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Electronic Effects on Photochemistry: The Diverse Reaction Dynamics of Highly Excited Stilbenes and Azobenzene

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ABSTRACT: Ultrafast time-resolved mass spectrometry and structural dynamics experiments on *trans*-stilbene, *cis*-stilbene, and azobenzene, with excitation to high-lying electronic states, reveal a rich diversity of photochemical reaction dynamics. All processes are found to be quite unlike the well-known photochemistry on lower electronic surfaces. While in *trans*-stilbene, excitation at 6 eV induces a phenyl twisting motion, in *cis*-stilbene it leads to an ultrafast ring-closing to form 4a,4b-dihydrophenanthrene. Azobenzene dissociates on an ultrafast time scale, rather than isomerizing as it does on a lower surface. The photochemical dynamics of the sample molecules proceed along steep potential energy surfaces and conical intersections. Because of that, the dynamics are much faster than vibrational relaxation, the randomizing effects from vibrational energy scrambling are avoided, and excitation-energy specific reaction dynamics results.

Stilbenes and azobenzenes frequently serve as prototypical models for studies of fundamental *trans*−*cis* isomerization and ring-forming reactions.[1−6] Spectroscopic and time-resolved dynamics studies, both experimental and theoretical, have revealed the nature of the reactions in their lowest excited electronic states.[6−19] As summarized in Scheme 1, these reactions include the *trans*-stilbene (TS) to *cis*-stilbene (CS) isomerization,[9,10,20−24] the CS to 4a,4b-dihydrophenanthrene (DHP) ring-closing reaction (known as the Mallory reaction),[5,25] as well as the dehydrogenation reactions of DHP to produce hydrophenanthrene (HPT) and phenanthrene (PT) upon photoexcitation[26,27−30] (oxygen is required for such a reaction to take place in solution[31]). Azobenzene (AZB), which is structurally very similar to stilbene, can also isomerize between a *trans*- and a *cis*- form.[1,12,17] However, azobenzene does not perform a ring-forming reaction unless it is in a protonated state.[32] In blocking one of the interesting reactions, the photochemistry of azobenzene is confined to be a pure *trans-cis* isomerization. This is especially important for applications involving molecular motors and machines, since the ring formation reduces the quantum yield of the *cis-trans* isomerization and thus limit the functionality of the motors.[33]

While the photochemistry of these molecules on their lowest excited states is thus well explored, our knowledge of their dynamics on highly excited molecular electronic states is quite limited. Since the reaction paths of the molecules on the lower potential energy surfaces are determined by the shapes of the surfaces, it stands to reason that placing the molecules onto different surfaces might dramatically alter the dynamics.[34−37] The present report documents such electronic excitation effects on the photochemistry of CS, TS, and AZB. This study also shows how subtle chemical changes, mediated by the structurally sensitive electronic energy surfaces, result in dramatic variations of the photochemistry.[1,38] Although the photochemistry is usually dependent on the medium, the results presented in this paper could provide important information to organic semiconductor researchers. Derivatives of stilbenes and azobenzenes are two of the commonly used building blocks of organic semiconductors and are used to construct photovoltaic cells, optical amplifiers, lasers, and other applications involving light and electricity.[39] Under prolonged optical illuminations, even a minor photochemical instability can have a sizable impact on the device lifetime. This report illuminates the nature of photochemical instabilities in these materials.

The experimental technique has been described in detail previously.[40,41] The structure-sensitivity of the method has been discussed.[42−44] For the time-resolved pump−probe experiments, a regeneratively amplified laser system (Positive Light, Spitfire) operating at 5 kHz with pulse durations of about 100 fs was used. The output beam of 828 nm was upconverted to the second (2ω, 414 nm, 3.0 eV) and fourth (4ω, 207 nm, 6.0 eV) harmonics with BBO crystals. Inside a vacuum chamber, the laser beams cross a molecular beam that is generated by seeding the molecules of interest in helium at 1.1 bar and expanding through a 100 μm nozzle and a 150 μm skimmer. The 4ω photons elevate the *cis*-stilbene, *trans*-stilbene, and azobenzene to the 7^1B state, the 3^1B_u state, and the 2^1A_u state, respectively. Using a time-delayed second harmonic (2ω, 414 nm, 3.0 eV) pulse, photoelectrons and photoions are produced through resonant multiphoton ionization, providing us with time-resolved photoelectron spectra (PES) and mass spectra (MS). *trans*-Stilbene (98%), *cis*-stilbene (97%), and azobenzene (97%+) were used as purchased from Alfa-Aesar without further purifications.

Our results reveal major differences in the dynamics of the investigated molecules on their highly excited surfaces compared to that on lower surfaces. Specifically, *cis*-stilbene decays very rapidly from the originally pumped 7^1B state down to its 3^1B state, on which it undergoes only the ring-forming reaction to DHP. Subsequently, dehydrogenation reactions of DHP to hydrophenanthrene (HPT) and phenanthrene take place on the ion surface of the molecule. In *trans*-stilbene, the 3^1B_u state is populated upon excitation. This molecule remains in the *trans*-form until it decays to lower states that are invisible to our technique. Finally, azobenzene, upon excitation to its 2^1A_u state, rapidly fragments by breaking the C−N bond.

The ionization pathway of *cis*-stilbene is revealed by the photoelectron spectrum, which shows a very broad transition

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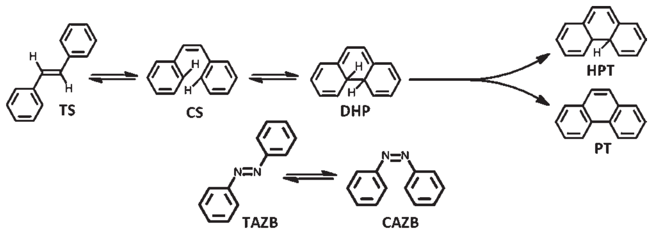
Scheme 1. Summary of Photochemical Reactions of Stilbenes and Azobenzenes in the Gas Phase[a]



[a] Shown in the top part are the reactions for TS, CS, and DHP. The bottom shows the photoisomerization reaction between *trans*-azobenzene (TAZB) and *cis*-azobenzene (CAZB).

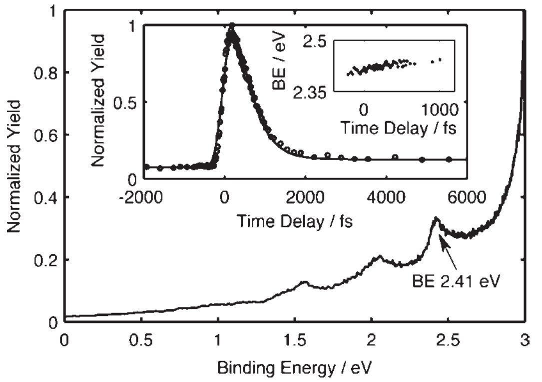


Figure 1. Photoelectron spectrum of *cis*-stilbene. Shown is the normalized two-color pump−probe signal for CS, summed over all delay time points. (Inset) Time-dependent signal of the BE = 2.41 eV peak. It features a 169 (±29) fs rise and a 407 (±41) fs decay, which represents the lifetime of its 7^1B state and its 3^1B state, respectively. Plotted in circles are the experimental data, while the solid line is a fit. (Small inset, top right) Time-dependence of the BE = 2.41 eV peak.

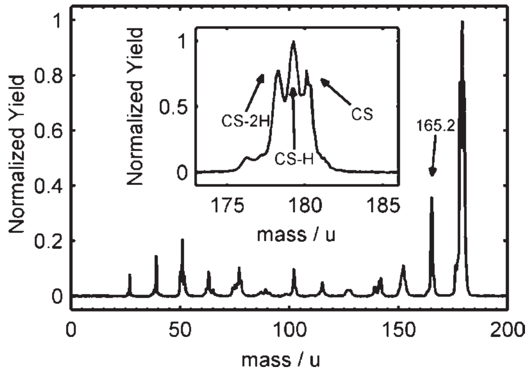


Figure 2. Mass spectrum of *cis*-stilbene, plotted as the normalized two-color ion yield for CS summed over all pump−probe delay time points. The CS parent mass is at 180.2, while the masses 179.2 and 178.2 correspond to CS losing one or two hydrogen atoms, respectively. They have intensities comparable to that of the *cis*-stilbene parent.

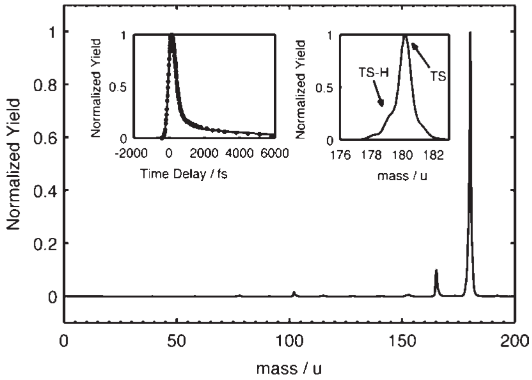


Figure 3. The mass spectrum of *trans*-stilbene, plotted as the normalized ion yield with the pump−probe two-color signals summed over delay times. The TS parent mass peak (MW = 180.2) is dominant. (Upper right inset) Details of the mass 180 region. (Upper left inset) Plots of time dependence of the parent peak of TS, where the black circles are the experimental data, and the solid line is a fit with a fast decay of 265 (±23) fs, representing the lifetime of the 3^1B_u state. There also is a slow decay component with a lifetime of 5 ps.

with binding energies (BE) from 1.5 to 3.0 eV (Figure 1). This reflects the initial excitation to the 7^1B state, which, according to previous calculations,[45] corresponds to a core excited state. Due to the instability of such core excitations, the 7^1B state decays rapidly, with a lifetime of 169 fs, to the 3^1B state, which in turn has a lifetime of 407 fs. The ring-closing process of CS to DHP was captured by resonant two-photon ionization out of the 3^1B state using the $3p_z$ Rydberg state (BE = 2.41 eV) as a reporter of the structure. Being structurally sensitive,[42−44] the Rydberg state binding energy maps the reaction dynamics with a time-dependent BE shift as shown in the top right inset of Figure 1. However, we did not find any evidence in the PES for the dehydrogenation reactions to HPT or PT on the 3^1B state. Yet, as shown in Figure 2, the MS data shows very intense peaks at mass units of 179.2 and 178.2, indicating the generation of HPT and PT. Loss of a methyl group can also be seen in the MS data (mass 165.2), following mechanisms similar to those discussed previously.[46,47] We conclude that the dehydrogenation reactions take place on the ion surface. The MS reveals important pathway dynamics in this reaction, as has been shown in previous studies of stilbenes and related aromatic compounds.[46−48]

In *trans*-stilbene, the molecules are first pumped to the 3^1B_u state and then ionized with one probe photon. Although possessing a carbon skeleton very similar to that of CS, TS displays very different MS even though the ionization scheme uses photons of the same energies. First, as presented in Figures 2 and 3, fragmentation in TS has a much lower yield compared to CS. This difference can be explained by the total number of photons absorbed by the molecule as it gets ionized. For CS, ionization requires two probe photons after cyclization, whereas in TS one probe photon suffices. While the ionization potentials for TS and CS are almost identical (7.76 eV versus 7.80 eV),[49,50] the rapid relaxation of the core excitation in CS redistributes electronic energy very rapidly, so that an additional 3 eV photon is required for ionization. Beyond that, the most significant difference between the MS of TS and CS is that the yield of dehydrogenation from TS is far smaller than that in CS, as shown in the insets in Figures 2 and 3. This suggests that TS maintains its overall geometry on the 3^1B_u surface until it decays to a lower state (with a lifetime of 265 fs). Only a very small portion undergoes isomerization to CS, which, as explained earlier, would quickly react to DHP and dehydrogenate upon ionization, as well as producing a little demethylated product. This result is further supported by the PES of TS, which revealed that two types of vibrations are excited in the pump−probe process: a coherent

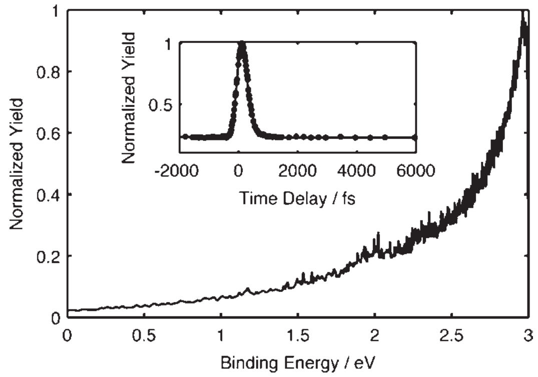


Figure 4. Photoelectron spectrum of azobenzene, with the pump−probe two-color signals summed over all delay time points. (Inset) Time dependence of the photoelectron intensity summed over all binding energies. Plotted in circles are the experimental data, and the solid line is the fit. The lifetime for the 2^1A_u state is close to the instrument function; the fit shown gives a decay time of 170 (±10) fs.

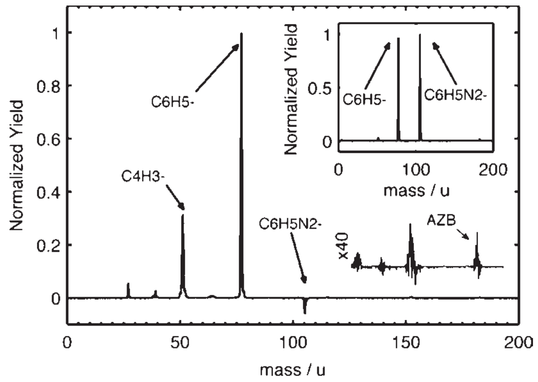


Figure 5. Mass spectrum of azobenzene. Shown is the normalized ion yield for AZB with the pump−probe, two-color signals summed over all delay time points, and with the one-color signals subtracted. The parent ion (182.2) has only 0.2% of the intensity of the dominant peak at 77.1 ($-C_6H_5$). (Inset) Mass spectrum acquired with the pump beam alone, showing a 1:1 ratio for 105.1 ($-N_2C_6H_5$) and 77.1 ($-C_6H_5$). The $C_6H_5N_2-$ peak in the two-color spectrum is negative because the $C_6H_5N_2-$ ions generated by the pump beam alone are fragmented by absorption of a probe photon, leading to a depleted signal.

wave packet motion of the phenyl rotations on the S_5 (3^1B_u) state and the C═C stretching vibrational progression on the D_0 (1^2A_u) state.[51] No indication for an isomerization or dehydrogenation reaction was seen in the PES.

The PES and MS show that highly excited azobenzene behaves very differently, not only from its lower excited species, but also from TS and CS. The PES of AZB, Figure 4, representing ionization out of the initially populated 2^1A_u state, shows no major peak but instead a very broad feature with a rapid decay of 170 fs. As had been observed in other molecules, such as NO_2[52,53] or amyl nitrite,[54] the broad and unstructured photoelectron spectrum suggests that a direct molecular bond dissociation event takes place immediately after photoexcitation of the molecule. This conclusion is further supported by AZB's mass spectrum, Figure 5, in which the parent ion for AZB (182.2) is almost completely missing. A careful examination of the resonant two-photon ionization by the pump beam alone, which has a much lower intensity than the probe beam, uncovers the originally generated ion. As shown in the inset of Figure 5, the nearly exact 1:1 ratio for 105.1 ($-N_2C_6H_5$) and 77.1 ($-C_6H_5$) peaks unambiguously reveals the fracture of the C−N bond linkage between the phenyl group and the azo group. The breakage of the C−N bond in the 2^1A_u state is consistent with the calculation of Conti et al.,[55] whose work showed that the electronic configuration for this excitation is partially due to a $n_+ \rightarrow \pi_2^*$ transition, creating well-defined nodes between the C−N bonds linking phenyl groups and the azo group. These nodes significantly weaken the bond upon excitation to the 2^1A_u state, making them prone to rupture.

The comparative study of the molecular dynamics of highly excited *cis*-stilbene, *trans*-stilbene, and azobenzene shows very different dynamics compared to their lower excited states. On its 1^1B state, *cis*-stilbene reacts in a parallel reaction mechanism to form both *trans*-stilbene and DHP. We find that from the 7^1B state, *cis*-stilbene quickly decays to 3^1B, from where it cyclizes to form DHP. After the ionization it reacts further to generate hydrophenanthrene and phenanthrene. No dehydrogenation reactions were observed on the highly electronically excited states.

trans-Stilbene is well-known for its isomerization to the *cis*-isomer via the conical intersection on the 1^1B_u state. However, we find that in its 3^1B_u state, it retains its structure while performing only vibrational movements. As for azobenzene, although a similar *trans*−*cis* isomerization reaction occurs in the 1^1B state, the molecule breaks apart at the C−N bond as soon as it is lifted to the 2^1A_u state and before any isomerization reaction can occur. Therefore, *trans*-stilbene proves to be most photostable under UV excitations, whereas the *cis*-stilbene is more prone to photochemical reactions. When replacing the photochemical active carbon by nitrogen atoms, the adjacent C−N bonds become extremely unstable.

Responsible for the excitation-specific photochemistry is the electronic nature of the initially prepared states. In the selected systems, where the photochemistry is governed by the rapid motion of wave packets down steeply sloping potential surfaces and through conical intersections, the exact topography of the surface at the excitation energy matters. In *cis*-stilbene, it is the core excitation that ushers in very rapid dynamics. In azobenzene the excitation to a repulsive surface with a shape that is distinctly different from that of lower electronic states seems to be responsible. These rapid dynamics into different directions compete effectively against the well-known dynamics on the lower electronic states.

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