

Fourier transform emission spectroscopy at 13 μm : Vibration-rotation spectrum of SiS

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The vibration-rotation emission spectrum of the high temperature molecule SiS was recorded with a Fourier transform spectrometer. The observation of a high resolution emission spectrum at 13 μ (750 cm^{-1}) is unusual but we believe this technique is generally applicable to high temperature species. Seven bands (1-0 through 7-6) of the main isotopic form, $^{28}\text{Si}^{32}\text{S}$, were observed along with three bands (1-0, 2-1, and 3-2) for each of the minor species, $^{29}\text{Si}^{32}\text{S}$, $^{30}\text{Si}^{32}\text{S}$, and $^{28}\text{Si}^{34}\text{S}$. Mass-reduced Dunham parameters, including Watson's correction due to the breakdown of the Born-Oppenheimer approximation, were derived from the data.

I. INTRODUCTION

Silicon monosulfide is a closed-shell molecule isovalent with carbon monoxide. SiS is, however, a solid at room temperature rather than a gas but high concentrations are readily achieved at elevated temperatures in a furnace.

Silicon monosulfide is an important astrophysical molecule. Morris *et al.*¹ discovered SiS in the envelope of the infrared carbon star IRC + 10216. There have been many additional astronomical microwave observations²⁻⁶ of SiS including a $J = 1 \rightarrow 0$ maser transition⁶ in IRC + 10216. More recently, SiS has been detected in oxygen-rich circumstellar shells⁷ and in the interstellar medium.⁸

The first laboratory spectra of SiS were recorded by Barrow and Jevons⁹ in the ultraviolet region of the spectrum. Since then there have been numerous analyses,¹⁰⁻²⁰ including a deperturbation of the $A^1\Pi-X^1\Sigma^+$ transition by Harris *et al.*²⁰ and the observation of $a^3\Sigma^+-X^1\Sigma^+$ and $b^3\Pi-X^1\Sigma^+$ chemiluminescence.^{21,22} He I photoelectron spectra²³ provided additional information about the electronic and vibrational structure of SiS and SiS^+ .

Microwave spectra of SiS are available²⁴⁻²⁹ and the ground state dipole moment of 1.73 D was determined by two groups from Stark effect measurements.^{27,28} Even the molecular g -factors are known.²⁹

Numerous theoretical calculations of the molecular properties of SiS have been published. Some of the more recent calculations were completed by Li *et al.*,³⁰ Müller-Plathe and Laaksonen,³¹ Lima and Canuto.³² In addition, Robbe *et al.*³³ interpreted the excited state perturbations with the help of *ab initio* theory. *Ab initio* calculations were also helpful in assigning the photoelectron spectra²³ and in the determination of the proton affinity.³⁴

Missing from this extensive body of work on SiS is the infrared vibration-rotation spectra. Atkins and Timms³⁵ recorded a low resolution spectrum of the fundamental mode of SiS isolated in a Kr matrix. However, no gas-phase spectra are available although some diode laser measurements are in progress.³⁶

Very recently, some lines of the fundamental band were identified in the infrared absorption spectrum³⁷ of IRC + 10216. In that work the vibrational constants were estimated from the electronic spectra⁹⁻²⁰ but a direct high-

resolution laboratory confirmation is desirable. We recorded our spectrum on the suggestion of the astronomer, J. Keady.

II. EXPERIMENT

The vibration-rotation spectrum of SiS in the ground electronic state was recorded with the Fourier transform spectrometer associated with McMath Solar Telescope at Kitt Peak. The unapodized resolution was 0.005 cm^{-1} with liquid helium cooled Si:As detectors and a KCl beam splitter. The spectral bandpass was limited to $550\text{--}1400\text{ cm}^{-1}$ by an InSb filter at the upper limit and with the lower limit set by the detector band gap and the KCl transmission. Three scans were co-added in 14 min of integration.

Gas phase SiS was produced in an alumina tube furnace. The furnace consisted of a 0.9 m long, 50 mm diameter ceramic tube (Coors) to which the gas inlet, pumping port, and KBr windows were attached with "O-ring"-sealed fittings. The gas inlet and the pumping ports were closed and no gas circulation was allowed while the spectra were recorded. The deposition of solid material on the 5 mm thick KBr windows was avoided by pressurizing the system with 5 Torr of argon. The temperature of the oven was increased at a rate of about $2\text{ }^\circ\text{C}/\text{min}$. by regulating the voltage applied to eight clamshell heaters which covered the central part of the tube.

A mixture of Si solid and SiS_2 (ESPI) was uniformly distributed on a fine mesh stainless steel wire gauze placed in the middle of the oven. The mixture was heated to a final temperature of about $1000\text{ }^\circ\text{C}$, as measured by a chromel-alumel thermocouple placed between the heaters and the ceramic tube. The best spectrum was recorded as the furnace cooled at a temperature of about $900\text{ }^\circ\text{C}$.

The heat pipe oven was placed in the front of the entrance aperture of the instrument and light from a glower was passed through the tube and focussed at the entrance plane. We expected to detect SiS absorption spectra rather than the observed emission spectra (Fig. 1).

III. RESULTS AND ANALYSIS

Data analysis was carried out on a 386/25 MHz based microcomputer using PC-DECOMP, a spectral analysis program developed by J. W. Brault of the National Solar

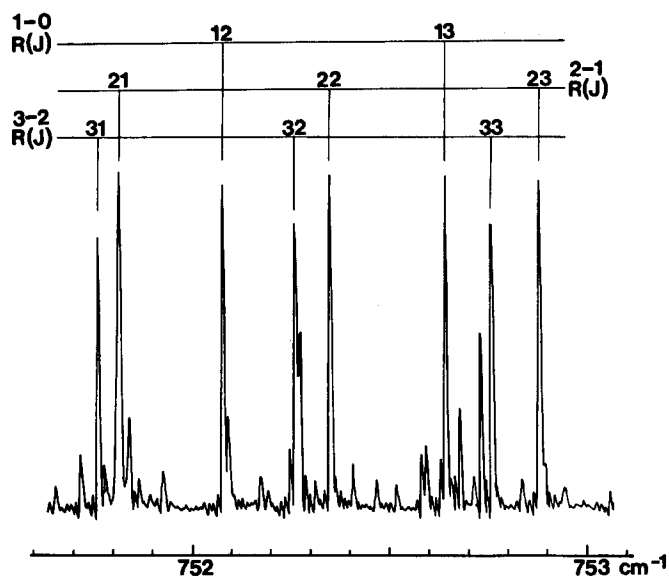


FIG. 1. A portion of the vibration-rotation emission spectrum of SiS. The small features in the spectrum belong to the minor Si and S isotopes.

Observatory. The rotational line profiles of all the emission features were fitted to Voigt functions although the large majority of the strong lines showed a predominant Gaussian line profile with an average full width at half maximum of 0.007 cm^{-1} . The strong lines showed substantial "ringing" near the base line. The ringing is caused by the $\sin x/x$ instrument line shape function of the Fourier transform spectrometer. The ringing was removed using a filtered fit option available in PC-DECOMP in which the resolution was improved by removing the effects of the instrumental *sinc* function line shape.

The signal-to-noise ratio was about 100 for the strongest lines (Fig. 1) of the fundamental band. The precision of these line positions is, therefore, better than 0.0001 cm^{-1} , but many of the weaker lines were determined to only about $\pm 0.001 \text{ cm}^{-1}$. The absolute calibration of the wave number scale was accomplished with some impurity H_2O lines³⁸ in the cell near 1300 cm^{-1} . Our absolute calibration accuracy is about $\pm 0.0001 \text{ cm}^{-1}$ for the SiS line positions.

The assignment of the vibrational bands of the main isotopomer $^{28}\text{Si}^{32}\text{S}$ from 1-0 to 6-5 was straightforward. However, the assignment of the remaining ten vibration-rotation bands (the 7-6 band of $^{28}\text{Si}^{32}\text{S}$; 1-0, 2-1, and 3-2 bands of $^{28}\text{Si}^{34}\text{S}$, $^{29}\text{Si}^{32}\text{S}$, and $^{30}\text{Si}^{32}\text{S}$) proved to be more difficult due to a high density of weak lines with many blended lines and many lines with a poor signal-to-noise ratio of only 3:1. An interactive color Loomis-Wood³⁹ assignment program (running on a 386 based microcomputer) was employed to pick out these weak bands. The ^{29}Si , ^{30}Si , and ^{34}S isotopes have natural abundances of 4.7%, 3.1% and 4.2%, respectively.

A total of 2468 lines of SiS were measured with PC-DECOMP. The line positions are available through PAPS⁴⁰ or directly from the authors. One thousand four hundred and eight lines of the main isotopomer $^{28}\text{Si}^{32}\text{S}$ were fitted to

the usual Dunham expression⁴¹ for the energy levels of a diatomic molecule.

$$F(v, J) = \sum Y_{ij} (v + \frac{1}{2})^i [J(J+1)]^j. \quad (1)$$

The microwave lines reported by Tiemann²⁶ were included in the fit. The Dunham coefficients obtained from this fit are shown in Table II.

The rotational constants for the remaining isotopomers were predicted from the isotopic relationships from the Dunham constants of $^{28}\text{Si}^{32}\text{S}$. The final rotational assignment of these bands was carried out by comparing the line positions from a predicted spectrum with the unassigned series of lines obtained with the Loomis-Wood program. A separate fit was performed for each isotopomer in order to adjust the weights of each rotational line. Finally, all the infrared and microwave lines were combined and fitted to the mass reduced Dunham expression including Watson's correction due to the break down of the Born-Oppenheimer approximation⁴²

$$Y_{ij} = \mu^{-(i+2j)/2} U_{ij} [1 + (m_e/m_{\text{Si}}) \Delta_{ij}^{\text{Si}} + (m_e/m_{\text{S}}) \Delta_{ij}^{\text{S}}], \quad (2)$$

where μ is the reduced mass, U are the mass-independent parameters, m_{Si} and m_{S} are the atomic masses, m_e is the mass of the electron, and Δ 's are the mass scaling factors for the nuclei. The data required four Δ 's (Δ_{10}^{Si} , Δ_{01}^{Si} , Δ_{10}^{S} , Δ_{01}^{S}) in all, two for each nucleus with one for " B_e " (Δ_{01}) and one for " ω_e " (Δ_{10}). The final mass-independent coefficients and the Δ 's are shown in Table I.

In Table II the individual Dunham fits using Eq. (1) are reported for each isotopomer. Many of the Dunham parameters (Y_{40} , Y_{21} , Y_{31} , Y_{22} , Y_{03} , and Y_{13}) were not well determined for the minor isotopomers. These constants were fixed at values calculated from the corresponding U 's of Table I using the isotopic relationships [Eq. (2)].

The Dunham coefficients (Y_{00} and Y_{11}) for $^{28}\text{Si}^{32}\text{S}$ were used to determine the potential energy function using the

TABLE I. Mass-reduced Dunham constants for SiS (in cm^{-1}). One standard deviation is in parentheses.

U_{10}	2 895.639 3(21)
Δ_{10}^{Si}	0.929(22)
Δ_{10}^{S}	-0.257(27)
U_{20}	-38.588 33(43)
U_{30}	0.060 09(34)
$10^2 U_{40}$	-0.164 9(91)
U_{01}	4.529 103 0(69)
Δ_{01}^{Si}	-1.203(52)
Δ_{01}^{S}	-1.944(58)
$10 U_{11}$	-0.849 051 9(76)
$10^5 U_{21}$	-0.628(99)
$10^5 U_{31}$	-0.800(34)
$10^4 U_{02}$	-0.443 095(22)
$10^6 U_{21}$	-0.159 7(12)
$10^7 U_{22}$	-0.102 4(66)
$10^{11} U_{03}$	-0.44(18)
$10^{11} U_{13}$	-0.826(69)

TABLE III. RKR turning points for the ground state of $^{28}\text{Si}^{32}\text{S}$.

v	E_v (cm^{-1})	R_{min} (\AA)	R_{max} (\AA)
0.0	374.211 6	1.876 68	1.986 65
0.5	747.095 5	1.856 15	2.011 89
1.0	1 118.687 8	1.840 87	2.031 89
1.5	1 488.989 4	1.828 30	2.049 19
2.0	1 858.000 8	1.817 46	2.064 78
2.5	2 225.722 9	1.807 84	2.079 16
3.0	2 592.156 4	1.799 15	2.092 63
3.5	2 957.301 9	1.791 18	2.105 39
4.0	3 321.160 3	1.783 81	2.117 57
4.5	3 683.732 1	1.776 94	2.129 27
5.0	4 045.018 1	1.770 49	2.140 56
5.5	4 405.018 8	1.764 40	2.151 50
6.0	4 763.735 1	1.758 63	2.162 13
6.5	5 121.167 5	1.753 15	2.172 50
7.0	5 477.316 6	1.747 91	2.182 64

RKR procedure. The classical turning points for the first seven vibrational levels are given in Table III.

IV. DISCUSSION

The vibration-rotation spectrum of SiS was observed in emission at 13μ (750 cm^{-1}). This is very unusual because the conventional wisdom is that emission spectroscopy below 1800 cm^{-1} (5.5μ , the InSb detector cutoff) is difficult to observe. Indeed, a survey of the literature⁴³ indicates that for only three other molecules (FO,⁴⁴ InF,⁴⁵ and GeS⁴⁶) have midinfrared vibration-rotation emission spectra been observed. The work of Uehara and co-workers on the high-temperature molecules InF (Ref. 45) and GeS (Ref. 46) corresponds closely to our SiS observations but at somewhat lower resolution.

One of the main problems with midinfrared emission spectra is that the emission rates, Einstein A factors, are very small. We calculated the Einstein A factors (in s^{-1}) using the following equation:⁴⁷

$$A_{ij} = 3.137 \times 10^{-7} \nu^3 |\mu_{ij}|^2, \quad (3)$$

where μ_{ij} is the transition dipole moment matrix element in Debyes, and ν is the transition frequency in cm^{-1} . The dipole matrix elements of Lopez Piñeiro *et al.*⁴⁸ are used. The calculated values of the A_{ij} coefficients were small, as expected, and found to range from 2.2 s^{-1} for the 1-0 band to 8.9 s^{-1} for the 4-3 rotation-vibration band.

In addition, blackbody emission from the hot cell walls is very bright in the midinfrared and contributes to the noise. In our case, no cold filter was used in front of the detector, so the entire $550\text{--}1400 \text{ cm}^{-1}$ interval was observed and, to make matters worse, our spectra were recorded with the glower on. Because we expected absorption spectra the glower was left on to provide continuum radiation and it contributed nothing but noise to the measurement. In spite of these obstacles a very strong (Fig. 1) emission spectrum of SiS was recorded in only a few minutes of observation.

The rotational temperatures for 1-0, 2-1, 3-2, 4-3, and 5-4 bands of SiS were derived from the integrated intensities of the rotational lines assuming thermal equilibrium and a Boltzmann distribution of the rotational populations.³⁹ The Boltzmann plots were found to be linear. The rotational temperatures were found to be $1139 \text{ K} \pm 6 \text{ K}$, $1203 \text{ K} \pm 16 \text{ K}$, $1213 \text{ K} \pm 15 \text{ K}$, $1231 \text{ K} \pm 29 \text{ K}$, and $1286 \text{ K} \pm 240 \text{ K}$ for the $v = 1, 2, 3, 4,$ and 5 vibrational levels, respectively, close to the approximate wall temperature of about 900°C . There is a small trend to increasing temperature with increasing vibrational excitation.

A vibrational temperature analysis was also carried out. To a good approximation the integrated intensity of a rovibrational emission line is given by⁴⁹

$$I = K \nu^4 N_{\nu'} \frac{\exp(-E_j hc/kT)}{Q_{\text{rot}}} |\mu_{\nu\nu'}|^2 S_{J,J'} F(m), \quad (4)$$

where ν is the transition frequency, $N_{\nu'}$ is the number density of molecules in the upper vibrational state ν' , E_j is the energy of the upper state, $\mu_{\nu\nu'}$ is the rotationless transition dipole moment, $S_{J,J'}$ is the rotational line strength, and $F(m)$ accounts for the interaction between vibration and rotation (Herman-Wallis factor). Since the R lines and the P lines fell on the same straight line for the rotational Boltzmann plots, no Herman-Wallis effect was present and $F(m) = 1$.

TABLE II. Dunham parameters for SiS (in cm^{-1}). Each isotopomer was fitted independently.

Constant	$^{28}\text{Si}^{32}\text{S}$	$^{28}\text{Si}^{34}\text{S}$	$^{29}\text{Si}^{32}\text{S}$	$^{30}\text{Si}^{32}\text{S}$
Y_{10}	749.645 653(64)	739.296 90(15)	742.717 29(12)	736.207 27(15)
Y_{20}	-2.586 222(34)	-2.515 454(91)	-2.538 553(71)	-2.494 515(89)
$10^3 Y_{30}$	1.040 8(66)	1.030(16)	0.995(12)	1.019(15)
$10^6 Y_{40}$	-7.30(43)	-7.008 ^a	-7.139 ^a	-6.892 ^a
Y_{01}	0.303 527 884(11)	0.295 205 728(27)	0.297 944 032(22)	0.292 744 133(34)
$10^3 Y_{11}$	-1.473 159(14)	-1.412 974(33)	-1.432 681(26)	-1.395 279(42)
$10^8 Y_{21}$	-3.11(46)	-2.667 ^a	-2.717 ^a	-2.623 ^a
$10^9 Y_{31}$	-9.08(40)	-8.677 5 ^a	-8.880 2 ^a	-8.497 8 ^a
$10^7 Y_{02}$	-1.990 30(10)	-1.882 13(28)	-1.917 70(28)	-1.851 14(38)
$10^{10} Y_{12}$	-1.864(13)	-1.728(54)	-1.764(44)	-1.848(89)
$10^{11} Y_{22}$	-0.292(20)	-0.284 ^a	-0.292 ^a	-0.277 ^a
$10^{15} Y_{03}$	-1.31(55)	-1.229 2 ^a	-1.263 7 ^a	-1.198 7 ^a
$10^{16} Y_{13}$	-6.20(52)	-5.843 ^a	-6.035 ^a	-5.674 6 ^a

^aThese constants were fixed to the values obtained from the mass-reduced Dunham constants (U_{ij} 's) of Table I.

If a single rotational temperature is assumed and the harmonic approximation is made for the transition dipole moments, then for a single J value in all the vibrational transitions it can be shown that the intensities of the rotational lines relative to the intensity of the 1-0 band line is

$$\frac{I_v}{I_1} = \frac{\nu_v^4}{\nu_1^4} v \frac{N_v}{N_1}, \quad (5)$$

where v is the upper state vibrational quantum number. Assuming a Boltzmann distribution of the vibrational populations, the vibrational temperature can be calculated. Selecting $R(39)$ as the rotational line for the calculations because this line was found to be free of blending in all the vibrational bands of the $^{28}\text{Si}^{32}\text{S}$, we found the vibrational temperature to be $1858 \text{ K} \pm 185 \text{ K}$. Although the vibrational temperature is not very well determined, it seems to be slightly higher than rotational temperature of about 1200 K . Perhaps some of the energy of the reaction⁵⁰



is not completely dissipated. There is some precedent for this in, for example, the oxidation of CO on Pt surfaces and the subsequent desorption of vibrationally hot CO_2 (Refs. 51 and 52) but this seems improbable for our system.

Initially we believed that excess vibrational excitation from an exothermic chemical reaction [Eq. (6)] was necessary to observe midinfrared emission. For example, Hammer *et al.* used the $\text{F} + \text{O}_3$ reaction⁴⁴ to provide vibrationally hot FO molecules. However, the observed vibrational temperature in the SiS system is rather close to the rotational temperature when the measurement errors are considered. Also, our best spectrum of SiS was recorded as the oven cooled, probably after reaction 6 had converted all of the SiS_2 to SiS. Moreover, we have recently detected the infrared emission spectrum of gas-phase BeF_2 near 1530 cm^{-1} . In the BeF_2 system, there were no chemical reactions occurring. We now believe that the emission from hot SiS, in approximate equilibrium with the walls of the cell, is responsible for our spectrum.

The observation of the high resolution infrared and microwave spectra of the minor isotopes of Si and S allows the effects of Born-Oppenheimer breakdown to be estimated in SiS. The Δ values (Table I) correct the rotational ($Y_{01} \approx B_e$) and vibrational ($Y_{10} \approx \omega_e$) constants for the various types of Born-Oppenheimer breakdown effects^{42,53} as well as for the Dunham corrections.⁴¹ The Δ_{01}^{Si} and Δ_{01}^{S} values (Table I) of $-1.203(52)$ and $-1.944(58)$ agree reasonably well with the values of Tiemann *et al.*,⁵³ $-1.392(59)$ and $-1.870(65)$. As expected, the values for the Δ_{10} parameters (Table I) are also of order one, similar to the other Δ 's of the IV-VI family of molecules.⁵³⁻⁵⁵ Only for the Pb-containing molecules are the Δ 's large^{54,55} because of the "field effect" caused by modifications to the Coulomb potential.⁵⁶ The Pb nucleus is sufficiently large so that the different nuclear volumes of the different Pb isotopes give rise to large Δ values.⁵⁶

The U_{01} value allows a "true Born-Oppenheimer" internuclear separation, r_e^{BO} , to be calculated from the formula $U_{01}(r_e^{\text{BO}})^2 = 16.857 631 3 \text{ cm}^{-1} \text{ amu} \text{ \AA}^2$. The r_e^{BO} value is

$1.929 266 3(15) \text{ \AA}$, identical to Tiemann *et al.*'s value,⁵³ because we included the same microwave data in our analysis.

It is interesting to test the mass-reduced version of Kratzer's relationship, $U_{02} = -4U_{01}^3/U_{10}^2$, which should be exact since the U 's correct for Born-Oppenheimer breakdown.⁴² The right-hand side of this equation is $-4.432 081(10) \times 10^{-5} \text{ cm}^{-1}$ compared to the observed value of $-4.430 95(22) \times 10^{-5} \text{ cm}^{-1}$ (Table I). Presumably, the small difference between the observed and calculated U_{02} values is caused by the correlations among the U 's in our fit of the experimental data.

V. CONCLUSION

The observation of high resolution vibration-rotation emission spectra of high temperature molecules in the mid-infrared is unusual but remarkably easy. With the exceptions of the groups led by C. Howard and H. Uehara, this technique has been overlooked. The method is also applicable to high temperature polyatomic molecules. We recently recorded the emission spectrum of BeF_2 , the first high resolution infrared spectrum of a metal dihalide.

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