (~ 2.4 eV) is consistent with the energy separation between the T_1 and S_0 state (2.2 and 2.4 eV for *trans*- and *cis*-stilbene, respectively) of the neutral molecules. Thus, the decay should be that of the D_2 population, but with different probing (probe photon detaches the anion to the neutral T_1 , instead of S_0 , and results in electron of lower eKE), as observed here.
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