Development of a Fluorescence Excitation Spectroscopy System

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Background

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.

Absorption Spectroscopy

In the present work, we have implemented a sensitive experimental technique, fluorescence excitation spectroscopy, to study the molecule 2-cyclopenten-1-one (2CP) in its lowest electronic excited state. 2CP is a simple cyclic enone analogous to the prototype acrolein.

Conventional Absorption Spectrum

In a conventional absorption spectroscopy experiment, the sensitivity is limited because of unavoidable random fluctuations in the laser light intensity. The result is a noisy baseline that makes it difficult to identify weak absorption peaks.

Fluorescence Excitation Method

In this project we have implemented fluorescence excitation spectroscopy\(^2\) (FES) as a highly sensitive alternative to the conventional absorption technique. In FES, the detector does not monitor the absorption of laser light, but rather the fluorescence, or emission of light from the molecules that occur subsequent to the absorption event. FES is a “dark-background” technique, because the light detector only registers a signal when an absorption event occurs. As a result, the baseline in FES is much less noisy than in conventional absorption spectroscopy.

Signal Processing

A sophisticated signal-processing system is required to realize the maximum benefit of FES. The laser produces a short (10-nanosecond) pulse of light that is absorbed by the molecule at specific wavelengths. Following the absorption event, the molecules respond by emitting light with an exponentially decaying time dependence over 1-5 microseconds. The photomultiplier detector produces a time-dependent voltage in response to the light emission. The voltage signal is viewed on an oscilloscope and sent to a gated integrator, an electronics module that produces an analog voltage proportional to the integrated light intensity. The voltage output from the gated integrator is sent to an analog-to-digital converter. The digitized signal is displayed and stored on a computer.

Current Results

The spectra above were recorded with our newly implemented FES system. The signal-to-noise level was maximized by adjusting several experimental parameters related to the alignment of the laser beam and the signal-processing electronics. The green curve has much higher signal-to-noise ratio than the same spectrum recorded using conventional absorption spectroscopy.

We plan to use our FES system to extend and refine results obtained in our previously published studies\(^3\) of 2CP and related molecules.

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