

Rotational Analysis of the $A^1\Sigma^+ - X^1\Sigma^+$ Transition of SrS

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The previously unobserved $A^1\Sigma^+ - X^1\Sigma^+$ transition of gas phase SrS was studied by dye laser spectroscopy. The 0-0, 0-1, 1-1, 2-1, 3-0, 3-2, 4-1, 5-1, and 5-2 bands were rotationally analyzed at high resolution. The $A^1\Sigma^+$ state is extensively perturbed. Spectroscopic constants of individual vibrational levels and equilibrium molecular constants were determined. Ground state ($X^1\Sigma^+$) constants derived from the analysis include: $\omega_e = 388.2643(11) \text{ cm}^{-1}$, $B_e = 0.1208034(33) \text{ cm}^{-1}$, and $r_e = 2.43969 \text{ \AA}$. Excited state ($A^1\Sigma^+$) constants determined include: $T_e = 13932.7068(10) \text{ cm}^{-1}$, $\omega_e = 339.1454(20) \text{ cm}^{-1}$, $B_e = 0.1139895(38) \text{ cm}^{-1}$, and $r_e = 2.51155 \text{ \AA}$. © 1988 Academic Press, Inc.

INTRODUCTION

In the course of our work on SrSH, we discovered the previously unobserved $A^1\Sigma^+ - X^1\Sigma^+$ transition of SrS. The only previous high-resolution work on the SrS molecule is the absorption study of Marcano and Barrow (1). In this work the $B^1\Sigma^+ - X^1\Sigma^+$ absorption spectrum in the 3600- to 3900-Å region was rotationally analyzed, and extensive perturbations were observed in the $B^1\Sigma^+$ state. We present here a rotational analysis of the $A^1\Sigma^+ - X^1\Sigma^+$ transition by dye laser excitation spectroscopy.

Partridge *et al.* (2) used ab initio calculations to determine spectroscopic constants (ω_e , D_e , and r_e) for the $X^1\Sigma^+$, $a^3\Pi$, and $A'^1\Pi$ states of the alkaline earth sulfides, including SrS. The transition energies, T_e , for the $a^3\Pi - X^1\Sigma^+$ and $A'^1\Pi - X^1\Sigma^+$ transitions were calculated to be 6870 and 7179 cm^{-1} , respectively.

The dissociation energy of 80 kcal/mole (3-5) is known from high-temperature mass spectrometry. Martin and Schaber (6) have recorded the infrared spectrum of matrix-isolated SrS and related metal sulfides.

Electronic transitions for BeS (7-9), MgS (10), CaS (11), and BaS (12-15) have been previously analyzed. The corresponding oxide spectra, including the SrO $A^1\Sigma^+ - X^1\Sigma^+$ transition (16-18), are also known.

EXPERIMENTAL DETAILS

The strontium sulfide molecule was produced in a Broida oven (19) by the reaction of strontium with carbon disulfide. The strontium metal was vaporized in a resistively heated crucible, carried to the reaction region by argon, and mixed with the oxidant (CS_2). A dye laser, tuned to the $^3P_1 - ^1S$ strontium atomic transition at 6892.6 Å, was required to promote the reaction. The pressures were approximately 1 Torr argon and a few mTorr carbon disulfide.

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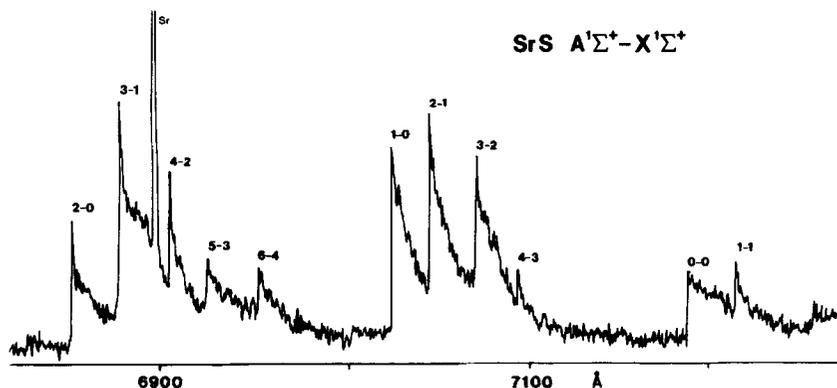


FIG. 1. Low resolution spectrum of SrS $A^1\Sigma^+ - X^1\Sigma^+$. The low resolution SrS laser excitation spectrum consists of a progression of vibrational band sequences. The $\Delta v = 2$, $\Delta v = 1$, and $\Delta v = 0$ sequences are shown, in order of increasing wavelength. The relative intensities of the bands have not been corrected for the variation in laser power.

Two types of spectra were recorded. Low-resolution laser excitation spectra were obtained by scanning a broadband (1 cm^{-1}) continuous wave dye laser and detecting the total fluorescence through a red pass filter with a photomultiplier tube. High-resolution (0.003 cm^{-1}) laser excitation spectra were obtained by scanning a computer-controlled ring dye laser (Coherent Autoscan 699-29) while detecting fluorescence through a 0.64-m monochromator. The monochromator was used as a narrow band-pass filter to select the rotational lines of interest.

The wavemeter of the computer-controlled dye laser is calibrated with an iodine cell, and the absolute accuracy of the line positions was approximately $\pm 0.003 \text{ cm}^{-1}$.

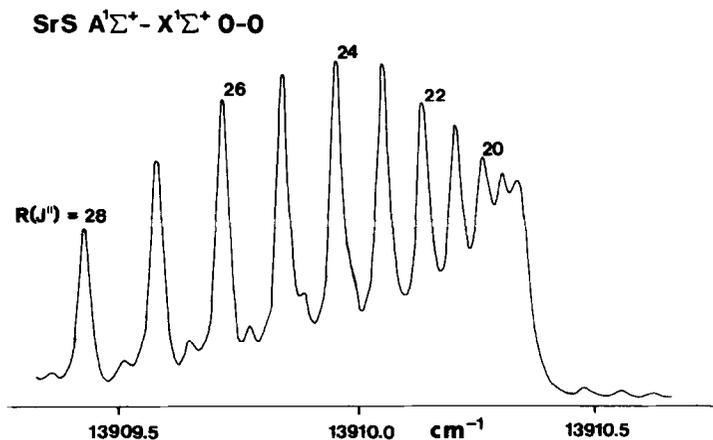


FIG. 2. High resolution spectrum of SrS $A^1\Sigma^+ - X^1\Sigma^+$. The high resolution spectrum near the R -branch bandhead of the $0-0$ band is shown. Rotational lines of high J values coming out of the bandhead are labeled. Low J , R -branch lines going into the bandhead are the smaller features. A monochromator was used as a narrow band-pass filter, and its wavelength setting determined the relative intensities of the rotational lines.

TABLE I
Observed Line Positions for SrS $A^1\Sigma^+ - X^1\Sigma^+$ (in cm^{-1})

a					b				
0-0 Band					0-1 Band				
J^*	P(J^*)	$\Delta\nu^a$	R(J^*)	$\Delta\nu$	J^*	P(J^*)	$\Delta\nu^a$	R(J^*)	$\Delta\nu$
0			13908.5562	0.0003	4	13521.5876	0.0015		
1	13908.0868	-0.0004	13908.7713	0.0014	5	13521.2991	0.0005		
2	13907.8333	0.0008	13908.9698	-0.0006	6	13520.9989	0.0034		
3	13907.5648	0.0005	13909.1599	0.0025	7	13520.6803	0.0005		
4	13907.2832	0.0007	13909.3334	0.0026	8	13520.3518	0.0002		
5	13906.9878	0.0005	13909.4918	0.0011	9	13520.0099	-0.0009		
6	13906.6742	-0.0042	13909.6369	-0.0001	10	13519.6581	0.0008		
7	13906.3547	-0.0013	13909.7703	0.0006	11	13519.2931	0.0018		
8	13906.0244	0.0042	13909.8888	-0.0001	12	13518.9120	-0.0008		
9	13905.6691	-0.0016	13909.9955	0.0009	13	13518.5222	0.0006		
10	13905.3055	-0.0023	13910.0889	0.0022	14	13518.1200	0.0021		
11	13904.9324	0.0011	13910.1656	0.0004	15	13517.7013	-0.0003		
12	13904.5427	0.0014			16	13517.2715	-0.0012		
13	13904.1382	0.0005			17	13516.8326	0.0014		
14	13903.7215	0.0009			18	13516.3763	-0.0009		
15	13903.2923	0.0024			19	13515.9106	0.0000		
16	13902.8477	0.0019			20	13515.4307	-0.0006		
17	13902.3903	0.0022			21	13514.9455	0.0009	13524.7183	-0.0033
18	13901.9189	0.0021			22	13514.4336	-0.0016	13524.6683	-0.0035
19	13901.4343	0.0023			23	13513.9201	0.0019	13524.6097	0.0004
20	13900.9344	0.0007			24	13513.3886	-0.0001	13524.5346	0.0004
21	13900.4222	0.0004			25	13512.8471	0.0005	13524.4444	-0.0021
22	13899.8987	0.0022			26	13512.2929	0.0011	13524.3450	-0.0010
23	13899.3597	0.0022	13910.0472	-0.0014	27	13511.7234	-0.0011	13524.2336	0.0006
24	13898.8040	-0.0010	13909.9505	-0.0001	28	13511.1424	-0.0022	13524.1069	-0.0004
25	13898.2359	-0.0031	13909.8387	-0.0002	29	13510.5507	-0.0014	13523.9695	0.0006
26	13897.6585	-0.0009	13909.7120	-0.0017	30	13509.9461	-0.0009	13523.8177	-0.0001
27	13897.0655	-0.0008	13909.5719	-0.0029	31	13509.3291	-0.0002	13523.6521	-0.0019
28	13896.4594	-0.0002	13909.4218	-0.0005	32			13523.4748	-0.0028
29	13895.8377	-0.0017	13909.2550	-0.0012	33	13508.0524	-0.0038	13523.2864	-0.0021
30	13895.2034	-0.0022	13909.0765	0.0001	34	13507.3971	-0.0036	13523.0826	-0.0041
31	13894.5596	0.0013	13908.8797	-0.0033	35	13506.7291	-0.0035	13522.8680	-0.0042
32	13893.8952	-0.0022	13908.6729	-0.0031	36	13506.0473	-0.0046	13522.6436	-0.0014
33	13893.2201	-0.0029	13908.4523	-0.0030	37	13505.3572	-0.0014	13522.3989	-0.0062
34	13892.5304	-0.0046	13908.2173	-0.0037	38	13504.6463	-0.0063	13522.1373b	-0.0152
35	13891.8311	-0.0023	13907.9678	-0.0053	39	13503.9251	-0.0090	13521.8408b	-0.0464
36	13891.1139	-0.0044	13907.7030	-0.0084	40	13503.1864b	-0.0166	13521.6298b	0.0206
37	13890.3847	-0.0049	13907.4279	-0.0082	41	13502.3337b	-0.1255	13521.3252	0.0068
38	13889.6404	-0.0069	13907.1312b	-0.0160	42	13501.7186b	0.0158	13521.0203	0.0054
39	13888.8874	-0.0041	13906.7231b	-0.1215	43	13500.9425	0.0088	13520.7011	0.0024
40	13888.1085b	-0.0135	13906.5442b	0.0159	44	13500.1594	0.0073	13520.3718	0.0021
41	13887.2176b	-0.1214	13906.2067	0.0084	45	13499.3631	0.0053	13520.0310	0.0030
42	13886.3603b	0.0179	13905.8587	0.0041	46	13498.5501	-0.0008	13519.6760	0.0024
43	13885.7410	0.0087	13905.5004	0.0032	47	13497.7350	0.0037	13519.3068	0.0005
44	13884.9136	0.0051	13905.1280	0.0019	48	13496.9000	0.0009		
45	13884.0738	0.0027	13904.7421	0.0008	49	13496.0549	0.0007		
46	13883.2241	0.0039	13904.3373	-0.0055	50	13495.1979	0.0012		
47	13882.3575	0.0019	13903.9266	-0.0040	51	13494.3271	0.0006		
48	13881.4784	0.0010	13903.5056	0.0009	52	13493.4448	0.0011		
49	13880.5861	0.0005	13903.0650	0.0000	53	13492.5469	-0.0013		
50	13879.6805	0.0002	13902.6108	-0.0007	54	13491.6387	-0.0014		
51	13878.7607	-0.0005	13902.1460	0.0016	55	13490.7191	-0.0001		
52	13877.8294	0.0008	13901.6638	0.0004	56	13489.7871	0.0014		
53	13876.8853	0.0030	13901.1693	0.0006	57	13488.8392	-0.0003		
54	13875.9246	0.0022	13900.6607	0.0004	58	13487.8788	-0.0018		
55	13874.9511	0.0022	13900.1392	0.0012	59	13486.9081	-0.0010		
56	13873.9625	0.0008	13899.6015	-0.0005	60	13485.9232	-0.0016		
57	13872.9614	0.0005	13899.0528	0.0006	61	13484.9248	-0.0030		
58	13871.9458	-0.0006	13898.4874	-0.0012	62	13483.9156	-0.0026		
59	13870.9198	0.0015	13897.9118	0.0007	63				
60	13869.8779	0.0014	13897.3212	0.0013	64	13481.8641	0.0034		
61	13868.8214	0.0003	13896.7147	-0.0001	65	13480.8154	0.0025		
62	13867.7501	-0.0018	13896.0983	0.0024	66	13479.7535	0.0012		
63	13866.6687	-0.0004	13895.4635	0.0003	67	13478.6777	-0.0013		
64	13865.5755	0.0029	13894.8170	0.0004	68	13477.5926	-0.0004		
65	13864.4614	-0.0010	13894.1528	-0.0034	69	13476.4929	-0.0013		
66	13863.3360	-0.0026	13893.4821	0.0002	70	13475.3828	0.0001		
67			13892.7948	0.0011					
68			13892.0904	-0.0013					
69			13891.3731	-0.0026					
70			13890.6454	-0.0005					

^a Observed-Calculated line positions using the constants of Table IV.
^b Perturbed.

RESULTS AND DISCUSSION

A portion of the low-resolution laser excitation spectrum of the SrS $A^1\Sigma^+ - X^1\Sigma^+$ transition is shown in Fig. 1. The spectrum consists of a progression of band sequences.

Each individual band exhibits a bandhead degraded to the red, implying a larger bond length in the excited state than in the ground state. Since the $A^1\Sigma^+$ and $X^1\Sigma^+$ vibrational frequencies differ by 50 cm^{-1} , the vibrational assignment of the bands was straightforward.

Following the vibrational assignment, the 0-0, 0-1, 1-1, 2-1, 3-0, 3-2, 4-1, 5-1, and 5-2 bands were recorded at high resolution. The bandhead in the R -branch of the 0-0 band is shown in Fig. 2. To select out this bandhead, the monochromator filter was set to detect fluorescence from the connecting 0-1 band. Low J lines can be seen as the small features going into the bandhead.

The frequencies of 682 rotational lines from the nine bands are presented in Table I, and the bandhead frequencies from both low- and high-resolution spectra are presented in Table II.

Perturbations were observed in most of the vibrational levels in the excited $A^1\Sigma^+$ state. The local perturbations observed are evident in the line positions in Table I. The exact assignment of the perturbing states was not possible, since both homogeneous ($\Delta\Lambda = 0$) and heterogeneous ($\Delta\Lambda = \pm 1$) interactions fit the perturbations equally well. In all cases, the perturbations appeared to be sharp, suggesting that the perturbing states have rotational constants quite different from that of the perturbed $A^1\Sigma^+$ excited state. By analogy with other alkaline earth oxides and sulfides, perturbations from the unknown $A'^1\Pi$, $a^3\Pi$ states and, perhaps, the $b^3\Sigma^+$ state are possible.

A perturbation in the P branch of the 5-1 band is shown in Fig. 3. The perturbed $P(32)$ line is shifted a small amount lower in frequency while the perturbing line is shifted to higher frequency. A similar pattern was observed in the R branch of the 5-1 band and in the P and R branches of the 5-2 band. These observations show that $v' = 5$, $J' = 31$ of the $A^1\Sigma^+$ state is perturbed. A list of the observed local perturbations is provided in Table III.

The 682 lines from the nine bands (Table I) were simultaneously fit using the customary $^1\Sigma^+$ energy level expression,

$$T_v(J) = T_v + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3.$$

TABLE II
Vibrational Bandhead Positions for SrS $A^1\Sigma^+ - X^1\Sigma^+$ (in cm^{-1})

v, v''	0	1	2	3
0	13910.3435(50) ^a	13524.7884(50)		
1	14244(5) ^b	13862.7019(50)		
2	14594(5) ^b	14199.5340(50)		
3	14921.0962(50)	14541(5) ^b	14152.4687(50)	
4		14870.0406(50)	14487(5) ^b	14103(5) ^b
5		15205.0073(50)	14821.9450(50)	14446(5) ^b

^a The numbers in parentheses represent one standard deviation uncertainty.

^b The positions of these bandheads were determined from a low-resolution laser excitation spectrum.

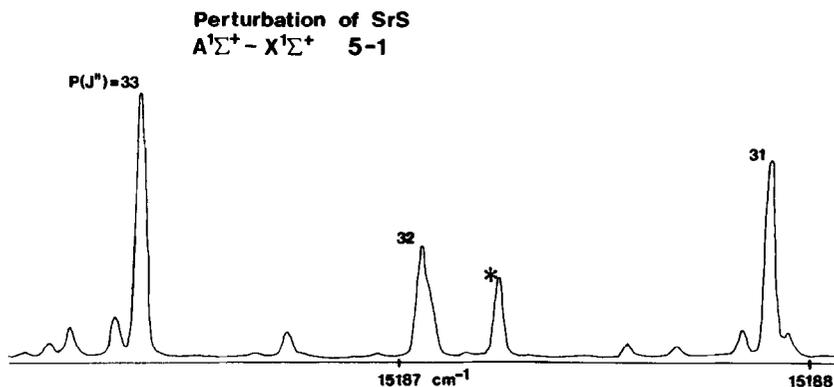


FIG. 3. Perturbation of the SrS $A^1\Sigma^+ - X^1\Sigma^+$ spectrum. The perturbation shown here is in the P branch of the 5-1 band. The perturbation occurred at the rotational level $J = 31$ of the vibrational level $v = 5$ in the $A^1\Sigma^+$ state. In this case, the perturbed line, $P(32)$, is shifted by a small amount (around 0.1 cm^{-1}) lower in frequency from its expected position as a result of the perturbation. The perturbing line, marked by the asterisk, is shifted to higher frequency.

The molecular constants resulting from the fit for vibrational levels in both the ground and excited states are presented in Table IV. The ground state constants agree reasonably well but are more accurate than those from the work of Marcano and Barrow (1). The excited state centrifugal distortion constants D_v and H_v (especially for $v = 3, 4$, and 5) are not physically reasonable molecular rotational constants but only effective constants because of the severe perturbations observed in these levels.

Lines from the 0-0, 0-1, 1-1, 2-1 bands and ground state vibrational combination differences between the 3-0 and 3-2 bands and between the 5-1 and 5-2 bands were also fit with a Dunham-type energy level expression (20) to determine equilibrium molecular constants (Table V),

$$E_{vJ} = \sum Y_{kl}(v + 1/2)^k [J(J + 1)]^l.$$

Due to the perturbed nature of the upper vibrational levels in the excited state, the 4-1 band was not included. The use of ground state combination differences essentially

v'	J'
0	40
1	0
3	43
3	59
5	31
5	45

TABLE IV
Molecular Constants for the $A^1\Sigma^+ - X^1\Sigma^+$ Transition of SrS (in cm^{-1})

Level	T_v	B_v	$D_v \times 10^8$	$H_v \times 10^{10}$
<u>$X^1\Sigma^+$</u>				
$v = 0$	0.0	0.1205652(29) ^a	4.894(64)	-
$v = 1$	385.70299(55)	0.1200876(29)	4.919(58)	-
$v = 2$	768.84690(69)	0.1196035(35)	4.86(13)	-
<u>$A^1\Sigma^+$</u>				
$v = 0$	13908.3283(3)	0.1137945(30)	5.355(60)	-
$v = 1$	14246.3691(8)	0.1134215(31)	4.779(74)	-
$v = 2$	14583.3051(8)	0.1130825(33)	6.29(11)	-
$v = 3$	14919.3935(4)	0.1126042(34)	1.81(14)	-
$v = 4$	15254.0297(8)	0.1122499(55)	2.44(75)	-0.440(32)
$v = 5$	15589.2504(14)	0.1109100(65)	-44.38(60)	-0.948(17)

^a The numbers in parentheses represent one standard deviation uncertainty.

TABLE V
Equilibrium Molecular Constants for the $A^1\Sigma^+ - X^1\Sigma^+$ Transition of SrS (in cm^{-1})

Constant ^a	$X^1\Sigma^+$	$A^1\Sigma^+$
Y_{00} (T_e)	0.0	13932.7068(10) ^b
Y_{10} (ω_e)	388.2643(11)	339.1454(20)
$-Y_{20}$ ($\omega_e x_e$)	1.28032(38)	0.55237(67)
Y_{01} (B_e)	0.1208034(33)	0.1139895(38)
$-Y_{11}$ (α_e)	0.00047463(70)	0.0004048(38)
Y_{21} (γ_e) $\times 10^6$	-2.07(28)	16.6(14)
$-Y_{02}$ (D_e) $\times 10^8$	4.870(63)	6.16(11)
$-Y_{12}$ (β_e) $\times 10^8$	---	-2.56(16)
$-Y_{22}$ $\times 10^8$	---	1.024(61)
Y_{03} (H_e) $\times 10^{13}$	---	-2.71(58)
r_e (Å)	2.439687(14)	2.511548(17)

^a As defined in Ref. 21, pg. 92, 107 and 108.

^b The numbers in parentheses represent one standard deviation uncertainty.

resulted in the removal of the most badly perturbed vibrational levels of the excited state ($v' = 3, 5$) from the fit, while allowing the $v'' = 2$ level of the ground state to be included. Again, the higher order excited state rotational constants (particularly the D 's and the H) are not actual molecular constants, but only effective constants.

Transitions involving the ^{86}Sr and ^{87}Sr isotopes of SrS were also observed in natural abundance (9.86, 7.00%). The positions of the isotopic transitions were accurately predicted from the constants of Table V. Only a few of the isotopic lines were measured and they were not included in the fits.

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