The High-Resolution Emission Spectrum of S₂ in the Near Infrared: The $b^1 \Sigma_q^+ - X^3 \Sigma_q^-$ System¹

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Bands of the $b^1 \Sigma_g^* - X^3 \Sigma_g^*$ system of S₂ have been excited in a discharge flow system by reacting ground state S₂ molecules with metastable O₂($^1\Delta_g$) molecules. The 0-0, 0-1, and 1-1 bands have been recorded in emission with a Bomem interferometer, together with the 0-0 band of $^{32}S^{34}S$. The rotational structures of the bands are determined by magnetic dipole selection rules. Detailed analysis has yielded accurate values for the molecular constants of the $b^1\Sigma_g^*$ and $X^3\Sigma_g^*$ states. The rotational line intensities are well reproduced by the line strength formulae of Watson. © 1986 Academic Press, Inc.

I. INTRODUCTION

The S₂ molecule, which is isovalent with the O₂ molecule, has low-lying $b^1\Sigma_g^+$ and $a^1\Delta_g$ electronic states which arise from the same electron configuration as the $X^3\Sigma_g^-$ ground state (1). Molecular constants for the $X^3\Sigma_g^-$ ground state of S₂ have been derived from studies of ultraviolet spectra (2-4), rotational Raman spectra (5), millimeter-wave spectra (6), and electron paramagnetic resonance (EPR) studies of the molecule in the gas phase (7). Data for the $a^1\Delta_g$ state have been obtained from electronic transitions involving higher singlet states, but information on the $b^1\Sigma_g^+$ state is rather fragmentary (1). Recently, the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ system, which is the analog of the atmospheric O₂ bands, has been observed in emission in the near infrared using a discharge flow system in which metastable O₂($^1\Delta_g$) molecules sensitized the emission of the S₂ molecules (8, 9). In the present paper the 0-0, 0-1, and 1-1 bands of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ emission system are studied with high resolution using a Bomem interferometer, and accurate molecular constants are derived for the $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ states. The line intensities in the four branches are fitted using the rotational line strength formulae of Watson (10).

II. EXPERIMENTAL DETAILS

The S₂ emission was recorded using a chemiluminescence flow system in which $S_2(b^1\Sigma_8^+)$ molecules were excited by near-resonant electronic energy transfer from

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metastable oxygen $O_2(a^1\Delta_g)$ molecules (8, 9). Due to the limited energy available, spectra from this source are virtually free from atomic lines and emissions from highlying molecular states.

The flow system was made of Pyrex glass and consisted of a tube, 100 cm long and 15 cm in diameter, with quartz windows at both ends. Ground state S₂ molecules were produced by passing a mixture of helium carrier gas and sulfur chloride (S₂Cl₂) vapor through a microwave discharge, and entered the tube through a sidearm. Oxygen containing 5–10% of metastable $O_2(a^1\Delta_g)$ molecules was introduced through a second sidearm. The oxygen was passed over warm mercury ($T \approx 330$ K) before entering a second microwave discharge. A deposit of mercuric oxide formed after the discharge and served to catalyze the recombination of oxygen atoms and to increase the concentration of oxygen molecules in the $a^1\Delta_g$ state. The system was pumped at the other end with a 500 m³ hr⁻¹ roots pump in series with a 40 m³ hr⁻¹ forepump resulting in flow velocities of about 5 msec⁻¹ in the tube. The total pressure was measured with a Baratron capacitance manometer and was in the range 1–3 Torr (1 Torr \cong 133 Pa). The gas mixture usually consisted of approximately equal amounts of oxygen and helium carrier gas and a few mTorr of S₂Cl₂ vapor.

The radiation emitted from the tube was focused onto the entrance diaphragm of a Bomem DA3.002 Fourier transform spectrometer using a 5-cm-diameter CaF₂ lens. To increase the intensity, a flat aluminum mirror was situated behind the rear window. The front window was purged with helium to avoid the deposit of sulfur which formed on the walls of the tube. Spectra were recorded in the region 7000-8200 cm⁻¹ at a resolution of 0.02 cm⁻¹ using a liquid-nitrogen-cooled germanium detector (Applied Detector Corp. Model 403S). Through a small hole in the rear mirror the S₂($b \rightarrow X$) 0-0 band at 1.25 μ m was monitored with a small grating monochromator (Spex Minimate), a second germanium detector, a mechanical light chopper, and a lock-in amplifier. This system served to optimize the S₂ chemiluminescence intensity by varying the gas flow rates and to control the intensity during the sampling of the interferograms.

A reproduction of the 0–0 band of the $S_2(b^1\Sigma_g^+ \to X^3\Sigma_g^-)$ system near 8000 cm⁻¹ is shown in Fig. 1. The spectrum is the result of 52 co-additions and the recording time was 51 min. The wavenumbers of the lines were calibrated using the measurements of Amiot and Verges (11) for the lines of the 0–0 band of the $a^1\Delta_g - X^3\Sigma_g^-$ system of O_2 which appeared on the same run. The latter measurements are considered to have an absolute wavenumber accuracy of ± 0.005 cm⁻¹; the internal precision of the S_2 measurements is of the order of 4×10^{-4} cm⁻¹ for the stronger lines.

The peak intensities of the lines were used as a measure of their relative intensities. The response curve of the germanium detector is a smooth function of wavelength and changes by less than 30% over the range 7000-8200 cm⁻¹. The relative sensitivity of the system was therefore assumed to be constant over the frequency range of a single band (\sim 75 cm⁻¹).

III. ANALYSIS

An energy level diagram for a ${}^{1}\Sigma_{g}^{+}{}^{3}\Sigma_{g}^{-}$ transition is shown in Fig. 2. Since the transition is of the type $g \leftrightarrow g$, the observed rotational transitions obey magnetic dipole selection rules (12); viz,





FIG. 2. Energy level diagram showing the first lines of the four branches for a ${}^{1}\Sigma_{g}^{+}-{}^{3}\Sigma_{g}^{-}$ magnetic dipole transition. Dashed lines indicate levels which are not populated for a homonuclear diatomic molecule with zero nuclear spin. The ground state is shown for a molecule with a moderately large value of λ/B as is found for S₂. The quantum number N is not well defined for the lower values of J.

$$\Delta J = 0, \pm 1, \quad \text{with the restriction} \quad J = 0 \leftrightarrow J = 0, \quad (1)$$

and

$$+ \leftrightarrow +, - \leftrightarrow -, + \leftrightarrow -.$$
 (2)

Since ³²S atoms have zero nuclear spin, alternate levels are missing for the homonuclear diatomic molecule and only levels with + symmetry are present. For the isotopic species ³²S³⁴S all the levels in Fig. 1 are populated. It is readily seen that each band has four branches designated ${}^{R}Q$, ${}^{R}R$, ${}^{P}Q$, and ${}^{P}P$ for which the first lines are ${}^{R}Q(2)$, ${}^{R}R(1)$, ${}^{P}Q(2)$, and ${}^{P}P(1)$.³ The first lines are observed in three of the branches for the 0-0 band, but the ${}^{R}Q$ branch is somewhat weaker and has not been observed for low J values. The observation of the ${}^{P}P(1)$ line confirms that the upper state is indeed the $b^{1}\Sigma_{g}^{+}$ state and not the $a^{1}\Delta_{g}$ state. Vacuum wavenumbers and rotational assignments for lines of the 0-0 and 0-1 bands are given in Tables I and II, respectively. The 1-1 band was identified later in the analysis; its vacuum wavenumbers and rotational assignments are given in Table III.

The $X^3\Sigma_g^-$ state lies intermediate between Hund's case (b) and case (c) coupling cases. Matrices were set up for each value of J using the matrix elements given by Amiot and Verges (AV, 11) for a case (b) basis set. Terms involving B, D, γ , λ , and λ_D were used (AV use μ_0 , λ_0 , and λ_1 for the last three terms). It was found that the term involving the centrifugal distortion correction to γ was not required. The matrices were diagonalized by means of a simple computer program. For the $b^1\Sigma_g^+$ state the

³ Assignments are given in terms of J rather than N since N is not well defined for low quantum numbers.

TABLE I

J	RR(J)	PP(J)	J	RQ(J)	PQ(J)
1	7981.7434 (23)*	7980.0154 (6)	2		7980.4704 (2)
3	7982.8240 (12)	7978,7960 (9)	4		7980.1604 (-4)
5	7983.8498 (4)	7977.5198 (-4)	6		7979.6820 (-2)
7	7984.8213 (7)	7976.1898 (-5)	8	8004.1630 (-1)	7979.0439 (5)
9	7985.7366 (1)	7974.8057 (5)	10	8004.4268 (-17)	7978.2543 (-3)
11	7986.5976 (7)	7973.3658 (6)	12	8004.7213 (-10)	7977.3273 (3)
13	7987.4024 (6)	7971.8697 (-4)	14	8005.0339 (0)	7976.2715 (2)
15	7988.1507 (-4)	7970.3197 (-2)	16	8005.3542 (8)	7975.0967 (~5)
17	7988,8447 (-1)	7968.7141 (-6)	18	8005.6719 (2)	7973.8140 (1)
19	7989.4825 (-2)	7967.0542 (-2)	20	8005.9804 (-3)	7972.4290 (1)
21	7990.0649 (2)	7965.3385 (-5)	22	8006.2743 (5)	7970.9489 (-1)
23	7990.5910 (3)	7963.5687 (1)	24	8006.5451 (~2)	7969.3797 (~3)
25	7991.0601 (-5)	7961.7428 (-2)	26	8006.7900 (~1)	7967.7270 (4)
27	7991.4744 (1)	7959.8627 (4)	28	8007.0034 (~5)	7965.9923 (-5)
29	7991.8320 (3)	7957.9269 (6)	30	8007.1835 (2)	7964.1825 (5)
31	7992.1322 (-4)	7955.9347 (-4)	32	8007.3258 (5)	7962.2970 (0)
33	7992.3773 (4)	7953.8887 (1)	34	8007.4277 (6)	7960.3407 (3)
35	7992.5648 (3)	7951.7862 (-5)	36	8007.4924 (58)*	7958.3146 (5)
37	7992.6953 (1)	7949.6291 (-2)	38	8007.4924 (-96)*	7956.2202 (5)
39	7992.7763 (75)*	7947.4160 (-4)	40	8007.4924 (208)*	7954.0576 (-9)
41	7992.7763 (-89) *	7945.1475 (-4)	42	8007.3925 (-14)	7951.8324 (3)
43	7992.7453 (10)	7942.8238 (0)	44	8007.2660 (-15)	7949.5410 (-2)
45	7992.6460 (2)	7940.4445 (6)	46	8007.0911 (-3)	7947.1864 (-2)
47	7992.4891 (-4)	7938.0072 (-8)	48	8006.8634 (-13)	7944.7699 (6)
49	7992.2748 (-6)	7935.5147 (-15)	50	8006.5861 (-3)	7942.2904 (6)
51	7992.0044 (13)	7932.9668 (-15)	52		7939.7493 (9)
53	7991.6731 (6)	7930.3615 (-27)*	54		7937.1440 (~18)
55	7991.2785 (-49)*	7927.7031 (-6)	56		7934.4826 (5)
57	7990.8329 (-27)*	7924.9859 (-10)	58		7931.7620 (43)*
59		7922.2112 (-21)*			

Vacuum Wavenumbers and Rotational Assignments for Lines of the 0–0 Band of the $b^1 \Sigma_g^* - X^3 \Sigma_g^-$ System of ${}^{32}S_2$ (in cm⁻¹)

* NOT USED IN THE LEAST SQUARES FIT. NOTE THE THO HEADS AT 8007.4924 AND 7992.7763 CM-1. NUMBERS IN PARENTHESES DENOTE THE (DBS-CALC) DIFFERENCES IN UNITS OF 0.0001 CM-1.

TABLE II

Vacuum Wavenumbers and Rotational Assignments for Lines of the 0-1 Band of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ System of ${}^{32}S_2$ (in cm⁻¹)

J	RR(J)	PP(J)	J	RQ(J)	PQ(J)
1			2		7260.4387 (-8)
3		7258.7736 (13)	4		7260.1550 (-10)
5	7263.8541 (-13)	7257.5247 (-15)	6		7259.7167 (-11)
7	7264.8664 (-17)	7256.2390 (13)	8		7259.1326 (-9)
9	7265.8371 (~11)	7254.9083 (14)	10		7258.4139 (7)
11	7266.7656 (0)	7253.5336 (-2)	12		7257.5681 (6)
13	7267.6493 (~10)	7252.1181 (-4)	14	7285.4352 (17)	7256.6070 (1)
15	7268.4924 (2)	7250.6611 (2)	16	7285.8426 (2)	7255.5417 (6)
17	7269.2917 (6)	7249.1623 (14)	18	7286.2641 (13)	7254.3785 (-4)
19	7270.0488 (18)	7247.6172 (-15)	20	7286.6856 (-13)	7253.1272 (~7)
21	7270.7582 (-16)	7246.0335 (-8)	22	7287.1080 (1)	7251.7941 (~7)
23	7271.4306 (10)	7244.4076 (1)	24	7287.5222 (22)	7250.3851 (0)
25	7272.0564 (6)	7242.7409 (26)	26	7287.9152 (-31)	7248.9047 (10)
27	7272.6382 (-6)	7241.0262 (-5)	28	7288.2993 (5)	7247.3560 (14)
29	7273.1777 (-5)	7239.2730 (2)	30	7288.6571 (~6)	7245.7399 (-12)
31	7273.6727 (-13)	7237.4758 (-6)	32	7288.9886 (-35)	7244.0653 (-10)
33	7274.1256 (-4)	7235.6359 (-17)	34	7289.3004 (10)	7242.3253 (-70)
35	7274.5347 (7)	7233.7577 (16)	36	7289.5785 (11)	7240.5402 (-11)
37	7274.9008 (29)	7231.8303 (~18)*	38	7289.8257 (15)	7238.6953 (4)
39	7275.2187 (10)		40	7290.0445 (64)*	7236.7956 (9)
41	7275.4934 (3)		42		7234.8414 (-3)

NUMBERS IN PARENTHESES DENOTE THE (DBS-CALC) DIFFERENCES IN UNITS OF 0.0001 CM-1. * NOT USED IN THE LEAST SQUARES FIT.

TABLE III

Vacuum Wavenumbers and Rotational Assignments for Lines of the 1-1 Band of the $b^{1}\Sigma_{e}^{*}-X^{3}\Sigma_{e}^{*}$ System of ${}^{32}S_{2}$

Line		$v (cm^{-1})$		Line		v (cm ⁻¹)	
PQ (10)	7925.4650	(+2) ^a	PP	(9)	7922.0276	(+12)
P _Q (12)	7924.5383	(+12)	PP	(11)	7920.5862	(+6)
P _Q (14)	7923.4802	(+1)	Pp	(13)	7919.0897	(+16)
PQ (16)	7922.3047	(+9)	PP	(15)	7917.5324	(-16)
P _Q (18)	7921.0161	(-5)	PP	(17)	7915.9225	(-10)
PQ (20)	7919.6253	(-12)	Pp	(19)	7914.2567	(+3)
PQ (22)	7918.1376	(-22)	PP	(21)	7912.5328	(0)
P _Q (24)	7916.5607	(-17)	Pp	(27)	7907.0255	(+34)
PQ (26)	7914.8998	(+8)	PP	(29)	7905.0725	(+7)

^a Obs-Calc in units of 10^{-4} cm⁻¹.

usual formula involving B and D was used (12). The frequencies of the assigned lines for the 0-0 band were fitted by the method of least squares, each line being weighted according to the square of its intensity since the precision of measurement is inversely proportional to intensity. The molecular constants for the ground state are given in the first column of Table IV; the weighted standard deviation of the fit is 0.0004 cm⁻¹. The molecular constants derived from microwave studies (6) are given in the second column of Table IV. It is seen that there are significant differences in the values of λ and γ derived from the optical and microwave determinations. The frequencies of the microwave transitions were calculated using the optical constants, and systematic differences were found. The values for the (obs. - calc.) frequencies ranged from

TABLE IV

Molecular Constants for the $X^{3}\Sigma_{g}^{-}$ Ground State of ${}^{32}S_{2}$ (in cm⁻¹)

Constant	Optical ^a	Microwave ^b	Optical + Microwave
В	0.294595 (6) ^c	0.2945994 (2) ^d	0.2945923 (4)
10 ⁷ D	1.97 (3)	1.97 (23)	1.96 (2)
10 ³ γ	-7.151 (13)	-6.701 (23)	-7.157 (9)
λ	11.7931 (8)	11.7761 (9)	11.7931 (4)
$10^5 \lambda_{\rm D}$	1.06 (9)	-	1.05 (5)

a This work.

b From Reference (6).

^c Error limits are 3σ.

¹ Error limits based on 40 kHz uncertainty in frequency measurements. -0.74 to -1.73 MHz, well within the standard deviation of the fit of the optical data (11.8 MHz). A simultaneous fit of the optical and microwave data was carried out, the microwave data being given a weight consistent with a precision of measurement of 40 kHz. The resulting molecular constants are given in column 3 of Table IV and agree very closely with the optical constants in column 1. The frequencies of the microwave transitions were calculated with the molecular constants in column 3 of Table IV and agree closely with the observed frequencies (Table V); the standard deviation of the fit is approximately 30 kHz.

The molecular constants for the 0–0 band derived from the simultaneous fit of the optical and microwave data are summarized in the first column of Table VI. The 0-1 band was next fitted keeping the upper state constants fixed at the values obtained from the 0–0 band. The molecular constants are given in the second column of Table VI.

Some weak unassigned lines in the region of the 0–0 band were next assigned to the ${}^{32}S^{34}S$ isotopic species which is present in ~8% abundance. The assignments for 28 lines are given in Table VII and the molecular constants obtained from the analysis of the band are given in Table VIII. The weighted standard deviation of the fit is 0.0017 cm⁻¹.

After the analysis of the vibrational isotope shift (see Discussion), a further 18 weak unassigned lines were then assigned to the two strongest branches of the 1–1 band of ${}^{32}S_2$ (Table III). The analysis of the band was carried out keeping the constants for the lower state fixed at the values obtained from the 0–1 band and varying only the upper state *B* value and the band origin. The values obtained are given in the third column of Table VI.

A summary of derived molecular constants for the $b^1 \Sigma_g^+$ and $X^3 \Sigma_g^-$ states is given in Table IX.

Formulae for the rotational line strengths in a ${}^{1}\Sigma_{g}^{+}-{}^{3}\Sigma_{g}^{-}$ magnetic dipole transition have been given by Watson (10) and are reproduced in Table X. A preliminary attempt to fit the experimental intensities with these formulae was satisfactory, hence a least squares fit was performed using the equation

$$I_{I' \to I} = C \nu^4 S_{I'I} e^{-\{[hcB'J'(J'+1)]/kT\}}$$
(3)

TABLE V

Observed and Calculated Frequencies for Microwave Transitions of ³²S₂ (in MHz)

J,	N '	J"	N "	α v(obs)	v(calc)	o-c
4	5	3	3	79805.30	79805.29	+0.01
5	5	4	5	79163.83	79163.82	+0.01
6	7	5	5	124928,77	124928.79	-0.02
7	7	6	7	104686.60	104686.54	+0.06
9	9	8	9	127054.98	127054.99	-0.01
11	11	10	11	146581,90	146581.93	-0.03

a. From Reference (6).

TABLE VI

Molecular Constants Derived From the Analysis of Bands of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ Transition of ${}^{32}S_2$ (in cm⁻¹)

		Band		
Constant	0-0	0-1	1-1	
в'	0.2877037 (7) ^a	0.2877037 ^d	0.2859192 (33)	
10 ⁷ D'	2.12 (2)	2.12 ^d	2 • 1 2 ^d	
в "	0.2945923 (4)	0.2929975 (23)	0.2929975 ^d	
10 ⁷ D"	1.96 (2)	1.97 (2)	1.97 ^d	
10 ³ Y"	-7.157 (9)	-7.148 (28)	-7.148 ^d	
λ "	11.7931 (4)	11.8659 (10)	11.8659	
10 ⁵ λ" D	1.05 (5)	1.05 ^d	1.05 ^d	
٥	7980.6041 (4) ^b	7260.5622 (9)	7927.8101 (14)	
σ ^c	0.0004	0.0010	0.0014	

^a Error limits are 3σ.

 $^{\rm b}$ The term value of the hypothetical ground state level F $_2,$ N=J=0 was set to zero.

 $^{\rm c}$ Weighted standard deviation of the fit of the optical data. $^{
m d}$ Fixed.

TABLE VII

Vacuum Wavenumbers and Rotational Assignments for Lines of the 0–0 Band of the $b^1\Sigma_g^+-X^3\Sigma_g^-$ System of ${}^{32}S^{34}S$

Line		v (cm.	L	ine	v (cm ⁻¹)		
PQ	(7)	7979.8263	(+27) ^a	PQ	(30)	7965.2070	(+20)
PQ	(8)	7979.5006	(+4)	PQ	(31)	7964.3042	(+4)
PQ	(9)	7979.1403	(-6)	ΡQ	(33)	7962.4488	(+6)
PQ	(10)	7978.7469	(+1)	RR	(16)	7988.6520	(-42)
PQ	(12)	7977.8571	(-22)	^R R	(17)	7988.9856	(-4)
PQ	(14)	7976.8464	(-13)	RR	(18)	7989.3013	(-10)
PQ	(16)	7975.7218	(+5)	RR	(20)	7989.8900	(-43)
PQ	(18)	7974.4911	(+27)	R _R	(23)	7990.6816	(+12)
PQ	(20)	7973.1534	(-31) ^b	R _R	(25)	7991.1376	(+10)
PQ	(22)	7971.7323	(+4)	RR	(27)	7991.5384	(+2)
PQ	(23)	7970.9870	(+4)	R R	(31)	7992.1755	(-19)
PQ	(24)	7970.2226	(+25)	Pp	(21)	7966.1695	(-15)
PQ	(25)	7969.4378	(+48) ^b	PP	(23)	7964.4508	(-22)
PQ	(28)	7966.9533	(+3)	Ρ _Ρ	(27)	7960.8552	(-16)
PQ	(29)	7966.0869	(-13)	Pp	(31)	7957.0438	(-32)

^a Obs-Calc in units of 10^{-4} cm⁻¹.

^b Overlapped line not used in the least squares fit.

Const	ant	b ^l Σ+g	x ³ Σ_{g}^{-}
	B ₀	a 0.279271 (56)	0.285959 (55)
107	D ₀	2.31 (40)	2.18 (37)
10 ³	Υ ₀		-7.157 ^b
	λ _o		11.793 ^b
105	^x D ₀		1.05 ^b
	т	7980.9874 (16)	0.0 ^c
a Erro	r li	mits are 3σ.	
b Fixe	d at	the value for ³² S	2.
c The leve	term 1 F ₂	value of the hypo , N=J=0, was set a	thetical t zero,

TABLE VIII

Molecular Constants for the $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ States of ${}^{32}S^{34}S$ (in cm⁻¹)

where $S_{J'J}$ is the rotational line strength. All lines were given equal weight except overlapped lines which were given zero weight. For the 0–0 band, 99 line intensities were fitted with a standard deviation of 1.3% of the intensity of the strongest line, which corresponds closely to the noise level observed. The temperature obtained was $310.7 \pm 1.4 \text{ K} (1\sigma)$. The quality of the fit is therefore comparable to the accuracy of the measurements.

IV. DISCUSSION

The molecular constants for ${}^{32}S_2$ and ${}^{32}S^{34}S$ derived from the present work and given in Tables IV, VI, VIII, and IX are more accurate than any which have hitherto appeared in the literature. In the ground state the value of $\Delta G_{1/2}$ (720.042 cm⁻¹) supersedes earlier values derived from bandhead measurements of electronic band

TABLE IX

Derived Molecular Constants for the $b^1 \Sigma_g^+$ and $X^3 \Sigma_g^-$ States of ${}^{32}S_2$

Constant	b ¹ Σ ⁺ g	x ³ Σ _g
B_e (cm ⁻¹)	0.2885959 (18) ^a	0.2953897 (12)
α _e (cm ⁻¹)	0.0017845 (34)	0.0015948 (23)
r _e (Å)	1.911537 (6)	1.889427 (4)
$\Delta G_{\frac{1}{2}}$ (cm ⁻¹)	667.2479 (17)	720.0419 (10)

a. Error limits are 3σ

TABLE	Х
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Rotational Line Strengths in a ${}^{1}\Sigma_{g}^{+} {}^{3}\Sigma_{g}^{-}$ Magnetic Dipole Transition^a

Li	lne	Triplet Component	b Line Strength	
R _R	(J)	F ₂	J M ²	
RQ	(J)	F_1 $s_J^2(2J+1)M^2$		
PQ	(J)	F ₃	$c_{J}^{2}(2J+1)M^{2}$	
Pp	(J)	F ₂	(J+1)M ²	
a.	From	Reference (10).		
b.	c _J ² =	$\frac{F_2 (J) - F_1 (J)}{F_3 (J) - F_1 (J)}$, $s_{J}^{2} = \frac{F_{3}(J) - F_{2}(J)}{F_{3}(J) - F_{1}(J)}$	
	and M	is the magnetic	dipole transition moment	

systems [719.96 cm⁻¹, (1)] and Raman studies in the gas phase [718 cm⁻¹, (13)]. The value of D_0 (=1.96 × 10⁻⁷ cm⁻¹) is in excellent agreement with the value calculated from the relation $D = 4B^3/\omega^2$ (viz 1.97 × 10⁻⁷ cm⁻¹). In the excited state the value of $\Delta G_{1/2}$ (667.248 cm⁻¹) replaces the value (693 ± 15 cm⁻¹) derived from low-resolution emission studies (8). Once again the value of D (=2.12 × 10⁻⁷ cm⁻¹) is in excellent agreement with the value calculated from the relation $D = 4B^3/\omega^2$ (viz 2.14 × 10⁻⁷ cm⁻¹).

The *B* values for ${}^{32}S^{34}S$ can be compared with values calculated by means of isotope relations. The value of $\rho^2 = \mu({}^{32}S^{34}S)/\mu({}^{32}S_2) = 1.0302669$. For the $b^1\Sigma_g^+$ and $X^3\Sigma_g^-$ states the *B* values for ${}^{32}S^{34}S$ calculated from those for ${}^{32}S_2$ are 0.279252 and 0.285938 cm⁻¹, respectively, in excellent agreement with the experimental values of 0.279271(56) and 0.285959(55) cm⁻¹, respectively.

The sign of the vibrational isotope shift for the 0–0 band indicates that the vibrational frequency in the $b^1\Sigma_g^+$ state is smaller than in the $X^3\Sigma_g^-$ ground state. From the magnitude of the shift (0.3833 ± 0.0016 cm⁻¹) the change in the vibrational frequency is calculated to be -51.0 ± 0.2 cm⁻¹; i.e., that $\Delta G'_{1/2} = 669$ cm⁻¹. This preliminary value was of considerable assistance in finding some weak lines of the 1–1 band (see Analysis) and proved to be accurate to ~2 cm⁻¹.

The intensities of the rotational lines in the 0–0 band and the derived rotational temperature of 310.7 ± 1.4 K indicate that the *b*-state population is completely rotationally relaxed under the conditions of the experiment. If the vibrational levels are also completely relaxed, then the 1–1 band is expected to have ~4.6% of the intensity of the 0–0 band assuming that the Franck-Condon factors are similar. From a comparison of the intensities of corresponding lines in the two bands, a value of 4.4% is obtained for the ratio of the intensities of the two bands. These results are consistent with the long radiative lifetime for the *b* state which has been calculated to be of the order of 3.4 sec (14).

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