Detailed dynamics of a complex photochemical reaction: Cis–trans photoisomerization of stilbene

Yusheng Dou and Roland E. Allen

Physics Department, Texas A & M University, College Station, Texas 77843

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Detailed simulations are reported for the dynamics of electrons and nuclei during the cis to trans photoisomerization of stilbene. Our method, which employs a semiclassical description of both the nuclear motion and the radiation field, is described in the text. After excitation of electrons from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) by a femtosecond-scale laser pulse, two principal avoided crossings are observed between the HOMO and LUMO levels, each of which leads to substantial depopulation of the LUMO. Based on our results and those of other groups, we propose that the first such HOMO–LUMO coupling can lead to the formation of 4a,4b-dihydrophenanthrene (DHP). The second coupling, on the other hand, leads to the formation of trans-stilbene. It is found that pyramidalization of the two carbon atoms of the vinyl group is involved significantly in both couplings, and that rotation of the two phenyl rings, together with their interaction, plays an important role in the first coupling. The occurrence along the same trajectory of two couplings, one leading to DHP and the other leading to isomerization, is a significant observation, and one which indicates that further theoretical and experimental investigations would be of considerable interest. © 2003 American Institute of Physics. [DOI: 10.1063/1.1621621]

I. INTRODUCTION

Since stilbene is a prototype molecule for investigating substantial photoisomerization, it has been the subject of a substantial number of experimental and theoretical studies.1–5 Stilbene is a model for understanding the behavior of more complicated systems, such as retinal,6 the chromophore of rhodopsin, and for understanding the effects of different environments on photoisomerization.7–10 Isomerization of stilbene can start from either the cis or the trans geometry. After electronic excitation, the molecule undergoes rotation about its ethylene bond. When rotated through about 90° from either the cis or trans conformation, stilbene arrives at a minimum of potential energy, called the phantom state, from which it decays to the ground state through nonadiabatic transitions. After reaching the ground state, the molecule can follow a trajectory which leads on to the formation of a product, or alternatively a trajectory which leads back to the reactant. Experiment indicates an energy barrier of ~0.15 eV in the isolated molecule for the trans-to-cis reaction.11,12 But a barrier of no more than 0.05 eV for cis-to-trans.13,14 Consequently, photoisomerization proceeds much faster from the cis than from the trans conformation, in roughly 0.3–0.5 ps versus 10–20 ps.15–17 This makes cis-stilbene a logical starting point for studying the excited-state dynamics involved in photoisomerization.

When the cis isomer is excited, the reaction may also end with a new product, 4a,4b-dihydrophenanthrene (DHP). Based on their experimental observations, Petek et al. have proposed that the initial motion of the wave packet on the potential energy surface for the first electronically excited state is along the reaction path for the formation of DHP, rather than cis–trans isomerization.18 However, there is only very limited information about the excited state dynamics along the path leading to the formation of DHP.

Experimental evidence1,18,19 shows that the cis–trans photoisomerization process is actually more complicated than the one outlined earlier, partially because of the steric interaction between two phenyl rings. This interaction results from the nonplanar arrangement of these rings in the molecule. Based on their potential energy surface study of electronically excited and ground states, using the molecular mechanics valence bond (MMVB) method, Robb and co-workers predicted that the interaction between the two phenyl rings may lead to a photocyclization path to DHP with almost no energy barrier.20 This prediction may form the basis of a new mechanism for nonadiabatic transitions involving cis-stilbene. More detailed investigation of this idea requires reliable dynamical simulations.

Based on ab initio molecular dynamics studies of the photoisomerization of ethylene,21 the groups of Martinez22 and Roos23 have proposed that, in addition to rotations about the vinyl bond and vinyl–phenyl bond, pyramidalization of the CHphenyl group also plays an important role in this process. It is clearly of interest to investigate this mechanism by means of reliable dynamical simulations.

Various models and approximate approaches have, of course, already been employed in dynamical simulations of the photoisomerization of cis-stilbene,7,21,24–28 Examples include the quasiclassical molecular dynamics approach of Frederick and co-workers24–26 and the ab initio potential energy surface approach of van Gunsteren and co-workers.7,27,28 The former used the potential energy sur-
faces for both the electronic ground and the first excited states based on experimental measurements, whereas the latter used an ab initio quantum approach. These studies have made significant progress in understanding the mechanisms involved in photoisomerization of stilbene, and the effects of environments. However, both approaches have some rather severe limitations. When pre-established potential energy surfaces are employed, molecular dynamics simulations have limited predictive ability. The calculations of van Gunsteren and co-workers do not take nonadiabatic quantum effects into consideration. Moreover, their potential energy surfaces are determined in a space with only a limited set of nuclear coordinates. The interaction of the two phenyl rings and pyramidalization of the CH phenyl group are therefore outside the scope of these previous studies.

In this paper, we report a realistic dynamical simulation of the cis–trans photoisomerization of stilbene using a relatively new method.29–32 All the nuclear coordinates are included in the calculation, the forces are computed at every time step, and nonadiabatic electronic transitions are treated quantum mechanically. As will be seen in the following, the technique is capable of revealing a detailed dynamical picture for the entire process, including electronic excitation, nonadiabatic deexcitation, response of the molecular geometry to changes in the population of different molecular orbitals, intramolecular vibrational energy redistribution, and the intricate interplay between the various electronic and vibrational degrees of the freedom.

Our method is briefly described in Sec. II. Results are presented in Sec. III, and a summary is given in Sec. IV.

II. METHODOLOGY

The technique used in this study is called semiclassical electron-radiation-ion dynamics, in order to emphasize both its strengths and its limitations. The valence electrons are treated quantum-mechanically, but both the radiation field and the motion of the ion cores are treated classically. A semiclassical treatment effectively includes n-photon and n-phonon transitions in absorption and stimulated emission, and this allows us to study some nontrivial processes, such as multiple electronic and vibrational excitations, intramolecular vibrational energy redistribution, and interdependence of the various electronic and vibrational degrees of freedom.

The forces on the atomic nuclei (or ion cores) are calculated at every time step, using the electronic wave functions with multiple electronic excitations. The wave functions are updated at each time step by solving the time-dependent Schrödinger equation in a nonorthogonal basis:

\begin{equation}
\frac{i\hbar}{\partial t}\Psi_j = S^{-1} \cdot H \cdot \Psi_j,
\end{equation}

where \( S \) is the overlap matrix for the atomic orbitals. The interaction of the laser pulse with the molecule is introduced by coupling a time-dependent vector potential to the electronic Hamiltonian via the Peierls substitution:

\begin{equation}
H_{ab}(\mathbf{X} - \mathbf{X}') = H_{ab}(\mathbf{X} - \mathbf{X}') \exp \left( \frac{i q}{\hbar c} \mathbf{A}(t) \cdot (\mathbf{X} - \mathbf{X}') \right),
\end{equation}

where \( \mathbf{X} \) and \( \mathbf{X}' \) are nuclear coordinates, \( a \) and \( b \) label atomic orbitals, \( \mathbf{A}(t) \) is the vector potential for the radiation field, and \( q = -e \) is the charge of the electron. The coupling of the vector potential has been found to provide a proper treatment of the laser excitation process,29 with the laser pulse having its specific properties, including wavelength, fluence, and duration. The motion of the nuclei (or ion cores) is described by Ehrenfest’s theorem, again in a nonorthonormal basis:

\begin{equation}
M_{ij} \frac{d^2 X_{\alpha,i}}{dt^2} = -\frac{1}{2} \sum_j \left[ \frac{\partial H}{\partial X_{\alpha,j}} - i\hbar \frac{\partial S}{\partial X_{\alpha,j}} \right] \cdot \Psi_j + \text{h.c.} \frac{\partial U_{\text{rep}}}{\partial X_{\alpha,i}}.
\end{equation}

With the one-electron wave function \( \Psi \) represented by atomic orbitals, the parameters determining the Hamiltonian matrix \( H \) and ion–ion interaction \( U_{\text{rep}} \) are fitted to first-principles density-functional calculations.33 In previous simulations for fullerenes responding to laser pulses in various intensity regimes, this approach was found to yield a good description of various ground-state and excited-state phenomena.31 Since the time-dependent Schrödinger equation is solved at every time step, the laser excitation and nonadiabatic events involving electronic transitions are treated automatically, with no need to force “hopping” of electrons from one energy surface to another. The most severe limitation of the present method is that it is based on a mean-field picture, which inherently neglects many-body effects. When configuration interaction effects are important, therefore, the results for electronically-excited states may not be accurate. However, in the case of the cis–trans photoisomerization of stilbene, the only crucially important electronically excited state is the one which results from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO),34 so the results are qualitatively reliable even when the quantitative accuracy of the excited-state levels may be questionable.

Equation (3) is numerically integrated with the velocity Verlet algorithm (which preserves phase space), and (1) is solved with an improved Cayley algorithm developed by Graves and Torralva29 (which conserves probability and ensures that the Pauli principle always holds). A time step of 50 as was used because energy was well conserved and the results were found to be unaffected by further reductions in the size of the time step.

The internal coordinates are defined in Fig. 1. All nuclear coordinates are included in the calculation, but we label only the ones discussed in the following. Before the molecule is coupled to the vector potential, the cis-stilbene molecule is given 2000 fs to relax to its ground state geometry at 300 °C. The resulting geometry is in good agreement with that obtained in an ab initio CI study.35 The laser pulse was taken to have a full-width at half-maximum (FWHM) duration of 150 fs, a Gaussian profile, a fluence of...
0.90 kJ/m², and a wavelength corresponding to a photon energy of 3.80 eV. (The pulse thus starts at time \( t = 0 \) and ends at \( t = 300 \) fs.) This wavelength matches the density-functional energy gap between the HOMO and LUMO levels of \( \text{cis} \)-stilbene. 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. Simulations with slightly different initial conditions, including slightly different temperatures, lead to results which differ in detail from those presented in this paper, but to no significant changes.

### III. CIS–TRANS PHOTOOISOMERIZATION

The variations with time of the torsional angles for the vinyl bond and the two vinyl–phenyl bonds are presented in Fig. 2(a), and the change in the intramolecular distances between \( C_1 \) and \( C_9 \) in the two phenyl rings in Fig. 2(b). Figure 2(a) shows that, starting from the equilibrium geometry for the electronic ground state, the torsional angle about the vinyl bond reaches approximately 180° shortly after 500 fs, and then stays near this value. The two vinyl–phenyl torsional angles evolve to approximately 0° and 180°, respectively, and then fluctuate around these new values. These results clearly demonstrate that the \( \text{trans} \) isomer is formed after about 500 fs, but the HOMO–1 and LUMO+1 energies are relatively unaffected during the course of the isomerization. Several couplings between HOMO and LUMO levels occur as time progresses, and those at 195 fs and 440 fs, marked by 1 and 2 in Fig. 3(a), lead to nonadiabatic electronic transitions from LUMO to HOMO, also marked by 1 and 2 in Fig. 3(b). The energy gaps are found to be 0.10 eV for 1 and 0.14 eV for 2. Shortly after 440 fs, the energy gap between LUMO and HOMO increases to approximately 3 eV, and then maintains this value until the end of the simulation. Figure 3(b) shows that the laser pulse promotes about 1.7 electrons from HOMO to LUMO, and that the majority of promoted electrons return to the HOMO after the two nonadiabatic electronic transition events. The rise in the LUMO population after 200 fs is due to HOMO–LUMO transitions. From 440 fs to the end of the simulation, there are no further events involving HOMO–LUMO transitions.

The changes in vinyl and vinyl–phenyl bond lengths can be understood in terms of the characters of HOMO and LUMO orbitals vary substantially until about 500 fs, but the HOMO–1 and LUMO+1 energies are relatively unaffected during the course of the isomerization. Several couplings between HOMO and LUMO levels occur as time progresses, and those at 195 fs and 440 fs, marked by 1 and 2 in Fig. 3(a), lead to nonadiabatic electronic transitions from LUMO to HOMO, also marked by 1 and 2 in Fig. 3(b). The energy gaps are found to be 0.10 eV for 1 and 0.14 eV for 2. Shortly after 440 fs, the energy gap between LUMO and HOMO increases to approximately 3 eV, and then maintains this value until the end of the simulation. Figure 3(b) shows that the laser pulse promotes about 1.7 electrons from HOMO to LUMO, and that the majority of promoted electrons return to the HOMO after the two nonadiabatic electronic transition events. The rise in the LUMO population after 200 fs is due to HOMO–1 to LUMO transitions. From 440 fs to the end of the simulation, there are no further events involving HOMO–LUMO transitions.

The bond length variations of the vinyl and two vinyl–phenyl bonds with time are shown in Figs. 4(a) and 4(b). Figure 4(a) demonstrates that the vinyl bond length increases from 1.34 Å to an average value of 1.48 Å during the first 100 fs; then remains at this length until about 440 fs; and finally undergoes a gradual decrease to its initial value. In contrast, the vinyl–phenyl bond lengths [Fig. 4(b)] decrease from 1.48 to 1.42 Å on average by 100 fs, increase to an average length of 1.44 Å after 200 fs, fluctuate at this new value until about 440 fs, and finally drop to the initial values rather quickly.

The changes in vinyl and vinyl–phenyl bond lengths can be understood in terms of the characters of HOMO and...
LUMO orbitals, as demonstrated in Fig. 5, which depicts the molecular orbitals before application of the laser pulse. It can be clearly seen that excitation of \( \pi \) electrons from HOMO to LUMO causes the vinyl bond to change from double to single bond in character. On the other hand, comparison of the same two figures shows that the vinyl–phenyl bonds undergo the opposite change of character, from single to double bond.

It is also noteworthy from Fig. 5 that this \( \pi \pi^* \) excitation also alters the bond orders of \( C_1-C_2 \) and \( C_1-C_6 \) in one phenyl ring, and \( C_9-C_{10} \) and \( C_9-C_{14} \) in another ring, and therefore changes the lengths of these bonds. Figure 6 demonstrates the variations of some bond lengths in one phenyl ring: The \( C_1-C_2 \) and \( C_1-C_6 \) bonds enlarge from 1.41 Å to an average of 1.44 Å, and the \( C_1-C_4 \) and \( C_4-C_5 \) bonds expand from 1.40 Å to an average length of 1.42 Å. This result indicates that the electronic excitation is delocalized over the whole molecule, rather than localized in only the vinyl part. The obvious enhancement in the amplitudes of the vibrational modes of these bonds shortly after 200 fs must result from the laser radiation, since some electronic excitation still occurs after 200 fs (Fig. 3).

Notice in Fig. 4(b) that a sudden deposition of energy into \( C_1-C_7 \) and \( C_8-C_9 \) bond-stretching modes occurs just at 200 fs, as evidenced by the increase in their stretching vibrational amplitudes. This result suggests a strong coupling of these modes to the nonadiabatic electronic transition 1.

More detailed inspection of Figs. 2(a) and 3(b) indicates that cis-stilbene starts to rotate about its vinyl bond and two vinyl–phenyl bonds as soon as electrons are excited. This is consistent with the nature of the fast isomerization process from cis to trans. On the other hand, for the isomerization starting from the trans isomer, it is observed that torsional motion about the vinyl bond is activated by the excess vibrational energy of other nonreactive modes, via intramolecular vibrational energy redistribution (IVR). IVR has also been investigated for other molecules using dynamical simulations. By using an \( \textit{ab initio} \) molecular dynamics technique, Ben-Nun and Martinez found that the initial motion in photoisomerization of ethylene is C–C double bond stretching, and that torsional motion is activated by energy flowing out from this C–C stretching. Our recent results for the trans to cis photoisomerization of 1,3-butadiene suggest that torsional motion about one single C–C bond and two double C–C bonds is similarly activated by energy released from other vibrational modes. The rotations about vinyl and vinyl–phenyl bonds in stilbene, which here are observed to immediately follow electronic excitation, must be associated with barrierless reaction paths along the reaction coordinates starting from the cis isomer. This is in contrast with the photoisomerization reaction starting from the trans conformer, where the molecule starts to twist around the vinyl bond at a much later time due to the potential barrier along the reaction.
coordinate. Molecular orbital coupling 2 occurs for a geometry with \( \theta = 110^\circ, \phi_1 = -20^\circ, \) and \( \phi_2 = 150^\circ, \) as shown in Fig. 7. This is one of a series of molecular orbital couplings corresponding to a molecular geometry change from \( \theta = 90^\circ, \phi_1 = -30^\circ, \) and \( \phi_2 = 160^\circ \) to \( \theta = 120^\circ, \phi_1 = -20^\circ, \) and \( \phi_2 = 155^\circ. \) These couplings are clearly in close proximity to the phantom state, for which \( \theta = 90^\circ, \phi_1 = -8^\circ, \) and \( \phi_1 = 160^\circ. \)

Coupling 1 of Fig. 3, which produces only modest electronic deexcitation, arises for a geometry with \( \theta = 45^\circ, \phi_1 = 180^\circ, \) and \( \phi_2 = 0^\circ. \) This geometry is shown in Fig. 8(a), together with its HOMO in Fig. 8(b) and LUMO in Fig. 8(c). This geometry is far from the phantom state, and it is therefore not immediately obvious what product would result from a path through this state with more substantial deexcitation.

The empirical potential energy surface of the first electronically excited state of stilbene, in the \( \theta \) and \( C_1-C_7-C_8 \) space constructed by Frederick et al.\textsuperscript{24} and later modified by Pedersen et al.,\textsuperscript{16} demonstrates the following: At smaller torsional angles about the vinyl bond, there exist two minima, corresponding respectively to \textit{cis}-stilbene and DHP. As \( \theta \) increases, the stilbene well becomes more stable and DHP more unstable. The small value of \( \theta \) in the geometry that we find at 195 fs suggests that the molecular orbital coupling 1 must lead to formation of DHP. Based on their MMVB calculations, Robb and co-workers proposed\textsuperscript{20} that a quinoid minimum in the potential energy surface leads to a conical crossing, along the photocyclization reaction path to DHP, with almost no barrier. Table I shows a comparison of some parameters for the quinoid geometry calculated by Robb and co-workers\textsuperscript{37} (third column) and the geometry that we find at 195 fs (center column). The similarity between two geometries is obvious. Even the enlargement of some C–C bond
The interaction between them due to this rotation. partially result from the rotation of the two phenyl rings and 200 fs, which lead to the coupling 1 of Fig. 3, must at least changes in HOMO and LUMO energies during a period 80– changes, until these two levels experience the avoided crossing 1 of Fig. 3, and Fig. 10, as well in the torsional action is of minor importance at $t \approx 400$ fs, because these atoms are much further apart than at their point of closest approach, as shown in Fig. 9.

There continue to be large oscillations in the phenyl ring separation coordinates of Fig. 9, as well in the torsional angles of Fig. 2, but it is clear that the trans structure, with a larger distance between the phenyl rings, has been achieved. This conclusion also follows from the stability of the $C_1–C_9$ distance in Fig. 2(b).

One of the notable features in Fig. 8 is the pyramidalization of the CHphenyl group [Fig. 8(a)], and the change in the distribution of $\pi$ electrons around the vinyl bond due to this pyramidalization [Figs. 8(b) and 8(c)]. Figure 10(a) shows the variations with time of the two pyramidalization angles $\tau_1$ and $\tau_2$, as defined in Fig. 1, and Fig. 10(b) is an expanded view of Fig. 10(a) from 150 to 500 fs. It can be seen in Fig. 10(a) that strong variations in both pyramidalization angles occur after about 180 fs. Figure 10(b) demonstrates that pyramidalization is involved in both of the molecular orbital couplings that lead to the nonadiabatic events with

### TABLE I. Comparison of geometric parameters for the quinoid configuration and the configuration of the atoms in the simulation at 195 fs.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Data taken at 195 fs</th>
<th>Quinoid geometry</th>
</tr>
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<tr>
<td>$C_7–C_8$</td>
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<td>1.45</td>
</tr>
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<td>$C_7–C_8$</td>
<td>1.42</td>
<td>1.42</td>
</tr>
<tr>
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<td>1.44</td>
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<td>$C_7–C_8–C_4$</td>
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<td>122</td>
</tr>
<tr>
<td>$C_7–C_8–C_4–C_9$</td>
<td>40</td>
<td>28</td>
</tr>
<tr>
<td>$C_7–C_8–C_4–C_9$</td>
<td>5</td>
<td>13</td>
</tr>
</tbody>
</table>

*Bond distances are in angstroms, and angles in degrees. See Fig. 1 for the labeling of atoms.

*Data are averaged.

*From Reference 20.

lengths of the phenyl ring, found for the calculated quinoid geometry, is also observed in our geometry at 195 fs, as can be seen in Figs. 6(a) and 6(b). Some slight differences between the two geometries may reflect the fact that the calculated quinoid geometry does not generate an intersection like the one observed in our results at 195 fs.

It can be seen from Fig. 2(a) that $\theta$ increases from $11^\circ$ to $45^\circ$ during the first 80 fs, and then fluctuates about this angle until $t = 200$ fs. The vinyl and vinyl–phenyl bond lengths exhibit similar behavior, as can be seen in Fig. 4. These degrees of freedom—$\theta$ and the principal bond lengths—are therefore relatively constant in the vicinity of $t = 200$ fs, whereas the bond angles $\phi_1$ and $\phi_2$ are steadily evolving during this period, as can be seen in Fig. 2. It follows that the changes in HOMO and LUMO energies during a period 80–200 fs, which lead to the coupling 1 of Fig. 3, must at least partially result from the rotation of the two phenyl rings and the interaction between them due to this rotation.

The interaction between the phenyl rings is dominantly associated with $C_2–C_{14}$ and $H_{17}–H_{18}$, where the labeling of these atoms is defined in Fig. 1. It can be seen in Fig. 8 that the lobes of the LUMO pointing toward each other for $C_2$ and $C_{14}$ have the same sign, indicating no node, or bonding behavior and an attractive interaction. In the same figure, the lobes of the HOMO have opposite signs, indicating a node, or antibonding behavior and a repulsive interaction.

There is a quite intricate interplay between the electronic and nuclear degrees of freedom: Up to about $t = 195$ fs, the attractive force discussed earlier pulls the phenyl rings together, with rotations about the vinyl–phenyl bonds. The energies of the HOMO and LUMO evolve as the geometry changes, until these two levels experience the avoided crossing 1 of Fig. 3(a). There are then LUMO to HOMO transitions, seen in Fig. 3(b), with the creation of vibrational excitations.

After this first electronic deexcitation, the interaction of the phenyl rings becomes dominantly repulsive, primarily because of the interaction of the positively charged $H_{17}$ and $H_{18}$ as they closely approach each other. The $C_2–C_{14}$ interaction is of minor importance at $t \approx 400$ fs, because these atoms are much further apart than at their point of closest approach, as shown in Fig. 9.

FIG. 8. (a) Molecular geometry at $t = 195$ fs, again determined from the nuclear coordinates. (b) HOMO of cis-stilbene at $t = 195$ fs. (c) LUMO of cis-stilbene at $t = 195$ fs.
electronic transitions which are marked in Fig. 3. This conclusion is based on the facts that $\tau_1$ has a minimum and $\tau_2$ has a shoulder at 190 fs, labeled 1 in Fig. 10(b), and $\tau_1$ has another minimum at 440 fs, labeled 2.

Figure 11 shows the variations of the $\text{C}_1$–$\text{C}_7$–$\text{C}_8$ and $\text{C}_7$–$\text{C}_8$–$\text{C}_9$ bending angles with time. The excitations of both C–C–C bond bending vibrations mainly occur just after 195 fs. These excitations most likely result from the electronic energy released in the nonadiabatic process at 200 fs in Fig. 3(b), although the laser radiation may also play a role. The couplings of both C–C–C bond bending vibrations to the nonadiabatic electronic transition at 195 fs are clearly evident, and the increase in their vibrational amplitudes demonstrates the transfer of energy from electrons to vibrational modes. Another significant feature in Fig. 11 is that both C–C–C bending angles increase from 124° to more than 130° immediately after $t = 200$ fs, and then decrease until approximately 400 fs. This period of time is the same as the interval between the two couplings of molecular orbitals shown in Fig. 3. The expansion of these two C–C–C bending angles therefore accounts (at least in part) for the variations in the energy gap between the HOMO and LUMO orbitals during this interval. One would then like to understand why these two bending angles become more open, and with this goal we examined the HOMO and LUMO orbitals for the molecular geometry at 220 fs. These are presented in Fig. 12. Notice first that, as indicated by Fig. 12(a), the molecular geometry after 200 fs changes in such a way that the vinyl bond is parallel to both phenyl rings. With this geometry, the interactions between $\text{C}_1$ and $\text{C}_8$ and between $\text{C}_7$ and $\text{C}_9$ are repulsive for both HOMO and LUMO orbitals, and this explains the increase in the two C–C–C bending angles seen in Fig. 11.

**IV. CONCLUSION**

We have performed detailed simulations of the cis to trans photoisomerization of stilbene following a laser pulse with a FWHM of 150 fs. After this pulse produces electronic excitations from HOMO to LUMO, the vinyl and vinyl–phenyl bonds, respectively, undergo an increase and decrease in length, as can be seen in Fig. 4. At the same time, the molecule begins to rotate simultaneously about all three of these bonds, as can be seen in Fig. 2(a). Although the detailed motion is rather intricate, the elongation of the molecule during the cis-to-trans transition is quite evident in Fig.
FIG. 12. (a) Side view of molecular geometry at t = 222 fs. (b) HOMO of cis-stilbene at t = 222 fs. (c) LUMO of cis-stilbene at t = 222 fs.

2(b), where the carbon atoms at the ends of the vinyl–phenyl bonds are observed to move steadily away from each other.

There are two principal avoided crossings for the HOMO and LUMO levels in Fig. 3, each of which leads to downward electronic transitions with a release of energy to the vibrational modes. The first is 195 fs, for a geometry with θ = 40°, where θ is the torsional angle about the vinyl bond. This first HOMO–LUMO coupling was not found to be of dominant importance in determining the final outcome. However, we propose that this coupling can lead to the formation of 4a, 4b-dihydrophenanthrene (DHP) when the molecule follows a different trajectory. This proposal is based on both our own results and the empirical potential energy surface for the first electronically excited state of stilbene.16,24 Even more importantly, it is also supported by the MMVB calculation of Bearpark et al.20 The pyramidalization of the CHphenyl group clearly plays a significant role in this coupling, as do the rotation and interaction of the two phenyl rings.

It is the second principal HOMO–LUMO coupling of Fig. 3, at 440 fs, which dominantly determines the final outcome in the process considered here: cis-to-trans isomerization. After depopulation of the LUMO at this avoided crossing 2, the molecule is stabilized in its new geometry. The central vinyl bond returns to its original double-bond status (with a shorter bond length in Fig. 4 after t = 440 fs). Rotation about this bond is then effectively inhibited: In Fig. 2, θ attains its new value of approximately 180°, corresponding to the new trans structure, and then merely exhibits torsional oscillations about this value.

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