

Direct Investigation of the Photochemical Ring-Opening Dynamics of Cyclobutene with Resonance Raman Intensities

Mary K. Lawless, Steven D. Wickham, and Richard A. Mathies*

Department of Chemistry
University of California
Berkeley, California 94720

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The Woodward–Hoffmann (WH) rules^{1a} and complementary theories^{1b} have provided a powerful framework for predicting the stereochemistry of thermal and photochemical pericyclic reactions. A classic example is the electrocyclic ring-opening of cyclobutene (CB) to 1,3-butadiene, whose photochemistry is predicted to occur with a disrotatory motion of the CH₂ groups.¹ This reaction has been investigated experimentally² and theoretically.³ Photolysis of CB at 185 nm^{2d} leads to 1,3-butadiene ($\phi = 0.43$) and methylenecyclopropane ($\phi = 0.12$); the latter is thought to arise from a low-lying Rydberg state.^{2e} While the thermal reaction proceeds with conrotatory stereochemistry,⁴ only one study of a substituted CB has indicated that the disrotatory route is photochemically preferred.^{2b,f,g} No experimental investigations of the stereochemistry and dynamics of CB itself have been reported. We present here the 200-nm resonance Raman spectrum of cyclobutene, which exposes the excited-state nuclear dynamics that occur immediately after excitation.

We have used resonance Raman scattering intensities to examine the excited-state dynamics of the conrotatory and disrotatory ring-opening reactions of 1,3-cyclohexadiene⁵ and 1,3,5-cyclooctatriene,⁶ respectively, and the [1,7] sigmatropic hydrogen shift of 1,3,5-cycloheptatriene,⁷ revealing mode-specific information on how each molecule moves out of the Franck–Condon region. When excitation is on resonance with an allowed electronic transition, the intensity of resonance Raman vibrational scattering depends upon the changes in the nuclear potential energy surface that occur upon electronic excitation.⁸ For a non-totally symmetric mode, a change in excited-state frequency will

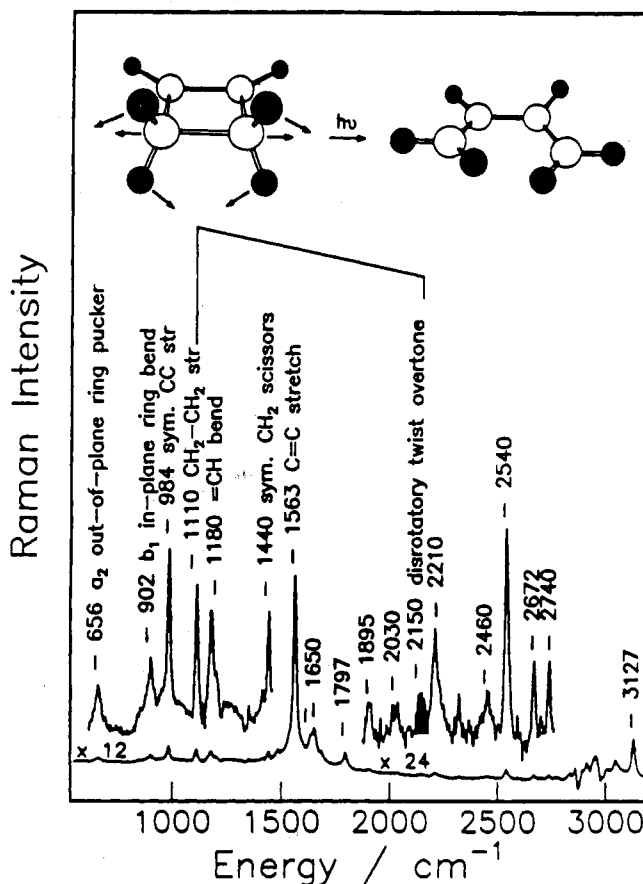


Figure 1. Resonance Raman spectrum of a liquid jet of cyclobutene¹⁰ in cyclopentane excited with a Nd:YAG laser that was H₂-shifted to 200 nm (15 μ J/pulse, 20 Hz, $\sim$ 30- μ m-diameter beam) obtained following the methods of ref 6. The full spectrum has been corrected for the wavelength dependence of the detection system, self-absorption, and chromatic aberration, but no fluorescence background has been subtracted. The residual features from solvent subtraction at 2900–3000 cm⁻¹ are $\sim$ 2% of their original intensity. The arrows superimposed on the ground-state structure of cyclobutene give the geometry changes that occur $\sim$ 30 fs after excitation as a result of evolution along the indicated CH₂–CH₂ stretch and b₂ CH₂ twist normal modes.

give rise to even overtone scattering, resulting from the spreading of the wavepacket on the excited-state surface. For fundamental scattering in a totally symmetric mode, the difference in equilibrium geometry (Δ) causes the excited-state wavepacket to move along that coordinate, leading to the development of overlap with the final state of the Raman process and resonance Raman intensity in that fundamental.⁸ The resonance Raman spectrum of 1,3-cyclohexadiene reveals an intense symmetric CH₂ twist, indicating that motion along the conrotatory reaction coordinate occurs immediately after excitation,⁵ while the spectra of the nonplanar 1,3,5-cyclooctatriene and 1,3,5-cycloheptatriene molecules indicate evolution mainly along ring-planarization coordinates.^{6,7} This led to the hypothesis that a planar carbon skeleton was required before pericyclic rearrangements would occur. The resonance Raman spectrum of CB presented here completes the series and provides a unique chance to examine the disrotatory ring-opening reaction of a planar⁹ system, thereby directly testing our hypothesis.

Figure 1 presents the resonance Raman spectrum of cyclobutene excited at 200 nm.¹⁰ From this spectrum and normal mode

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(10) Cyclobutene was prepared following Salaun and Fadel: Salaun, J.; Fadel, A. *Org. Synth.* **1986**, *64*, 50–56. Purity and structure were determined by solvent-decoupled ¹H NMR; only NMR spectral lines for CB were observed ($\delta = 2.56$ ppm, s, 4H; $\delta = 6.01$ ppm, s, 2H).

* Address correspondence to this author.

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assignments¹¹ we can describe the nuclear dynamics that occur immediately after excitation. As expected for a $\pi-\pi^*$ transition, the most intense peak is the ethylenic mode at 1563 cm^{-1} , indicative of an increase in its equilibrium bond distance upon excitation.¹² Enhancement of the 984- and 1110- cm^{-1} modes indicates changes in the equilibrium bond lengths of the three C-C single bonds, including the CH_2-CH_2 bond, which breaks as the ring-opening proceeds. The symmetric CH_2 scissors mode at 1440 cm^{-1} parallels the change in hybridization of the methylene carbons as the CH_2-CH_2 bond breaks: the HCH bond angle must change from 109° (sp^3) for CB^9 to 120° (sp^2) for 1,3-butadiene. The most intriguing feature of the spectrum is the intensity of the 2150- cm^{-1} peak in the overtone region;¹⁴ this corresponds to the first overtone of the non-totally symmetric CH_2 twist (b_2 in the C_{2v} point group), whose fundamental is not observed because it is symmetry forbidden for A-term resonance Raman scattering. *This mode projects directly onto the disrotatory twist of the CH_2 groups, indicating that evolution along the reactive coordinate occurs directly out of the Franck-Condon region via a decrease in the excited-state frequency of this mode.*¹⁵ This evolution is depicted by the arrows on the molecular model of CB in Figure 1. Also, the symmetric CH_2 twist at 1145 cm^{-1} is not observed, indicating that no initial evolution occurs along the conrotatory reaction coordinate. The low fluorescence background beneath the resonance Raman spectrum suggests a very low fluorescence quantum yield due to a short electronic state lifetime (T_1). This phenomenon has been observed in previous studies of pericyclic photochemical reactions and can be explained by a femtosecond internal conversion to a lower-lying excited electronic state of A_1 symmetry.^{5-7,16}

In addition to the disrotatory twist, the 200-nm spectrum reveals activity in other non-totally symmetric modes. The peak at 656 cm^{-1} corresponds to the first overtone of the 328- cm^{-1} a_2 out-of-plane ring pucker. Due to Rayleigh interference, we were unable to determine if the 328- cm^{-1} fundamental is enhanced at 200 nm. However, from the small intensity of the combination of the 328- and 1563- cm^{-1} modes at 1895 cm^{-1} , we infer that the fundamental is deriving some B-term resonance enhancement via vibronic coupling,¹⁷ suggesting that the initial dynamics of the ring-opening reaction in CB also involve a torsion about the C=C bond. This makes sense since the CH_2 groups in the *s-cis* product are expected to assume a gauche conformation¹⁸ and a torsion would be necessary to bring the planar CB ring to this geometry. The B-term intensity of the non-totally symmetric (b_1) in-plane ring-bending fundamental at 902 cm^{-1} indicates involvement of this mode in the vibronic coupling of two electronic transitions.¹⁷ We also see a very intense mode at 1797 cm^{-1} which can only be assigned as the first overtone of the 902- cm^{-1} mode.¹⁹ This in-phase ring-bending mode projects strongly onto the motion necessary to produce the methylenecyclopropane photoproduct, suggesting that initial motion along this reaction coordinate also begins in the Franck-Condon region.

The resonance Raman intensities of cyclobutene indicate that the initial photochemical dynamics are directed along the Woodward-Hoffmann-predicted disrotatory ring-opening reaction coordinate. The disrotatory twisting of the CH_2 groups is accompanied by changes in the bond lengths of the carbon skeleton, changes in the HCH bond angles of the methylene groups, and an out-of-plane pucker of the carbon ring about the C=C bond. This concerted motion does not support the sequential mechanism predicted by *ab initio* calculations for substituted cyclobutenes in which the stereochemistry is determined by the ground-state surface after the system has passed through a conical intersection.^{3e} However, the importance of both disrotatory twists²⁸ and C=C torsional motion^{3e} in the photochemistry has been suggested previously. It is also interesting that the initial dynamics of CB show no evolution along the conrotatory reaction coordinate, since many examples of nonstereospecific photochemical ring-openings in substituted CBs have been documented.²⁸ Besides changing the reduced mass of the system, thus altering the reaction dynamics, it is also possible that the substituents required to identify the stereochemistry perturb the ordering and interactions of the two low-lying excited states ($2A_1$ and $1B_2$ for C_{2v} symmetry) through inductive or hyperconjugative mechanisms, resulting in a system which is guided by a different set of forces than those of the unsubstituted ring.²⁰ However, it is also possible that nonstereospecific dynamics could occur farther along the reaction coordinate, at a time that cannot be probed by resonance Raman intensities (>50 fs); yet the forces which would direct such a mechanism, in which one methyl group reverses its rotation direction after significant evolution has already occurred, are difficult to imagine.

This analysis of the photochemical ring-opening dynamics of CB illustrates how resonance Raman intensities can be used to reveal the excited-state dynamics of photochemical systems without relying on perturbative substituents. Our observation that, after excitation, planar cyclobutene evolves directly and immediately along the WH-predicted reaction coordinate has important implications for the mechanism of pericyclic rearrangements. 1,3-Cyclohexadiene, a system which is only slightly nonplanar, also evolves immediately along the conrotatory reaction coordinate.⁵ However, the nonplanar systems 1,3,5-cyclooctatriene and 1,3,5-cycloheptatriene evolve out of the Franck-Condon region along ring-planarization coordinates.^{7,8} *Comparison of the excited-state dynamics of these four systems strongly suggests that a planar or near-planar carbon skeleton must be established before the reactive pericyclic changes occur.*

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(12) The intensity of the 1640- cm^{-1} ethylenic peak, due to scattering from *s-cis*-1,3-butadiene,^{13a} depends quadratically on laser power, indicating that the *s-cis* conformer is the direct product of the ring-opening and is formed in <5 ns. The 1650- cm^{-1} peak, due to scattering from the *s-trans* conformer, is due to the accumulated photolysis of the solution. The fact that no resonance Raman peaks are observed due to the methylenecyclopropane photoproduct (C=C stretch = 1736 cm^{-1})^{13b} could be due to a small concentration of this species ($\phi \sim 0.12$), a low Raman cross section at this wavelength, and/or a time scale for ground-state formation that is longer than ~ 5 ns.

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(14) Overtone and combination band assignments are as follows: 656 cm^{-1} = 328 $\times$ 2; 1797 = 902 $\times$ 2; 1895 = 1563 + 328; 2030 = 1110 + 902; 2150 = 1075 $\times$ 2; 2210 = 1110 $\times$ 2; 2460 = 1563 + 902; 2540 = 1563 + 984; 2672 = 1563 + 1110; 2740 = 1563 + 1180; 3127 = 1563 $\times$ 2.

(15) Calculations of the relative resonance Raman intensities of the fundamentals and overtones in Figure 1 using methods outlined previously⁸ were used to provide estimates for excited-state displacements (Δ 's): 1536 cm^{-1} , $\Delta = 1$; 1440 cm^{-1} , $\Delta = 0.16$; 1180 cm^{-1} , $\Delta = 0.30$; 1110 cm^{-1} , $\Delta = 0.27$; 986 cm^{-1} , $\Delta = 0.33$. The observed intensity of the 2150- cm^{-1} overtone was reproduced by lowering the frequency of the disrotatory CH_2 twist mode from 1075 cm^{-1} in the ground state to 850 $\pm$ 100 cm^{-1} in the excited state. Although this frequency change is not sufficient to make the excited state unbound about this coordinate, once the system moves further from the Franck-Condon region, additional changes of the electronic structure are likely to occur.

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