Jet-Cooled Fluorescence Excitation Spectrum of γ-Pyrone

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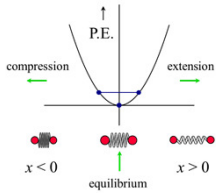
Introduction

The overall goal of our research program is to determine bond properties experimentally for small molecules in their excited states.

Excited states are key intermediates in many photochemical reaction mechanisms. An excited state results when a molecule absorbs energy from a light source, causing electrons to be displaced from their most stable locations. These destabilized molecules tend to be very reactive. [a] Computational chemistry is emerging as a powerful tool for elucidating photochemical mechanisms, but it requires benchmark experimental data on excited states. Ultimately, the increased accuracy of computed excited-state properties will permit a theoretical description of complex photochemical events.

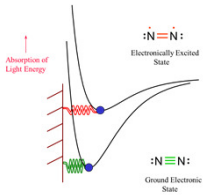
A common way physical chemists describe bond properties, for ground or excited states, is through a curve that shows potential energy (P.E.) as a function of the distance between the nuclei (x):

Potential Energy of a Bond

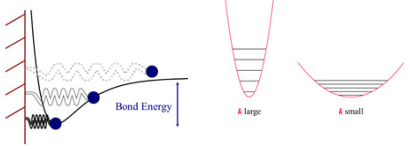


Diatomic nitrogen is shown below as a simple illustration of a potential energy curve. The "stiffness" of a bond changes upon excitation. This causes the spacings between quantum vibrational energy levels to change. By determining these spacings experimentally, we can ascertain changes in the potential energy curve quantitatively.

Photoexcitation

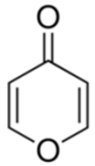


Energy Level Patterns and Changes



$$\Delta E \propto \sqrt{\frac{k}{\mu}}$$

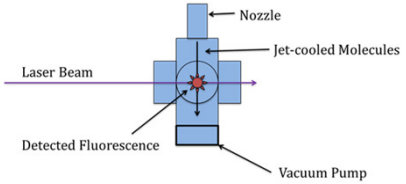
γ-Pyrone



We have focused our work on γ-pyrone ($C_5H_4O_2$), which is a conjugated enone. Small molecules such as pyrone serve as important models for larger systems, with similar bonding, that undergo a variety of photochemical processes or which are used as photosynthetic components. The advantage of studying the small prototype molecules is that they possess similar photochemical reactivity as the larger ones, but are much more straightforward to study spectroscopically and computationally.

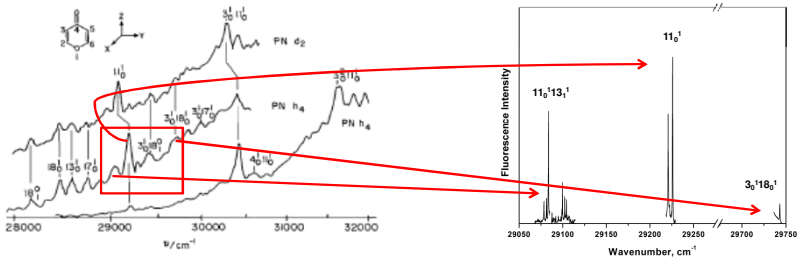
Another key characteristic of the molecule under study is that it is cyclic, or ring-shaped. The effects of excitation on the ring, such as loss of rigidity, can be subtle. Experimental investigation of these effects is critical because we are uncovering structural details that are very challenging to model computationally. A given modeling technique must be extremely good in order to pick up the effects. Our experimental results therefore offer a most rigorous test for computational models.

Laser-Induced Fluorescence Spectroscopy



Our current work employs a technique known as jet-cooled Laser-Induced Fluorescence spectroscopy (LIF). Tuneable laser light perpendicularly intersects a stream, or "jet," of gas-phase molecules that exit a small nozzle into a vacuum chamber. The molecules can fluoresce, or emit light, subsequent to the absorption of the laser light. A light detector captures the intensity of the fluorescence and transmits the signal to a computer, which displays our spectrum. The jet formation leads to a cooling effect (discussed below) that helps us interpret the spectral data.

Room-Temperature Spectrum **Jet-cooled spectrum**



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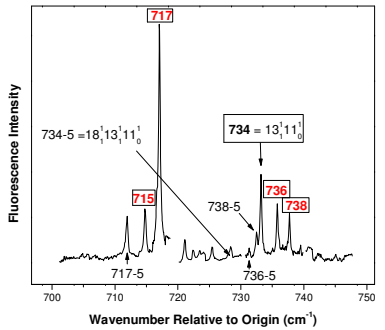
The measured spectral region, near 350 nm (or 30,000 cm^{-1} in wavenumber units), includes the $S_1(n,\pi^*) \leftarrow S_0$ band system. This work complements and refines a previously published investigation[b] of the $S_1(n,\pi^*) \leftarrow S_0$ spectrum measured at room temperature. We have assigned about 15 vibronic bands in the jet-cooled spectrum, improving the precision of the previous[b] assignments, making several corrections in the earlier work, and assigning several bands that were not observed previously due to hot-band congestion at room temperature.

Hot bands are unwanted artifacts in the spectrum attributable to excessive vibrational motion that molecules undergo in the room-temperature sample. Our jet-cooling apparatus sprays molecules into a vacuum chamber, allowing the vibrational motion to be quelled via collisions within the small (0.5 mm) nozzle orifice. The jet-cooling approach is extremely beneficial because it eliminates the hot band artifacts while keeping the molecular sample gaseous; *i.e.*, without freezing it into an impenetrable solid. In the jet-cooled spectrum we recorded (above, right), several hot bands have been eliminated from the original room-temperature spectrum, and new cold bands have been revealed by virtue of the high laser resolution.

Analysis of Jet-Cooled Spectrum



The observed peak position minus the wavenumber of the vibrationless transition gives the fundamental frequencies of various vibrational modes in the excited state. Satellite bands at –5 cm^{-1} indicate excitation in combination with a low frequency mode.

Fundamental Frequencies Observed for S_1

- 715 cm^{-1}
- 717 cm^{-1}
- 736 cm^{-1}
- 738 cm^{-1}

Ground State Frequencies from IR Spectroscopy[b,c]

720 cm^{-1}	bending ring deformation
790 cm^{-1}	out of plane CH twist
960 cm^{-1}	CH bend (out of plane)
847 cm^{-1}	C=O wag (out of plane)

Summary

The known ground-state frequencies suggest vibronic assignments for the newly observed excited-state spectrum. The ground-state descriptions are candidates for assigning the excited-state spectrum, but a one-to-one correspondence is not implied. We are pursuing computational studies in order to confirm the vibrational mode descriptions and appropriate correspondences above.

References. **(a)** Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Sausalito, CA, 1991; pp 232-295. **(b)** Gordon, R.D.; Park, W.K.C. *Canadian Journal of Chemistry* 1993, *71*, 1672-1675. **(c)** Csaszar, P.; Csaszar, A.; Somogyi, A.; Dinya, Z.; Holly, S.; Gal, M.; Boggs, J.E. *Spectrochimica Acta Part A: Molecular Spectroscopy* 1986, *42*, 473-486.

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