Another important coordinate in the photoisomerization of cis-stilbene

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Abstract

Detailed simulations are reported for the coupled dynamics of electrons and nuclei in the isomerization reaction of cis-stilbene stimulated by laser excitation. The results demonstrate that, in addition to the traditional vinyl and vinyl–phenyl torsions, the HCCH torsional coordinate of the vinyl group also makes a significant contribution to the HOMO and LUMO couplings that yield nonradiative electronic transitions to the ground state. Moreover, variations in the CCH angles of the vinyl group in the vicinity of the HOMO–LUMO couplings indicate that pyramidalization of the vinyl-group carbon atoms is strongly involved in these molecular orbital couplings.

1. Introduction

Photoisomerization of stilbene serves as a model for understanding both the natural processes that convert light into molecular motion on a femtosecond time scale, as observed in rhodopsins, and the effects of different solvents on these processes [1–3]. Isomerization can start from either the cis or the trans conformer. Following electronic excitation, the stilbene molecule undergoes rotational motion simultaneously about its vinyl and vinyl–phenyl bonds in the electronically excited state, as a result of forces generated by the redistribution of electronic charge. When the torsional angle around the vinyl bond reaches about 90°, corresponding to the so-called phantom state, the molecule decays to its ground state through nonadiabatic processes. After the molecule has fallen to the electronic ground state, its trajectory can follow either a branch which leads back to the reactant or one which leads on to the product. Pump–probe experiments have revealed that, if the reaction starts from the cis conformer, the photoexcited molecule in the gas phase decays to the ground state on a femtosecond time scale [4–6]. The process is fast enough to compete with vibrational energy relaxation or redistribution [7,8] and no fluorescence emission generally can be detected [9]. This rapid decay has been ascribed to a barrierless path from the cis conformer, along the reaction coordinate in the electronically excited state [10,11]. This reaction coordinate is not well
understood, however, because of the complexity due to the couplings among the lower-frequency vibrational modes in the electronically excited state [7,10,12]. Theoretical studies of the photodynamics of isomerization for stilbene have mainly focused on the torsional motions, with the majority involving a one-dimensional model of the vinyl C–C bond rotation [13–17].

Recently Molina et al. [18,19] performed more accurate theoretical calculations for the ground and electronically excited states of the cis and trans conformers of stilbene using multiconfigurational second-order perturbation theory (CASPT2). They additionally discussed some static features along the photoisomerization path on the excited-state potential energy surface.

Quenneville and Martínez [20] also performed ab initio calculations. They suggested that vinyl torsion, and pyramidalization of the vinyl carbons in the twisted state as a result of hydrogen motion, are essential for generating a minimal energy intersection in a low-lying electronically excited state. This work provides an incentive to further investigate the reaction coordinate for cis–trans photoisomerization of stilbene.

With this motivation, we have performed detailed simulations of the isomerization process for cis-stilbene following irradiation with an ultrashort laser pulse. We find that the HCCH torsion of the vinyl group is in fact strongly involved in the molecular orbital couplings that lead to decays of electronically excited cis-stilbene.

2. Methodology

Time-dependent density-functional theory [21] is now well established and has been successfully used to calculate photoabsorption spectra and excitation energies of atoms and small molecules. However, in the present context one needs a complementary approach which is suitable for larger systems and multiphoton processes.

Here we use a method for realistic simulations of the interaction of light with molecules, which combines the virtues of tight-binding electron-ion dynamics [22–24] and density-functional-based tight-binding (DFTB) [25,26]. (There are also connections with time-dependent density-functional theory [21] and other density-functional-based schemes [27].) Both the effective one-electron Hamiltonian and the effective repulsive forces between ion cores are accurately determined in local-density-functional calculations [25]. I.e., we employ the DFTB ansatz, which can be seen as a stationary approximation to DFT [26], and which has been found to yield accurate results in a variety of different systems, including molecules, clusters, solids, and surfaces [25,26].

Our general method is called semiclassical electron-radiation-ion dynamics (SERID) [28], since the valence electrons are treated quantum-mechanically but both the radiation field and the motion of the ion cores are treated classically. Such a semiclassical treatment effectively includes absorption and stimulated emission of photons and vibrational quanta, in the sense that electronic transitions involve energies \( \pm \hbar \omega \), where \( \omega \) is a characteristic frequency associated with the radiation field or vibrational motion. In the version of the method used in the present work, as mentioned above, the values of the parameters determining both the one-electron Hamiltonian \( \mathbf{H} \) and the repulsion between ion cores were determined in local-density-functional calculations [25]. This approach yielded a very good description for the response of fullerenes to laser pulses of various intensities [29] and for the C–H bond in various systems [25]. Since stilbene only involves C–C and C–H bonds, it should be quite well described by this approach.

The electronic wavefunctions are updated at each time step by solving the time-dependent Schrödinger equation in a nonorthogonal basis

\[
\frac{i\hbar}{\partial t} \Psi_j = S^{-1} \cdot \mathbf{H} \cdot \Psi_j, \tag{1}
\]

where \( \mathbf{H} \) is the one-electron Hamiltonian matrix, \( S \) is the overlap matrix, and \( \Psi_j \) is the state vector for the electron labeled by \( j \). The ion forces are calculated from Ehrenfest’s theorem

\[
M_i \frac{d^2 X_{ij}}{dt^2} = -\frac{1}{2} \sum_j \Psi_j^\dagger \left( \frac{\partial \mathbf{H}}{\partial X_{ij}} - i\hbar \frac{\partial S}{\partial X_{ij}} \frac{\partial}{\partial t} \right) \cdot \Psi_j + \text{h.c.} - \frac{\partial U_{\text{rep}}}{\partial X_{ij}}, \tag{2}
\]
where \( X' \) is one coordinate of the ion core (or atomic nucleus) labeled by \( \ell \) (with \( \ell = x, y, z \)), \( U_{\text{rep}} \) is the repulsive ion–ion interaction, and h.c. represents the Hermitian conjugate of the first term in Eq. (2). The coupling of the electrons to the radiation field is accomplished by the time-dependent Peierls substitution [23,30]

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

where \( \mathbf{A}(t) \) is the vector potential for the radiation field and \( q = -e \) is the charge of the electron. Eq. (2) is numerically integrated using the velocity Verlet algorithm (which preserves phase space), and Eq. (1) is solved with an improved Cayley algorithm developed by Graves and Torralva [24] (which conserves probability and ensures that the Pauli principle always holds). A time step of 50 attoseconds was used because the results were then found to be well converged.

A much longer description of the methodology, its strengths, its limitations, and its suitability for the present class of problems is given elsewhere [28].

The internal coordinates are defined in Fig. 1. All nuclear coordinates are included in the calculation, but only some of them are labeled for discussion in the text below. Before coupling to the vector potential, the molecule is allowed to relax to its equilibrium geometry for 2000 fs. The resulting geometry is in good agreement with one obtained in an ab initio study with configuration interaction [31]. The laser pulse was taken to have a 150 fs FWHM duration (or a total duration of 300 fs), a Gaussian profile, a fluence of 0.85 kJ/m², and a wavelength corresponding to a photon energy of 3.80 eV. This wavelength matches the density-functional energy gap between the HOMO and LUMO levels in 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.

3. Results and discussion

Energy variations with time for the HOMO − 1, HOMO, LUMO, and LUMO + 1 levels are shown in Fig. 2a, and the time-dependent population of the LUMO is shown in Fig. 2b. The rather violent variations in the energies of the HOMO and LUMO after 200 fs indicate strong changes in the molecular structure following the intense laser pulse. Several avoided crossings, or couplings, between the HOMO and LUMO levels occur between 250 and 450 fs. At later times the gap between these levels stays roughly constant. Four couplings, marked by 1, 2, 3, and 4 in Fig. 2a, lead to nonadiabatic electronic transitions, also marked by 1, 2, 3, and 4 in Fig. 2b. The energy gaps are, respectively, found to be 0.01, 0.05, 0.1, and 0.07 eV. The downward electronic transitions 1, 2, and 4 involve emission of vibrational quanta, whereas vibrational quanta are absorbed in the upward transition 3. Fig. 2b shows that the laser pulse promotes approximately 1.3 electrons from HOMO to LUMO, and that the majority of this excited-state occupancy is lost back to the HOMO by about 450 fs, through nonradiative transitions. The molecule is then essentially locked into its electronic ground state.

It is interesting that the CASPT2 calculation of Molina et al. [19] also predicts that the initial event
in the cis–trans photoisomerization reaction of stilbene involves a HOMO → LUMO transition, since high oscillator strength is found in the 2^1B state corresponding to this transition. It should be mentioned, however, that the HOMO–LUMO energy gap for the initial geometry is 0.81 eV less in the density-functional-based calculation of the present study than in the CASPT2 calculation of Molina et al.

The variations with time of vinyl and vinyl–phenyl bond lengths and the three principal torsional angles, \( \theta_2 \), \( \phi_1 \), and \( \phi_2 \), are presented in Fig. 3. Following the excitation of electrons from HOMO to LUMO, the vinyl bond and vinyl–phenyl bonds exhibit an effective inversion of single and double bond characters: the former is lengthened from 1.35 Å to an average value of 1.47 Å, while the latter is shortened from 1.48 Å to an average of 1.40 Å, as can be seen in Figs. 3a and b. At the same time, the C–C bond stretching frequency is found to decrease for the vinyl bond and increase...
for the vinyl–phenyl bonds. These changes are due to the antibonding character of the LUMO. After the LUMO is depopulated through nonradiative transitions, the lengths and vibrational frequencies of both vinyl and vinyl–phenyl bonds revert to their initial characters, but the vibrational amplitudes of these bonds increase as electronic energy is converted to kinetic energy of nuclear motion.

The increase in the vinyl bond length facilitates its rotation. As can be seen in Fig. 3c, starting from its initial equilibrium value, $\theta_2$ reaches approximately 90° at about 250 fs, and then maintains this angle for about 400 fs, before returning to its initial value and fluctuating about this value until the end of simulation. The angles $\phi_1$ and $\phi_2$, on the other hand, start from 50° to 235°, respectively, and then, after passing through minima near 400 fs, come back to their initial values, about which they continue to oscillate. These results clearly demonstrate that the cis-stilbene has completed an isomerization process: following electronic excitation, the molecule rotates towards the phantom state, and essentially reaches this state shortly after 200 fs. It moves in the vicinity of the phantom state for about 250 fs, before decaying to the ground state and finally propagating back to the reactant (i.e., the cis isomer) after nonradiative decay.

The torsional angle $\theta_1$, compared with $\theta_2$, is plotted in Fig. 4a as a function of time. Fig. 4b shows a comparison between $\theta_1$ and the HOMO and LUMO energies for the time interval 240–450 fs. It is clear that there is one significant difference between the variations in $\theta_1$ and $\theta_2$: $\theta_1$ remains near 90° during the time interval 250–450 fs, demarcated by two bars in Fig. 4a, and this indicates that the molecule moves in the vicinity of the phantom state. On the other hand, $\theta_1$ varies over a range of about 100°.

It is especially interesting that the maximum and minimum of $\theta_1$ occur in conjunction with two maximum energy gaps between the HOMO and LUMO, as can be seen in Fig. 4b. This figure provides direct and dramatic evidence that the torsional angle $\theta_1$ strongly affects the HOMO and LUMO couplings.

It is further noteworthy that each of the four molecular orbital couplings in Fig. 2, all of which lead to pronounced nonradiative electronic transitions, corresponds to values of the torsional angle $\theta_1$ in the range 70–80°.

Finally, let us turn to the variations with time of the two CCH bending angles of the vinyl group, defined as the pyramidalization of the vinyl carbons in [20]. These angles are plotted in Fig. 5. One very pronounced feature in Fig. 5 is the sharp drop in these two bending angles after about 420 fs, when the fourth HOMO–LUMO coupling occurs, indicating that pyramidalization of the vinyl carbons plays a strong role in causing the HOMO–LUMO gap to shrink. Enhancements in the amplitudes of the two bending vibrations after 253 fs, and again after 440 fs, are due to the electronic energy released via nonradiative downward electronic transitions. This is direct evidence that these two modes couple to the nonradiative electronic transitions 1 and 4 of Fig. 2b.
4. Conclusion

We have investigated the coupled electronic and nuclear dynamics involved in the photoisomerization of cis-stilbene, using a semiclassical dynamical simulation technique (SERID). We found that, in addition to the traditional vinyl and vinyl–phenyl torsions, the HCCH torsion of the vinyl group also makes a significant contribution to the HOMO and LUMO couplings which are responsible for nonadiabatic decays to the ground state.

We also found that the two CCH angles of the vinyl group are about 10° smaller near one molecular orbital coupling (see Fig. 5). This result confirms a very recent proposal that both torsion and pyramidalization of vinyl carbons are involved in producing the minimal energy conical intersection which is conjectured to dominate a nonadiabatic decay of the electronically excited molecule to the ground state [20]. Finally, we showed that both CCH bending vibrations of the vinyl group are strongly coupled to the nonradiative downward electronic transitions. All of these results provided new understanding of this model photochemical reaction.

The most important conclusion of this Letter is that the HCCH torsional angle of the vinyl group plays a significant role in the HOMO–LUMO nonadiabatic couplings which lead to depopulation of the LUMO. It would be of considerable interest to perform ab initio calculations of the potential energy surfaces, for both the electronic ground state and excited states, which would provide more detailed understanding of how this coordinate affects the photoisomerization process.

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References


