Analysis of Rotation-Vibration Bands of Sulfine, (CH_2SO), by FT-IR and Microwave Spectroscopy

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The rotation-vibration bands of a transient molecule, sulfine, (methanethial S-oxide), have been observed by FT-IR and analyzed with the aid of microwave data, a part of which has been newly obtained in this study. The band center frequencies for ν_5 and ν_9 are determined to be 1175.75 cm^{-1} and 762.07 cm^{-1}, respectively. The good agreement between the observed and simulated band contours clarifies that the origin of these bands is sulfine.

The recent development of FT-IR spectroscopy has enabled us to observe high-resolution infrared spectra of less abundant species such as unstable molecules. If the observed rotation-vibration bands are analyzed to give reasonable values for the molecular constants, it will become evident that the spectrum is due to a particular unstable molecule. However, since many parameters are necessary for the analysis of infrared band envelopes, it is generally very difficult unless some of them have been determined previously from other sources. Since microwave spectroscopy gives the rotational and centrifugal distortion constants in the excited vibrational state as well as in the ground state, the joint study of FT-IR and microwave spectroscopy can be a powerful tool for the analysis of rotation-vibration bands. In the present study we applied this method to the analysis of the rotation-vibration bands of a transient molecule, sulfine.

The spectroscopic investigation of sulfine was first done by Block *et al.*[1] with microwave and infrared spectroscopy using flash vacuum pyrolysis of thiethane S-oxide or 1,3-dithiethane 1-oxide. The detailed analysis of the microwave spectrum of this molecule was carried out and reported by Penn and Olsen.[2] Later, the infrared spectrum of sulfine was studied by Powers *et al.*[3] using a matrix isolation method, and all the fundamental vibrations have been observed. However, only limited results on infrared spectra have been reported for gas phase sulfine.[1] They observed the two rotation-vibration bands at 1170 and 760 cm^{-1} which seemed to be due to sulfine, but they presented no support for their assignments of these bands to sulfine.

Since sulfine is produced by pyrolysis and has a fairly short lifetime, the spectra are naturally disturbed by the parent and decomposed materials. Therefore, it is very difficult to identify the spectrum unambiguously. In the present study, we observed the same two bands of sulfine in the gas phase as observed by Block *et al.* using FT-IR with relatively high resolution, and were able to identify them from the analysis of the band contours by the use of the rotational constants determined by microwave spectroscopy.

Experimental

Infrared Spectra. The infrared spectra were measured by the use of a Digilab model FTS-20C/D spectrophotometer. The optical system was modified as shown in Fig. 1. The collimated beam is taken out through the window attached to the side cover of the instrument. It is reflected by a flat mirror M_1 (80 mmϕ) and a spherical mirror M_2 (80 mmϕ and f=500 mm), and focused at the center of a gas cell. Then the image of the source is focused onto a detector by an off-axis ellipsoidal mirror M_3 (80 mmϕ, f_1=35 mm, and f_2=555 mm). The distance between the source and the detector is about 2.8 meters, and the separation between the mirrors M_2 and M_3 is about 1 meter. Thereby, a 700 mm sample cell with 40 mm diameter can be placed without disturbing the optical path. The detector, the mirrors, and the sample cell were set in the compartment covered with acrylic resin plates, and atmospheric water vapor was purged by dried air. A HgCdTe detector cooled with liquid nitrogen and a globar source were used in all measurements. The accuracy of the frequency of the FT-IR spectrometer was estimated to be better than 0.03 cm^{-1} from the comparison of the observed values for carbon monoxide with the data listed in Ref. 4.

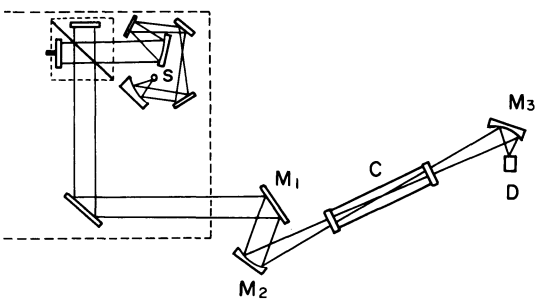

Fig. 1. Modified optical system.
S: glober, M_1: flat mirror, M_2: spherical mirror, M_3: off-axis ellipsoidal mirror, C: infrared cell, D: detector.

For the measurements of the sulfine spectrum, dimethyl sulfoxide was passed through a quartz tube heated up to 700 °C and the products of thermal decomposition were introduced into the cell and pumped through. The heated part of quartz was 20 cm long and 5 mm i.d. The pressure of dimethyl sulfoxide was carefully regulated by a needle valve and, thereby, a steady stream of the products was obtained in the flow-through system. The best sulfine spectrum was obtained at the $(CH_3)_2SO$ pressure of *ca.* 450 mTorr (1 Torr≈133.322 Pa) which was the maximum vapor pressure obtainable in the flow-through system at room temperature. The spectrum was measured at 0.1 cm^{-1} resolution using a 350 mm gas cell with 30 mm diameter and averaging over 512 scans. A triangular apodization function was used in the calculation of spectra.

In the observed spectra, C_2H_4 and SO_2 with medium intensity, along with CH_4 with strong intensity, were clearly identified. These molecules are known to be decomposition products of sulfine or dimethyl sulfoxide by the work of

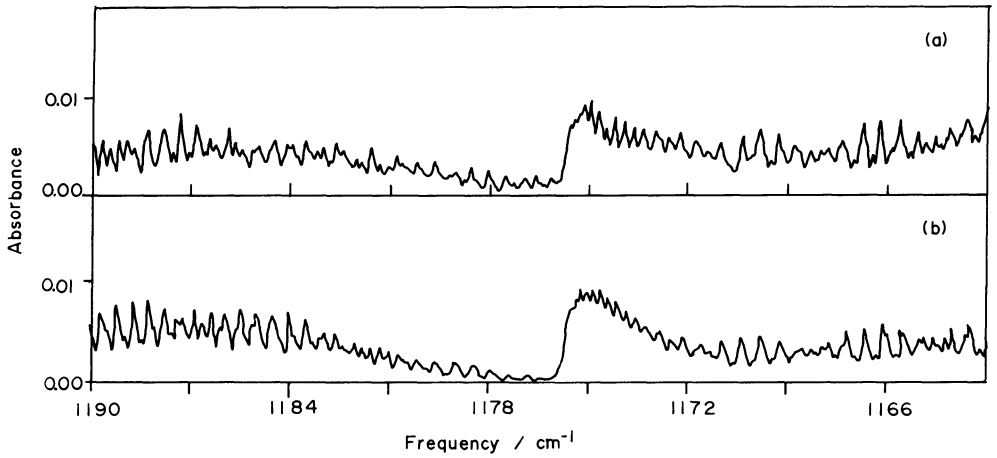

Fig. 2. Spectrum of ν_5 band of sulfine.
(a) Obsd. (b) Calcd.

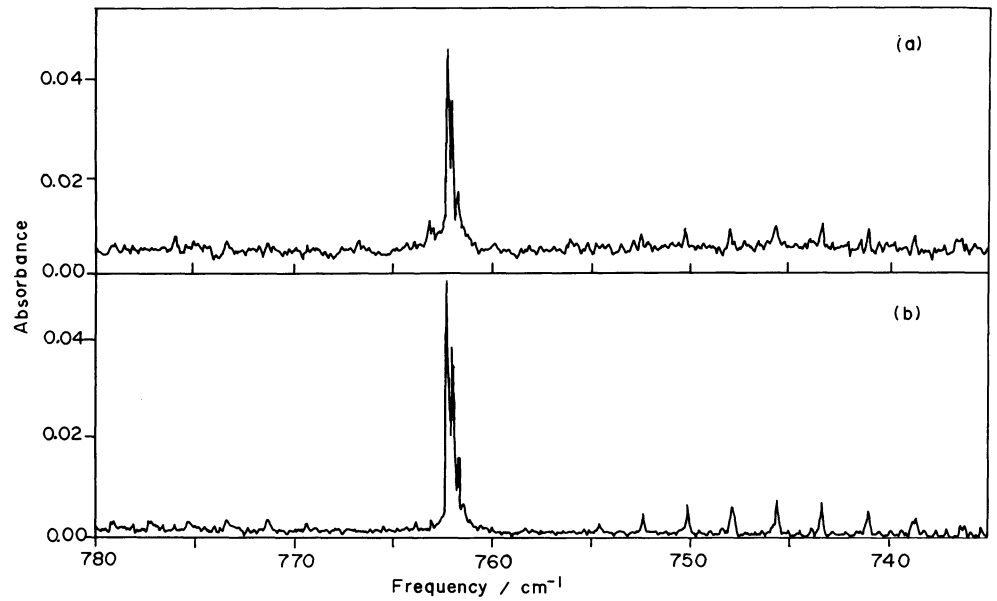

Fig. 3. Spectrum of ν_9 band of sulfine.
(a) Obsd. (b) Calcd.

Thyrion and Debecker[5] on the pyrolysis of $(CH_3)_2SO$. Besides the absorption bands due to these molecules, the rotation-vibration bands centered at 1175 cm^{-1} and 762 cm^{-1} were observed as shown in Figs. 2 and 3. These band positions agree with those reported by Block *et al.* The half-life of the molecular species giving these bands was about 25 min in the infrared cell, which was comparable with that in X-band copper waveguide cell reported by Penn and Olsen.[2] Although the lifetime of this molecule is much longer compared to the pumping speed, the strong infrared spectrum was obtained when the heated quartz tube was placed very near the inlet of the infrared cell. This suggests that this molecule tends to be lost in the narrow glass tube.

Microwave Spectra. The microwave spectrum was measured by a conventional Stark modulation spectrometer with a 3-meter X-band copper waveguide cell. The microwave sources are an HP-8672A frequency synthesizer and an HP-8690 microwave sweeper phase locked to the synthesizer. The sweeping was performed through an HP-IB system controlled by an HP-9835 desk-top computer.

The sample flow-through system was almost the same as used for the IR spectroscopy. However, the vapor pressure was optimum at about 20 mTorr. According to the results of the IR spectroscopy of matrix isolated sulfine,[3] the lowest fundamental vibration is ν_7 (394 cm^{-1}). The microwave spectrum in the excited ν_7 state was first searched for and several low-J transitions were easily identified from their characteristic Stark patterns. The spectral lines for the $2\nu_7$ state were also observed at the expected frequencies. Since the intensity of the ν_9 excited state spectrum was expected to be nearly the same as of $2\nu_7$, the assignment of the spectral lines was done by comparing them with corresponding $2\nu_7$, lines. All the observed transition frequencies and the rotational constants derived from them by least-squares fitting are listed in Table 1. Since the μ_b of sulfine is small, no b-type transitions for the vibrational satellites were observed and the A' rotational constants were not determined precisely.

Results and Discussion

The sulfine is a planar asymmetric top molecule with an asymmetry parameter $\kappa=-0.891$ and belongs to the

TABLE 1. OBSERVED MICROWAVE TRANSITIONS AND ROTATIONAL CONSTANTS OF SULFINE IN VARIOUS VIBRATIONAL STATES (MHz)

Transition	Ground[a]	ν_7		$2\nu_7$		ν_9	
	Obsd	Obsd	Δ[b]	Obsd	Δ	Obsd	Δ
1_{01}—0_{00}	17001.86	16988.85	0.13	16974.98	−0.04	16979.75	0.05
2_{02}—1_{01}	33928.87	33902.16	0.03	33874.96	0.01	33885.77	0.04
2_{12}—1_{11}	32216.49	32183.32	−0.01	32149.39	0.06	32201.41	0.02
2_{11}—1_{10}	35791.41	35771.52	−0.02	35750.70	−0.04	35717.42	0.01
3_{13}—2_{12}	48278.11	48228.82	−0.05	48178.01	−0.01	48256.90	−0.06
3_{12}—3_{13}	10723.27	10762.66	−0.01	10802.27	0.02	10546.13	−0.01
A	40404.500	40535(130)		40861(80)		39936(84)	
B	9394.837	9391.41(5)		9387.86(3)		9368.86(3)	
C	7607.120	7597.30(4)		7587.16(3)		7610.84(3)	

a) Obtained by R. E. Penn and R. J. Olsen. b) Δ=Obsd−Calcd.

C_s point group. Simulation spectra for the two bands observed in this work were obtained with the computer program written for calculating the rotation-vibration spectrum of the asymmetric top molecule. The details of the program have been described elsewhere.[6] After the line positions and intensities of the individual transitions were calculated the spectrum was simulated using a Lorentz type line shape function and a triangular slit function. A comparison of the two bands observed at 1175 and 762 cm^{-1} with the simulated ones leads to their unambiguous assignment to the CSO symmetric stretching mode (ν_5) and the CH_2 wagging mode (ν_9), respectively, of sulfine. The lower part of the ν_5 band was overlapped by the ν_1 band of SO_2 produced by pyrolysis. Nevertheless, PQR-structure of sulfine was readily distinguished from the mixed spectra. In principle, the ν_5 band is expected to be an a- and b-type hybrid band. However, the observed spectrum clearly shows that this band consists mainly of a-type band because of the weak line strength of the b-type band. In the course of simulation calculation, three excited state rotational constants (A'_5, B'_5, and C'_5) and the band center ν_5 were adjusted to fit the observed spectrum, keeping the ground state rotational and centrifugal distortion constants fixed at their microwave values,[2] and the excited state centrifugal distortion constants equal to the ground state values. In the analysis of the spectrum, 44 prominent peak positions in the absorption band were chosen to use in a least-squares fit for the determination of the molecular parameters. The molecular parameters derived are listed in Table 2, and the observed and calculated frequencies along with the assignments are given in Table 3. Each of the prominent peaks is assigned to the transition which makes the largest contribution to that particular peak. In Fig. 2 the observed and simulated spectra of ν_5 band are shown. The band center is determined as 1175.75 cm^{-1} which is slightly higher than the value of 1170 cm^{-1} reported by Block *et al.*,[1] while it is fairly different from the matrix value (1165 cm^{-1}).[3]

The ν_9 band should be a c-type band which corresponds to the perpendicular band in a prolate symmetric top and, therefore, a fairly strong Q-branch is expected at its center. In Fig. 3 the observed band is compared with the calculated spectrum. It is clearly seen that this band is of typical c-type and is compatible with the vibrational mode of the CH_2 wagging as has been estimated by Powers *et al.*[3] The prominent series of $^{r,p}Q$ branches were easily assigned from comparison with the calculated spectrum, whereas ^pP, ^pR, ^rP, and ^rR in many subbands were not resolved in the present measurements. Consequently, it was difficult to determine the three excited state rotational constants of this band only from the observed spectrum. Therefore, the measurement of the microwave spectrum in the excited ν_9 state was carried out. Since the A' rotational constant obtained by microwave spectroscopy had a large uncertainty as described previously, both the A' and band center were adjusted to fit the observed infrared spectrum, keeping all the other constants fixed at the microwave values. The determined molecular constants are listed in Table 2. Table 4 compares the observed and calculated values of the prominent peaks in the ν_9 band. The band center of ν_9 thus determined is 762.07 cm^{-1} which is close to the value of 760 cm^{-1} obtained by Block *et al.* and also near the matrix value (767 cm^{-1}).

In conclusion, the good agreement between the observed and calculated spectra of the ν_5 and ν_9 bands with the reasonable molecular parameters was obtained

TABLE 2. ROTATIONAL CONSTANTS AND BAND CENTERS OF ν_5 AND ν_9 (cm^{-1})

Ground state[a]	Band center	Excited state[b]
A''=1.3477493(10)	ν_5=1175.75(3)	A'=1.33686(41)
B''=0.31337495(23)		B'=0.31200(136)
C''=0.25374587(20)		C'=0.25314(148)
	ν_9=762.07(4)	A'=1.33684(119)
		B'=0.31251135(97)[c]
		C'=0.2538704(87)[c]

a) See Ref. 1. b) Standard deviations (3σ) are given in parentheses. c) These values were determined by MW measurement in this work.

Table 3. Observed and calculated wavenumbers of ν_5 band (cm^{-1})

Obsd	Δ[a]	J''	K_a''	K_c''	$-J'$	K_a'	K_c'	Obsd	Δ[a]	J''	K_a''	K_c''	$-J'$	K_a'	K_c'
1164.52	−0.02	21	0	21	20	0	20	1175.31	−0.01	6	6	0	6	5	1
1165.60	0.02	19	0	19	18	0	18	1175.48	0.03	5	5	0	5	4	1
1166.15	0.03	18	0	18	17	0	17	1177.42	0.01	2	0	2	3	0	3
1166.69	0.05	17	0	17	16	0	16	1177.96	0.00	3	0	3	4	0	4
1167.25	0.04	16	0	16	15	0	15	1178.50	0.00	4	0	4	5	0	5
1167.75	0.02	15	0	15	14	0	14	1179.04	0.01	5	2	4	6	4	3
1168.74	0.00	13	0	13	12	0	12	1179.28	0.00	5	1	4	6	1	5
1169.82	0.02	11	0	11	10	0	10	1179.59	0.03	6	0	6	7	0	7
1170.37	0.00	10	1	10	9	3	7	1180.13	0.00	7	2	6	8	4	5
1170.97	0.03	9	1	9	8	3	6	1180.55	0.02	8	0	8	9	0	9
1171.33	−0.03	8	0	8	7	0	7	1180.97	0.02	9	1	9	10	3	8
1171.69	−0.03	7	2	6	6	4	3	1181.21	−0.01	9	2	8	10	4	7
1172.17	−0.01	18	18	0	18	17	1	1181.51	0.02	10	0	10	11	0	11
1172.54	0.01	6	1	6	5	3	3	1181.94	−0.03	11	0	11	12	0	12
1172.90	−0.01	17	16	1	17	15	2	1182.54	0.07	12	0	12	13	0	13
1173.26	0.00	15	15	0	15	14	1	1182.78	0.03	12	2	11	13	4	10
1173.56	−0.01	14	14	0	14	13	1	1183.44	0.02	14	0	14	15	0	15
1173.86	−0.01	13	13	0	13	12	1	1183.93	−0.01	15	0	15	16	0	16
1174.12	−0.01	13	12	1	13	11	2	1184.41	−0.02	16	0	16	17	0	17
1174.39	0.00	11	11	0	11	10	1	1184.89	0.01	17	0	17	18	0	18
1174.60	−0.02	10	10	0	10	9	1	1185.37	0.01	18	0	18	19	0	19
1174.83	0.00	9	9	0	9	8	1	1185.85	0.00	19	0	19	20	0	20
1175.01	−0.01	8	8	0	8	7	1	1186.34	0.05	20	0	20	21	0	21
1175.19	0.01	7	7	0	7	6	1	1186.76	−0.04	21	0	21	22	0	22

a) Δ = Obsd − Calcd.

Table 4. Observed and calculated frequencies of ν_9 band peaks (cm^{-1})

Obsd	Obsd − Calcd	Assignment
775.29	0.00	$^rQ_6$
773.30	0.02	$^rQ_5$
771.12	−0.02	$^rQ_4$
769.31	0.01	$^rQ_3$
762.05	−0.02	$^rQ_0$
752.31	−0.01	$^pQ_5$
750.12	0.01	$^pQ_6$
747.85	0.00	$^pQ_7$
745.55	−0.02	$^pQ_8$
743.28	0.01	$^pQ_9$
740.92	−0.02	$^pQ_{10}$
738.56	−0.01	$^pQ_{11}$

by the joint analysis of FT-IR and microwave spectroscopy and it definitely confirmed that the origin of these bands is the sulfine molecule. In addition, the vibrational frequencies of ν_5 and ν_9 of sulfine were determined precisely.

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