

# Effect of C-C-C Bond Bending on Photodissociation of Cyclobutane

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## Abstract

The potential energy surfaces for the electronic ground state and lowest excited state of cyclobutane, during photodissociation into two molecules of ethylene, were calculated at the CASSCF/MYPT2 level with 6-31G\* basis sets, along the reaction path determined in semiclassical dynamics simulations. The calculations show that there are well-defined energy minima and maxima in the intermediate state region and 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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## I. Introduction

The dissociation of cyclobutane to form two ethylene molecules is a prototype of an addition/elimination reaction which follows the Woodward-Hoffmann rules [1]. Such a reaction might proceed 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 yielding two molecules of ethylene.

Early experimental evidence strongly suggested the existence of the diradical intermediate [2-7]. Later, using femtosecond laser techniques, together with a time-of-flight mass spectrometry approach, Zewail's group identified the tetramethylene diradical as the intermediate state [8] and found that its lifetime varies from 340 to 840 fs depending on the energy of the laser pulse.

A large number of quantum calculations have been conducted, focusing on 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 [11,12] found two minima and six saddle points on the tetramethylene PES. Computations at a higher level indicate [19] that these stationary points and their relative energies are significantly dependent on the level of theory employed. The stationary points in these investigations were determined along a reaction path which involves only rotation of the diradical about the central C-C bond, together with dissociation of the second C-C bond.

Here we report a study of the potential energy surfaces for the electronic ground state and lowest excited state, at the CASSCF/MYPT2 level with 6-31G\* basis sets. These potential energy surfaces are calculated by following the path from reactant to product as determined in a semiclassical dynamics simulation, which is performed using the methods described in the next section. The energy surfaces calculated in this way involve all the nuclear degrees of freedom, and allow 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.

## II. Methodology

In our semiclassical dynamics simulations, the time-dependent quantum states are calculated for the valence electrons, but both the radiation field and the motion of the nuclei are treated classically. The forces acting on the nuclei are calculated from Ehrenfest's 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

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

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

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

The laser pulse was taken to have a full-width-at-half-maximum (FWHM) duration of 100 fs, a fluence of 0.90 kJ/m<sup>2</sup>, 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 enough 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, and with 4 electrons and 4 orbitals 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  $\beta$ . First the energies and corresponding eigenvectors were obtained in standard CASSCF calculations:

$$\mathbf{E}_0^i, \Psi_0^i = \sum_{R \in CAS} \mathbf{C}_R^i \Phi_R \quad (i=1, 2, \dots). \quad (4)$$

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

$$\mathbf{E}^i = \mathbf{E}_0^i + \sum_{\beta \notin CAS} \frac{|\langle \Psi_0^i | \mathbf{H} | \Phi_\beta \rangle|^2}{\mathbf{E}_0^i - \mathbf{E}_\beta} \quad (5)$$

where the  $\mathbf{E}_\beta$  are the energies calculated in the previous iteration.

### III. 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  $t = 0$ , at about 190 fs the C<sub>1</sub>-C<sub>3</sub> 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 1e. At about 380 fs, the C<sub>2</sub>-C<sub>4</sub> bond is broken and two ethylene molecules are produced. The lifetime of the tetramethylene intermediate found in the simulation, as defined by the time until the second C-C bond is broken, is comparable to the experimental value of 340 fs. After 450 fs, the two ethylenes move away each other.

The variation of the C<sub>1</sub>-C<sub>2</sub> bond with time is presented in Fig. 2. This is a single bond in cyclobutane, but it becomes a double bond in ethylene. One can clearly see that the C<sub>1</sub>-C<sub>2</sub> bond initially is about 0.155 nm, the length of a typical C-C single bond, and that it starts to vibrate after the laser pulse is applied. After 190 fs, the C<sub>1</sub>-C<sub>2</sub> 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, at about 400 fs, the C<sub>1</sub>-C<sub>2</sub> bond is shortened to about 0.135 nm, and it 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 electronic ground state and the first excited state of the molecule as a function of time are presented in Fig. 3, compared with the variation of the C<sub>1</sub>-C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> torsional angle. It should be noted that the energy curves of Fig. 3 are one-dimensional 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<sub>1</sub>-C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> 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<sub>2</sub>-C<sub>4</sub> bond, from 0° to about -100° during the next 100 fs, and then turns back. It passes through 0° at about 365 fs and continues trivially to increase after the C<sub>2</sub>-C<sub>4</sub> bond is broken. Two energy wells of the electronic ground state PES, near the torsional angles of about -100° and 100°, suggest that these large deviations of the C<sub>1</sub>-C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> torsional angle from its initial value of 0° lower the potential energy of the reaction intermediate.

Fig. 4 presents two PES curves as a function of time, compared with the time dependence of the C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> angle. It can be seen that, between 200 and 400 fs, the C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> angle experiences large-amplitude angle-bending vibrations due to the breaking of the C<sub>1</sub>-C<sub>3</sub> 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  $90^\circ$  (the initial value in cyclobutane), while the higher energy regions at about 240, 350 and 440 fs are associated with C-C-C angles substantially different from  $90^\circ$ . 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 features of the ground state potential energy surface in the intermediate state region: Expansion 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  $0^\circ$ ) lowers it. The same discussion can be applied to the first excited state, whose PES is also presented in Figs. 3 and 4.

#### **IV. Conclusions**

The PES of the electronic ground state for cyclobutane during photodissociation, 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 bond-bending angles greatly affect the features of the ground state PES for the diradical intermediate. Increase of the C-C-C angle appears to raise the ground state energy, while the rotation of the molecule about the  $C_2-C_4$  bond away from its initial value lowers it.

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## FIGURE CAPTIONS

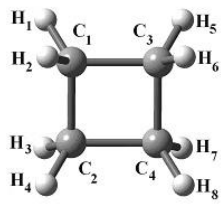
**FIG. 1.** Snapshots from semiclassical dynamics simulation of the photodissociation of cyclobutane to form two ethylene molecules. Note that the first C-C bond is broken at about 190 fs, and the second at about 365 fs. All atoms are labeled in a. The rotation of tetramethylene about the central C-C bond is also indicated. An animation file for this reaction is available at [http://www.nicholls.edu/phsc/you/ring\\_opening\\_cyclobutane.htm](http://www.nicholls.edu/phsc/you/ring_opening_cyclobutane.htm)

**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.

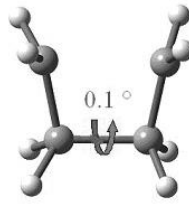
**FIG. 3.** Potential energy surfaces (as defined in the text) for the electronic ground state and lowest excited state of the molecule, calculated at the CASSCF/MRPT2 level with 6-31G\* basis sets, compared with the time-dependent  $C_1-C_2-C_3-C_4$  dihedral angle.

**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.

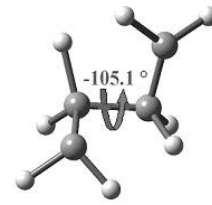
FIG. 1.



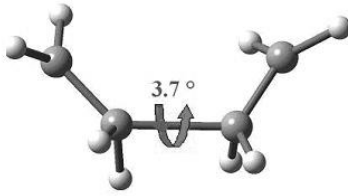
a  $t = 0.0$  fs



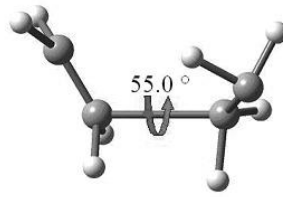
b  $t = 191.2$  fs



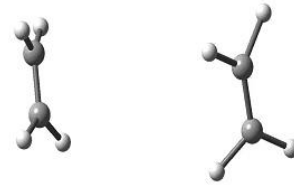
c  $t = 304.8$  fs



d  $t = 364.8$  fs



e  $t = 380.0$  fs



f  $t = 700.0$  fs

FIG. 2.

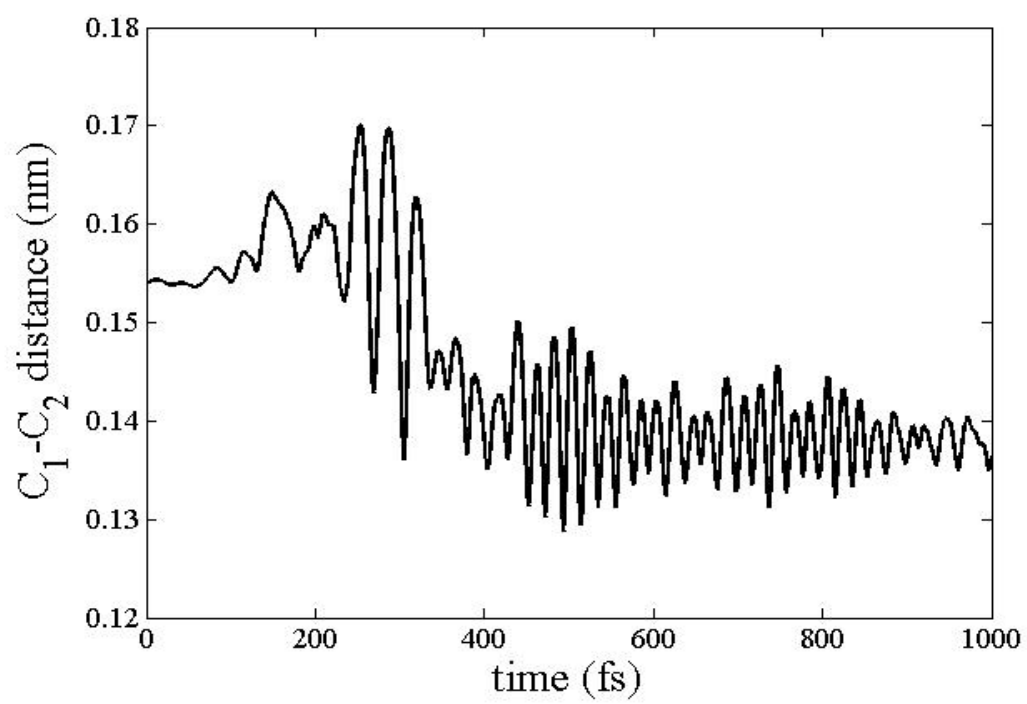


FIG. 3.

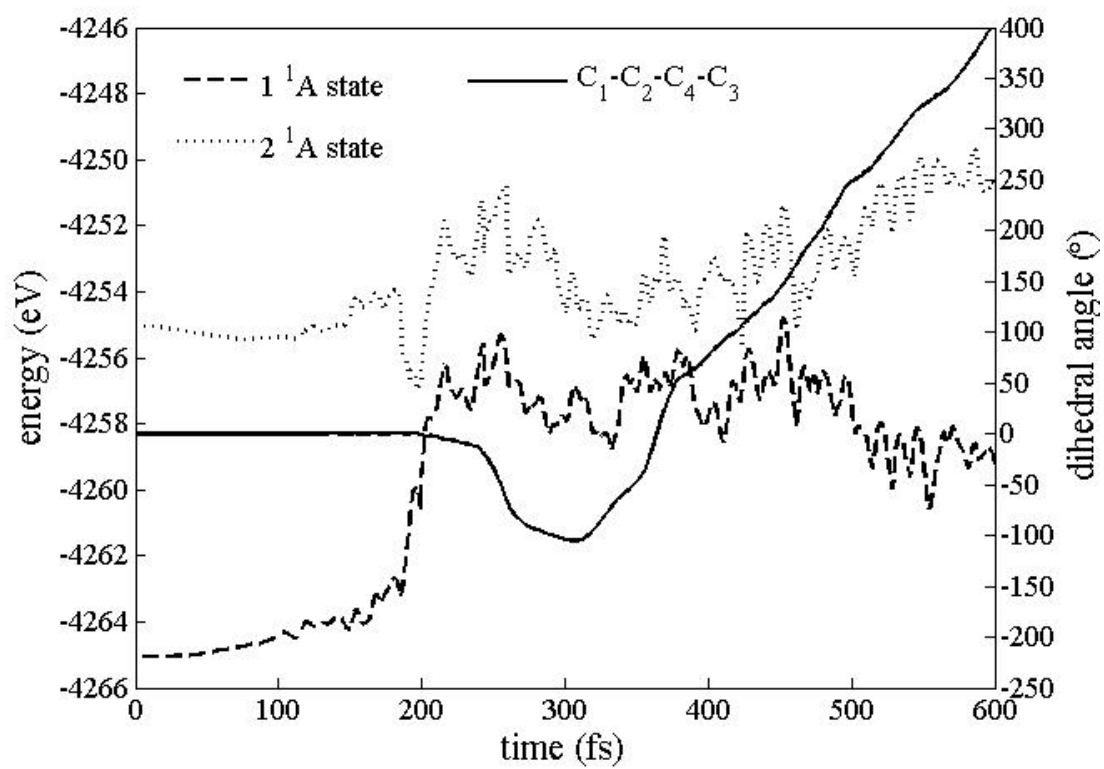


FIG. 4.

