Photocyclization of trans-stilbene induced by an ultrafast laser pulse

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Abstract

We predict that photocyclization of trans-stilbene to 4a,4b-dihydrophenanthrene (DHP) can be achieved with a femtosecond-scale laser pulse. Specifically, we have performed dynamical simulations in which the original trans-stilbene molecule is observed first to isomerize to cis-stilbene (as an excited-state intermediate) after more than one picosecond, and then to form a new bond to become DHP, after a few hundred additional femtoseconds. The process is initiated by excitation from the S₀ electronic state to S₁, with subsequent de-excitation at avoided crossings.

1. Introduction

During the past two decades there has been considerable interest in photoinduced ring-opening and ring-closing of molecules [1–5], largely because of potential applications in, e.g., molecular electronics. As a model for understanding the behavior of more complicated systems, stilbene has been the subject of numerous experimental [6–16] and theoretical [17–24] investigations of photoisomerization and other photoinduced processes.

Photoexcited cis-stilbene has three decay routes: (1) cis-to-trans isomerization, (2) cis-to-cis, and (3) cis to the closed-ring structure 4a,4b-dihydrophenanthrene (DHP). Experiments show that, at room temperature, 35% of excited cis-stilbene isomerizes to trans-stilbene, 55% returns to the original reactant, and only 10% changes to DHP [25]. cis-to-trans isomerization of stilbene has been well studied by our group [26] and others [6,7,18]. The other two reactions have also attracted some attention [25,27–33]. Photocyclization of trans-1-(1’-naphthyl)-2-(3-hydroxyphenyl)-ethene (another stilbene analog) has also been reported by Bortolus et al. [36].

In addition, after irradiation of cis-stilbene, Saltiel et al. [37] observed fluorescent emission from the singlet excited state of trans-stilbene, which may be evidence of adiabatic cis-to-trans isomerization in the excited state. The following question therefore arises: does an excited-state reaction pathway from trans-stilbene to DHP exist, with reasonably high probability so that it should be experimentally observable? I.e., besides the trans-to-trans and trans-to-cis decay routes for excited trans-stilbene, is there a reaction pathway from trans-stilbene to DHP which passes through the excited state of cis-stilbene?

Here we describe the results of realistic simulations which clearly exhibit photoinduced ring-closing, from trans-stilbene to DHP, in which excited cis-stilbene is indeed just a short-lived intermediate state of the molecule.

Our method, semiclassical electron-radiation-ion dynamics (SERID), has been described in detail elsewhere [38–40], and has been used to successfully study a variety of ultrafast phenomena in various chemical systems. The dynamics of the valence electrons is treated via solution of the time-dependent Schrödinger equation in a nonorthogonal basis, with a time step of 50 attoseconds. The Hamiltonian matrix, overlap matrix, and effective ion–ion repulsive potential are derived from the density-functional-based approach of Frauenheim and co-workers [41,42]. The nuclear motion is obtained from Ehrenfest’s theorem [43], and the vector...
potential \( A(t) \) of the radiation field is coupled to the electrons through the time-dependent Peierls substitution [44,45].

2. Results

Before subjecting the stilbene molecule to a femtosecond-scale laser pulse, we first used our (SERID) method to obtain the optimized geometrical parameters of \( \text{trans-stilbene} \), \( \text{cis-stilbene} \), and DHP, and the results are given in Table 1. For comparison, the corresponding values calculated with \( \text{GAUSSIAN 03} \) [46], with B3LYP/6-31G(d,p), are also given in this table. One can see that the results obtained with our method are in quite good agreement with those obtained in the full density-functional calculations.

Let us now turn to the results of simulations in which the molecule responds to an ultrafast laser pulse. The full simulation time, 8500 fs, consists of two parts: first, in order to obtain the ground-state equilibrium geometry (of \( \text{trans-stilbene} \)), a 1500 fs simulation at room temperature was performed before applying the laser pulse. The final optimized geometry is shown in Fig. 1a. The optimized geometries of \( \text{cis-stilbene} \) and DHP, obtained in the same way but in separate simulations, are shown in Fig. 1b and c. These three geometries are all in good agreement with the results of other calculations [47].

A laser pulse was then applied to the molecule in the trans geometry and in the electronic ground state, but with vibrations corresponding to room temperature. The duration of the pulse was 150 fs full-width-at-half-maximum (FWHM), so that the entire duration spans the time interval from 0 fs to 300 fs in the figures, with an effective photon energy of 3.1 eV and a fluence of 0.21 kJ/m². This photon energy matches the density-functional energy gap between the HOMO and LUMO levels of \( \text{trans-stilbene} \) (so that HOMO to LUMO is a one-photon transition). The fluence was chosen such that the forces on the nuclei are large enough to produce a change of geometry, but not a dissociative reaction. The pulse shape was the same as in Ref. [38]:

\[
A(t) = A_0 \sin \left( \frac{\pi t}{t_0} \right) \sin(\omega t), \quad 0 \leq t \leq t_0.
\]

The resulting geometrical changes are represented by Figs. 2 and 3, with the variations with time of the three torsional angles, \( \text{C}_6-\text{C}_7-\text{C}_8-\text{C}_9 \), \( \text{C}_5-\text{C}_6-\text{C}_7-\text{C}_8 \) and \( \text{C}_7-\text{C}_8-\text{C}_9-\text{C}_{10} \) shown in Fig. 2. The behavior of the \( \text{C}_1-\text{C}_{14} \) distance is shown in Fig. 3a. The \( \text{C}_1-\text{C}_{14} \) distance decreases from 5.4 to 1.5 Å. The \( \text{C}_5-\text{C}_6-\text{C}_7-\text{C}_8 \) and \( \text{C}_7-\text{C}_8-\text{C}_9-\text{C}_{10} \) dihedral angles never fully achieve their optimized values for \( \text{cis-stilbene} \) in the electronic ground state (210.6°) because the intermediate \( \text{cis-stilbene} \) remains in an excited state.

The time dependence of the electronic energy levels (i.e., eigenvalues of the instantaneous electronic Hamiltonian) are shown in Fig. 4a for those levels nearest the initial energy gap – i.e., HOMO–2 to LUMO+2, where ‘HOMO’ means ‘highest occupied molecular orbital’ and ‘LUMO’ means ‘lowest unoccupied molecular orbital’, with ‘HOMO–1’ designating the level immediately below the HOMO. The electron populations in the HOMO and LUMO levels are presented in Fig. 4b. The populations in other states are not shown here, since they were found to be unimportant in the present context. As can be seen in Fig. 4a, for \( \text{trans-stilbene} \) the HOMO–1 and HOMO–2 states are degenerate, as are the LUMO+1 and LUMO+2 states. But for \( \text{cis-stilbene} \) and DHP the degeneracy is removed, with a quite pronounced separation after the isomerization approaches completion, near 1000 fs.

During the course of the simulation, there are several avoided crossings between HOMO and LUMO. Specifically, in the interval 750–1025 fs one can observe four non-adiabatic couplings between the HOMO and LUMO, and the corresponding electronic transitions between these two levels, although weak, are visible.

### Table 1

<table>
<thead>
<tr>
<th>Geometrical Parameters</th>
<th>trans-Stilbene</th>
<th>cis-Stilbene</th>
<th>DHP</th>
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</thead>
<tbody>
<tr>
<td>( \text{C}_1-\text{C}_6 )</td>
<td>1.41 (1.41)</td>
<td>1.41 (1.41)</td>
<td>1.51 (1.53)</td>
</tr>
<tr>
<td>( \text{C}_6-\text{C}_7 )</td>
<td>1.46 (1.47)</td>
<td>1.47 (1.48)</td>
<td>1.37 (1.37)</td>
</tr>
<tr>
<td>( \text{C}_7-\text{C}_8 )</td>
<td>1.36 (1.35)</td>
<td>1.35 (1.35)</td>
<td>1.44 (1.43)</td>
</tr>
<tr>
<td>( \text{C}<em>1-\text{C}</em>{14} )</td>
<td>5.37 (5.46)</td>
<td>3.01 (3.25)</td>
<td>1.53 (1.54)</td>
</tr>
<tr>
<td>( \text{C}_6-\text{C}_7-\text{C}_8-\text{C}_9 )</td>
<td>180 (180)</td>
<td>8.2 (7.0)</td>
<td>8.1 (8.5)</td>
</tr>
<tr>
<td>( \text{C}_5-\text{C}_6-\text{C}_7-\text{C}_8 )</td>
<td>181.3 (180.3)</td>
<td>210.6 (209.8)</td>
<td>181.3 (180.3)</td>
</tr>
<tr>
<td>( \text{C}_7-\text{C}_8-\text{C}<em>9-\text{C}</em>{10} )</td>
<td>181.3 (180.3)</td>
<td>210.6 (209.8)</td>
<td>181.3 (180.3)</td>
</tr>
</tbody>
</table>

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Fig. 1. Equilibrium geometries of (a) \( \text{trans-stilbene} \), (b) \( \text{cis-stilbene} \), and (c) 4a,4b-dihydrophenanthrene (DHP). The black atoms are carbons, and white atoms hydrogens, with all atoms labeled.
in Fig. 4b. Also, as can be observed in Fig. 2, the C₆–C₇–C₈–C₉ dihedral angle passes through 90° during this time interval. I.e., the stilbene molecule passes through a minimum of the excited-state potential energy surface, called the phantom state, as is consistent with previous studies [7,14]. One can see in Fig. 4b that there is a small decrease in the electron occupation of the LUMO after these four avoided crossings, from 1.24 to 1.10, but the molecule is still in an excited state. Two more avoided crossings occur between

Fig. 2. Variation with time of the three torsional angles C₆–C₇–C₈–C₉, C₅–C₆–C₇–C₈, and C₇–C₈–C₉–C₁₀. A line at 8.1° (the value of the C₆–C₇–C₈–C₉ dihedral angle in the optimized 4a,4b-dihydrophenanthrene geometry) is also plotted.

Fig. 3. (a) Variation with time of C₁−C₁₄ distance. (b) Variation of C₁−C₆ and C₆−C₇ bondlengths. (c) Variation of C₇−C₈ bondlength.
1500 and 1600 fs, with a further transfer of 0.1 electron from LUMO to HOMO. Variations in bond length with time, for the C1–C6; C6–C7, and C7–C8 bonds, are shown in Fig. 3b and c. From 0 to 120 fs, the vinyl (C7–C8) bond length increases from 1.36 Å to an average value of 1.47 Å, while the vinyl–phenyl (C6–C7) bond length decreases from 1.48 to 1.42 Å on average, retaining this value until the end of the simulation. After 1000 fs, the vinyl bond length decreases to 1.45 Å, and continues to decrease to an average value of 1.43 Å as the DHP molecule forms. The excitation of \( p \) electrons from HOMO to LUMO thus weakens the vinyl bond and strengthens the vinyl–phenyl bond. This behavior is similar to that in our previous calculations for other molecules [26,48,49]. The C1–C6 bond length is also enlarged, from 1.42 to 1.45 Å (on average), during the first 120 fs of the laser pulse, and then to 1.52 Å when the DHP molecule forms.

A simplistic scheme for the trans-stilbene to DHP reaction pathway is shown in Fig. 5. In this diagram, the ground-state (\( S_0 \)) and first-excited-state (\( S_1 \)) potential energy surfaces are presented qualitatively. The traditional model suggests that, after excitation of trans-stilbene to its singlet excited state (trans-stilbene\(^*\)), the molecule can twist around the central \( C-C \) bond into the excited singlet state with a perpendicular geometry. Subsequently, internal conversion to the ground state in this (perpendicular) geometry can be followed by rotational relaxation to either the cis or trans ground state. Our earlier dynamical simulations [38] indicate that trans-to-trans and trans-to-cis are indeed the main de-excitation processes for excited trans-stilbene.

In the present Letter, on the other hand, we have found another decay route for photoexcited trans-stilbene: trans\(^*\)-to-cis\(^*\)-to-DHP. This process should be experimentally observable, although it may have only a small quantum yield.

In the results presented here, the molecule stays in the vicinity of a local minimum in the \( S_1 \) potential energy surface for about 275 fs, before passing over the second energy barrier (labeled II
in the figure). Specifically, in Fig. 2, the C6–C7–C8–C9 dihedral angle remains around 90° from 750 to 1025 fs, with four avoided crossings between HOMO and LUMO during this time interval, as can be seen in Fig. 4a.

We conclude this section by emphasizing several points about the present dynamical simulations: (i) they are complementary to static calculations of potential energy surfaces, which are more quantitative, but which are limited to a small number of nuclear degrees of freedom, and which do not directly treat the dynamics of electronic states and nuclear motion. (ii) The present simulations predict various products, with various quantum amplitudes, or branching ratios, just as is the case in nature. Furthermore, the outcome depends on the initial atomic configuration (in a room-temperature simulation). The implications of these two sources of uncertainty in the outcomes for cis-stilbene are mentioned in the second paragraph of Section 1. For the present initial system, trans-stilbene, Fig. 5 demonstrates that there are three possible outcomes, all of which are realized in both our simulations and nature: a return to trans-stilbene, with no isomerization or change in bonding; simple isomerization to cis-stilbene; and isomerization to cis-stilbene as only an intermediate state, followed by ring-closing to form DHP. (iii) However, the relative probabilities certainly depend on the laser pulse parameters, and it is therefore natural that simple isomerization to form cis-stilbene was observed in Ref. [38], whereas in the present results the molecule proceeds past cis-stilbene in Fig. 5 to form DHP, since the higher fluence (0.210 J/m² in the present 300 K simulation, as compared to 0.176 J/m² in the 300 K simulation of Ref. [38]) was sufficient to surmount the barrier labeled II in Fig. 5.

It may be worthwhile to emphasize one point: at room temperature, the molecular vibrations break the symmetry of the ground-state trans geometry, permitting electronic transitions that are forbidden at 0 K. One therefore expects both photoisomerization and photocyclization to occur more readily at the higher temperature, and this is exactly what happens in the present simulations.

3. Conclusions

Dynamical simulations were performed in which a trans-stilbene molecule is subjected to a femtosecond-scale laser pulse. trans-to-cis isomerization is achieved after a picosecond, but is followed within the next few hundred femtoseconds by a photocyclization reaction to form 4a,4b-dihydrophenanthrene. We thus predict that photocyclization of trans-stilbene, through an excited cis intermediate state, should be experimentally observable.

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References
