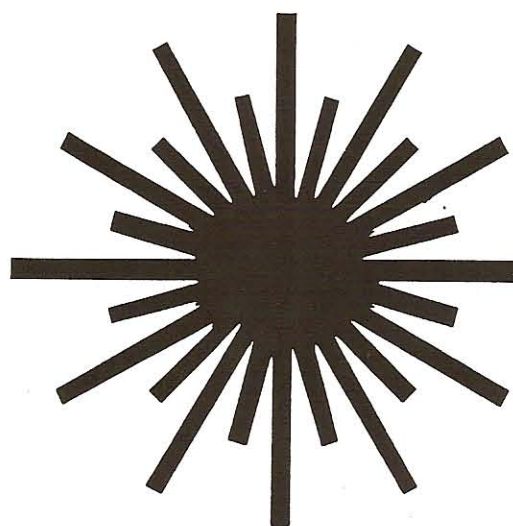


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WAVELENGTH-RESOLVED EMISSION SPECTROSCOPY OF THE ALKOXY AND ALKYLTHIO RADICALS IN A SUPERSONIC JET

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Abstract

Wavelength-resolved emission spectra of methoxy (CH_3O) and methylthio (CH_3S) radicals have been obtained in a supersonic jet environment with a resolution of 0.3 nm by dispersing the total laser-induced fluorescence with a 0.6 m monochromator. A detailed analysis of the single vibronic level dispersed fluorescence spectra yields the following vibrational frequencies for CH_3O in the X^2E state: $\nu_1''=2953\text{ cm}^{-1}$, $\nu_2''=1375\text{ cm}^{-1}$, $\nu_3''=1062\text{ cm}^{-1}$, $\nu_4''=2869\text{ cm}^{-1}$, $\nu_5''=1528\text{ cm}^{-1}$ and $\nu_6''=688\text{ cm}^{-1}$. A similar analysis of the wavelength-resolved emission spectra of CH_3S provides the following ground state vibrational frequencies: $\nu_2''=1329\text{ cm}^{-1}$, $\nu_3''=739\text{ cm}^{-1}$ and $\nu_6''=601\text{ cm}^{-1}$. An experimental uncertainty of 20 cm^{-1} is estimated for the assigned frequencies.

Introduction

The methoxy (CH_3O) radical is a highly reactive transient molecular species that is a key chemical intermediate in the combustion of hydrocarbon fuels and in atmospheric reaction chemistry.¹ It belongs to a larger family of molecules called the alkoxy (RO , $\text{R}=\text{CH}_3$, C_2H_5 , $i\text{-C}_3\text{H}_7$) radicals. The alkoxyes have widespread occurrence in combustion and atmospheric processes. If the O atom in the alkoxy molecules is replaced by the S atom, one obtains the alkylthio (RS) radicals. The alkylthio species are chemical intermediates in the combustion of sulfur-rich fossil fuels.^{1,2} Investigations³ have shown that the methylthio (CH_3S) radical is a key intermediate in the reaction of reduced sulfur compounds (for example, RSH and RSR') with OH radicals in the troposphere.

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CH₃O has an orbitally degenerate ground electronic state (X ²E) and is therefore expected to exhibit Jahn-Teller distortion.⁴ A first order Jahn-Teller distortion leads to spontaneous breaking of the nominal C_{3v} symmetry in CH₃O. CH₃O is an intriguing free radical which possesses a quenched electronic angular momentum; and the associated reduction in spin-orbit splitting gives rise to striking features in the A ²A₁ - X ²E spectral transitions. The spin-orbit interaction in CH₃O splits the X ²E electronic level into two components ²E_{1/2} and ²E_{3/2}. As a result, any vibronic level belonging to the A ²A₁ state can have possible transitions to both spin-orbit components of the X ²E state. CH₃S is analogous⁵ to CH₃O and also has a first electronically excited state A ²A₁ which is known to be predissociative.

Laser-induced fluorescence (LIF) spectroscopy in conjunction with a supersonic jet expansion has been used to study the RO and RS radicals at low temperatures. Fluorescence from the A ²A₁ state of CH₃O and CH₃S was dispersed using a 0.6 m monochromator with 0.3 nm resolution. Several vibrational frequencies have been obtained for both these molecules in the X ²E state; and the experimental uncertainty in the assignments is estimated for the most part to be about 20 cm⁻¹.

Experimental

The alkoxy (RO) radicals were generated *in situ* in the jet expansion by excimer laser (KrF @ 248 nm) photolysis of freshly synthesized RONO.⁶ Jet-cooled alkylthio (RS) radicals were produced by the photodissociation of commercially available precursors R₂S₂ with excimer laser pulses at 248 nm.⁵ The photolysis excimer pulse energy was typically 70-80 mJ. A YAG-pumped dye laser was frequency-doubled to obtain the excitation spectra of CH₃O and C₂H₅O, whereas an excimer-pumped dye laser was employed to record the LIF spectra of *i*-C₃H₇O and the RS (R=CH₃, C₂H₅, *i*-C₃H₇) radicals. Typically, the dye laser pulse energy in the UV was about 1-3 mJ. Wavelength-resolved emission spectra for CH₃O and CH₃S were obtained by exciting the radicals at the wavelength of a rotational transition near a specific band maximum. The LIF was focused onto the entrance slit of a 0.6 m monochromator (Jobin Yvon HRS 2) with 0.2 mm wide slits that had a resolution of 0.3 nm. The output signal at the exit slit was collected by a photomultiplier tube and subsequently relayed to a microcomputer-aided data acquisition system. Both the photolysis and probe lasers were run at 10 Hz and each of the data points was averaged over 10 events. The scan speed of the monochromator grating was maintained at 24 Å per minute and it was calibrated using known mercury lines and a 0.025 mm wide entrance slit. A least-squares fit of the data provided an equation for the calibrated wavenumbers versus the reading of the monochromator dial.

Results and Discussion

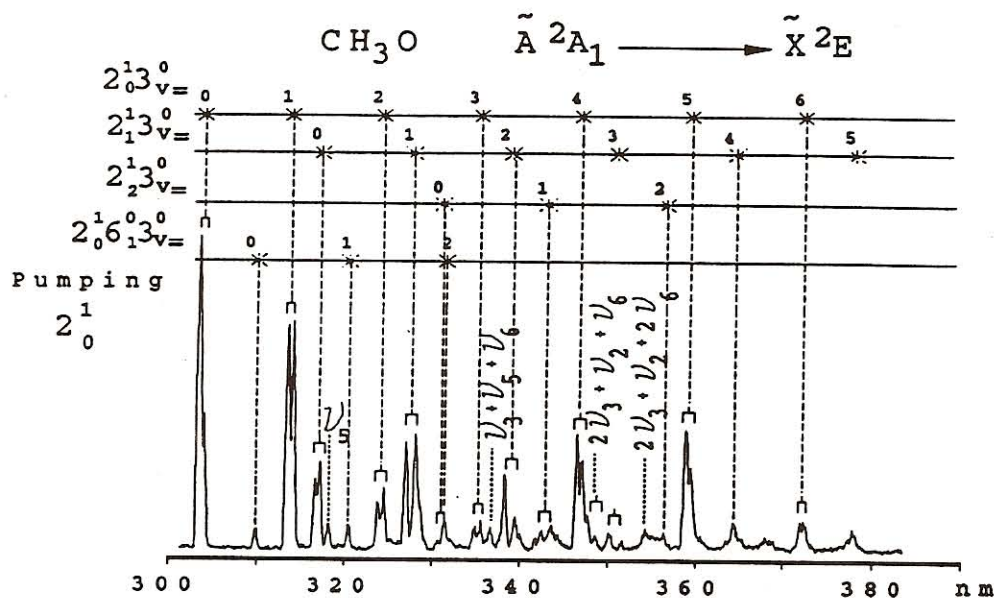


Figure 1. Laser-excited dispersed fluorescence spectrum of CH_3O observed when the 2_0^1 band was pumped. A helium backing pressure of 200 psi was maintained behind the nozzle and the time delay between the photolysis and probe lasers was 6 μs .

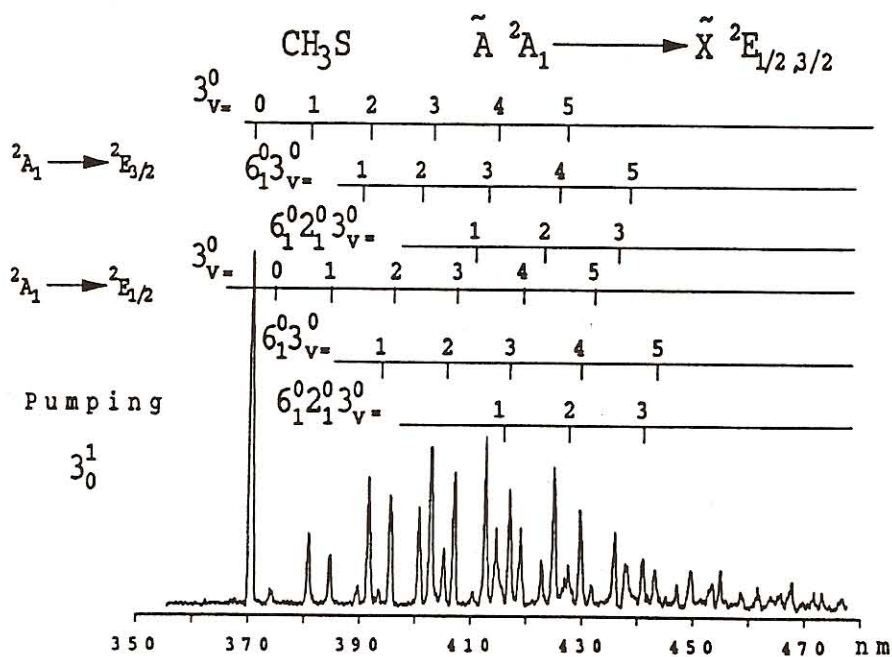


Figure 2. Laser-excited wavelength-resolved emission spectrum of CH_3S observed when the 3_0^1 band was pumped. Two sets of ν_3 progressions were seen and correspond to $\text{A } 2A_1 - \text{X } 2E_{3/2}$ and $\text{A } 2A_1 - \text{X } 2E_{1/2}$ transitions, respectively.

Figure 1 is an illustrative dispersed fluorescence scan for the 2^1_0 band of CH_3O . The first doublet on the left of the scan corresponds to a mix of the pump laser wavelength and the fluorescence arising from the CH_3O transition from the vibrational level in the excited $^2\text{A}_1$ state to levels in the lower $^2\text{E}_{1/2}$ and $^2\text{E}_{3/2}$ states. The second doublet in Fig. 1 shows a pair of transitions separated by 61 cm^{-1} (akin to the first 65 cm^{-1} wide doublet feature) and these doublets are characteristic of the spin-orbit splitting of methoxy in the ground electronic state. Several ν_3 progressions are visible in Fig. 1 and have been assigned in conjunction with ν_2 , ν_5 and ν_6 vibrations. A detailed analysis of the dispersed fluorescence spectra recorded for CH_3O yields the following vibrational frequencies for the X ^2E state: $\nu_1''=2953\text{ cm}^{-1}$, $\nu_2''=1375\text{ cm}^{-1}$, $\nu_3''=1062\text{ cm}^{-1}$, $\nu_4''=2869\text{ cm}^{-1}$, $\nu_5''=1528\text{ cm}^{-1}$ and $\nu_6''=688\text{ cm}^{-1}$.

Figure 2 shows a typical wavelength-resolved emission spectrum for the 3^1_0 band of CH_3S . Two sets of ν_3 progressions are clearly visible corresponding to the $^2\text{A}_1 \rightarrow ^2\text{E}_{3/2}$ and $^2\text{A}_1 \rightarrow ^2\text{E}_{1/2}$ transitions, respectively. The separation between the X $^2\text{E}_{3/2}$ and the X $^2\text{E}_{1/2}$ states gives an accurate value of -267 cm^{-1} for the spin-orbit splitting of the CH_3S ground electronic state. In addition to the independent ν_3 progression in Fig. 2, two other ν_3 progressions are seen; one in combination with ν_6 , and the other in combination with ν_6 and ν_2 . A detailed vibrational analysis of the dispersed fluorescence data for CH_3S has provided the following values for certain fundamental vibrations in the ground state: $\nu_2''=1329\text{ cm}^{-1}$, $\nu_3''=739\text{ cm}^{-1}$ and $\nu_6''=601\text{ cm}^{-1}$.

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References

1. S.C. Foster and T.A. Miller, *J. Phys. Chem.* **93**, 5986 (1989).
2. S.-Y. Chiang and Y.-P. Lee, *J. Chem. Phys.* **95**, 66 (1991).
3. S. Hatakeyama and H. Akimoto, *J. Phys. Chem.* **87**, 2387 (1983).
4. S.C. Foster, P. Misra, T.-Y. D. Lin, C.P. Damo, C.C. Carter, and T.A. Miller, *J. Phys. Chem.* **92**, 5914 (1988).
5. Y.-C. Hsu, X. Liu, and T.A. Miller, *J. Chem. Phys.* **90**, 6852 (1989).
6. A.H. Blatt, ed., *Organic Syntheses*, Collective Vol. 2, Wiley, New York, 1943.