for their help in obtaining the laser flash photolysis data.

References


Observation of Electronic Emission Spectra of CH₃S

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Received January 13, 1993

The combination of Fourier Transform spectroscopy with a technique of supersonic expansion has been employed to examine the vibronic structure of the transition A²Π→X²Σ of CH₃S radical. CH₃S was produced by an electric 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 reported to be an intermediate in combustion and atmospheric chemistry of organosulfur compounds. Theses 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 CH₃S, CH₃SSCH₂ and CH₂SH, 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 ³E 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,⁷ microwave,⁷ matrix infrared,⁸ electronic paramagnetic resonance,⁹ laser photodetachment,¹⁰¹¹ and laser induced fluorescence.¹²¹³ The emission experiment estimated the possible position of the band origin of the transition A²A₁→X²E 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 A²A₁→X²E 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 A²A₁→X²E 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 produced by photolyzing a geometrically ideal precursor dimethyl disulfide, CH₃SSCH₃ by using strong radiation sources such as excimer lasers.¹⁴ 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 (CH₃SCH₃:CH₃S=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.](image)

![Figure 2. A portion of the CH₃S spectrum obtained with the FT-spectrometer at the resolution of 20 cm⁻¹. The numbers without parenthesis and with parentheses indicate the vibrational quantum numbers of the transitions A₁→Eₓ₂ and A₁→E₁₂, respectively.](image)
Figure 3. Typical bandshape exemplified by the CH$_3$S spectrum. The band having bandhead in the right side is from the $^2A_1 \rightarrow ^2E_{2g}$ (3G) transition and the other having more symmetric shape in the left side is from $^2A_1 \rightarrow ^2E_{1u}$ (3I) transition.

2 cm$^{-1}$. The frequency of the spectrometer was calibrated with the $I_2$ transitions in the $I_2$ atlas$^{16}$ and believed to be better than 0.01 cm$^{-1}$ in this spectrum.

The Q$\bar{0}$ bandhead of the transition $^2A_1 \rightarrow ^2E_{2g}$ of CH$_3$S 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$_3$S, 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$_3$S emission spectrum obtained with the FT-spectrometer at the resolution of 2 cm$^{-1}$. Most of CH$_3$S bands are found in the range of 20000-27000 cm$^{-1}$. In some frequency regions, CH$_3$S bands are heavily overlapped with the peaks of CH. The peaks of CH at 23200 and 25600 cm$^{-1}$ are from the transitions of $A^3X^3 \rightarrow X^3\Pi$ and $B^3\Sigma^- \rightarrow \chi^3\Pi$, respectively.$^{11}$ Since the CH and He peaks appears as sharp and strong compared to those of CH$_3$S, we have no problem in distinguishing the CH$_3$S bands from those of CH and He. The molecular radical CH was produced from the precursor (CH)$_2$S by electric discharge in the decomposing processes. The He peaks are from the buffer gas. The position of the maxima of CH$_3$S bands were measured within ±0.1 cm$^{-1}$. In the emission of CH$_3$S, the characteristics of the doublet bands are attributed to the transitions of $^2A_1 \rightarrow ^2E_{2g}$ and $^2A_4 \rightarrow ^2E_{1g}$, respectively. Thus, the interval between the doublet bands are easily identified as the spin-orbit splitting ($E_{2g}$, $E_{1g}$) of the ground electronic state. The tentative assignment of the bands has been made with the LIF data$^{13}$ 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 Hamiltonian shown below

\[
F'(v') = T + \omega_3(v' + 0.5) - \omega_2 x_3 (v' + 0.5)^2
\]

for $^2A_1$ state

\[
F''(v_i, v_f) = \omega_3 (v_f + 0.5) - \omega_2 x_3 (v_i + 0.5)^2
+ \omega_1 x_2 (v_f + 0.5) - \omega_1 x_2 (v_i + 0.5)^2
+ \omega_3 x_3 (v_i + 0.5) (v_f + 0.5)
\]

for $^2E_{2g}$ state

Table 1. CH$_3$S Band Positions and Assignments$^a$

<table>
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<tr>
<th>Position (cm$^{-1}$)</th>
<th>Assignments$^b$</th>
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</tr>
<tr>
<td>25080.4</td>
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<td>23668.5</td>
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</tr>
<tr>
<td>22292.0</td>
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<td>21519.8</td>
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</table>

$^a$ N.O. stands for no observation due to the weak intensity or overlap. $^b$ The assignment 3I means the transition of the $v_1$ 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

<table>
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<th>Parameters</th>
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<th>Previous Work</th>
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<td>27322.59</td>
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<td>402.68(101)</td>
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</tr>
<tr>
<td>\omega</td>
<td>742.98(24)</td>
<td>744.8</td>
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<tr>
<td>\omega\tau</td>
<td>4.72(3)</td>
<td>5.45</td>
</tr>
<tr>
<td>\omega\tau'</td>
<td>1326.83(71)</td>
<td>1322.3</td>
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<td>\omega'\tau</td>
<td>5.56(19)</td>
<td>3.32</td>
</tr>
<tr>
<td>\omega'\tau'</td>
<td>-7.40(8)</td>
<td>-8.5</td>
</tr>
<tr>
<td>A</td>
<td>260.4 \pm 2.0</td>
<td>-255.5</td>
</tr>
</tbody>
</table>

Number of data: 45, 24

*a in units of cm⁻¹. b Number in parenthesis is one standard error in units of last digit in the parameter. c Reference (12). d Reference (13).

The electronic bands have been identified in each electronic transition \( ^2A_1 \rightarrow ^2E_{18} \) and \( ^2A_1 \rightarrow ^2E_{14} \) 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 \( ^2A_1 \rightarrow ^2E_{18} \) and \( ^2A_1 \rightarrow ^2E_{14} \) are nearly constant over the whole range observed. It turned out that the intensity of the transition \( ^2A_1 \rightarrow ^2E_{14} \) is weaker than that of the \( ^2A_1 \rightarrow ^2E_{18} \).

The molecule, CH₃S has the \( ^2E \) ground electronic state (\( ^2E_{18} \) and \( ^2E_{14} \)) and a relatively large spin-orbit splitting. The spin-orbit interaction has been estimated to be about \(-280 \pm 20 \text{ cm}^{-1} \) by LIF method\(^{12} \), \(-221.0 \pm 2.0 \text{ cm}^{-1} \) by microwave spectroscopy,\(^{18} \) and \(-255.5 \text{ cm}^{-1} \) by low temperature LIF method.\(^{19} \) In this work, the spin-orbit coupling constant (A) has been determined to be \(-260.4 \pm 2.0 \text{ cm}^{-1} \) from the differences in the frequencies between \( ^2A_1 \rightarrow ^2E_{18} \) and \( ^2A_1 \rightarrow ^2E_{14} \). The value obtained in this work agrees well with the result of the previous work\(^{12} \) 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 (\(-377 \text{ cm}^{-1})^{10} \). The trend is said as the case of CH₂O (\(-82 \text{ cm}^{-1})^{10} \) and OH (\(-139 \text{ cm}^{-1})^{10} \).

In addition, it has been shown in Figure 3 that the bandshape for the \( ^2A_1 \rightarrow ^2E_{18} \) transition is quite different from that for \( ^2A_1 \rightarrow ^2E_{14} \). 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 \( ^2E_{18} \) and \( ^2E_{14} \) states are different, and that the rotational constant of the \( ^2E \) 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 spectroscopy 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 has 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 \( A = -260.4 \text{ cm}^{-1} \). With these parameters, we could predict the positions of vibrational peaks within a few wavenumber.

**Acknowledgement.** This work was supported by the Korea Science and Engineering Foundation (Grant No. 923-0300-007-2). The author thanks The Ohio State University for letting use the FT-spectrometers (Bruker IFS120HR).

**References**

15. S. K. Lee, unpublished data on CN emission.
The Electronic Structure and Chemical Bonding between Metal and Oxygen Atoms: TlI22-Based Copper Oxide Superconductors

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Received September 30, 1992

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 TlI22-based copper oxide. The interaction between the s orbital of Tl atom and the p_z and p_y orbitals of O3w atom in the Tl layers results in nonbonding. The interaction between the s orbital of Tl atom and the p_y orbital of O2 and O3w atoms in Ba and Tl layers results in antibonding. The interaction between the d_{z^2} orbital of Cu atom and the p_y orbital of O2 atom also results in antibonding. The TlI22-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 TlI-based copper oxide superconductors show the highest superconducting transition temperatures T_c=2-3. The TlI-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 TlI22-based copper oxide superconductors has space group P4/mmm. Type II that is TlI22-based copper oxide superconductors has the space group I4/mmm. The ideal superconducting phases of TlI22-based and TlI22-based copper oxide superconductors may be classified into six groups, TlBa2CaCu3O8(TlI212 system)5, TlBa2CaCu4O8(TlI223)5, TlBa2Ca2Cu4O8(TlI234)5, Tl2Ba2Cu3O6(Tl201)5, Tl2Ba2Cu4O8(Tl2212)5, and Tl2Ba2Ca2Cu4O8(Tl2223)5.

The structures of these systems are separated by Tl-O monolayer and Ti-O bilayers for TlI22-based and TlI22-based copper oxide superconductors. Figure 1 shows nominal unit cells 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 TlI22-based copper oxide superconductors, copper-oxide chains are present in a YBa2Cu3O7 superconductor, while these chains are absent in TlI22-based copper oxide superconductors.

Using ABED-MO5 of the tight-binding molecular orbital method, we studied electronic structures and chemical bonding of the thallium-oxygen and copper-oxygen atoms for TlI22-based copper oxide superconductors.

The Cluster Size and Calculation Methods

The oxygen atoms in different layers of superconductors are crystallographically inequivalent. TlI22-based copper oxide 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, Cu', and O1'. These labels are shown in Figure 1. We also use atoms O3w and O3z, which stand for equatorial and axial positions in the TlI double layer for TlI22-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 TlI22-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