

NEW DEVELOPMENTS
IN INTRACAVITY LASER ABSORPTION SPECTROSCOPY

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In the last two decades, observation of extremely weak vibrational overtone transitions by high sensitivity techniques has opened a window over molecular dynamics of the electronic ground state. In fact, overtone transitions in the visible spectrum correspond to excitation energies sufficiently elevated to induce vibrational redistribution, isomerization and even unimolecular dissociation.

Intracavity Laser Absorption Spectroscopy (ICLAS) is one of the most performant techniques used to detect and measure weak transitions. We have employed this technique for more than a decade to study overtone transitions of intermediate size molecules such as CH₄, C₂H₂, SiH₄, GeH₄, NO₂, N₂O, CO₂, etc... in the near infrared and visible ranges. More recently several groups have adopted this technique and I will try to present the state of the art in ICLAS and discuss briefly its sensitivity limitations.

To reduce the rotational (and to a less extent vibrational) congestion which prevents rotational analysis, we have combined our ICLAS spectrometer either with a cell cooled at liquid nitrogen temperature or a slit jet expansion. Some selected examples of data obtained with this system will be presented and discussed.

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TIME-RESOLVED ROTATIONAL SPECTROSCOPY OF REACTIVE MOLECULES

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Ions, radicals and other reactive molecules of short lifetime studied in the laboratory by rotational spectroscopy must first be produced in-situ by dissociation of stable or quasi-stable precursors. Often a variety of stable and reactive molecules may be formed simultaneously, leading to a complicated spectral pattern. In spite of recent advances in ab-initio calculations, or the availability of rotational constants calculated from vibrational or electronic spectra, the lack of accurate higher order constants for new molecules can make their identification very difficult. Even if optimum production conditions are known (and they can only be found after identification of the molecule) these short-lived species are invariably formed with time-averaged densities many orders smaller than that of the precursor. However, the very fact that these molecules have a short lifetime presents a new tool; that of time-resolved spectroscopy.

A widely used method for producing reactive species is that of electric glow discharge in a low pressure gas mix. By modulating the discharge on/off the lifetime of each molecule produced may be measured and the spectral pattern hence disentangled. These measurements not only allow lines of a particular molecule to be grouped together but also give valuable information on the nature of the species formed.

With the availability of high-power pulsed excimer lasers, UV photolysis can now be used to produce reactive species by breaking selected molecular bonds of photosensitive precursors. This method should be well adapted to the study of reactive species involved in atmospheric pollution cycles, and to large reactive molecules too easily broken by electric discharge. Unfortunately the precursor molecules envisaged often have very dense spectra which can swamp smaller absorption lines. It will be shown that the use of time-resolved techniques can increase sensitivity to short-lived species and eliminate the precursor spectrum.