

Dynamics of the photocyclization of *cis*-stilbene to dihydrophenanthrene

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Abstract. Semiclassical simulations are reported for the dynamics of the photocyclization of *cis*-stilbene, leading to the formation of 4a,4b-dihydrophenanthrene. Photo-excited *cis*-stilbene rotates about its vinyl and vinyl-phenyl bonds simultaneously. The structural changes result in a series of strong couplings between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. These couplings cause the formation of a new chemical bond between the two phenyl rings of stilbene. The length changes of different C—C bonds, corresponding to the formation of the new molecule, are presented and discussed in detail.

1. Introduction

Stilbene is a prototype molecule for investigating photo-isomerization, and has been the subject of a substantial number of studies [1–4]. The photo-isomerization process is of interest because it is the primary event in vision [5]. Isomerization of stilbene can start from either the *cis* or the *trans* geometry. When the reaction proceeds from the *cis* isomer, the photo-excited molecule has two competing reaction pathways: one is a torsional *cis*–*trans* isomerization reaction, and the other is a photocyclization reaction due to electronic rearrangement. The product is *trans*-stilbene for the former and 4a,4b-dihydrophenanthrene (DHP) for the latter.

Recently, the ring closure reaction of *cis*-stilbene to form DHP has also attracted attention [6, 7]. It is generally believed [8] that this reaction proceeds on the electronically excited singlet state from *cis*-stilbene, through an intermediate state with a perpendicular orientation in the geometry, before the molecule decays to the electronic ground state non-adiabatically. However, there is only very limited information about the excited state dynamics along the reaction pathway leading to the formation of DHP.

Very recently, we have performed a series of simulation studies on the molecular response to ultrashort laser irradiation [9–12]. These include the photo-isomerization of *cis*- and *trans*-butadiene [9, 10], and *cis*-stilbene [11, 12] using a semiclassical approach. The simulation results provide insights into the dynamics of these complicated photoreactions. In this paper, we report some initial results of a simulation of the photocyclization of *cis*-stilbene to form the

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DHP molecule. The technique is described briefly in the next section. The results of the simulation are presented in section 3, and a summary is given in section 4.

2. Methodology

The technique used in this study is semiclassical electron-radiation-ion dynamics (SERID). A detailed description of the technique is published elsewhere [10] and here we give only a brief introduction. In this method, the valence electrons are treated quantum mechanically, but both the radiation field and the motion of the ion cores are treated classically. Since a semiclassical treatment in time-dependent perturbation theory effectively includes n -photon and n -phonon processes in absorption and stimulated emission, the present model provides detailed insight into some molecular processes, including electronic excitation, vibrational mode excitation, intra-molecular vibrational energy redistribution, and interdependence of the various electronic and vibrational degrees of freedom.

The electronic wavefunctions are constructed by solving the time-dependent Schrödinger equation in a non-orthogonal basis at every time step:

$$i\hbar \frac{\partial \psi_j}{\partial t} = \mathbf{S}^{-1} \cdot \mathbf{H} \cdot \psi_j, \quad (1)$$

where \mathbf{S} is the overlap matrix for the atomic orbitals. The laser excitation is described by coupling a time-dependent vector potential to the electronic Hamiltonian via the Peierls substitution:

$$H_{ab}(\mathbf{X} - \mathbf{X}') = H_{ab}^0(\mathbf{X} - \mathbf{X}') \exp\left(\frac{iq}{\hbar c} \mathbf{A}(t) \cdot (\mathbf{X} - \mathbf{X}')\right), \quad (2)$$

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. This approximation has been found to properly describe the laser excitation process in solids and molecules. The laser pulse can be input with different wavelengths, fluences, and durations. The motion of the nuclei (or ion cores) is presented by the mean field approximation, again in a non-orthogonal basis:

$$M_\ell \frac{d^2 X_{\ell\alpha}}{dt^2} = -\frac{1}{2} \sum_j \psi_j^\dagger \cdot \left(\frac{\partial \mathbf{H}}{\partial X_{\ell\alpha}} - i\hbar \frac{\partial \mathbf{S}}{\partial X_{\ell\alpha}} \frac{\partial}{\partial t} \right) \cdot \psi_j + \text{h.c.} - \frac{\partial U_{\text{rep}}}{\partial X_{\ell\alpha}}, \quad (3)$$

where M and X are any nuclear mass and coordinate, and U_{rep} is the ion-ion repulsive potential.

The Hamiltonian matrix, overlap matrix, and ion-ion repulsive potential are determined in density-functional calculations [13]. The basis functions used in the present simulations are the 1s atomic orbital of H and the valence s and p orbitals of C. (Spin-up and spin-down states are not distinguished.) This basis set excludes the ionized states that play a crucial role in many photochemical reactions. In the present study, however, the photon energy is chosen to match the energy for a transition to the lowest excited state, and the laser fluence is sufficiently low that multiphoton processes are found to occur with little amplitude, so ionization processes are not significant. In previous work, the approach described above was found to properly describe various non-trivial ground-state and excited-state

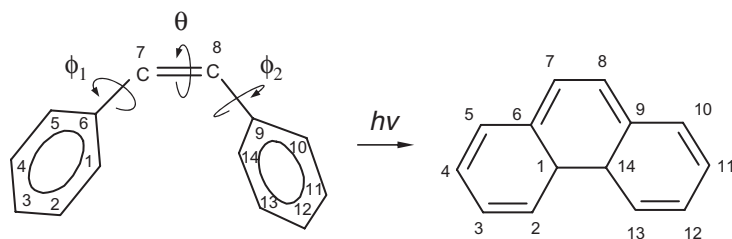


Figure 1. Definitions of the internal coordinates of *cis*-stilbene and 4a,4b-dihydrophenanthrene (DHP). Note that all nuclear coordinates are included in the simulation, but only those discussed in the text are labelled.

phenomena of fullerenes reacting with laser pulses of various intensities, ranging from low to very high [13]. (Photofragmentation, like other processes, is treated semiclassically in the present description: laser excitation promotes some valence electrons from bonding to antibonding states, giving rise to strong repulsive forces if the fluence is high. In the present work, however, we have focused on less violent processes.) This same approach has also been successful in modeling the photo-isomerization processes of butadiene and *cis*-stilbene.

In the present model, the time-dependent Schrödinger equation is solved at every time step. Therefore, laser excitation, non-adiabatic electron transition, and energy conversion between electronic and nuclear motion can be treated automatically. The most severe limitation of the present approach is neglecting many-body effects, or using a the mean-field approximation. When the photo-reaction involves many electronically excited states, the absence of configuration interaction may seriously affect the energy levels of the excited states. However, the photocyclization of *cis*-stilbene to form DHP is believed to proceed adiabatically on the electronically excited singlet state, and therefore the results of the present study are qualitatively reliable even when the energy levels of the excited states are not accurate.

The time-dependent Schrödinger equation (1) is solved with an improved Cayley algorithm [14] and (3) is integrated with the velocity Verlet algorithm. A time step of 50 attoseconds was chosen based on the test of energy conservation and result stability.

Figure 1 presents the definitions of the internal coordinates of both *cis*-stilbene and DHP. All the nuclear coordinates are included in the calculation, but only those discussed in the text are labelled. Before the laser pulse is applied, the *cis*-stilbene molecule is simulated for 2000 fs so it can relax to its ground-state geometry at 300°C. The geometry thus obtained is in good agreement with that calculated by an *ab initio* CI approach [15]. The laser pulse for this study has a full-width at half-maximum (FWHM) duration of 150 fs with a Gaussian profile, a fluence of 0.95 kJ m⁻² and a wavelength of 3.80 eV. This wavelength matches the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels as calculated with density-functional theory. Using a standard method [16], we find the absorption cross section of the molecule to be about 0.33 × 10⁻¹⁶ cm². The fluence used in this study is one that ultimately leads to the DHP molecule rather than the *trans* isomer or dissociated products.

3. Results and discussion

The variation with time of the torsional angles for the vinyl bond and the two vinyl–phenyl bonds are shown in figure 2(a) and the time dependence of the electronic energy levels for the four important molecular orbitals HOMO-1, HOMO, LUMO and LUMO+1 are shown in figure 2(b). As shown in figure 2(a), the *cis*-stilbene molecule rotates over 90° in about 300 fs from the onset of the laser pulse, and then gradually rotates back to about 0°, finally staying near this value until the end of the simulation. On the other hand, both vinyl–phenyl torsional angles evolve to approximately 0° before 200 fs, and then essentially maintain this geometry until the end. These results clearly show the formation of the DHP molecule within the first 650 fs. Figure 2(b) demonstrates that there are six non-adiabatic couplings between the HOMO and LUMO orbitals. Two strong couplings between the HOMO and LUMO at about 590 and 705 fs result from the formation of a new chemical bond between the two phenyl rings, and therefore the formation of the photocyclization product, DHP. This conclusion is supported by

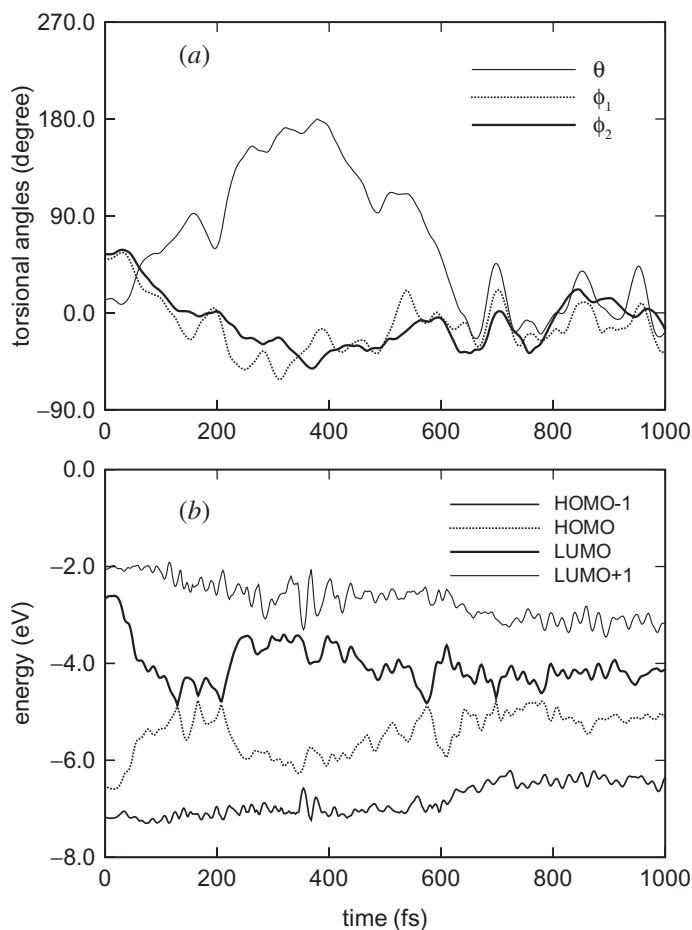


Figure 2. (a) Variation with time of the torsional angles θ , ϕ_1 and ϕ_2 of stilbene (as defined in figure 1). (b) Variation with time of HOMO-1, HOMO, LUMO and LUMO+1 energy levels.

the observation of geometrical changes in the stilbene molecule, as demonstrated in figure 2 (a), which shows that the three C—C rings are coplanar at about 600 fs. The formation of the DHP molecule also modifies the relative energy levels of the HOMO-1 and LUMO+1 orbitals, as shown in figure 2 (b).

The bond length variations of the vinyl and two vinyl-phenyl bonds with time are presented in figure 3 (a) and (b). Figure 3 (a) demonstrates that the vinyl bond length increases from 1.34 Å to an average value of 1.45 Å shortly after the laser pulse is applied to the molecule, and then remains at this length until 1200 fs. In contrast, the vinyl-phenyl bond lengths (figure 3 (b)) decrease from 1.48 Å to an average of 1.42 Å by about 100 fs, and then fluctuate about this value until 1200 fs.

Upon excitation of π electrons from HOMO to LUMO, the vinyl bond changes from effectively double bond to single bond in character. On the other hand, the vinyl-phenyl bonds experience the opposite change of character, from single to double bond. The couplings between HOMO and LUMO orbitals do not

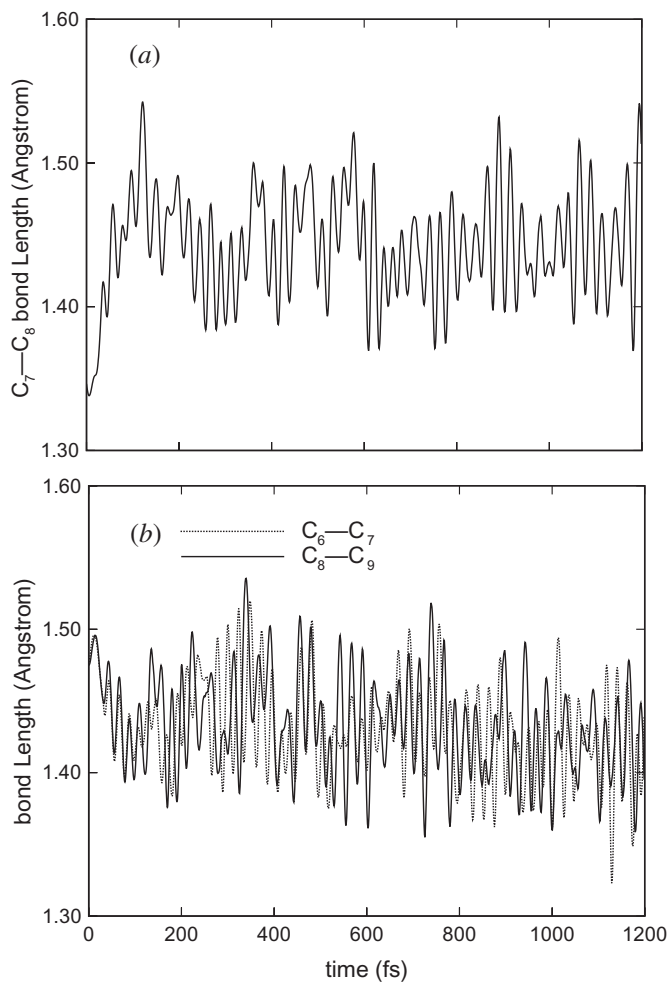


Figure 3. (a) Variation of the C₇—C₈ (vinyl) bond length with time. (b) Variation of the C₆—C₇ and C₈—C₉ (vinyl-phenyl) bond lengths.

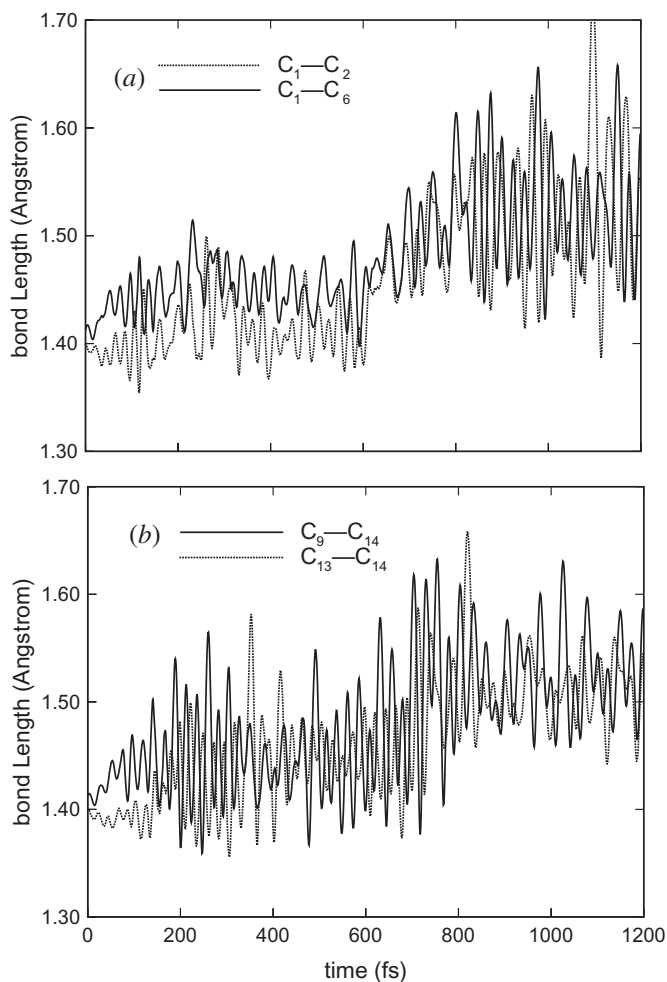


Figure 4. (a) Variation of the C_1-C_2 and C_1-C_6 bond lengths with time. (b) Variation of the C_9-C_{14} and $C_{13}-C_{14}$ bond lengths with time.

change the lengths of these bonds significantly. These bonds maintain their new character in the new molecule that is formed at about 600 fs.

Figure 4 (a) demonstrates the variation of the bond lengths of C_1-C_2 and C_1-C_6 , while figure 4 (b) shows the variation in C_9-C_{14} and $C_{13}-C_{14}$. These four C—C bonds exhibit similar trends in length variations. First, the bonds are elongated from 1.41 Å to an average of 1.44 Å immediately after 100 fs. They remain at their new lengths for about 600 fs, then start to increase again, reach about 1.52 Å shortly after about 700 fs, and finally maintain the new lengths until the end of the simulation.

The first increase in the bond lengths is a consequence of electron redistribution due to laser excitation. This result reveals that the electronic excitation is delocalized over the two phenyl rings, rather than localized in only the vinyl bond. The constant lengths of the four C—C bonds in the phenyl rings from about 100 fs to around 600 fs suggests that the molecule is still in the electronically excited state

during this period of time. The formation of the new chemical bond between the two phenyl rings changes these four C—C aromatic bonds to single bonds, resulting in the further bond-length expansion after about 600 fs.

4. Conclusion

We have performed detailed simulations of the photocyclization of *cis-stilbene* to form the DHP molecule following a laser pulse with a FWHM of 150 fs. After electronic excitations from HOMO to LUMO, the vinyl and vinyl–phenyl bonds, respectively, undergo an increase and decrease in length. This facilitates rotations of the molecule about the vinyl bond and two vinyl–phenyl bonds. Before reaching an angle of rotation of about 180° about the vinyl bond, the molecule undergoes a back rotation about this bond. The new chemical bond between two phenyl rings is formed at about 600 fs, as a result of the electronic rearrangement. Specifically, laser excitation of electrons across the HOMO–LUMO gap causes the vinyl bond and two vinyl–phenyl bonds to switch from single- and double-bond character, and the four aromatic C—C bonds to change to single bond in character.

Acknowledgments

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