

A theoretical study of cyclohexadiene/hexatriene photochemical interconversion: multireference configuration interaction potential energy surfaces and transition probabilities for the radiationless decays

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Abstract

The overall energetics and the feature of reactive potential energy surfaces for the photochemical interconversion between cyclohexadiene (CHD) and all-*cis*-hexatriene (cZc-HT) have been investigated using the multireference configuration interaction (MRCI) calculations. The adiabatic and the diabatic potential energy surfaces of the ground and the excited states have been calculated along the Jacobi coordinates. The conical intersections among the states are estimated and the corresponding non-adiabatic transition probabilities are calculated using the semiclassical Zhu–Nakamura formula. The $1^1\text{B} \rightarrow 2^1\text{A}$ decay occurs by C_2 -symmetry-breaking motion around the conical intersection. The non-adiabatic transition to 1^1A occurs by the motion toward the 5-membered ring. © 2004 Elsevier B.V. All rights reserved.

1. Introduction

Ring-opening/closure reactions of dialylethene by photoirradiation have attracted much attention to develop photochromic electronic device materials [1–3]. Photochemical interconversion between cyclohexadiene (CHD) and all-*cis*-hexatriene (cZc-HT) (Fig. 1) is known to be a good model system of the photochromism. The CHD molecule is excited by ultraviolet absorption and the ring-opening to cZc-HT occurs with the quantum yield of ~ 0.4 via radiationless decays to the ground state [4–9]. The following scheme has been proposed for the CHD/cZc-HT photochemical interconversion [4–9]:

- (1) The CHD is initially excited to the 1^1B state by photoirradiation.
- (2) The 1^1B state rapidly decays to the 2^1A state (within 10 [5] to 53 [9] fs).
- (3) The 2^1A state decays to the 1^1A (ground) state within ~ 1 ps in solution [6,7] or within ~ 200 fs in gas phase [9], and then CHD or cZc-HT are created.

The ring-closure from cZc-HT to CHD has not been experimentally observed, because cZc-HT scarcely remains in the thermal equilibrium due to the conformation change to the predominant *trans*-HT structures [4–9]. The important issues to be elucidated are the mechanisms determining the quantum yield and the lifetime on the excited state. Robb et. al. [10–12] have carried out the pioneering theoretical study using the complete active space self-consistent field (CASSCF) calculations. For the $1^1\text{B} \rightarrow 2^1\text{A}$ decay [12], the

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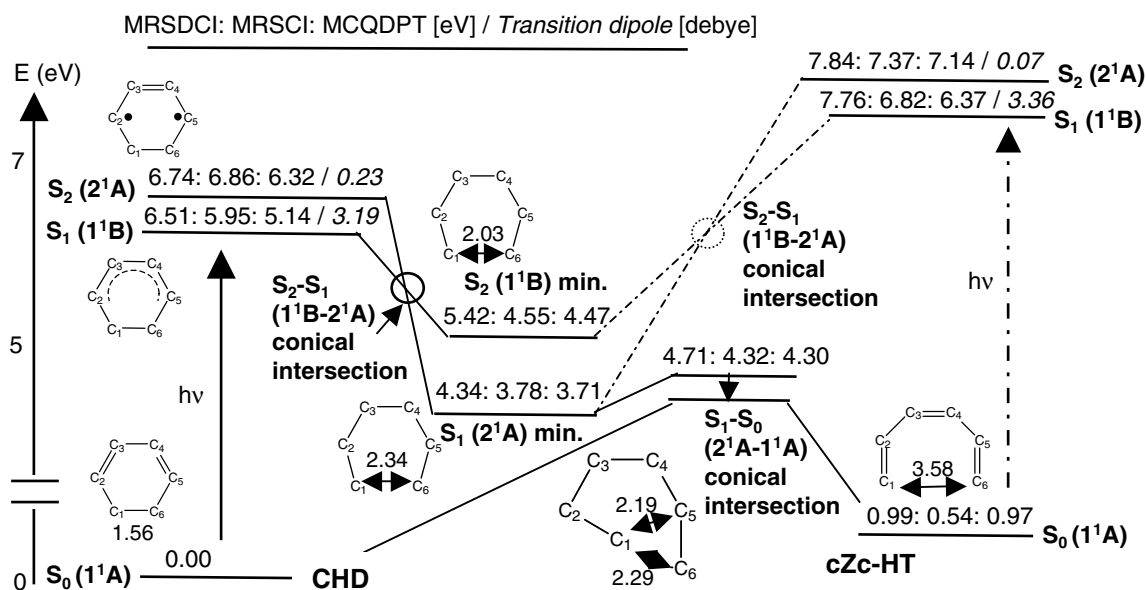


Fig. 1. Diagram of CHD/cZc-HT photochemical interconversion. MRSDCI, MRSCI and MCQDPT energies are relative values from those of the ground state CHD. Transition dipoles and equilibrium geometries are also shown.

multireference second-order perturbation theory (CASPT2F) has predicted that the ring-opening of CHD proceeds with barrierless descending on the 1^1B potential. The intersection between 1^1B and 2^1A states has been found at ~ 2 Å bond breaking C–C distance [12], which corresponds to the experimentally observed rapid radiationless decay. However, in this study, the 1^1B and 2^1A potentials were separately calculated within the constraint of C_2 symmetry and the transition probability from 1^1B to 2^1A was not elucidated. The CHD/cZc-HT production ratio has also been estimated by using the minimum energy path through the conical intersection based on the assumption that the thermal equilibrium is reached before the decay to the ground state [10]. However, the experimentally observed short lifetime [9] implies that the excited state decays to the ground state before it reaches the thermal equilibrium.

Accurate information of potential energy surfaces of the ground and the excited states is crucial to investigate the reaction dynamics, and the radiationless decay should be investigated by the proper theory of non-adiabatic transition. In the present Letter, the overall energetics and the feature of reactive potential energy surfaces for the CHD/cZc-HT photochemical interconversion have been investigated using the CASSCF method with dynamic correlation energies. The adiabatic and the diabatic potential energy surfaces of the ground and the excited states have been calculated using the Jacobi coordinates, which effectively describe the ring-opening/closure reactions. Since the CASSCF without dynamic correlation energies predicts wrong relative energies between the states as described later, the poten-

tial energy surfaces are calculated using the multireference configuration interaction (MRCI). The non-adiabatic transition probabilities among the states are estimated by the semiclassical Zhu–Nakamura formula [13,14]. The C_2 -symmetry-breaking potential energy surfaces have been calculated to investigate the 1^1B-2^1A decay. The transition probabilities along the seam line around the 2^1A-1^1A conical intersection have also been calculated to investigate the radiationless decay to the ground state.

2. Methods

The molecular orbitals are optimized using the (state-averaged) CASSCF method. The equilibrium geometries of the molecules in the ground and the excited states are optimized without symmetry constraint (C_1 symmetry) using the CASSCF energy gradient of the respective states. After that the single-point energy of each state at the equilibrium geometries is calculated using the MRCI [15] with single (MRSCI) and single-double (MRSDCI) excitations and also using the multi-configurational quasi-degenerated perturbation theory (MCQDPT) [16] to take into account dynamic correlation energies. The active space comprises of six active orbitals and six active electrons (CASSCF(6,6)); the active orbitals are composed of the $\pi(\pi^*)$ orbitals and the breaking $\sigma(\sigma^*)$ orbitals. The 6-31G (d,p) basis set with d and p polarization functions (6-31G (d,p)) is used for all the calculations. The ab initio calculations are performed using the MOLPRO2002 and the GAMESS codes [17]. The

diabatic potentials are calculated using the quasi-diabatization method [18]. While the wavefunction character of the adiabatic state is switched at the intersection between the diabatic potentials, the diabatic state keeps its wavefunction character. The two-dimensional MRSCI potential energy surfaces are calculated along the Jacobi coordinates (Figs. 2 and 4). All the other coordinates are optimized using the CASSCF energy gradient of the upper state. The conical intersection is defined as a real crossing point between the multi-dimensional adiabatic potential energy surfaces, which is an $n - 2$ dimensional hyperline (n is the number of degree of freedom) [13,19]. The minimum energy geometry on the conical intersection is optimized using the state-averaged CASSCF energy gradient [19]. The non-adiabatic transition probability (p_{ZN}) is calculated by using the semiclassical Zhu–Nakamura formula [13,14].

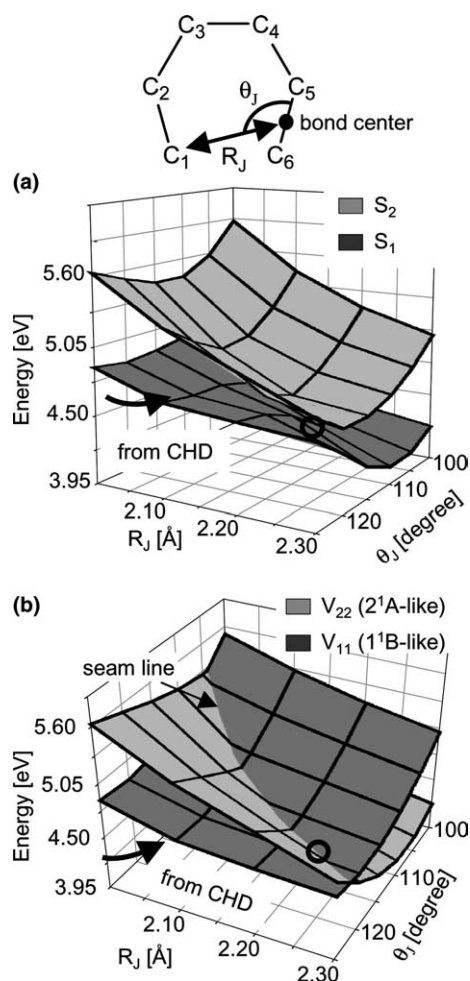


Fig. 2. (a) Adiabatic and (b) diabatic 2-dimensional potential energy surface in the Jacobi coordinate, where the other coordinates are optimized using the 1^1B CASSCF energy gradient at each R_j and θ_j . The ground state CHD corresponds to the $\sim 2 \text{ \AA}$ R_j and the $\sim 130^\circ$ θ_j in this Jacobi coordinate. The circle indicates the position of the S_2 – S_1 conical intersection ($\sim 2.25 \text{ \AA}$ R_j and $\sim 119^\circ$ θ_j).

3. Results and discussions

Fig. 1 shows the overall energetics of the photochemical interconversion of the present system. The equilibrium geometries of CHD and cZc-HT are found to be approximately in the C_2 symmetry. Consequently, the electronic states can be approximately classified by the C_2 rotation into symmetric (A) and anti-symmetric (B). We call these states 1^1A , 2^1A and 1^1B for convenience even at the asymmetric geometries to distinguish the state characters. We also use the notations of S_0 , S_1 and S_2 to indicate the ground, the first and the second excited adiabatic states (Fig. 1). The MRCI and the MCQDPT energies of the 1^1B state are lower than those of the 2^1A state at the ground state equilibrium geometries of CHD and cZc-HT, whereas the CASSCF without dynamic correlation energies incorrectly predicts that the 2^1A state is lower than the 1^1B state. The transition dipole of the $1^1\text{A} \rightarrow 1^1\text{B}$ excitation is larger than that of $1^1\text{A} \rightarrow 2^1\text{A}$ excitation and thus CHD is initially excited to the 1^1B state by photoabsorption (Fig. 1). The equilibrium geometry at the minimum of the 2^1A state is more stable than that of the 1^1B state and thus these two states must intersect at two different points (see the two S_2 – S_1 conical intersections in Fig. 1). The S_1 minimum geometry slightly deviates from the C_2 symmetry due to the asymmetric S_1 wavefunction.

The minimum energy path descending the S_1 potential corresponds to the C_2 symmetric ring-opening motion as described in [12]. However, the mixing of 1^1B and 2^1A states by breaking the C_2 symmetry is definitely necessary for the 1^1B – 2^1A decay, because the transition from S_1 to S_2 completely occurs (i.e. the 1^1B character is completely kept) along the C_2 symmetric minimum energy path. Fig. 2 shows the adiabatic and the diabatic 2-dimensional MRSCI potential energy surfaces around the S_2 – S_1 (1^1B – 2^1A) conical intersection. The ring-opening proceeds by descending the S_1 (1^1B) potential energy surface. The minimum energy gap between the adiabatic potentials is found at the C_2 symmetric molecular geometry (i.e. the S_2 – S_1 conical intersection). The 1^1B – 2^1A seam line is found around the S_2 – S_1 conical intersection. The wavefunction character on the S_1 adiabatic potential energy surface is switched from 1^1B -like to 2^1A -like on passing this seam line. As the molecular geometry deviates from the C_2 symmetric S_2 – S_1 conical intersection, the energy gap between the adiabatic potentials and the diabatic coupling increase. Fig. 3a shows the non-adiabatic transition probability (p_{ZN}) from S_1 to S_2 as a function of the displacement from the S_2 – S_1 conical intersection. Note that small p_{ZN} (i.e. difficult transition to the S_2 state) means easy 1^1B – 2^1A decay. The p_{ZN} decreases as the molecular geometry deviates from the C_2 symmetry. This means that the asymmetric molecular motion induces the gradual state

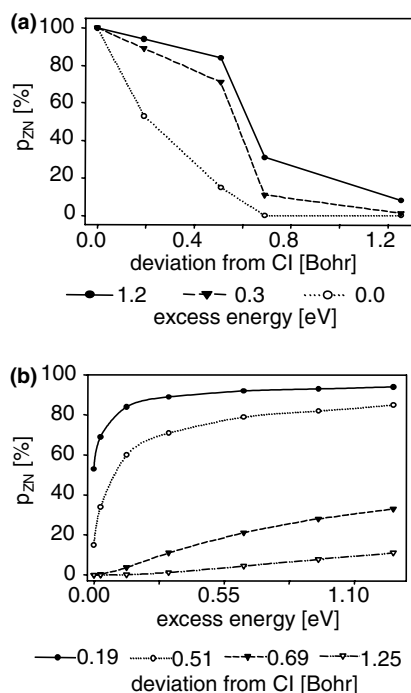


Fig. 3. Non-adiabatic transition probabilities (p_{ZN}) as a function of (a) deviation from the S_2 – S_1 conical intersection (CI) and (b) excess energy to cross the 1^1B – 2^1A seam line, where the directions to cross the seam line are assumed to be approximately perpendicular to the seam line.

character switching from 1^1B -like to 2^1A -like by descending the S_1 adiabatic potential, which corresponds to the experimentally observed rapid 1^1B – 2^1A decay. The relaxation from the ground state equilibrium geometry on the 1^1B potential is expected to generate substantial excess nuclear kinetic energies to cross the seam line (more than ~ 1 eV). As the molecular geometry deviates from the C_2 symmetric S_2 – S_1 conical intersection, the 1^1B – 2^1A decay becomes easier even at the high excess energy (Fig. 3b). On the other hand, even when the excess energy decreases, the 1^1B – 2^1A decay is not efficient in the vicinity of the S_2 – S_1 conical intersection.

Fig. 4 shows the adiabatic (S_1 and S_0) and the diabatic 2-dimensional MRSCI potential energy surfaces. Any local minima corresponding to CHD or cZc-HT are not found on the S_1 potential energy surface; thus these structures are not created before the decay to the S_0 state. The wavefunction character is switched by the motion toward the 5-membered ring and thus the seam line has been found along the C_1 – C_5 distances. Although the seam line along the C_1 – C_6 distance is also found, the non-adiabatic transition along this direction is negligible because of the large S_1 – S_0 energy gap. The relevant C_1 – C_5 distance at the seam line is in the range of 2.2–2.3 Å. The smallest S_1 – S_0 energy gap is found on this seam line, whose position is close to the CASSCF optimized S_1 – S_0 conical intersection. The p_{ZN} along the seam line (Figs. 5a,b) indicate that the S_1 – S_0 non-adiabatic transition

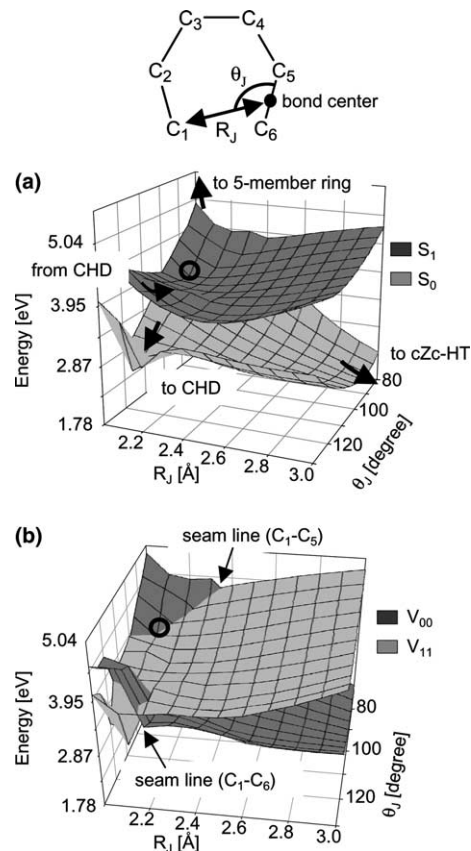


Fig. 4. (a) Adiabatic and (b) diabatic 2-dimensional potential energy surfaces in the Jacobi coordinate, where the other coordinates are optimized using the S_1 CASSCF energy gradient at each R_J and θ_J . The circle indicates the S_1 – S_0 minimum energy gap position (~ 2.1 Å R_J and $\sim 95^\circ$ θ_J).

efficiently occur in the vicinity of the S_1 – S_0 minimum energy gap position. The ring-opening direction after the 1^1B – 2^1A decay is downhill on the S_1 potential, then the molecular motion must swing round toward the 5-membered ring to reach the S_1 – S_0 conical intersection. The short lifetime of the S_1 state [9] implies that the S_1 – S_0 decay occurs before the molecule disperses its kinetic energy from the Franck–Condon region so that it can cross the seam line with sufficient kinetic energy. Although three channels, which correspond to CHD, cZc-H and 5-membered ring, are found on the S_0 potential energy surface, only CHD and cZc-HT can be created after the decay to the S_0 state. The quantum yield of the 5-membered ring is negligible due to the large energy barrier. The direction and the momentum to cross the seam line around the S_1 – S_0 conical intersection are determined by the dynamics on the S_1 potential energy surface starting from the Franck–Condon region. This multi-dimensional dynamics is crucial to determine the CHD/cZc-HT production ratio. This dynamics calculation is now under way and will be reported in a future publication together with the details of the electronic structure computations.

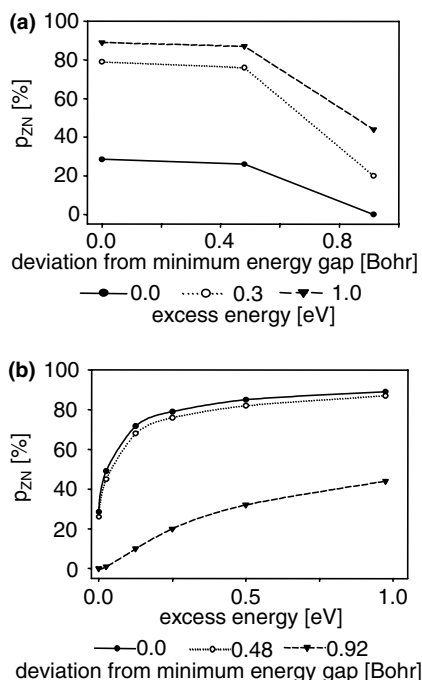


Fig. 5. Non-adiabatic transition probabilities (p_{ZN}) as a function of: (a) deviation from the S_1 – S_0 minimum energy gap position and (b) excess energy to cross the C_1 – C_5 seam line, where the directions to cross the seam line are assumed to be approximately perpendicular to the seam line.

4. Conclusions

In the present Letter, the overall reaction scheme of the CHD/cZc-HT photochemical interconversion has been elucidated using the MRCI calculations and the Zhu–Nakamura non-adiabatic transition probabilities. The CHD/cZc-HT interconversion proceeds via following consecutive steps; (1) photo excitation of CHD to the 1^1B (S_1) state, (2) state character switching from 1^1B to 2^1A with the asymmetric ring-opening motion, and (3) decay to the S_0 (ground) state via the seam line around the S_1 – S_0 conical intersection. The 1^1B and the 2^1A states are mixed by the C_2 -symmetry-breaking motion and the state character is gradually switched from 1^1B to 2^1A as experimentally observed rapid 1^1B – 2^1A decay [5,9]. The S_1 – S_0 non-adiabatic transition occurs along the molecular motion toward the 5-membered ring. The gentle slope on the S_1 potential toward the 5-membered ring and the excess kinetic energy in the region of conical intersection are considered to be responsible for the rapid decay to the ground state via the S_1 – S_0 non-adiabatic transition. The direction and the

momentum to cross the seam line around the S_1 – S_0 conical intersection are expected to play an important role on the CHD/cZc-HT ratio of the ground state product.

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