Direct Observation of Disrotatory Ring-Opening in Photoexcited Cyclobutene Using ab Initio Molecular Dynamics

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The electrocyclic ring-opening reaction of cyclobutene (to 1,3 butadiene) is a classic example of a pericyclic rearrangement whose outcome is predicted by the Woodward−Hoffmann (WH) rules[1] and complementary theories.[2,3] The WH rules predict that for reactants containing $4n + 2$ π-electrons the photochemical ring opening reaction will proceed with disrotatory stereochemistry, while for reactants with $4n$ π-electrons the photochemical ring opening will proceed in conrotatory fashion. For the case of cyclohexadiene, this prediction (conrotatory) has been experimentally confirmed[4] using both stereochemical analysis of the products in alkyl-substituted reactants[5−7] and resonance Raman spectroscopy.[8,9] Somewhat surprisingly, the results for the smaller cyclobutene (CB) molecule are less conclusive. Alkyl substitutions of CB have produced mixtures of allowed (disrotatory) and forbidden (conrotatory) photoproducts[10] and, because of controversies in the assignment of some bands,[11,12] the interpretation of resonance Raman experiments[13,14] (which provide a more direct probe of the excited-state dynamics) has been questioned.[15] On the basis of the original assignment of the vibrational force field of CB,[16] and a later assignment by Craig and co-workers,[11] the resonance Raman spectrum[13] has been interpreted to show traces of a disrotatory ring opening.[13,14] However, on the basis of their own assignment of the vibrational force field and on their interpretation of the assignment of Wiberg and Rosenberg,[12] Negri and co-workers[15] concluded that the resonance Raman spectrum does not show "any positive hint of the activity of distrotatory ring opening motion."

In this paper we present the results of ab initio "on the fly" molecular dynamics simulations which for the first time directly probe the photodynamics of CB, following $\pi \rightarrow \pi^*$ electronic excitation. This first principles investigation shows that the initial motion projects directly and significantly onto the disrotatory ring-opening reaction coordinate.

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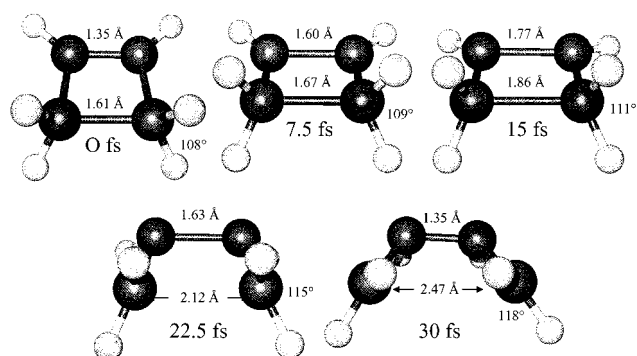(12) Wiberg, K. B.; Rosenberg, R. E. *J. Phys. Chem.* **1992,** *96,* 8282.
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Figure 1. Snapshots of a typical excited-state trajectory. The values of the CC double and single bond distances, as well as the HCH hybridization angle, are indicated.

The calculations detailed here use the ab initio multiple spawning (AIMS) method that we have developed for first-principles quantum dynamics.[17,18] Electronically nonadiabatic effects, that is, surface-crossing, are allowed in the nuclear dynamics but were not observed in the short-time dynamics which is the focus of this report. The longer time dynamics leading to ground state photoproduct is probably mediated by a conical intersection, as is found in the photochemical ring-closure of butadiene.[19] The electronic structure problem is solved using a single set of "best-compromise" molecular orbitals that are determined for the relevant electronic states ($\pi\pi$ and $\pi\pi^*$). These state-averaged orbitals are expanded in a double-ζ Gaussian basis set,[20] and they are determined by minimizing an energy expression in which one electron is placed in each of the orbitals which is of variable occupation in the relevant electronic states. For the present case, these are the π and π^* orbitals of the C=C bond, as well as the σ and σ^* orbitals of the C−C bond which is destined to break. All electronic configurations resulting from rearrangement of these four electrons in the four active orbitals are used as references in a multireference configuration interaction (MRCI) including single excitations. The use of a MRCI wave function provides the flexibility to describe the orbitals of both electronic states and additionally includes some electron correlation effects. Previous workers have found similar MRCI methods to be very effective in describing excited states.[21] At each time step the necessary potentials, gradients, and nonadiabatic coupling matrix elements are obtained using this procedure. Diffuse electronic basis functions are not included in the calculations. Thus, we do not expect to reliably model those (long time) features of the photochemistry (formation of ethylene, acetylene, and methylenecyclopropane photoproducts[10,22]) that are thought to arise from excitation to a low-lying $\pi \rightarrow 3$s Rydberg state. Instead, our treatment focuses on the features which arise due to the state with the strongest oscillator strength: the $\pi \rightarrow \pi^*$ excited state. We report averaged, short time (50 fs), results for four trajectories whose initial conditions were sampled from the Wigner distribution[23] for the ground-state molecule in the harmonic approximation.

A few snapshots of a typical excited-state trajectory are shown in Figure 1, and we discuss the observed geometrical changes in

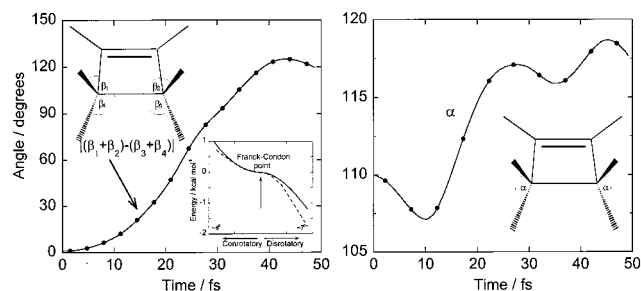(17) Ben-Nun, M.; Martínez, T. J. *Chem. Phys. Lett.* **1998,** *298,* 57.
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Figure 2. Left panel: The absolute value of the average disrotatory angle as a function of time in fs. The lower inset depicts a one-dimensional cut of the excited-state PES. The full and dashed lines correspond to two levels of electronic structure calculations (see text for details). Right panel: the average HCH hybridization angle (see inset for definition) as a function of time in fs.

chronological order. Following the electronic excitation the first motion is a stretching of the C=C bond. (Within 15 fs, the C=C bond extends by ~0.4 Å.) This is expected for a $\pi \rightarrow \pi^*$ transition and is in agreement with the resonance Raman spectrum[13] that is dominated by the totally symmetric C=C stretching mode. An impulsive change in the hybridization of the methylenic carbons is also observed. As the CH_2-CH_2 bond breaks the HCH angle changes from ~109° (sp³) to ~120° (sp²). The change in hybridization begins almost immediately after the electronic excitation and is completed within 50 fs (see right panel of Figure 2). In the resonance Raman spectrum,[13] this motion is manifested by a pronounced activity of the totally symmetric CH_2 scissors mode. Finally, and most importantly, Figure 1 clearly (and unambiguously) shows that the excited-state dynamics are directed along the WH-predicted disrotatory reaction coordinate. In fact, this is the most pronounced feature observed in Figure 1. In the left panel of Figure 2 we plot the absolute value of the average disrotatory angle as a function of time. The left inset of this panel defines the disrotatory coordinate, a coordinate that is *not* a normal mode of the molecule. The disrotatory motion begins approximately 10 fs after the electronic excitation and its amplitude is large (120°). No significant motion is observed along the conrotatory reaction coordinate. The right inset in the left panel of Figure 2 explains these observations. Here we show (solid line) a one-dimensional cut of the excited-state potential energy surface (PES) along the disrotatory and conrotatory coordinates (all other coordinates are kept at their ground-state equilibrium value). The Franck−Condon point on the excited electronic state remains a minimum with respect to conrotatory motion, but becomes unstable with respect to disrotatory motion. The dynamical conclusions we draw concerning the rapid onset of disrotatory motion arise largely because of the form of the excited-state PES shown in the inset. Thus, we have also computed this cut (dashed line) using the MOLPRO program[24] with a larger cc-pVTZ basis set[25] and a more sophisticated electronic wave function.[26] The same qualitative behavior is observed.

The interpretation of resonance Raman spectra is critically dependent on the assignment of the observed vibrational frequencies in the normal mode approximation. Hence it is crucial that (a) the coordinate of interest corresponds to a single normal mode

and (b) the frequency of this normal mode be correctly assigned. In the case of CB this has resulted in some controversy. The disrotatory motion is a nontotally symmetric coordinate (b_1 symmetry), projecting only on nontotally symmetric normal modes that may appear as odd overtones in the experimental spectra. Mathies and co-workers[13] observed an overtone of the 1075 cm^{-1} mode at 2150 cm^{-1}. Using the normal mode assignment of previous workers[11,16] they concluded that this mode is a nontotally symmetric CH_2 twist, projecting directly onto the disrotatory twist of the CH_2 groups. In 1995, this interpretation was challenged by Negri and co-workers,[15] who revisited the normal-mode analysis of CB. They concluded, in agreement with a previous assignment by Wiberg,[12] that the 1075 cm^{-1} mode is mainly a CH_2 deformation (and not twist), while the lower frequency 848 cm^{-1} mode is a CH_2 twist mode with a dominant disrotatory component. This conflicting assignment of the CB normal modes led to the conclusion that the overtone at 2150 cm^{-1} does not provide any proof of disrotatory motion. Instead, Negri argued that the overtone of the 848 cm^{-1} mode would provide such proof. Unfortunately, one cannot determine if this overtone is present because of the intense band at 1650 cm^{-1}, which is attributed to butadiene photoproduct.[13]

Since it is unlikely that any normal mode is solely disrotatory, we analyzed the projection of the symmetry adapted local modes on the normal modes as detailed in Supporting Information. The ground state normal modes were calculated using the Jaguar program[27] for a GVB(2/4) wave function[28] with the same basis set used in the AIMS dynamics. We find that two of the normal modes have significant disrotatory character, implying that analysis of the intensities of overtones in both modes is required for a quantitative statement about the extent of disrotatory motion during the resonance Raman experiment. Since one of these overtones is masked by butadiene scattering, one should instead turn to either pump−probe[29] or excited-state resonance Raman[30] experiments to find experimental evidence of early disrotatory motion in CB.

In summary, the results of excited state ab initio molecular dynamics simulations provide the first direct observation of ultrafast disrotatory ring-opening motion in CB. Our results show that the preference for the WH-predicted stereochemistry is established shortly (within ~15 fs) after the electronic excitation. Although we did not observe any motions in violation of the WH rules (e.g., conrotatory motion, rotation of single CH_2 groups), we cannot exclude the possibility that these motions would be observed on a longer time scale or with a larger ensemble of trajectories. Future studies will address this issue. Our results imply that disrotatory motion is in principle observable in the resonance Raman spectrum. However, analysis of the ground-state normal modes shows that the lowest overtone of interest will be masked by intense scattering from butadiene photoproduct. Therefore, further experiments are needed to confirm the theoretical predictions that we make here.

Supporting Information Available: Table of vibrational assignments and results of symmetry adapted internal coordinates analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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