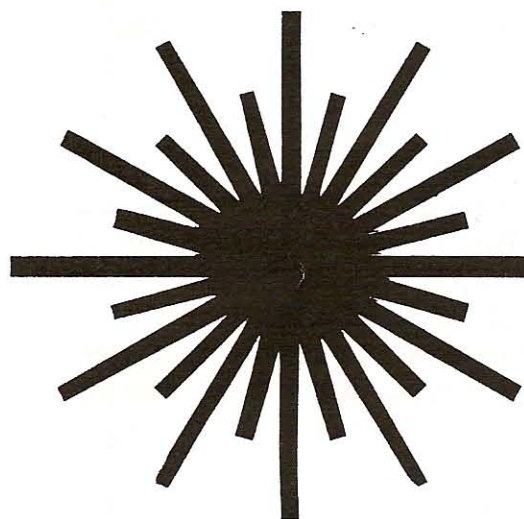


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# ROTATIONALLY-RESOLVED EXCITATION SPECTROSCOPY OF THE ALKOXY AND ALKYLTHIO RADICALS IN A SUPERSONIC JET

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## Abstract

Rotationally-resolved laser excitation spectra have been obtained for the alkoxy radicals ( $\text{CH}_3\text{O}$ ,  $\text{C}_2\text{H}_5\text{O}$ ,  $i\text{-C}_3\text{H}_7\text{O}$ ) and the alkylthio radicals ( $\text{CH}_3\text{S}$ ,  $\text{C}_2\text{H}_5\text{S}$ ,  $i\text{-C}_3\text{H}_7\text{S}$ ) in a supersonic jet expansion. Low resolution ( $0.2\text{ cm}^{-1}$ ) excitation spectra have helped identify several vibronic bands belonging to the A-X electronic system for these jet-cooled free radicals. High resolution ( $0.07\text{ cm}^{-1}$ ) laser-induced fluorescence excitation spectra have aided the unraveling of the associated rotational structure and in certain cases ( $\text{CH}_3\text{O}$  and  $\text{CH}_3\text{S}$ , for example) enabled explicit rotational (J,K) assignments of the transitions.

## Introduction

The alkoxy ( $\text{RO}$ ,  $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $i\text{-C}_3\text{H}_7$ ) radicals and the alkylthio ( $\text{RS}$ ) radicals are important chemical intermediates in combustion reactions and in photochemical air pollution.<sup>1,2</sup> It is well established that the combustion of organic fuels involves a complex sequence of reactions.<sup>3</sup> Interestingly, most of the reactions proceed via the involvement of free radicals as chemical intermediates.<sup>4</sup> Thus, a clearer understanding of their spectroscopy and the role these chemical intermediates play in the combustion chain will lead to the development of improved and efficient organic fuels. In the gas-phase oxidation of most hydrocarbons, the RO radicals undergo a series of reactions leading to the formation of ultimate combustion products such as alcohols, aldehydes and ketones.<sup>5</sup> The combustion of so-called dirty fuels (for example, sulfur-rich oil and coal) involves the thio analogs (RS) of the alkoxy radicals.

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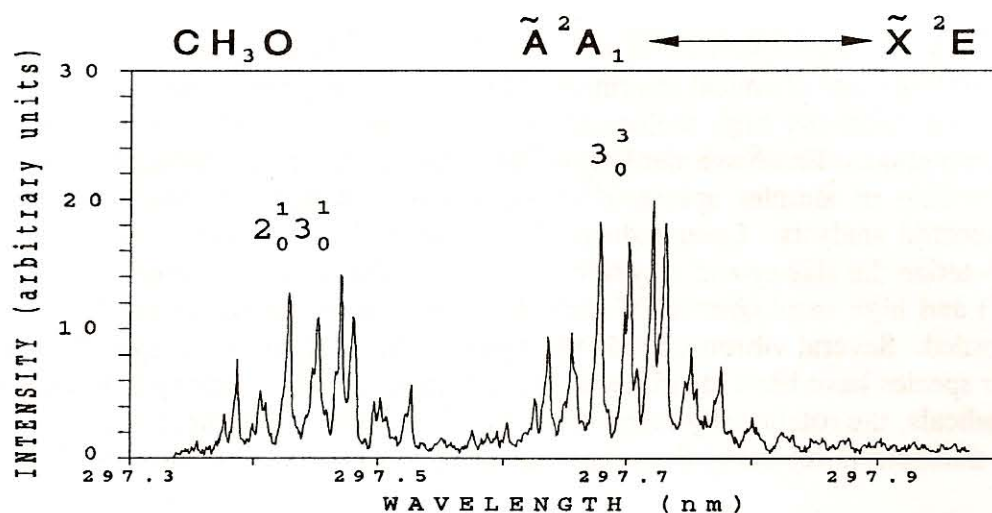
By generating these chemical intermediates *in situ* in a supersonic jet expansion, it is possible to study these relatively high molecular weight species under jet-cooled conditions and good spectral resolution. Extensive cooling of the translational and rotational degrees of freedom allow recording of simpler spectra of these complex polyatomic molecules and facilitate a detailed spectral analysis. Laser-induced fluorescence (LIF) spectroscopy was used to monitor and characterize the alkoxy and alkylthio radicals in a free jet environment. Both low resolution ( $0.2\text{ cm}^{-1}$ ) and high resolution ( $0.07\text{ cm}^{-1}$ ) laser excitation spectra of the RO and RS radicals were recorded. Several vibronic bands belonging to the A-X electronic system of these transient molecular species have been identified in the LIF spectra. For methoxy ( $\text{CH}_3\text{O}$ ) and methylthio ( $\text{CH}_3\text{S}$ ) radicals, the rotationally-resolved  $A^2A_1 - X^2E$  spectra have been explicitly assigned with quantum numbers (J,K) using the nomenclature for symmetric top transitions in spin-doublet states.<sup>6</sup>

### Experimental

The alkoxy (RO) radicals were produced by the excimer laser (KrF @ 248 nm or ArF @ 193 nm) photolysis of alkylnitrites (RONO). RONO was synthesized by the dropwise addition of dilute sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to a solution of sodium nitrite ( $\text{NaNO}_2$ ) and the corresponding alcohol (ROH).<sup>7</sup> Freshly synthesized RONO was stored at 77°K employing a liquid nitrogen bath. The alkylthio (RS) radicals were produced by the excimer laser (248 or 193 nm radiation) photolysis of either the dialkyl sulfide ( $\text{R}_2\text{S}$ ) or the dialkyl disulfide ( $\text{R}_2\text{S}_2$ ). Both the sulfide precursors are available commercially (Aldrich or Sigma Chemical Co.).

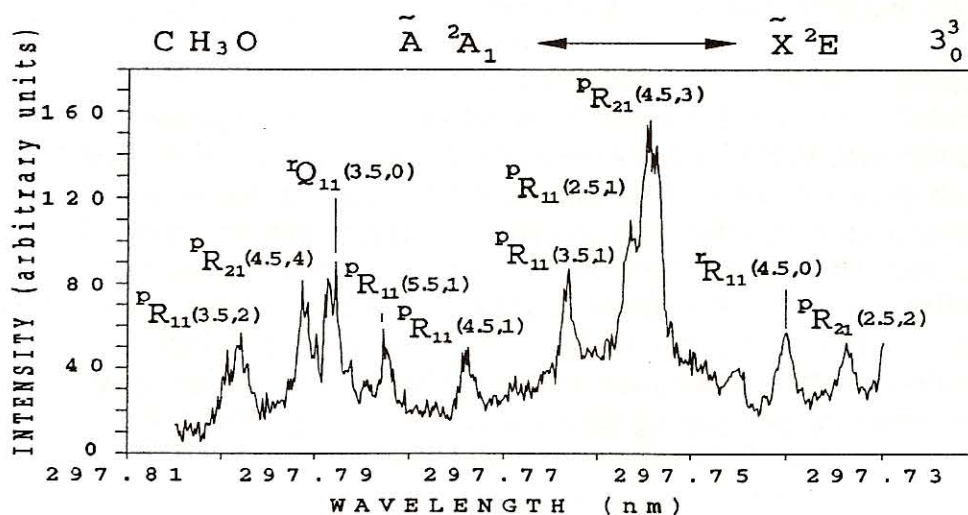
Each precursor was entrained in an inert gas flow of high-pressure ( $\sim 10\text{-}17\text{ atm}$ ) helium gas and the seeded flow was subsequently introduced into an expansion chamber through a commercial (General Valve) pulsed nozzle of 0.5 mm orifice. The RO and RS radicals were formed by directing a KrF or ArF excimer laser beam close to the expansion orifice so that the precursor molecules were effectively photolyzed. These fragments were probed by a pulsed tunable dye laser (either YAG- or excimer-pumped). Total fluorescence was detected by a photomultiplier tube and used as input to a gated integrator. The signals were accumulated and averaged by the boxcar integrator (Stanford Research Model 250) in association with a microcomputer-aided data acquisition system. Fluorescence excitation spectra for the free radicals were recorded by scanning the dye laser wavelength. The line-width afforded by the dye laser pulse was about  $0.2\text{ cm}^{-1}$  and could be improved to  $0.07\text{ cm}^{-1}$ .

## Results and Discussion



**Figure 1.** Low resolution ( $0.2\text{ cm}^{-1}$ ) laser excitation spectrum of  $\text{CH}_3\text{O}$  showing the  $2_0^1 3_0^1$  and  $3_0^3$  bands.

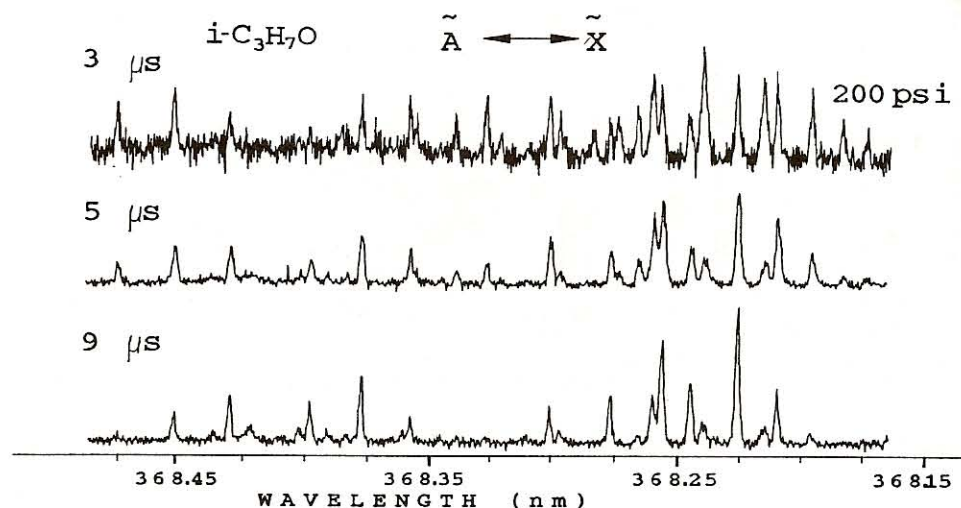
Figure 1 is a typical illustration of the low resolution ( $0.2\text{ cm}^{-1}$ ) excitation spectrum obtained for jet-cooled  $\text{CH}_3\text{O}$  in the wavelength region 297.3 - 298.0 nm. The backing pressure of the helium and nitrite mixture behind the pulsed valve was 120 psi and the time delay between the photolysis and probe lasers was  $8\ \mu\text{s}$ . The KrF photolysis excimer laser had an energy of 30 mJ per pulse, while the frequency-doubled Nd:YAG-pumped dye laser had an energy of 1 mJ per pulse. A high resolution ( $0.07\text{ cm}^{-1}$ ) excitation spectrum of the A-X  $3_0^3$  band of jet-cooled  $\text{CH}_3\text{O}$  is shown in Fig. 2. A mixture of dyes KR620 and R640 was used in the Nd:YAG-pumped



**Figure 2.** High resolution ( $0.07\text{ cm}^{-1}$ ) LIF excitation spectrum of the A-X  $3_0^3$  band of jet-cooled  $\text{CH}_3\text{O}$  showing assigned rotational transitions. A backing pressure of 250 psi for the helium and methyl nitrite mixture was maintained behind the pulsed nozzle.



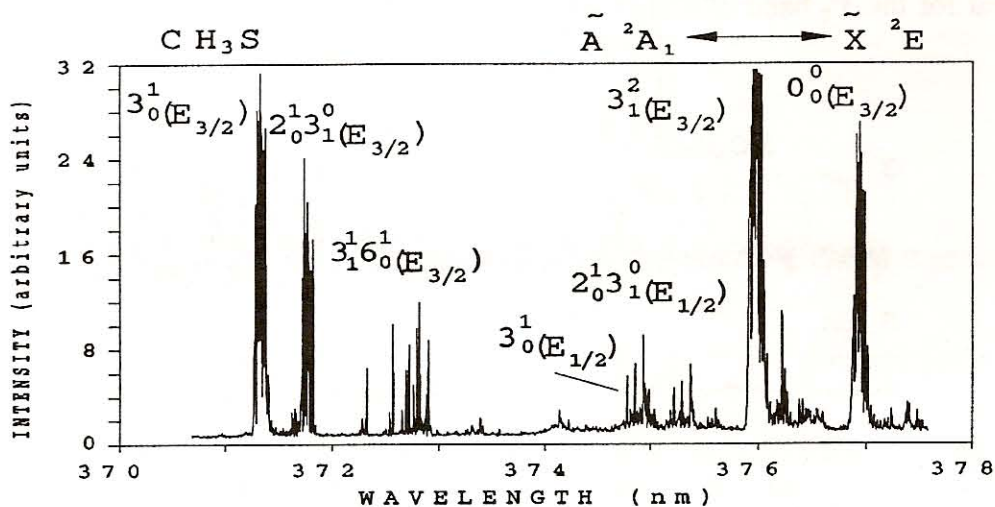
tunable dye laser to generate the requisite wavelength range for recording the  $3^3_0$  LIF spectrum, while the frequency-doubled UV pulse had an energy of about 0.5 mJ. The rotational transitions were identified and labeled following a least-squares fit<sup>8</sup> and employing the nomenclature for prolate symmetric top transitions in doublet states.<sup>6</sup> The upper state ( $A^2A_1$ ) rotational constants determined from the fit were  $A'=4.97\text{ cm}^{-1}$  and  $B'=0.74\text{ cm}^{-1}$ , while the ground state ( $X^2E$ ) rotational constants were fixed at the values previously reported for methoxy.<sup>8</sup> The band origin determined for the  $3^3_0$  band of  $\text{CH}_3\text{O}$  was  $\nu_0=33551.88\text{ cm}^{-1}$ .



**Figure 3.** Laser excitation scans showing the 368.15-368.50 nm spectral region for  $i\text{-C}_3\text{H}_7\text{O}$  obtained with 200 psi helium backing pressure for three separate time delays of 3  $\mu\text{s}$ , 5  $\mu\text{s}$  and 9  $\mu\text{s}$ , respectively, between the photolysis and probe lasers. The excimer-pumped dye laser using BPBD dye had an average energy of 2 mJ per pulse.

Figure 3 is an illustration showing three excitation scans for the isopropoxy ( $i\text{-C}_3\text{H}_7\text{O}$ ) radical in the wavelength domain 368.15-368.50 nm obtained with an excimer-pumped dye laser with an average energy of 2 mJ per pulse. A KrF photolysis excimer beam of 80 mJ per pulse photodissociated the nitrite precursor. The backing pressure of the helium and isopropyl nitrite mixture was maintained at 200 psi for three separate time delays of 3  $\mu\text{s}$ , 5  $\mu\text{s}$  and 9  $\mu\text{s}$ , respectively, between the photolysis and probe lasers. An examination of the composite scan display (Fig. 3) reveals the cooling effect realized in the supersonic jet expansion for longer time delays and the concomitant increase in spectral resolution.

The methylthio ( $\text{CH}_3\text{S}$ ) radical was produced by photolyzing the dimethyldisulfide ( $\text{CH}_3\text{SSCH}_3$ ) precursor with a KrF laser (@ 248 nm, 80 mJ/pulse). An excimer-pumped dye laser (3 mJ/pulse) beam was used to probe the  $\text{CH}_3\text{S}$  molecules downstream in the jet expansion. The dye Exalite 376 enabled the recording of the excitation spectrum of  $\text{CH}_3\text{S}$  in the 370-378 nm region and is shown in Fig. 4.



**Figure 4.** Low resolution ( $0.2\text{ cm}^{-1}$ ) LIF spectrum of  $\text{CH}_3\text{S}$  showing the various vibronic bands belonging to the  $\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{E}$  electronic system. A backing pressure of 200 psi helium was maintained behind the nozzle and there was a time delay of  $8\ \mu\text{s}$  between the photolysis and probe lasers.

The vibronic bands indicated in Fig. 4 primarily belong to the  $\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{E}_{3/2}$  electronic system of  $\text{CH}_3\text{S}$ . However, two fairly strong bands:  $3^1_0$  (@ 374.9 nm) and  $2^1_0 3^1_0$  (@ 375.3 nm) that belong to the  $\tilde{\text{A}}^2\text{A}_1 - \tilde{\text{X}}^2\text{E}_{1/2}$  electronic system of  $\text{CH}_3\text{S}$  have also been assigned (Fig. 4). The  $\nu_2$  (umbrella),  $\nu_3$  (C-S stretch) and  $\nu_6$  (rocking) modes of vibration of  $\text{CH}_3\text{S}$  were visible in the jet-cooled LIF spectra recorded. Analysis of the excitation spectra yield the following excited state vibrational frequencies for  $\text{CH}_3\text{S}$ :  $\nu_2' = 1085\text{ cm}^{-1}$ ,  $\nu_3' = 401\text{ cm}^{-1}$  and  $\nu_6' = 600\text{ cm}^{-1}$ .

Rotationally-resolved LIF excitation spectra of  $\text{C}_2\text{H}_5\text{O}$  ( $9^4_0$  band, 316.82-316.89 nm),  $\text{C}_2\text{H}_5\text{S}$  (398.73-398.93 nm) and  $i\text{-C}_3\text{H}_7\text{S}$  (398.68-398.92 nm, 403.68-403.88 nm) have been recorded with good signal-to-noise in a supersonic jet environment.

### Acknowledgements

Financial support from the Center for Terrestrial and Extraterrestrial Atmospheres (Grant# NASA NAGW-2950), Wright-Patterson Air Force Base (Grant# F33615-90-C-2038), and the Collaborative Core Unit of Howard University's Graduate School of Arts and Sciences is gratefully acknowledged.

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