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 $r_{e} = 2.43969$ Å. 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 $r_{e} = 2.51155$ Å. © 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 (CS₂). A dye laser, tuned to the ³P₁-¹S 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 bandpass 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 ± 0.003 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.

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TABLE I

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

a		0 - 0	Band		b		0-1 H	and	
J.	P(J")	Δν ^a	R(J")	Δν	J"	P(J")	Δν ^a	R(J")	۵۲
0 1	13908.0868	-0,0004	13908,5562 13908,7713	0.0003	4	13521.5876	-0.0015		
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		
7	13906.3547	-0.0013	13909.7703	0.0001	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		
13	13904.342/	0.0014			17	13517.2715	-0.0012		
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	0.0059	13524.7183	-0,0033
18	13901.9189	0.0021			22	13514.4336	-0.0016	13524.6683	-0.0035
20	13901.4343	0.0023			23	13513,9201	-0.0019	13524.6097	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	-0.001/	30	13509.9461	-0,0009	13523.6177	-0.0001
28	13896 4594	-0.0002	13909.3719	-0.0005	32	13309.3291	-0.0002	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
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	13907.1312Ъ	-0.0160	42	13501.7186Ъ	0.0158	13521.0203	0.0054
39	13888.8874	-0.0041	13906.7231Ь	-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	13886 56035	-0.1214	13906.2067	0.0084	46	13498.5501	-0.0008	13519 6760	0.0030
43	13885 7410	0.01/3	13905.5004	0.0041	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	13494,32/1	0.0006		
40	13880 5861	0.0010	13903.0056	0.0009	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	138/5.9246	0.0022	13900.6607	0.0004	59	13486 9081	-0.0018		
56	13873 9625	0.0022	13899 6015	-0.0012	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	~	12/01 0//2	0.000/		
60	13869.8779	0.0014	13897.3212	0.0013	64 65	13481.8641	0.0034		
62	13867 7503	-0.0003	13896./14/	-0.0001	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	134/5.3828	0.0001		
0/ 68			13892.7948	0.0011					
69			13891.3731	-0.0015					
70			13890.6454	-0.0005					

 $\stackrel{a}{\scriptstyle b}$ Observed-Calculated line positions using the constants of Table IV. 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.

TABLE I—Continued

	1-1 Band			d			2-1 Band		
J"	P(J")	Δν ^a	R(J")	ν	J"	P(J")	۵µª	R(J")	עם
1			13861.2266b	0.1202	28	14185.5801	0,0022	14198.4576	-0.0000
2			13861.3962b	0.0896	29	14184.9503	0.0056	14198.2743	-0.0012
3	13860.0244b	0.1188	13861.5547b	0.0612	30	14184.2967	-0.0007	14198.0783	-0.0009
4	13859.71255	0.0871	13861.70975	0.0428	31	14183.6353	-0.0007	14197.8672	-0.0014
5	13859.3988b	0.0669	13861 08805	0.0273	32	14182.9591	-0.0013	14197.6472	0.0033
5	13839.06600	0.0409	13862 1185b	0.0111	33	14182.2726	0.0018	14197.4000	-0 0014
Ŕ			13862.2319	0.0043	34	14181.3003	0.0004	14196 8885	0.0043
9	13858.0336b	0.0089	13862.3353	0.0009	36	14100.0474	0.0004	14196.6066	0,0042
10	13857.6676	0.0030	13862.4295	0.0017	37	14179.3689	-0.0016	14196.3072	0.0008
11	13857.2956	0.0044	13862.5079	-0.0000	38	14178.6108	0.0008	14195.9955	-0.0005
12	13856.9052	0.0008	13862.5740	-0.0007	39	14177.8354	0.0001	14195.6716	0.0002
13	13856.5031	-0,0012	13862.6247	-0.0035	40	14177.0468	0.0004	14195.3298	-0,0026
14	13856.0933	0.0023	13862.6662	-0.0020	41	14176.2452	0.0019	14194.9791	0.0001
15	13855.0049	0.0008			42	14175.4279	0.0020	14194.6080	-0.0034
17	13854 7705	-0.0005			e				
18	13854.3031	-0.0012					3-0 Bar	id	
19	13853.8285	0.0041							
20	13853.3286	-0.0026			T.*	P(17)	Au ^a	R(J")	Δμ
21	13852.8190	-0.0057			U U	1(0 /			
22	13852.3035	-0.0013			0			14919.6181	-0.0006
23	13851.7699	-0.0018			1	14919.1547	0.0023	14919.8320	0.0040
24	13851.2254	0.0001			2	14918.8977	0.0023	14920.0187	-0.0027
25	13850.6637	-0.0019			3	14918.6203	-0.0021	14920.2001	0.0013
26	13850.0859	-0.0066			4	14918.3322	-0.0013	14920.3624	0.0020
20	13849.0000	-0.0010	13861 8226	-0 0052	5	14918.0295	0.0008	14920.5063	0.0003
20	13848 2903	-0.0035	13861.6674	-0.0003	6	14917.7085	0.0005	14920.6359	0.0002
30	13847 6589	-0.0087	13861.4958	0.0016	7	14917,3683	-0.0031	14920.7521	0.0026
31	13847.0300	0.0018	13861.3075	0.0002	8	14917.0142	-0.004/	14920.8496	-0.0023
32	13846.3754	-0.0000	13861,1084	0.0013	10	14916.0504	-0.0001	14920.9292	0.0015
33	13845.7108	0.0014	13860.8942	0.0007	11	14915 8671	0.0011	14720.7707	0.0010
34	13845.0315	0.0013	13860.6667	0.0001	12	14915 4507	0.0007		
35	13844.3396	0.0020	13860.4285	0.0022	13	14915.0160	-0.0021		
36	13843.6297	-0.0021	13860.1747	0.0020	14	14914.5685	-0.0019		
37	13842.9111	-0.0016	13859.9046	-0.0011	15	14914.1057	-0.0011		
38	13842.1838	0.0035	13859.6265	0.0011	16	14913.6264	-0.0010		
39	13841.4370	0.0023	13839.3321	0.0004	17	14913.1331	0.0009		
40	13840,6769	0.0011	13859.0234	-0.0013	18	14912.6195	-0.0017		
41	13839.9048	0.0011	13858.7098	0.0033	19	14912.0916	-0.0028		
42	13839.1139	-0.0014	13858.0257	0.0022	20	14911.5495	-0.0023	14920.7816	-0.0025
45	13837 5069	-0.0008	13857.6639	0.0009	21	14910.9914	-0.0020	14920.6727	-0.0033
45	13836.6821	-0.0004	13857.2894	0.0002	22	14910.4211	0.0017	14920.3499	0.00022
46	13835.8420	-0.0022	13856.9049	0.0028	25	14909.0299	-0.0004	14920 2550	-0.0021
47	13834.9916	+0.0009	13856.5028	0.0012	24	14908 6030	0.0002	14920.0886	0.0025
48	13834.1260	-0,0016	13856.0908	0.0030	26	14907.9673	0.0013	14919.8989	-0.0004
49	13833.2463	-0.0032	13855.6592	-0.0014	27	14907.3140	0.0006	14919.6993	0.0024
50	13832.3540	-0.0041	13855.2207	0.0007	- 28	14906.6458	0,0005	14919.4818	0.0030
d					29	14905.9607	-0,0008	14919.2469	0.0018
*		2-1 Band			30	14905.2669	0.0047	14918.9975	0.0017
					_ 31	14904.5506	0.0033	14918.7307	-0.0002
		. 8			32	14903.8167	-0.0001	14918.4527	0.0023
J.	P(J")	<u>u</u>	K(J")	44	33	14903.0692	-0.0016	14918.1554	0.0011
	14107 3451	0.0031	14198 0430	0.0025	- 34	14902.3106	0.0012	14917.83/9	0.0049
2	14197.3031	0.0063	14198.2390	0,0004	35	14901.3342	-0.0010	14917.0100	-0.0009
3	14196.8392	-0,0004	14198.4240	0,0013	37	14899 9279	-0.0044	14916.8116	-0.0036
ŭ	14196.5588	0.0014			38	14899 1073	-0,0018	2.720.0120	
					39	14898.2659	-0.0047		
6	14195.9513	0.0003							
7	14195.6259	-0.0008			f				
8	14195.2874	-0.0011					3-2 Ba	ina	
9	14194.9347	-0.0016							
10	14194.5708	0.0008			1.	P(1")	Ava	R(1")	٨٧
11	14194.1863	-0.0034			J .	r(J)	13 8	m(o)	
12	14193.7929	-0.0020			2		_	14151.1791	-0.0012
17	14191 6123	-0.0014			3			14151.3625	-0.0010
18	14191 1322	-0.0031			4	14149.5079	0.0021	14151.5360	0.0033
19	14190.6416	-0.0012			5	14149.2137	0.0030	14151.6894	0.0015
20	14190.1365	0.0002			6	14148.9040	0.0025	14151.8295	0.0003
21	14189.6197	0.0040			7	14148.5768	-0.0016	14151.9596	0.0032
22	14189.0793	-0.0018			8	14148.2437	0.0025		
23	14188.5299	-0.0025	14199.1515	-0.0041	.9	14147.8892	-0.0010		
24	14187.9713	0.0016	14199.0411	-0.0032	10	14147.5237	-0.0014		
25	14187.3942	0.0014	14198.9163	-0.0026	11	1414/.1440	-0.0021		
26	14186.8014	-0.0005	14198.7778	-0.0015					
	A 1 A 4 1 1 1 1 1 1								

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TABLE I—Continued

f		3-2 Ba	nd		h		5-1 Band		
J.	P(J")	Δν ^a	R(J")	Δν	J.	P(J*)	Δν ⁸	R(J*)	Δν
20			14152.3372	-0.0039	14	15198.5310	0,0001		
21	14142.5897	-0.0011	14152.2730	-0.0003	15	15198.0341	-0.0049	15204.9188	-0.0088
22	14142.0565	-0.0025	14152.1896	-0.0022	16	15197.5243	-0.0056	15204.8583	-0.0062
23	14141.5120	-0.0014	14152.0930	-0.0034	17	15196.9967	-0.0069	15204.7773	-0.0072
24	14140 3935	0.0016	14151.9836	-0.0036	18	15196.4537	-0.0068	15204.6903	0.0024
25	14139 7952	0.0010	14151,8631	-0.0011	19	15195.89/0	-0.0035	15204.5685	-0.0062
27	14139.1940	0.0005	14151 5778	0.0033	20	15195.3196	0.0044	15204.4405	-0.0046
28	14138.5789	-0.0002	14151.4098	-0.0029	22	15194.1163	-0.0052	15204.2956	-0.0036
29	14137.9533	0.0022	14151,2331	-0.0016	23	15193.4938	-0.0020	15203,9593	-0.0000
30	14137.3161	0.0067	14151.0434	0.0004	24	15192.8556	0.0015	15203,7685	0.0030
31	14136.6571	0.0030	14150.8356	-0.0021	25	15192.1962	-0.0003	15203.5576	0.0016
32	14135.9870	0.0018	14150.6202	0,0015	26	15191.5249	0.0018	15203.3327	0.0019
33	14135.3049	0.0023	14150.3858	-0.0003	27	15190.8382	0.0042	15203.0917	0.0017
35	14134.6095	0.0030	14150.1413	0.0014	28	15190.1344	0.0051	15202.8348	0.0010
36	14133,0904	-0.0004	14149.8814	0.0012	29	15189.4141	0.0049	15202.5584	-0.0039
37	14132 4360	-0.0010	14147.0095	0.0025	31	15187 0232	0.0028	15202.1936b	-0.0817
38	14131.6819	-0.0049			32	15187 07816	0.0004	15201.99/30	0.0244
					33	15186.3940b	0 0188	15201.06770	0.0122
9					34	15185.5925b	0.0139	15200.9808	0.0065
		4-1 Ban	d		35	15184.7798b	0.0131	15200.6158	0.0053
					36	15183.9473	0,0078	15200.2337	0.0025
	D(1")	a	B(78)		37	15183.1028	0.0059	15199.8369	0.0008
3	£(J)	20	K(J ~)	200	38	15182.2450	0.0062	15199.4231	-0.0021
1	14868 0878	0.0012	14868 7603	0.0002	39	15181.3659	0.0008		
2	14867.8299	-0.0008	14868.9567	0.0035	40	15180.4753	-0.0004	15198.5477	-0.0071
3	14867.5590	-0.0002	14869.1283	-0.0024	41	151/9.5/15	0.0013	15198.0890	-0.0058
4	14867.2682	-0.0038	14869.2904	-0.0021	42	15178.0452	-0.0032	15197.6149	-0.0029
5	14866.9644	-0.0048	14869.4404	0.0018	45	151/6 7519	-0.0042	15197.1177	-0.0056
6	14866.6474	-0.0032	14869.5683	-0.0008	45	15175.7795	-0.0029	13130.00740	-0.0036
7	14866.3190	0.0025			46	15174.7887b	-0.0035		
8	14865.9/19	0.0053	14869.7823	-0.0007	47	15173.7846	0.0009		
10	14865.602/	0.0016	14869.8623	-0.0041	48	15172.7640	0.0076		
10	14864 8220	-0.0016			49	15171.7196	0.0100		
12	14864 4144	0.0036			50	15170,6539	0.0112		
13	14863.9827	0.0000			i				
14	14863.5404	0.0015					5-2 Band		
15	14863.0801	0.0005							
16	14862.6045	-0.0000			• •		. 8		
17	14862.1121	-0.0017			3	P(J")	$\Delta \nu$	R(J")	Δ <i>ν</i>
18	14861.6077	0.0002			0	14017 6340	0.0000		
19	14861.0862	0.0008	14869.8390	0.0010	10	14817 2376	0.0045		
20	14860.5488	0.0012	14869,7490	0.0005	11	14816 8247	0.0027		
21	14039.9902	0.0020	14960 5334	0 0012	12	14816.3978	0.0036		
23	14858 8414	0.0015	14869 3852	0.0013	13	14815.9478	-0.0019		
24	14858.2364	-0.0026	14869.2329	0 0010	14	14815.4866	-0.0021		
25	14857.6250	0.0028	14869.0619	-0.0008	15	14815.0050	-0.0062	14821.8983	-0.0016
26	14856.9864	-0.0031	14868.8788	0.0014	16	14814.5131	-0.0045	14821.8466	-0.0056
27	14856.3351	-0.0057	14868.6759	0.0000	17	14813.9992	-0.0086	14821.7846	-0.0041
28	14855.6751	-0.0009	14868.4589	0.0009	18	14813.4/50	-0.0071	14821.7039	-0.0056
29	14854.9919	-0.0031	14868.2230	-0.0006	20	14012.7334	-0.0071	14021.0089	-0.0058
30	14854.2954	-0.0023	14867.9749	0.0022	21	14811 8041	-0.0057	14021.4992	-0.0032
31			14867.7061	0.0010	22	14811 2197	-0.0027	14821 2381	-0.0010
32			14867 1200	0.0008	23	14810,6224	0.0034	1.0011.2001	0.0001
34			14866 8001	-0.0001	24	14810.0014	0.0009	14820.9129	0.0010
35			14866.4630	-0.0009	25	14809.3681	0.0010	14820.7295	0.0030
36			14866.1136	0.0036	26	14808.7204	0.0016	14820.5301	0.0036
37			14865.3480	-0.0002	27	14808.0601	0.0043	14820.3138	0.0020
38			14864.9378	-0.0019	28	14807.3848	0.0066	14820.0869	0.0042
					29	14805.0920	0.0059	14819.8404	0.0012
h		5-1 Band	d		31	14805 2634	0.0063	14819.00340	-0.0778
					32	14804 4478b	-0.0756	14819 03815	0.0154
					33	14803.7902b	0.0164	14818 72875	0.0075
1 °	P(J")	<u>م</u> بد	R(J*)	Δv	34	14803.0243b	0.0143	14818.4076	0.0019
			10001		35	14802.2448b	0.0129		
2			15204.1716	0.0137	36	14801.4501b	0.0106	14817.7283	-0.0029
د ۸			15204,3349	0.0102	37	14800.6397	0.0071	14817.3730	0.0011
5			15204.4630	0.0096	38	14799.8148	0.0036	14816.9940	-0.0036
6	15201.8427	0.0112	15204.7186	0.0025	39	14/98.9740	-0.0011	14816.6049	-0.0033
7	15201.4918	0.0102	15204.8152	0.0048	40	14/98.1213	-0.0030	14816.2002	-0.0032
8	15201.1209	0.0072	15204.8887	0.0019	42	14796 3753	-0.0018	14013.///2	-0.0058
9	15200.7335	0.0058			43	14795,4790	-0.0012	14814 8860	-0.0003
10	15200.3254	0.0016			44	14794.5695	0.0021	14814.4214h	-0,0022
11	15199.9027	0.0007			45	14793.6366	-0.0017	14813.9350b	-0.0013
12	13133.4018	-0.0008			46	14792.6908b	-0.0016	14813.4349	0.0039
					47	14791.7322	0.0030		

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 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,

$$T_{v}(J) = T_{v} + BJ(J+1) - D[J(J+1)]^{2} + H[J(J+1)]^{3}.$$

,×"	0	1	22	3
0	13910.3435(50) [@]	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

TABLE II

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

^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
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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>Χ¹Σ</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)	-
		A ¹ Σ ⁺		
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 $A^{\dagger}\Sigma^{+}-X^{\dagger}\Sigma^{+}$ Transition of SrS (in cm⁻¹)

Cons	stant ^a			X ¹ Σ ⁺	Α ¹ Σ ⁺
Yoo	(T_)			0.0	13932.7068(10) ^b
Y ₁₀	(w_)			388.2643(11)	339.1454(20)
-Y ₂₀	(w _e x _e)			1.28032(38)	0.55237(67)
Y ₀₁	(B _e)			0.1208034(33)	0.1139895(38)
-Y ₁₁	(a _e)			0.00047463(70)	0.0004048(38)
Y ₂₁	(7 _e)	x	106	-2.07(28)	16.6(14)
-Y ₀₂	(D _e)	x	10 ⁸	4.870(63)	6.16(11)
-Y ₁₂	(β _e)	x	10 ⁸	•••	-2.56(16)
-Y ₂₂		x	10 ⁸		1.024(61)
Y _{os}	(H _e)	x	1013		-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.

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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 ⁸⁶Sr and ⁸⁷Sr 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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