

for their help in obtaining the laser flash photolysis data.

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Observation of Electronic Emission Spectra of CH₃S

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The combination of Fourier Transform spectroscopy with a technique of supersonic expansion has been employed to examine the vibronic structure of the transition $A^2A_1 \rightarrow X^2E$ of CH₃S radical. CH₃S was produced by an electric *dc* discharge of the precursor (CH₃)₂S. The emission spectrum of CH₃S shows extensive progressions of CS stretching frequencies in the transitions. The molecular parameters describing the vibrational structure of CH₃S have been determined with high accuracy from the analysis of the emission spectrum.

Introduction

For a long time, alkylthio radicals (RS·) have been reported¹⁻³ to be an intermediate in combustion and atmospheric

chemistry of organosulfur compounds. These compounds also play an important role in the atmospheric sulfur cycle and contribute to the acidic rain problem. Particularly, CH₃S is considered an important intermediate in oxidative reaction

of CH₃SCH₃, CH₃SSCH₃, and CH₃SH, which may be related to the air pollution in the atmosphere.⁴

From the spectroscopic point of view, CH₃S has many interesting features. It has a ²E ground electronic state and thus is subjected to the Jahn-Teller distortion. CH₃S has a relatively large spin-orbit interaction compared to its counterpart CH₃O.⁵ Thus, an accurate determination of the magnitudes of the spin-orbit interaction and the Jahn-Teller distortion is very interesting.⁶ In addition, it provides a good opportunity to examine the interaction between the Jahn-Teller distortion and the spin-orbit splitting.

Until now, CH₃S has been investigated by several spectroscopic methods including emission,⁵ microwave,⁷ matrix infrared,⁸ electronic paramagnetic resonance,⁹ laser photodetachment^{10,11} and laser induced fluorescence.^{12,13} The emission experiment estimated the possible position of the band origin of the transition $A^2A_1 \rightarrow X^2E$ of CH₃S.⁵ The LIF experiment¹² could determine the lifetime at given vibronic states. In addition to its lifetime measurement, the vibrational structure of CH₃S was analyzed from the fluorescence dispersion spectra. On the other hand, high resolution LIF experiment¹³ employing a supersonic expansion system resolved the rotational structure of the transition $A^2A_1 \rightarrow X^2E$ of CH₃S and could obtain the molecular parameters at the ground and the excited electronic states.

However, to our surprise, there has been no extensive studies on the vibrational progressions of CH₃S in the ground and the excited electronic states. In this paper, we report the vibrational frequencies of the transition $A^2A_1 \rightarrow X^2E$ of CH₃S from the analysis of the emission spectrum obtained with a FT-spectrometer combined with a supersonic expansion system.

Experimental

CH₃S is a very unstable molecule and does not exist in the normal condition. Thus, it has been usually produced⁵ by photolyzing a geometrically ideal precursor dimethyl disulfide, CH₃SSCH₃ by using strong radiation sources such as excimer lasers.¹² However, an electric *dc* discharge of this precursor generates a large amount of S₂ molecule due to the easy cleavage of C-S bond rather than CH₃S radical. On the other hand, another precursor methyl sulfide, CH₃SCH₃ can be used for the generation of CH₃S by an electric *dc* discharge without producing S₂.

Figure 1 shows the experimental setup which is similar to those used previously.¹⁴ CH₃S radical was produced from the mixture of He buffer gas and the precursor (CH₃)₂S[He : (CH₃)₂S = 100 : 1] with an electric *dc* discharge in the supersonic expansion system. For the supersonic expansion system, 2 atm pressure of the gas mixture has been expanded through 0.2 mm diameter of nozzle into an expansion chamber which was made of 6-way cross Pyrex glass tube of 5.0 cm in diameter, and was maintained by a mechanical vacuum pump and a boost pump to less than 1.0 Torr of pressure. The nozzle was made by a glass capillary of thick wall, narrowed at one end to provide the desired hole size. The anode was a 2 mm diameter of stainless steel rod sharpened at the tip and inserted into the capillary through an O-ring to within 1 mm of the orifice. The copper pipe of 7.5 cm in diameter connecting the expansion to the pump

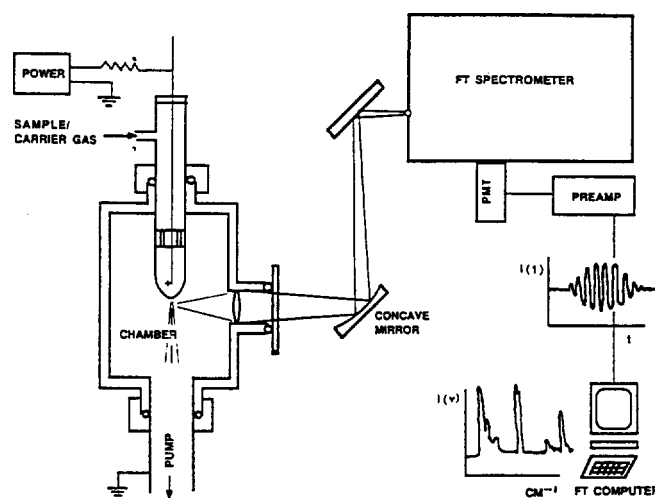


Figure 1. Schematic diagram of the experimental apparatus used for this work.

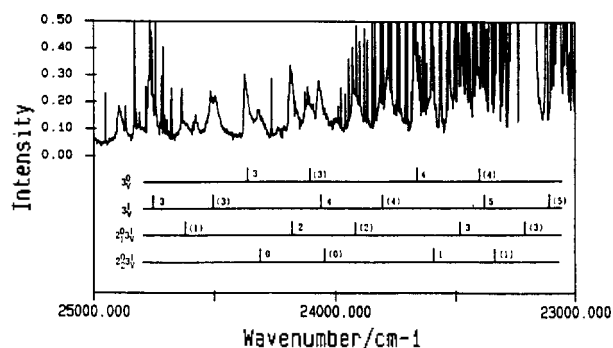


Figure 2. A portion of the CH₃S spectrum obtained with the FT-spectrometer at the resolution of 2.0 cm⁻¹. The numbers without parenthesis and with parentheses indicate the vibrational quantum numbers of the transitions $^2A_1 \rightarrow ^2E_{3/2}$ and $^2A_1 \rightarrow ^2E_{1/2}$, respectively.

was used as the cathode at the ground potential. The distance between the two electrodes was about 30 cm. The typical operating condition was about 5 mA discharge current and 3.0 KV of *dc*. The discharge was stabilized by using a 250 KΩ of current-limiting ballast resistor. With this operating conditions, we were able to obtain the rotational temperature to $T_{rot} = \sim 50$ K according to a theoretical calculation of the intensity distribution of the rotational spectrum.¹⁵ The discharge emission from an area of the jet below the nozzle orifice was focussed with several optics onto the emission port of a FT-spectrometer (Bruker model IFS120HR) and was detected with a PMT (Hamamatsu model 1P28). The optical alignment of the spectrometer was optimized by adjusting the position of the beamsplitter and the fixed mirror.

Since the emission from the He gas and fragment molecules, mostly CH radical in this case is much stronger than that of CH₃S, an optical filter of a suitable spectral range (Corning model number 5-57) was used to block off the unwanted emission. The color filter used for this purpose has spectral window range of about 18000-30000 cm⁻¹. Typically, 1000 spectra were averaged over 30 min to obtain the final emission spectrum shown in Figure 2 at the resolution of

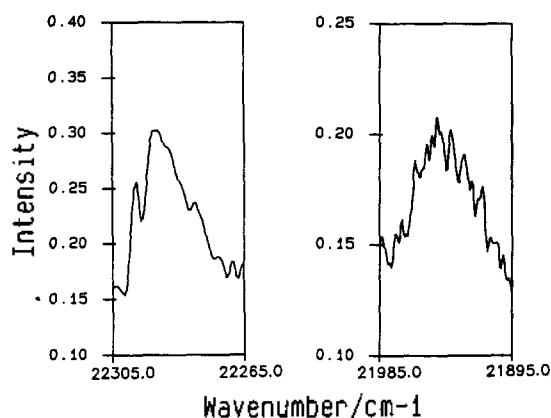


Figure 3. Typical bandshape exemplified by the CH_3S spectrum. The band having bandhead in the right side is from the ${}^2A_1 \rightarrow {}^2E_{3/2}$ (3_3^0) transition and the other having more symmetric shape in the left side is from ${}^2A_1 \rightarrow {}^2E_{1/2}$ ($2_3^0 3_3$) transition.

2 cm^{-1} . The frequency of the spectrometer was calibrated with the I_2 transitions in the I_2 atlas¹⁶ and believed to be better than 0.01 cm^{-1} in this spectrum.

The 0_0^0 bandhead of the transition ${}^2A_1 \rightarrow {}^2E_{3/2}$ of CH_3S was reported by Suzuki *et al.*¹² to be located at 26530 cm^{-1} . Since this experiment is to obtain the emission spectrum of CH_3S , which must lie in the lower frequency region of the band origin, the spectrum region from 17000 to 32000 cm^{-1} was scanned.

Results and Discussion

Figure 2 shows a portion of CH_3S emission spectrum obtained with the FT-spectrometer at the resolution of 2 cm^{-1} . Most of CH_3S bands are found in the range of 20000 – 27000 cm^{-1} . In some frequency regions, CH_3S bands are heavily overlapped with the peaks of CH. The peaks of CH at 23200 and 25600 cm^{-1} are from the transitions of $A^2\Delta \rightarrow X^2\Pi$ and $B^2\Sigma^- \rightarrow X^2\Pi$, respectively.¹⁷ Since the CH and He peaks appears as sharp and strong compared to those of CH_3S , we have no problem in distinguishing the CH_3S bands from those of CH and He. The molecular radical CH was produced from the precursor $(\text{CH}_3)_2\text{S}$ by electric discharge in the decomposing process. The He peaks are from the buffer gas. The position of the maxima of CH_3S bands was measured within $\pm 0.1 \text{ cm}^{-1}$. In the emission of CH_3S , the characteristics of the doublet bands are attributed to the transitions of ${}^2A_1 \rightarrow {}^2E_{3/2}$ and ${}^2A_2 \rightarrow {}^2E_{1/2}$, respectively. Thus, the interval between the doublet bands are easily identified as the spin-orbit splitting (${}^2E_{3/2}$, ${}^2E_{1/2}$) of the ground electronic state. The tentative assignment of the bands has been made with the LIF data¹² on this molecule. Since the emission spectrum, in general, is much more complicated compared to the LIF spectrum, the bands with weak intensity have been analyzed by using the Hamiltonian⁷ shown below

$$F'(v_3') = T_v + \omega_3'(v_3' + 0.5) - \omega_3'x_3'(v_3' + 0.5)^2 \quad \text{for } {}^2A_1 \text{ state}$$

$$F''(v_2'', v_3'') = \omega_3''(v_3'' + 0.5) - \omega_3''x_3''(v_3'' + 0.5)^2 \\ + \omega_2''(v_2'' + 0.5) - \omega_2''x_2''(v_2'' + 0.5)^2 \\ + \omega_{23}''x_{23}''(v_2'' + 0.5)(v_3'' + 0.5) \quad \text{for } {}^2E_{3/2} \text{ state}$$

Table 1. CH_3S Band Positions and Assignments^a

${}^2A_1 \rightarrow {}^2E_{3/2}$	${}^2A_1 \rightarrow {}^2E_{1/2}$	Assignments ^b
Position (cm^{-1})	Position (cm^{-1})	
25800.4	N.O.	3_3^0
25080.4	24818.5	3_3^0
24371.7	24111.6	3_3^0
23668.5	23408.1	3_3^0
22974.2	22713.2	3_3^0
22292.0	22032.0	3_3^0
21619.8	21358.6	3_3^0
20956.1	N.O.	3_3^0
26200.9	25936.0	3_3^1
25479.9	25218.4	3_3^1
24769.0	24509.7	3_3^1
24069.6	23810.2	3_3^1
23375.0	N.O.	3_3^1
22692.9	N.O.	3_3^1
22020.1	21757.4	3_3^1
26597.5	26337.8	3_3^2
25876.1	25617.9	3_3^2
25166.3	24905.8	3_3^2
25218.4	24957.6	2_3^0
24496.3	24235.5	$2_3^0 3_3^0$
23782.7	23522.3	$2_3^0 3_3^0$
23079.6	22820.7	$2_3^0 3_3^0$
22386.5	22126.5	$2_3^0 3_3^0$
21700.1	21440.6	$2_3^0 3_3^0$
21027.2	20763.0	$2_3^0 3_3^0$
20360.1	20100.1	$2_3^0 3_3^0$
25617.9	N.O.	$2_3^0 3_3^1$
24895.1	24634.7	$2_3^0 3_3^1$
24183.4	23923.4	$2_3^0 3_3^1$
23478.8	23217.3	$2_3^0 3_3^1$
22785.0	22525.3	$2_3^0 3_3^1$
23917.4	23658.5	2_3^1
22497.0	22235.9	$2_3^1 3_3^0$
21800.6	21541.7	$2_3^1 3_3^0$
21114.2	20854.9	$2_3^1 3_3^0$
20437.9	20178.6	$2_3^1 3_3^0$
19769.3	19508.9	$2_3^1 3_3^0$
24317.7	24057.3	$2_3^1 3_3^1$
23602.3	N.O.	$2_3^1 3_3^1$
22896.0	22636.5	$2_3^1 3_3^1$
22200.5	21942.0	$2_3^1 3_3^1$
21514.1	N.O.	$2_3^1 3_3^1$
23030.0	N.O.	$2_3^1 3_3^1$
22319.9	22060.0	$2_3^1 3_3^1$
21619.8	21358.6	$2_3^1 3_3^1$

^aN.O. stands for no observation due to the weak intensity or overlap. ^bThe assignment 3_3^0 means the transition of the v_3 vibrational mode from $v=0$ at the upper electronic state (2A_1) to $v=1$ at the ground electronic state (2E).

From these analyses, a total of 45 and 37 vibrational peaks belonging to the progressions of 4 fundamental and 5 combi-

Table 2. Determined Parameters and Spin-Orbit Coupling Constant (*A*) of CH₃S^a

Parameters	This work ^b	Previous Work ^c
T_e	27360.02(47)	27332.59
ω_3'	402.68(101)	410.0
$\omega_3'x_3'$	1.44(38)	3.44
ω_3''	742.98(24)	744.8
$\omega_3''x_3''$	4.72(3)	5.45
ω_2''	1326.83(71)	1322.3
$\omega_2''x_2''$	5.56(19)	3.32
$\omega_{23}''x_{23}''$	-7.40(8)	-8.5
<i>A</i>	260.4 ± 2.0	-255.5 ^d
Number of data	45	24

^ain units of cm⁻¹. ^bNumber in parenthesis is one standard error in units of last digit in the parameter. ^cReferences (12). ^dReference (13).

national bands has been identified in each electronic transition ${}^2A_1 \rightarrow {}^2E_{3/2}$ and ${}^2A_1 \rightarrow {}^2E_{1/2}$, respectively. Table 1 lists the frequencies and assignments of the CH₃S bands observed in the emission spectrum. With the accurate measurement of the positions of the peak maxima, we have found that the differences in frequencies between ${}^2A_1 \rightarrow {}^2E_{3/2}$ and ${}^2A_1 \rightarrow {}^2E_{1/2}$ are nearly constant over the whole range observed. It turned out that the intensity of the transition ${}^2A_1 \rightarrow {}^2E_{1/2}$ is weaker than that of the ${}^2A_1 \rightarrow {}^2E_{3/2}$.

The molecule, CH₃S has the 2E ground electronic state (${}^2E_{1/2}$ and ${}^2E_{3/2}$) and a relatively large spin-orbit splitting. The spin-orbit interaction has been estimated to be about -280 ± 20 cm⁻¹ by LIF method^{5,12}, -221.0 ± 2.0 cm⁻¹ by microwave spectroscopy,¹⁸ and -255.5 cm⁻¹ by very low temperature LIF method.¹³ In this work, the spin-orbit coupling constant (*A*) has been determined to be -260.4 ± 2.0 cm⁻¹ from the differences in the frequencies between ${}^2A_1 \rightarrow {}^2E_{3/2}$ and ${}^2A_1 \rightarrow {}^2E_{1/2}$. The value obtained in this work agrees well with the result of the previous work¹³ employing LIF method. The final vibrational parameters by the least squares fit to the Hamiltonian shown above are summarized in Table 2. With these parameters, the positions of the observed bands could be predicted within a few wavenumbers. Also, it is interesting to note that the value of *A* for CH₃S is smaller than that for SH (-377 cm⁻¹).¹³ The trend is same as the case of CH₃O (-62 cm⁻¹)¹⁹ and OH (-139 cm⁻¹).²⁰

In addition, it has been shown in Figure 3 that the bandshape for the ${}^2A_1 \rightarrow {}^2E_{3/2}$ transition is quite different from that for ${}^2A_1 \rightarrow {}^2E_{1/2}$. The former shows clear bandheads with red degradation and the latter exhibits broader and more symmetric peaks. This means that the molecular structures in the ${}^2E_{3/2}$ and ${}^2E_{1/2}$ states are different, and that the rotational constant of the ${}^2E_{1/2}$ levels is close to that of the excited 2A_1 state. Since, according to the Franck-Condon principle, the variation of peak intensities reflects the bond length at both states connected by the transition, the structure in the excited state can be estimated if we know the structure in the ground state and the intensity variation over the transition quantum numbers. The structure in the ground electronic state was already determined by using microwave spect-

roscopy on this molecule.⁷ The analysis of the intensity distribution of the vibronic transition in the emission spectrum is now in progress.

Conclusion

The emission spectrum of CH₃S has been obtained with an FT-spectrometer coupled with a supersonic expansion system. The spectrum shows vibrational progression of the fundamental and combinational bands in the frequency range of 20000-27000 cm⁻¹. The bands observed have been extensively assigned. The harmonic frequencies and anharmonic constant of the bands have been determined in the ground and the excited electronic states. Also the spin-orbit coupling constant (*A*) in the ground electronic state has also been estimated to be $A = -260.4$ cm⁻¹. With these parameters, we could predict the positions of vibrational peaks within a few wavenumber.

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The Electronic Structure and Chemical Bonding between Metal and Oxygen Atoms: Tl22-Based Copper Oxide Superconductors

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Using tight-binding molecular orbital methods for charged cluster models, we studied the electronic structure and chemical bonding of thallium-oxygen and copper-oxygen atoms in Tl22-based copper oxide. The interaction between the s orbital of Tl atom and the p_x and p_y orbitals of O3_{eq} atom in the Tl layers results in nonbonding. The interaction between the s orbital of Tl atom and the p_z orbital of O2 and O3_{ax} atoms in Ba and Tl layers results in antibonding. The interaction between the d_{z^2} orbital of Cu atom and the p_z orbital of O2 atom also results in antibonding. The Tl22-based copper oxide superconductors can be understood in terms of a local electron transfers from Cu layers to Tl layers along c -direction. The resulting electron transfers have the same patterns as those of YBa₂Cu₃O₇ and YBa₂Cu₄O₈ superconductors.

Introduction

At present Tl-based copper oxide superconductors show the highest superconducting transition temperatures T_c^{1-5} . The Tl-based copper oxide superconductors have Cu perovskite-like unit structures. These compounds can be divided into two types according to the space group. Type I that is Tl12-based copper oxide superconductors has space group P4/mmm. Type II that is Tl22-based copper oxide superconductors has the space group I4/mmm. The ideal superconducting phases of Tl12-based and Tl22-based copper oxide superconductors may be classified into six groups, TlBa₂CaCu₂O₇(Tl1212 system)⁶, TlBa₂Ca₂Cu₃O₁₀(Tl1223)⁷, TlBa₂Ca₃Cu₄O₁₁(Tl1234)⁸, Tl₂Ba₂CuO₆(Tl2201)³, Tl₂Ba₂CaCu₂O₈(Tl2212)⁴, and Tl₂Ba₂Ca₂Cu₃O₁₀(Tl2223)⁵.

The structures of these systems are separated by Tl-O monolayer and Tl-O bilayers for Tl12-based and Tl22-based copper oxide superconductors. Figure 1 shows nominal unit cells⁹ for Tl2201, Tl2212, and Tl2223 superconductors. Ca²⁺ cations are between adjacent Cu layers and Ba²⁺ cations between Cu layers and Tl layers. From the comparison of the crystal structures of YBa₂Cu₃O₇ and Tl22-based copper oxide superconductors, copper-oxygen chains are present in a YBa₂Cu₃O₇ superconductor, while these chains are absent in Tl22-based copper oxide superconductors.

Using ASED-MO¹⁰ of the tight-binding molecular orbital method, we studied electronic structures and chemical bonding of the thallium-oxygen and copper-oxygen atoms for Tl22-based copper oxide superconductors.

The Cluster Size and Calculation Methods

The oxygen atoms in different layers of superconductors are crystallographically inequivalent. Tl22-based copper oxide

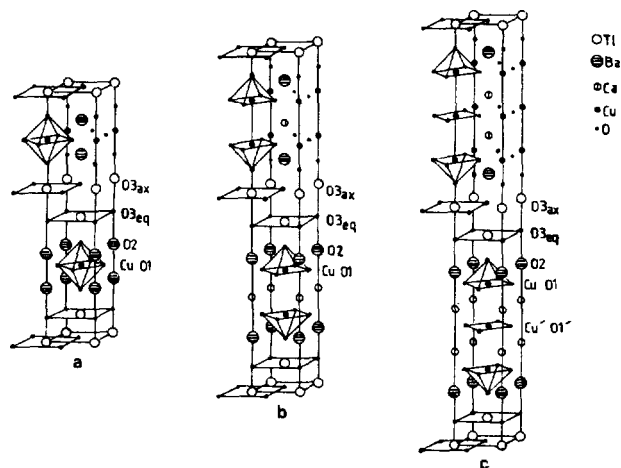


Figure 1. Nominal unit cells for Tl₂Ba₂CuO₆, Tl₂Ba₂CaCu₂O₈, and Tl₂Ba₂Ca₂Cu₃O₁₀ superconductors. (a) Tl₂Ba₂CuO₂ superconductors. (b) Tl₂Ba₂CaCu₂O₈ superconductor. (c) Tl₂Ba₂Ca₂Cu₃O₁₀ superconductors.

superconductors are labeled by O1 (in Cu layers), O2 (in Ba layers), and O3 (in Tl layers). The atoms in the two inequivalent Cu layers are labeled Cu, O1, Cu' and O1'. These labels are shown in Figure 1. We also use atoms O3_{eq} and O3_{ax} which stand for equatorial and axial positions in the Tl double layer for Tl22-based copper oxide superconductors.

Freeman *et al.*¹¹ and Kasowski *et al.*¹² calculated the band structure and electronic structure using the band theory for Tl22-based copper oxide superconductors. Their findings indicate that the Tl and Cu layers affect Fermi energy states. Using the full-potential linearized augmented plane-wave