

SPECTROSCOPIC CHARACTERIZATION OF COLD RADICALS USING THE LASER-INDUCED FLUORESCENCE TECHNIQUE

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Abstract

The technique of laser-induced fluorescence spectroscopy in tandem with a supersonic jet expansion has helped characterize spectroscopically several free radicals that are crucial for better understanding of combustion and atmospheric processes.

Introduction

Laser-induced fluorescence (LIF) spectroscopy is a versatile technique in which molecular species are irradiated with laser radiation in a specific wavelength range (normally in the ultraviolet for electronic spectroscopy) that is in resonance with the differences in molecular energy levels. Such resonantly tuned radiation has a fairly good probability of inducing a transition to the excited state of the molecule, which may be followed by relaxation of the molecules to the ground electronic state by spontaneous emission of a photon whose energy corresponds to the separation in molecular energy levels. Experimentally, the LIF technique involves scanning the wavelength of the probe laser (usually, a frequency-doubled tunable dye laser) and capturing the fluorescence intensity versus wavelength excitation spectrum.¹ An important advance associated with the LIF technique is to utilize a supersonic jet expansion to cool the precursor molecules, and subsequently followed by photodissociation of the precursor to produce rovibrationally cold gas phase free radical fragments. As a result of the low temperatures realized in the jet, collisional excitation and quenching phenomena are diminished, and thereby the laser-induced fluorescence process can dominate and simplified spectra of moderately-sized radicals can be recorded and analyzed in detail.²⁻³

Experimental

A timing control circuit was designed to first send a pulse (excimer charge) to an excimer laser that orders it to begin charging its capacitor bank. A discharge of the capacitors results in the energy needed to fire the excimer laser, which is used to photolyze a suitable precursor and produce the appropriate free radical; for e.g. ethyl nitrite (C_2H_5ONO) is photodissociated at 193 or 248 nm to generate the ethoxy (C_2H_5O) radical and nitric oxide (NO). Alkylthio (RS) radicals were produced by photolysis of either dialkyl sulfide (R_2S) or the dialkyl disulfide (R_2S_2). Each precursor was entrained in a flow of high pressure (8-10 atm) helium gas and the seeded flow was introduced into an expansion chamber through a 0.5 mm pulsed nozzle. Once the excimer laser fires, after a delay determined by the timing control circuit, a second trigger pulse orders the

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Nd:YAG laser to fire and the resulting laser pulse then causes the dye laser to fire at a suitably tuned wavelength. A typical separation of 10-12 mm was maintained between the photolysis and probe lasers. The optical laser beam emanating from the dye laser is frequency-doubled using a nonlinear crystal (e.g. KDP) to produce a UV pulse that excites the free radical. The molecular radical subsequently decays to the ground electronic state via spontaneous photon emission. An appropriate focusing lens is used to capture the laser-induced fluorescence photons onto a photomultiplier tube, which converts the optical signal into an electric current. A filter in front of the photomultiplier tube minimizes the scattered light entering it. The output from the photomultiplier tube is sampled by a boxcar integrator that produces a DC level, which is a measure of the LIF intensity. The timing control circuit used provides the trigger pulse to the boxcar and allows the synchronization of the boxcar gate with the fluorescence signal. The analog signal from the boxcar output is converted to digital and relayed to a personal computer for processing. A scan of the dye laser wavelength yielded the excitation spectrum of the free radical. The line-width afforded by the tunable dye laser pulse was about 0.2 cm^{-1} and could be improved to 0.07 cm^{-1} . Moderate resolution LIF spectra were used for vibronic assignments and the higher resolution spectra for rotational assignments. Frequency calibration of the excitation spectra was accomplished by simultaneously recording either the absorption spectrum of iodine or the optogalvanic spectra of neon and argon.

Results and Discussion

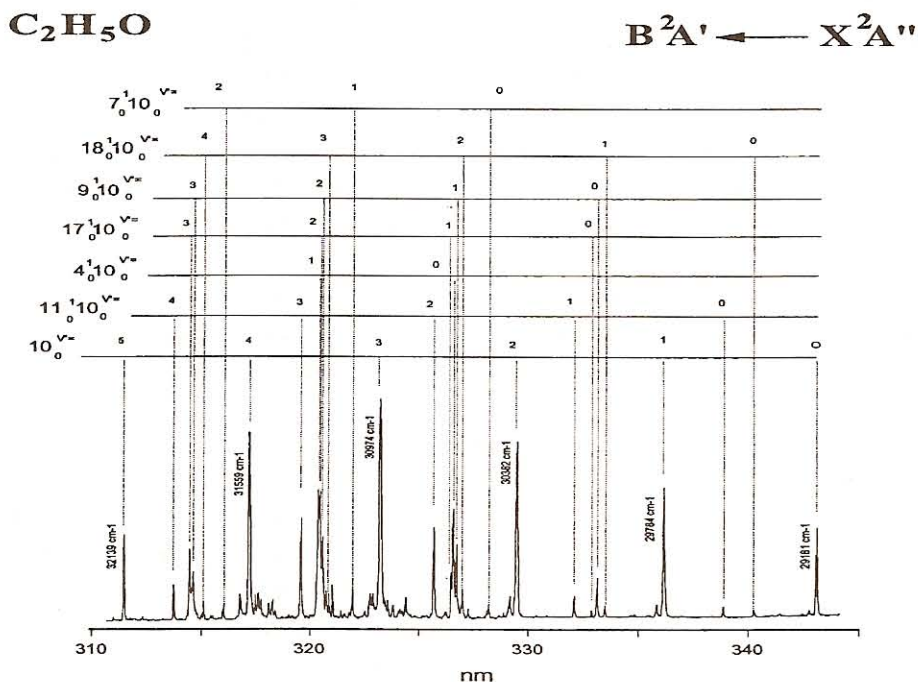


Fig. 1. Laser excitation fluorescence spectrum of the $\text{B}^2\text{A}' - \text{X}^2\text{A}''$ system of the jet-cooled ethoxy radical. The time delay between the excimer laser and the dye laser was $8 \mu\text{s}$.

Figure 1 is a typical laser excitation fluorescence spectrum of the jet-cooled ethoxy radical in the 310-345 nm region recorded at a resolution of 0.2 cm^{-1} . The time delay between the excimer laser and the dye laser was $8 \mu\text{s}$. Several vibrational modes have been identified and are indicated on the illustration (Fig. 1). The strongest CO progression lines are shown in Fig. 1. An examination of a specific individual band under high rotational resolution indicates that ethoxy exhibits a C-type perpendicular band structure of a near prolate symmetric top molecule. For comparison, the laser excitation spectrum of the jet-cooled methylthio (CH_3S) radical is shown in the $25,800\text{-}27,800 \text{ cm}^{-1}$ ($\sim 360\text{-}388 \text{ nm}$) region in Fig. 2. Figure 2 is a composite scan of two overlapping adjacent scans ($25,800\text{-}27,000 \text{ cm}^{-1}$ and $27,000\text{-}28,000 \text{ cm}^{-1}$) and shows vibronic bands involving both fundamental and combination modes. Figure 3 shows the resolved rotational structure for a typical band of the jet-cooled isopropylthio ($i\text{-C}_3\text{H}_7\text{S}$) radical recorded in the $24,766\text{-}24,780 \text{ cm}^{-1}$ region and separated into K-manifolds. The isopropylthio radical is an oblate symmetric top molecule. A detailed analysis of the spectra shown in Figs. 1-3 allows determination of significant molecular parameters for the upper and lower states of the various free radicals, which in turn proves very useful for chemical kinetics investigations involving the reactions of these radicals with other stable as well as unstable molecules.

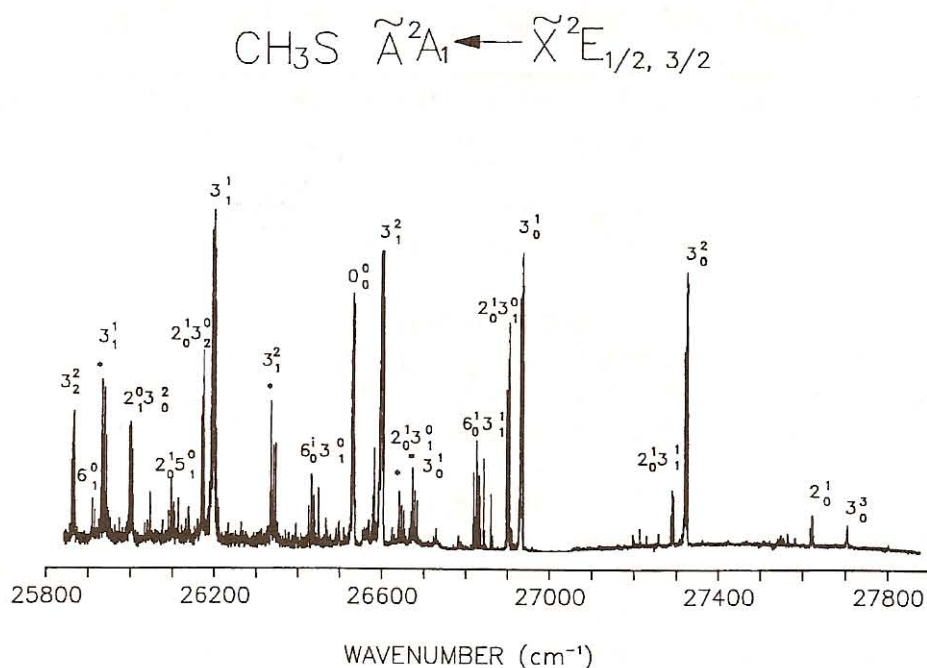


Fig. 2. A composite laser excitation scan of the jet-cooled methylthio radical in the $25,800 - 27,800 \text{ cm}^{-1}$ region.

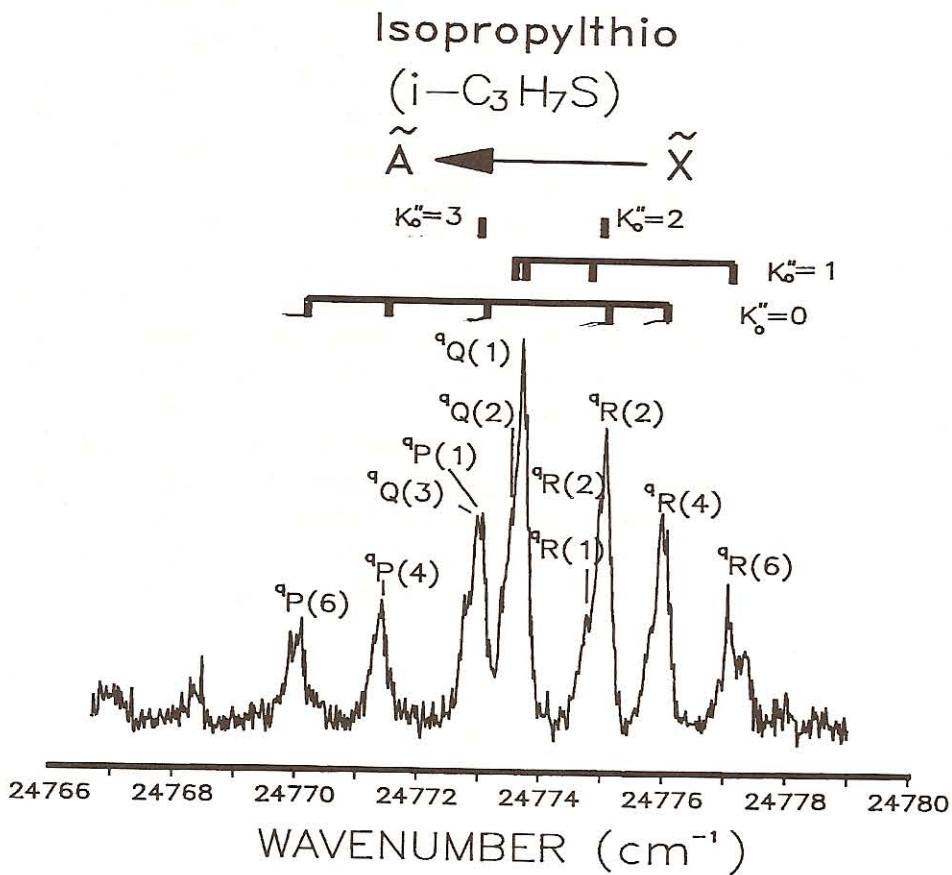


Fig. 3. A rotationally-resolved spectrum of the jet-cooled isopropylthio radical showing the K-manifolds of an oblate symmetric top molecule.

Acknowledgments

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