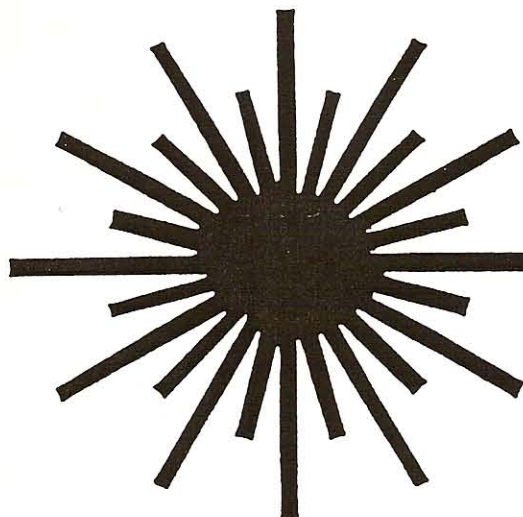


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# LASER SPECTROSCOPY OF ORGANIC FREE RADICALS OF ENVIRONMENTAL AND ATMOSPHERIC SIGNIFICANCE

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## Abstract

Laser excitation spectra of organic free radicals, namely the alkoxy and alkylthio molecules, were recorded in a supersonic jet expansion and analyzed. The members of the alkoxy family include methoxy ( $\text{CH}_3\text{O}$ ), ethoxy ( $\text{C}_2\text{H}_5\text{O}$ ), and isopropoxy ( $i\text{-C}_3\text{H}_7\text{O}$ ), while the alkylthio molecules studied were methylthio ( $\text{CH}_3\text{S}$ ), ethylthio ( $\text{C}_2\text{H}_5\text{S}$ ), and isopropylthio ( $i\text{-C}_3\text{H}_7\text{S}$ ). Extensive rovibronic spectra of these supersonically cooled radicals have helped determine important molecular parameters characterizing the upper and lower electronic states involved in the transitions. Several vibrational frequencies for the ground electronic state of  $\text{C}_2\text{H}_5\text{O}$  are being reported for the first time.

## Introduction

Organic radicals such as the alkoxies ( $\text{RO}$ ;  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$ ) and alkylthios ( $\text{RS}$ ) are significant chemical intermediates in environmental and atmospheric processes [1]. The alkoxy radicals play a leading role as oxidation intermediates in the combustion of hydrocarbons and in air pollution [2]. The alkoxies are also of considerable interest in the photochemistry of the upper atmosphere [3] and are important in astrophysical work. Alkylthio radicals, on the other hand, are important chemical intermediates in the oxidation of reduced sulfur compounds in the atmosphere and are involved in the combustion of sulfur-rich fuels [4].

Laser-induced fluorescence (LIF) excitation spectra of jet-cooled RO and RS radicals [5] were obtained with a frequency-doubled Nd:YAG-pumped dye laser. Low resolution ( $0.2 \text{ cm}^{-1}$ ) LIF spectra were used for vibronic assignments, while high resolution ( $0.07 \text{ cm}^{-1}$ ) rotationally-resolved spectra provided accurate rotational parameters characteristic of the upper and lower electronic states. Dispersed fluorescence spectra obtained employing a high resolution monochromator were used for vibrational assignments.

### Experimental

The RO radicals were generated *in situ* in a supersonic jet expansion by the excimer laser (KrF @ 248 nm) photolysis of alkyl nitrites (RONO). While, the RS radicals were produced by the excimer-induced photodissociation of  $\text{R}_2\text{S}_2$ . The precursors (typically 1-2% concentration by volume) were transported by helium in separate experiments under high pressure (12-14 atm) and seeded into an expansion chamber employing a pulsed valve. Nascent RO and RS radicals in the jet expansion were excited with a frequency-doubled Nd:YAG-pumped dye laser in the UV. The tunable dye laser had a nominal linewidth of  $0.07 \text{ cm}^{-1}$  and the typical time delay between the photolysis and excitation beams was 6-8  $\mu\text{s}$ . Optogalvanic transitions excited in an Fe-Ne hollow-cathode discharge lamp were used to calibrate the wavelength of the dye laser [6].

Dispersed fluorescence spectra of the RO and RS radicals were recorded by exciting the molecules at the wavelength of a rotational transition within a vibronic band. The total fluorescence was focused onto the entrance slit of either a 0.6 m monochromator (equipped with a 1800 grooves/mm grating of resolution 0.3 nm) used in conjunction with a photomultiplier tube, or a 0.275 m monochromator (with a 1200 grooves/mm grating of resolution 0.5 nm) connected to a Charge-Coupled-Device (CCD) detector. The grating dispersed the fluorescence and enabled recording of the wavelength-resolved emission spectra of the RO and RS radicals.

### Results and Discussion

Figure 1 shows a rotationally-resolved high resolution spectrum of ethoxy ( $\text{C}_2\text{H}_5\text{O}$ ).  $\text{C}_2\text{H}_5\text{O}$  shows a C-type perpendicular band structure [7] of a near prolate symmetric top molecule ( $|\kappa| \geq 0.9$ ) as illustrated by the rotational structure of the  $10^3_011^1_0$  band displayed in Fig. 1. The  $\nu_{10}$  mode corresponds to the symmetric C-O stretch vibration. Electronic wavefunctions of  $\text{C}_2\text{H}_5\text{O}$  transform according to one of the two irreducible representations of the  $C_s$  point group. A detailed high resolution analysis using optogalvanic transitions for calibration of the excitation spectrum and employing prolate symmetric top quantum numbers for the rotational assignments of the (A or B)  $-X 10^3_011^1_0$  band of ethoxy gave:  $\nu_0 = 31325.78 \text{ cm}^{-1}$ ,  $A' = 1.10 \text{ cm}^{-1}$ ,  $B' = 0.29 \text{ cm}^{-1}$ ,  $C' = 0.28 \text{ cm}^{-1}$ ,  $A'' = 1.26 \text{ cm}^{-1}$ ,  $B'' = 0.31 \text{ cm}^{-1}$ , and  $C'' = 0.28 \text{ cm}^{-1}$ .

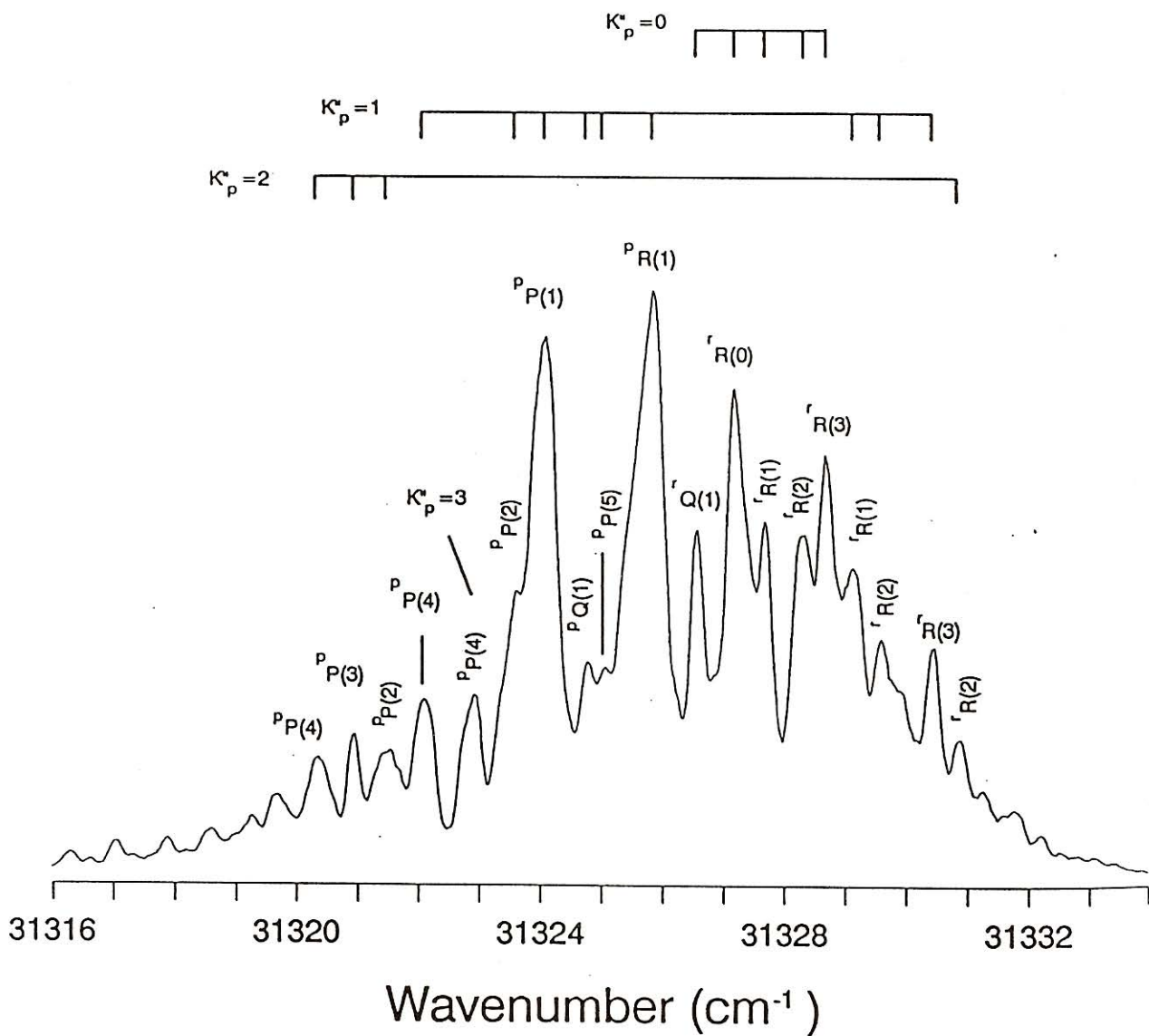
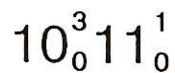
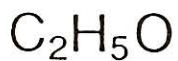


Figure 1. Rotationally-resolved LIF excitation spectrum of the  $10_0^3 11_0^1$  band of jet-cooled  $C_2H_5O$ . The wavenumber axis was calibrated using optogalvanic neon transitions.

Similar to  $C_2H_5O$ , the ethylthio ( $C_2H_5S$ ) radical is a prolate symmetric top molecule. Table I summarizes the molecular parameters for  $C_2H_5S$  obtained from the least-squares fit of the rotational transitions. Rotational parameters were also obtained for the isopropylthio ( $i-C_3H_7S$ ) radical and are collected together with those of  $C_2H_5S$  in Table I. In contrast to  $C_2H_5S$ , the jet-cooled spectrum of  $i-C_3H_7S$  exhibited rotational structure characteristic of an oblate symmetric top molecule.

Figure 2 is an illustrative dispersed fluorescence scan for the  $10^3_0$  band of  $C_2H_5O$ . Besides the main CO stretch progression, there were other distinct ground state frequencies that could be identified:  $CH_3$  s-stretch ( $\nu''_3 = 2251 \text{ cm}^{-1}$ ),  $CH_2$  scis ( $\nu''_4 = 1850 \text{ cm}^{-1}$ ),  $CH_3$  s-deform ( $\nu''_6 = 1720 \text{ cm}^{-1}$ ),  $CH_2$  wag ( $\nu''_7 = 1366 \text{ cm}^{-1}$ ), CO stretch ( $\nu''_{10} = 1073 \text{ cm}^{-1}$ ), CCO deform ( $\nu''_{11} = 450 \text{ cm}^{-1}$ ),  $CH_2$  rock ( $\nu''_9 = 943 \text{ cm}^{-1}$ ) and Torsion ( $\nu''_{18} = 386 \text{ cm}^{-1}$ ).

TABLE I

Molecular parameters (in  $\text{cm}^{-1}$ ) of alkylthio radicals

Parameter	$C_2H_5S$ Band at $25103.90 \text{ cm}^{-1}$	$i-C_3H_7S$ Band at $24773.66 \text{ cm}^{-1}$
$A''$	1.08	0.27
$B''$	0.73	0.26
$C''$	0.58	0.11
$A'$	0.99	0.27
$B'$	0.68	0.23
$C'$	0.57	0.04
$\nu_0$	25103.90	24773.66

In summary, the jet-cooled LIF spectra of the RO and RS radicals exhibit clearly-resolved rotational structure, which has allowed accurate determination of molecular parameters for the ground and excited electronic states involved in the transitions. In addition, the single vibronic level dispersed fluorescence spectra have provided information about the vibrational intervals in the ground state.

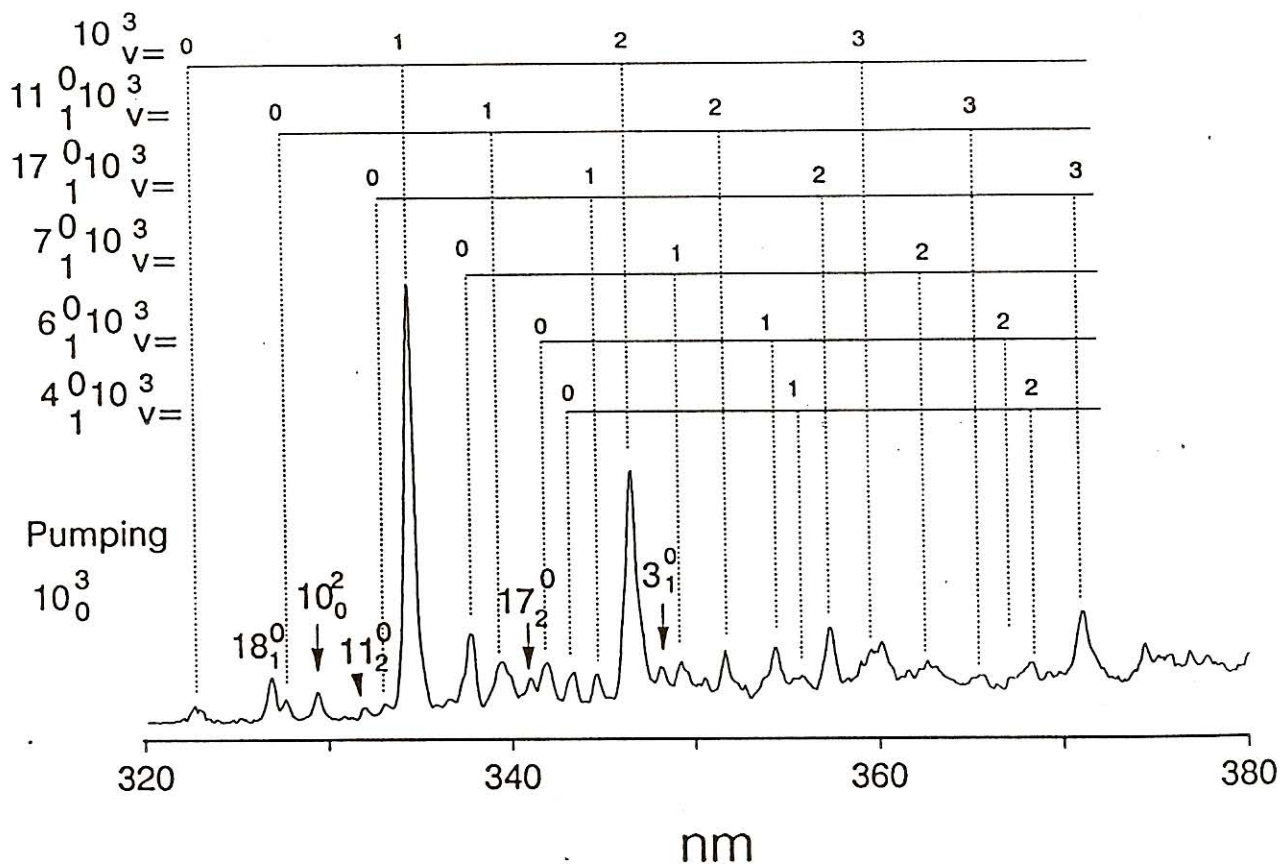


Figure 2. Dispersed fluorescence spectrum of the ethoxy radical obtained when the  $10_0^3$  band was pumped. A 0.275 m focal length monochromator equipped with a 1200 grooves/mm grating was used to record the spectrum and provided a resolution of 0.5 nm.

## Acknowledgments

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