Supporting Information

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

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The symmetry coordinates (S_1, S_2, …, S_{24}) were chosen as in Table VII of Ref. [1], using the appropriate **B** matrix[2] projected onto the ground state normal modes. The latter were calculated using the Jaguar program[3] for a GVB(2/4) wavefunction[4] with the same basis set used in the AIMS dynamics. The results of this analysis are summarized in the accompanying table. The disrotatory motion is given by the sum of the S_{15} and S_{16} symmetry coordinates and the wag motion is given by the difference of these two coordinates. The disrotatory component of the 1075cm^{-1} normal mode (ν_{15}) is 0.275, whereas that of the 848cm^{-1} (ν_{16}) is 0.590. The wag components of ν_{15} and ν_{16} are -0.635 and 0.18, respectively. *Both* modes have non-negligible 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. If a conclusion about disrotatory motion is to be drawn from the observation of intensity in only one of these overtones, it is the 848cm^{-1} mode that must be detected. The first overtone of the 848cm^{-1} mode is masked by butadiene photoproduct scattering and a resonance Raman experiment which avoids detection of this photoproduct is not feasible. Therefore, different experiments will be required to verify the predicted early onset of disrotatory motion in cyclobutene ring-opening.

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[1] Wiberg, K. B.; Rosenberg, R. E. *J. Phys. Chem.* **1992**, *96*, 8282.
[2] Wilson, E. B.; Decius, J. C.; Cross, P. C. *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*; Dover: New York, 1955.
[3] Jaguar v3.5, Schrodinger, Inc., Portland, OR, 1998.
[4] Goddard, W. A., III; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368.

Vibrational assignments and results of symmetry adapted internal coordinates analysis

Symmetry	Mode	Computed Frequency†	Experimental Frequency	Description: symmetry adapted internal coordinates
A_1	1	3085.7		$0.99S_4$
	2	2909.5		$0.99S_5$
	3	1509.8	1570	$-0.74S_1, -0.46S_6, 0.42S_7$
	4	1468.7	1449	$0.35S_1, -0.22S_6, -0.90S_7$
	5	1191.5	1185	$0.21S_1, 0.96S_8$
	6	1086.9	1113	$0.50S_1, 0.43S_2, -0.73S_6$
	7	959.6	983	$0.86S_1, 0.45S_6$
	8	750.1	875	$-0.97S_3$
A_2	9	2949.6		$0.99S_9$
	10	1128.5	1145	$0.34S_{10}, 0.93S_{11}$
	11	1009.4	1015	$0.88S_{10}, -0.35S_{11}, -0.30S_{13}$
	12	831.3	906	$-0.99S_{12}$
	13	298.7	328	$0.31S_{10}, 0.95S_{13}$
B_1	14	2963.6		$-0.99S_{14}$
	15	1070.8	1075	$-0.36S_{15}, 0.91S_{16}, 0.20S_{17}$
	16	808.6	848	$0.77S_{15}, 0.41S_{16}, -0.48S_{17}$
	17	611.7	635	$-0.52S_{15}, -0.85S_{17}$
B_2	18	3055.1		$0.99S_{19}$
	19	2901.8		$0.99S_{20}$
	20	1458.9	1432	$-0.97S_{22}$
	21	1292.8	1296	$0.39S_{18}, -0.85S_{21}, -0.33S_{23}$
	22	1244.0	1214	$-0.39S_{21}, 0.92S_{23}$
	23	863.3	888	$-0.89S_{18}, -0.32S_{21}, -0.22S_{24}$
	24	842.5	850	$0.95S_{24}$

† Scaled by 0.9