



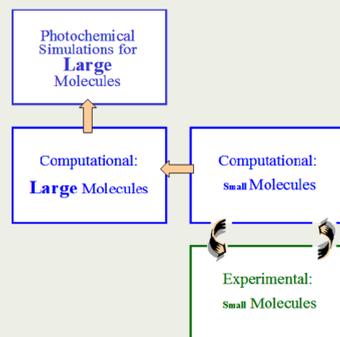
Cavity Ringdown Spectrum of 2-Cyclohexen-1-one in Its Lowest Singlet Excited State

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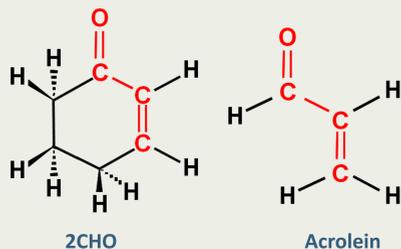
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Background Information

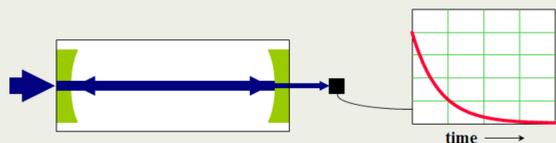


The overall goal of our experimental research program is to determine bond properties, such as vibrational frequencies, for small molecules. Such data may be used by computational chemists to verify their theoretical predictions for small molecules. This process can lead to refinement of computational techniques for treating larger molecules. Ultimately, the increased accuracy of computed excited-state properties will permit a theoretical description of complex photochemical events.



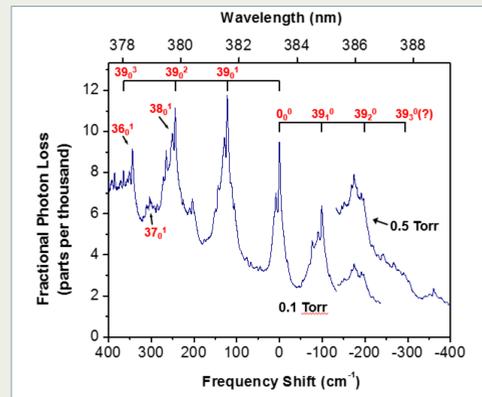
In the present work, we have used laser absorption spectroscopy to determine vibrational frequencies of 2-cyclohexen-1-one (2CHO) in its lowest singlet excited state. 2CHO is a simple cyclic enone analogous to the prototype acrolein. We use gas-phase samples in order to obtain targeted information about the molecular bonds in the absence of interactions between molecules.

Cavity Ringdown (CRD)



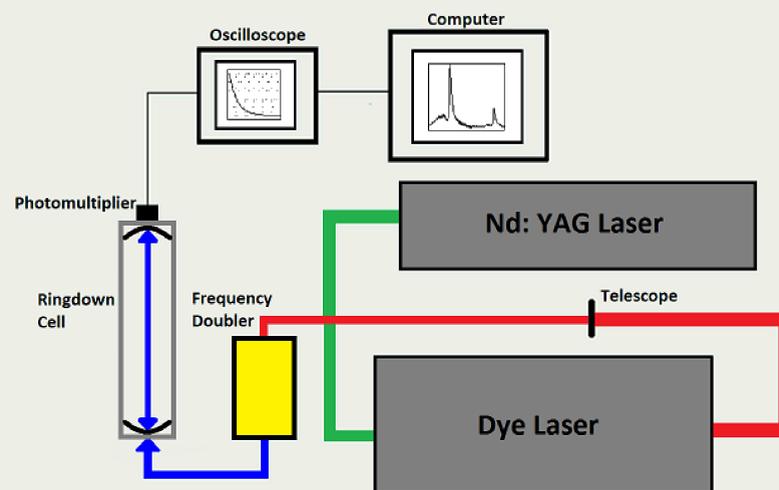
We use cavity ringdown (CRD) spectroscopy for enhanced sensitivity when studying the low-density gas-phase samples. In the CRD technique, we inject temporally short light pulses into an optical cavity filled with sample. The light is reflected back and forth thousands of times between high-reflectivity mirrors at the entrance and exit of the cell. These mirrors allow the light to leak out with exponential time dependence, and a detector placed outside of the exit mirror captures the exponential decay of the light. From this, we mathematically obtain a decay constant (k). The k value is decoupled from the decay amplitude, meaning it is unaffected by random fluctuations in laser light intensity. The CRD spectrum is created by plotting k values against wavelength. The peaks seen in the CRD spectrum are the result of a faster exponential decay, indicating molecular absorption.

Shortcomings of Previous Work



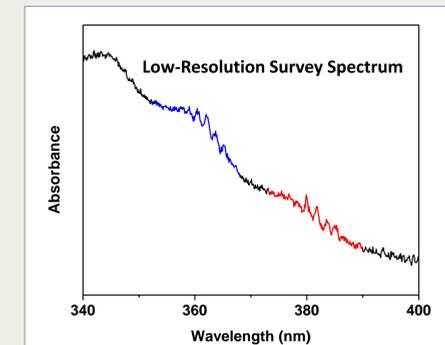
Previously resolved features in the CRD spectrum correspond to excitation of the ring-twisting vibration (mode 39) in either the ground state (low-frequency bands) or electronic excited state (higher-frequency bands).¹ The peaks corresponding to the ring-twisting vibration in the electronic excited state are separated by approximately 120 cm^{-1} . This interval was also anticipated in the higher-energy region of the spectrum, corresponding to the excitation of the C=O stretching vibration. This mode strongly influences the photochemistry of cyclohexenone. However, until recently, we were not able to access the higher-energy spectral region (350-370 nm). Our tuneable dye laser is equipped to generate light only in the visible region of the spectrum, with a wavelength minimum of 385 nm.

Experimental Advances

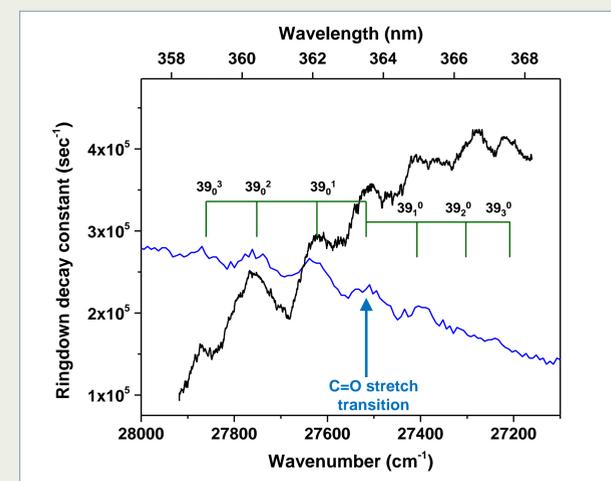


To extend the wavelength coverage of the dye laser, we have designed a computer interface for frequency doubling. The computer program drives a motor that turns a newly installed frequency doubler through very fine angular steps. With the new motor controller, we can now double the frequency (i.e., halve the wavelength) in an automated way, permitting us to operate efficiently in the ultraviolet region. The newly accessible range of wavelengths allows us to investigate the properties of the C=O stretching vibration in the excited-state CHO molecule.

Current Results



The spectral coverage of our previous CRD work was limited to the origin region, seen above in red. From the resolved features in this spectrum, we identified a fundamental frequency of 120 cm^{-1} for the ring-twisting vibration of cyclohexenone in its S_1 excited state. In the previous work, we also assigned the $S_0 \rightarrow S_1$ origin band near 385 nm. We used these results in the present work to verify the C=O stretching assignment, since its fundamental is built on the origin band. With the newly installed frequency doubler, we were able to probe the ultraviolet region of this spectrum corresponding to the C=O stretching vibration, which is highlighted above in blue.



The low-resolution spectrum seen in blue was recorded using a commercial instrument equipped with a broadband (non-laser) light source. This spectrum did not have low enough noise to determine vibrational frequencies, but was implemented as a guide to ensure our CRD spectrum (shown above in black) followed the expected absorption pattern. We have assigned the C=O stretching fundamental to the absorption peak at 27 511 cm^{-1} in the CRD spectrum. After subtracting the origin-band frequency, we determined the C=O stretch fundamental to be 1429.7 cm^{-1} . This experimentally determined value can be compared to results obtained via high-level computational predictions.²

Acknowledgements. Acknowledgement is made to the Office of Research and Sponsored Programs at the University of Wisconsin – Eau Claire for partial funding of this research. We also gratefully acknowledge funding from the National Science Foundation Grant # CHE-0848615.

References. (1) Rishard, M. Z. M.; Brown, E. A.; Ausman, L. K.; Drucker, S.; Choo, J.; Laane, J. *J. Phys. Chem. A* **2008**, *112*, 38-44. (2) McAnally, M. O.; Zabronsky, K. L.; Stupca, D. J.; Phillipson, K.; Pillsbury, N. R.; Drucker, S. *J. Chem. Phys.* **2013**, *139*, 214311