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Effect of C–C–C bond bending vibration on the photodissociation of cyclobutane

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Abstract

The effect of C–C–C bond bending on the photodissociation of cyclobutane to form two ethylene molecules was investigated by performing semiclassical electron-radiation-ion dynamics simulations and also by examining the potential energy surfaces of the electronic ground state and lowest excited states. These potential energy surfaces, calculated at the CASSCF/MRPT2 level with 6-31G* basis sets along a reaction path determined by the semiclassical dynamics simulations, show well-defined energy minima and maxima in the intermediate state region. It is found that in addition to rotation of the molecule around the central C–C bond, C–C–C bond bending plays an important role in determining the features of the potential energy surfaces for the intermediate species.

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1. Introduction

The dissociation of cyclobutane to form two ethylene molecules is a prototype of an addition/elimination reaction that follows the Woodward–Hoffmann rules [1]. The reaction proceeds either directly through a transition state at the saddle point of the activation barrier, or through a two-step process, with one of the C–C bonds first breaking to form the tetramethylene diradical, which then passes through a transition state, finally forming two molecules of ethylene.

Experimental evidence strongly suggested the existence of the diradical intermediate [2–7]. Using recently developed femtosecond laser techniques, together with a time-of-flight mass spectrometry approach, Zewail's group identified the tetramethylene diradical in the transition state [8] and found

that the lifetime of this immediate varies from 340 to 840 fs depending on the total energy used.

A large number of quantum calculations have been conducted with a focus on the minima and the saddle points of the potential energy surface (PES) for the electronic ground state of tetramethylene, but no consistent results regarding the existence of energy wells near the transition state of the reaction have been obtained [9–19]. Calculations at the CASSCF level found [11,12] two minima and six saddle points on the potential energy surface of tetramethylene. Computations at a higher level indicate [19] that these stationary points and their relative energies are significantly dependent on the level of theory employed. These investigations searched for stationary points exclusively along a reaction path involving only rotation of the diradical about the central C–C bond or dissociation of the second C–C bond.

Here, we report a PES study for the electronic ground state and lowest excited state at the CASSCF/MYPT2 level with 6-31G* basis sets. The potential energy surfaces are calculated by following the reaction path from reactant to product as determined in semiclassical dynamics simulations, as described below in Section 2. The PES calculated in this way involves all

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the nuclear degrees of freedom, and allows us to investigate how the reaction pathway, particularly near the transition state, is affected by different internal coordinates. It is found that the electronic ground state PES shows rather well-defined energy wells, and that both C–C–C bond bending and rotation of the molecule (around the central C–C bond) play important roles in determining the features of the potential energy surfaces for the intermediate species.

2. Methodology

In our semiclassical dynamics simulations, the time-dependent quantum states are calculated for valence electrons, but both the radiation field and the motion of the nuclei are treated classically. The forces acting on the nuclei are calculated using Ehrenfest's theorem, which yields an expression identical in form to that given by the Hellmann–Feynman theorem.

The details of this method have been presented elsewhere [20,21], so only a brief description is given here. The one-electron wavefunctions are updated at each time step by solving the time-dependent Schrödinger equation in a nonorthogonal basis,

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

where \mathbf{S} is the overlap matrix for the atomic orbitals. The laser radiation is included by coupling the vector potential \mathbf{A} of the radiation field to the electrons through the time-dependent Peierls substitution [22]

$$H_{ab}(\mathbf{X} - \mathbf{X}') = H_{ab}^0(\mathbf{X} - \mathbf{X}') \exp\left(\frac{iq}{\hbar c} \mathbf{A} \cdot (\mathbf{X} - \mathbf{X}')\right). \quad (2)$$

Here, $H_{ab}(\mathbf{X} - \mathbf{X}')$ is the Hamiltonian matrix element for basis functions a and b on atoms with position vectors \mathbf{X} and \mathbf{X}' , respectively, and $q = -e$ is the charge of the electron.

The Hamiltonian matrix, overlap matrix, and effective nuclear–nuclear repulsion are based on density-functional calculations [23].

The nuclear motion is determined by the Ehrenfest equation of motion

$$M_l \frac{d^2 X_{l\alpha}}{dt^2} = -\frac{1}{2} \sum_j \Psi_j^+ \cdot \left(\frac{\partial \mathbf{H}}{\partial X_{l\alpha}} - i\hbar \frac{1}{2} \frac{\partial \mathbf{S}}{\partial X_{l\alpha}} \cdot \frac{\partial}{\partial t} \right) \cdot \Psi_j - \frac{\partial U_{\text{rep}}}{\partial X_{l\alpha}}, \quad (3)$$

where U_{rep} is the effective nuclear–nuclear repulsive potential.

The time-dependent Schrödinger Eq. (1) is solved using a unitary algorithm which is based on the equation for the time evolution operator [24]. Eq. (3) is numerically integrated with the velocity Verlet algorithm (which preserves phase space). A time step of 50 as (where as represents attoseconds) was chosen because it was found to result in good energy conservation.

The laser pulse was selected to have a full-width-at-half-maximum (FWHM) duration of 100 fs with an approximately Gaussian profile, a fluence of 0.90 kJ/m², and a wavelength

corresponding to a photon energy of 6.50 eV. (This wavelength was selected to match the density-functional energy gap between the HOMO and LUMO levels of cyclobutane.) The fluence was chosen such that the forces on the nuclei are just sufficient to break two nonadjacent C–C bonds successively, but not to break any C–H bond.

The potential energy surfaces of both the electronic ground state and the first excited state were calculated at the CASSCF/MRPT2 level with 6-31G* basis sets, using the XIAN CI code [25] with no symmetry restriction; four electrons and four orbitals were included in the active space. For tetramethylene, the degeneracy due to states of the same symmetry and spin multiplicity are broken by including states outside the active space, labeled by β . First the energies and corresponding eigenvectors were obtained in standard CASSCF calculations:

$$E_0^i, \Psi_0^i = \sum_{R \in \text{CAS}} C_R^i \Phi_R (i = 1, 2, \dots). \quad (4)$$

Then Rayleigh–Schrödinger perturbation theory was used to obtain the nondegenerate energies using an iterative procedure:

$$E^i = E_0^i + \sum_{\beta \notin \text{CAS}} \frac{|\langle \Psi_0^i | \mathbf{H} | \Phi_\beta \rangle|^2}{E_0^i - E_\beta}. \quad (5)$$

In Eq. (5), the E_β are the energies calculated in the previous iteration.

3. Results and discussion

Six snapshots from the simulation at different times are shown in Fig. 1. Starting with the coupling of the laser pulse to the molecule at $t = 0$ fs, at about 190 fs the C₁–C₃ bond is broken and the tetramethylene intermediate is formed. The diradical rotates about the central C–C bond from 0° to –100°, as can be seen in Fig. 1c, and then turns back to 55°, as seen in Fig. 1d and e. At about 380 fs, the C₂–C₄ bond is broken and two ethylene molecules are produced. The lifetime of the tetramethylene intermediate, as defined by the time until the second C–C bond is broken, is found in the simulation to be comparable to the experimental value of 340 fs. After 450 fs, the two ethylenes move away from each other.

The variation of the C₁–C₂ bond with time is presented in Fig. 2. A single bond in cyclobutane becomes a double bond in ethylene. The results of this figure clearly show that the C₁–C₂ bond initially is about 0.155 nm, the length of a typical C–C single bond, and starts to vibrate after the laser pulse is applied. After 190 fs, the C₁–C₂ bond length decreases but is still longer than 0.135 nm, the length of a regular C–C double bond, indicating the formation of the diradical. Then the C₁–C₂ bond is shortened to about 0.135 nm until about 400 fs and remains at this length until the end of the simulation, indicating the dissociation of the diradical into two molecules of ethylene.

The potential energy surfaces for both the electronic ground state and the first excited state of the molecule as a function of time are presented in Fig. 3, where they are also compared with the variation of the C₁–C₂–C₄–C₃ torsional angle. It should be mentioned that the energy curves of Fig. 3 are one-dimensional

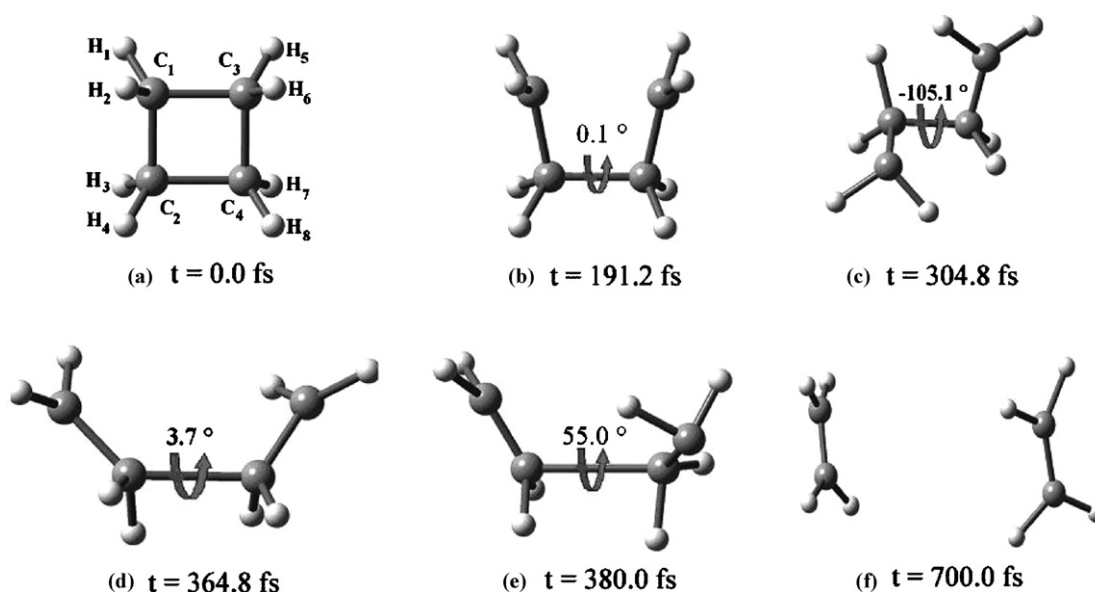


Fig. 1. Snapshots from semiclassical dynamics simulation of the photodissociation of cyclobutane to form two ethylene molecules. Note that the first C–C bond is broken at about 190 fs, and the second at about 380 fs. All atoms are labeled in (a). The rotation of tetramethylene about the central C–C bond is also indicated. An animation file for this reaction is available at http://www.nicholls.edu/phsc/you/ring_opening_cyclobutane.htm.

“potential energy surfaces”, corresponding to the classical nuclear trajectories determined “on the fly” in a simulation, for which the dynamics is given by Eqs. (1)–(3). Both PES curves show a reaction intermediate state, roughly between 200 and 450 fs. Two rather well-defined energy wells occur in the ground state PES, one at about 330 fs and another at about 410 fs. The C_1 – C_2 – C_4 – C_3 torsional angle does not vary significantly before the tetramethylene intermediate diradical is formed at about 200 fs. After this time, the diradical rotates about the C_2 – C_4 bond during the next 100 fs, from 0° to about -100° , and then turns back. It passes through 0° at about 365 fs and continues trivially to increase due to the fact that the C_2 – C_4 bond is broken. Two energy wells of the electronic ground state PES, occurring at torsional angles of about -100° and 100° , respectively, suggest that the large deviation of the C_1 – C_2 – C_4 –

C_3 torsional angle from its initial value of 0° acts to lower the potential energy of the reaction immediate.

Fig. 4 presents two PES curves as functions of time, compared with the time dependence of the C_2 – C_4 – C_3 angle. It can be seen that the C_2 – C_4 – C_3 angle experiences large-amplitude angle-bending vibrations, between 200 and 400 fs, due to breaking of the C_1 – C_3 bond to form the diradical. It can also be seen, in Fig. 4, that the electronic ground state PES is greatly affected by the variations in the C–C–C angles: the two energy wells are associated with C–C–C angles near 90° (the initial value in cyclobutane), while the higher energy regions, at about 240, 350 and 440 fs, respectively, are associated with C–C–C angles substantially different from 90° . These results suggest that the C_1 – C_2 – C_4 – C_3 torsional angle and the C–C–C angles are the main internal reaction coordinates that affect the

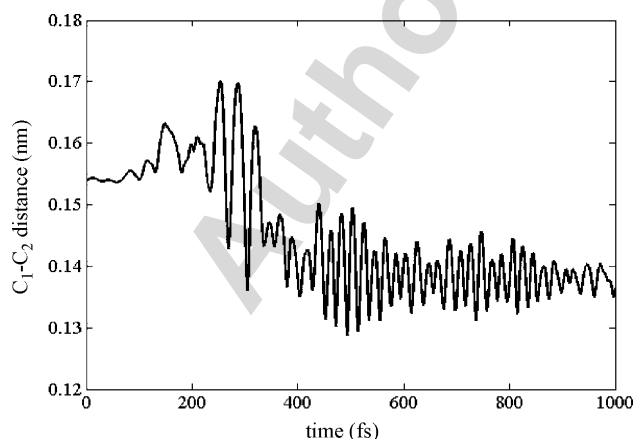


Fig. 2. Time dependence of a C–C bond ultimately associated with one ethylene molecule. Notice that this bond begins to shorten in the intermediate state, and becomes a double bond after dissociation.

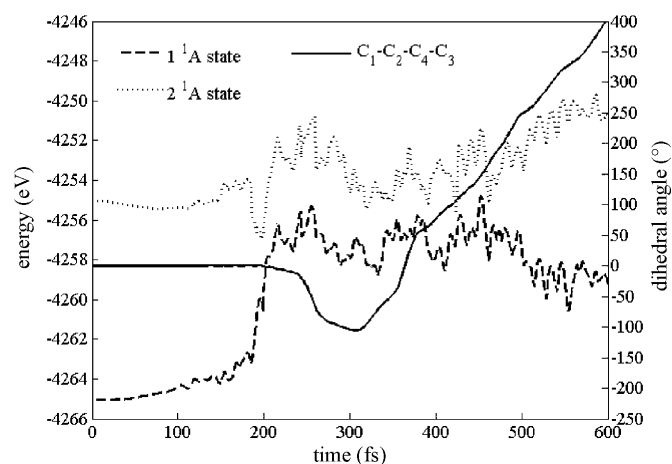


Fig. 3. Potential energy surfaces (as defined in the text) for the electronic ground state and lowest excited state of the molecule, calculated at the CASSCF/MRPT2 level with 6-31G* basis sets, compared with the time-dependent C_1 – C_2 – C_3 – C_4 dihedral angle.

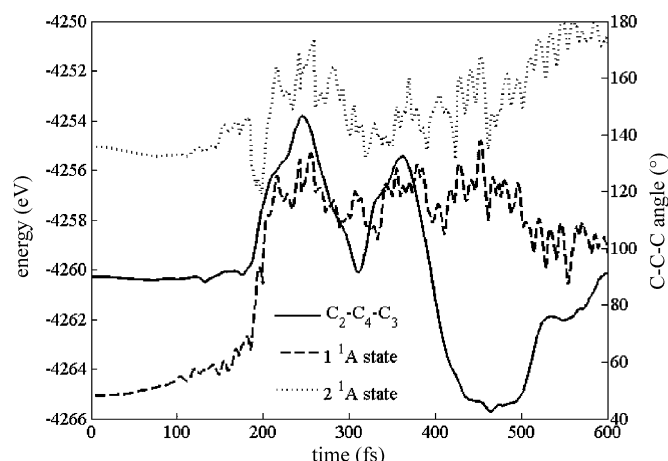


Fig. 4. Potential energy surfaces (as defined in the text) for the electronic ground state and lowest excited state of the molecule, compared with the time-dependent $C_2-C_4-C_3$ bond bending angle.

features of the ground state potential energy surface in the intermediate state region: expansion of the $C-C-C$ angle appears to rise the ground state energy, while rotation of the molecule about the C_2-C_4 bond (away from 0°) lowers it. The same discussion can be applied to the first excited state, whose PES is also presented in Figs. 3 and 4.

4. Conclusions

The PES of the electronic ground state in the photodissociation of cyclobutane, calculated along the reaction path determined in the semiclassical dynamics simulations, shows well-defined energy wells in the intermediate state region. The variations of both the $C_1-C_2-C_4-C_3$ torsional angle and the $C-C-C$ angles greatly affect the appearance of the ground state PES of the intermediate diradical. Enlargement of the $C-C-C$ angle appears to raise the ground state energy, while rotation of the molecule about the C_2-C_4 bond (away from the initial geometry) lowers it.

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