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Communications

Observation of High Resolution Emission Spectra of $\text{CH}_3\text{S}(A^2A_1 \rightarrow X^2E)$

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The methylthio radical CH_3S has been known to be an important intermediate^{1,2} in the atmospheric oxidation of dimethyl sulfide CH_3SCH_3 , which may be related to the air pollution in the atmosphere.³ CH_3S exhibits many interesting features from the spectroscopic point of view. It has an electronic ground state of orbitally degenerate 2E symmetry, as for the methoxy radical CH_3O ,⁴ and thus is subjected to the Jahn-Teller distortion. Also, CH_3S has a relatively large spin-orbit splitting of about -260 cm^{-1} .^{5,6} Thus, it is interesting to examine the interaction between spin-orbit coupling and Jahn-Teller distortion. It has been suggested that Jahn-Teller distortion quench the electronic orbital angular momentum and hence reduce the magnitude of the spin-orbit splitting.⁷

Up to the present, CH_3S has been studied by many spectroscopic methods including emission,^{6,8} microwave,⁹ matrix infrared,¹⁰ electron paramagnetic resonance,¹¹ laser photodetachment,^{12,13} and laser induced fluorescence.^{5,14,15} Although the rovibronic spectra of CH_3S were obtained in a jet using the laser induced fluorescence method,¹⁵ a high resolution emission spectrum has not been reported yet. This is due to the fact that the sensitivity of a Fourier transform (FT) spectrometer is lower than that of laser spectroscopy by an order of one or two, and that even a single noise of the electric discharge can spoil the whole spectrum. Nevertheless, it still seems desirable to obtain the high resolution emission spectrum of short-lived species such as CH_3S using a FT spectrometer, since the spectrum of a wide frequency range can be recorded easily, and more reliable values of the frequencies and the relative intensities of the transition lines can be obtained.¹⁶

In this study, the emission spectra of CH_3S in the transition of $A^2A_1 \rightarrow X^2E$ have been reexamined using a high reso-

lution FT-UV/VIS spectrometer coupled with a technique of supersonic expansion.

The observation of high resolution emission spectra of CH_3S has been carried out using the experimental setup similar to those previously described.^{6,17} The precursor CH_3SCH_3 was expanded with an inert carrier gas He through 0.2 mm diameter of quartz nozzle into the vacuum chamber made by a six-way cross Pyrex glass tube of 5.0 cm in diameter. The concentration of the precursor is believed to be about 1% in the gas mixture. The backing pressure of the nozzle was measured to be about 2 atm. The pressure in the expansion chamber during operation was maintained to lower than 1.0 Torr by using the mechanical vacuum pump. The CH_3S radical was generated in a jet by an electric dc discharge between the anode fixed inside the nozzle and the pump which acts as the cathode. The anode was connected to a 3.0 KV of dc power supply via a 500 K Ω current limiting ballast resistor. The typical operating condition was 5 mA discharge current at the 1.5 KV dc potential. For increased collection of the emission, a quartz lens ($f=5.0 \text{ cm}$, $d=3.8 \text{ cm}$) was placed inside the vacuum chamber. The emission from CH_3S radical in a jet was focussed onto the external port of the FT spectrometer (Bruker IFS-120HR). An area of the jet below the nozzle orifice of 2 mm in diameter was viewed by the PMT (Hamamatsu model 1P28) detector. For the improvement of signal to noise ratio of the spectrum, 410 nm narrow band interference optical filter has been used. The spectral region from 23,000 to 26,000 cm^{-1} was scanned at the resolution of 0.05 cm^{-1} . A total of 1000 scans have been added together over 8 hrs. to obtain the final spectra shown in Figures 1 and 2. The accuracy of the frequency is believed to be better than 0.005 cm^{-1} from the comparison with the I_2 transitions.

According to the low resolution study,⁶ the spectra shown in Figures 1 and 2 were already assigned to the transitions from the vibrational ground state in the excited electronic state 2A_1 to the same C-S stretching ($\nu_3=3$) vibrational states in the spin-orbit splitting levels, $^2E_{3/2}$ and $^2E_{1/2}$ of CH_3S , respectively.

It should be noted that the band shapes of both spectra shown in Figures 1 and 2 are quite different; the former exhibits a clear bandhead on the higher frequency side and is degraded to the red, while the latter shows broader and

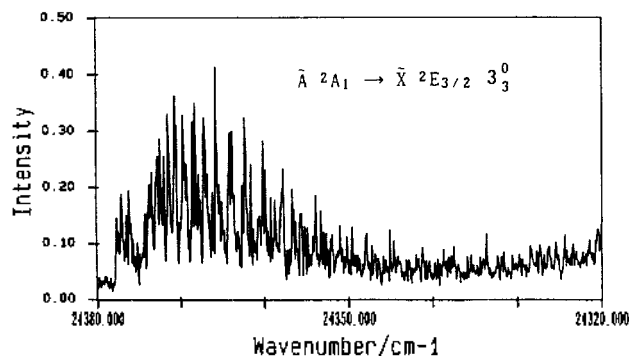


Figure 1. High resolution FT emission spectrum of CH₃S in the transition of $A^2A_1 \rightarrow X^2E_{3/2} (3_3^0)$. The spectrum was obtained from the average of 1000 scans over 8 hrs. at the resolution of 0.05 cm^{-1} .

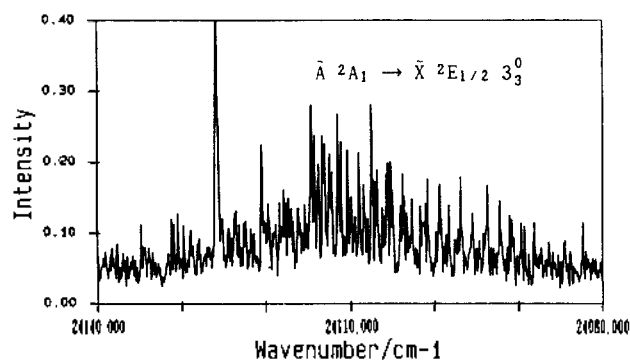


Figure 2. High resolution FT emission spectrum of CH₃S in the transition of $A^2A_1 \rightarrow X^2E_{1/2} (3_3^0)$. The spectrum was obtained from the average of 1000 scans over 8 hrs. at the resolution of 0.05 cm^{-1} . The strong peak located at $21125.8750 \text{ cm}^{-1}$ is from the inert carrier gas He.

symmetric peaks. The difference in the band shape can be ascribed to the difference in geometry between the $^2E_{3/2}$ and $^2E_{1/2}$ states. This suggests that the geometries at the $^2E_{3/2}$ and $^2E_{1/2}$ states be different, and that the rotational constants of the $^2E_{1/2}$ state be close to those of the 2A_1 state.

Janousek *et al.*¹³ have reported the equilibrium geometry of the ground state of CH₃S by *ab initio* calculation at the 4-31G level to be $r_{\text{C-S}}=1.76 \text{ \AA}$, $r_{\text{C-H}}=1.10 \text{ \AA}$, and $(\text{H-C-S})=110.9^\circ$ in strict C_{3v} symmetry. Because of the Jahn-Teller distortion, the potential minimum was obtained at the geometry such that the C-S bond makes an angle of 0.35° with the principal axis, and the energy at this geometry is 21 cm^{-1} lower than that for the strict C_{3v} symmetry. Also, Suzuki *et al.*¹⁴ roughly estimated the molecular geometries of CH₃S with C_{3v} symmetry such that the optimum angle is 100° for both the $^2E_{1/2}$ and 2A_1 states and 110.9° for the

$^2E_{3/2}$ state by assuming $r_{\text{C-S}}$ is constant in both $^2E_{1/2}$ and $^2E_{3/2}$ states and changing the H-C-S angle.

On the other hand, it has been found¹⁵ that C-S bond length increases by 0.3 \AA in the excited electronic 2A_1 state, which can be easily confirmed by the dramatic decrease in the vibrational frequency of the ν_3 band upon electronic excitation.⁶ Since the rotational constant B value is primarily determined by the C-S bond length with minor contributions from the position of the H's, the molecular geometry in the excited electronic 2A_1 state should be different from that in the $^2E_{1/2}$ state. Thus, more accurate molecular geometry should be determined by fitting the observed spectra to the appropriate molecular Hamiltonian⁴ which includes electronic, vibrational, rotational, centrifugal distortion, spin-orbit coupling and spin-rotation interaction terms. The analysis is now in progress.

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