Table S1. *The* vertical excitation energies with the $X^3\Sigma_g^-$ state for other states (cm^{-1}) in $R_{s\text{-}s}$=1.899Å

Basis	$a^1\Delta_g$	$b^1\Sigma_g^+$	$1^3\Pi_g$	$1^1\Pi_g$
aug-cc-pwCVTZ	4490.50	7700.96	38445.10	45534.13
aug-cc-pwCVQZ	4391.58	7552.95	38514.41	45429.61
aug-cc-pwCV5Z	4364.48	7511.62	38577.06	45458.34
CBS 345	4345.30	7481.78	38653.84	45521.28
CBS45	4342.48	7478.06	38627.93	45481.67
best CBS	4343.89±1.41	7479.92±1.86	38640.88±12.96	45501.47±19.81

best CBS = *X*±{CBS45 - *X* }

X=（CBS45 + CBS 345）/2

Table S2. Calculated spin-orbit matrix elements in S_2($R_{s\text{-}s}$=1.899Å)

Basis	Spin-orbit matrix elements with the $X^3\Sigma_g^-$ state for other states(cm^{-1})			Spin-orbit matrix elements with the $1^3\Pi_g$ state for other states(cm^{-1})	
	$b^1\Sigma_g^+$	$1^1\Pi_g$	$1^3\Pi_g$	$a^1\Delta_g$	$b^1\Sigma_g^+$
basis A	382.8	192.7	-193.2	-189.9	177.4
basis B	384.6	193.2	-193.8	-190.6	178.1
basis C	385.7	193.4	-194.1	-190.9	178.3
basis A_2	426.53	215.4	-216.8	212.6	201.2
basis A_1	426.62	214.9	-216.5	-212.1	200.5
basis B_1	427.94	215.3	-217.0	-212.6	201.1
basis C_1	428.90	215.6	-217.2	-212.7	201.3
CBS 345	430.02	215.95	-217.39	-212.74	201.47
CBS34	428.70	215.53	-217.29	-212.89	201.45
CBS45	429.68	215.84	-217.36	-212.78	201.46
best CBS	429.85±0.17	215.90±0.06	-217.38±0.01	-212.76±0.02	201.47±0.00
basis D [19, 38]	422.5	200.3	-203.1		
basis D1 (core2) [19]	423.0	202.7	-204.0		
basis E[19]	410.3	200.9	-200.8		
basis F[19]	416.6	203.9	-204.9		
basis G (core2) [20]				-200.2	188.6

basis D is the double-zeta set for sulfur given

basis D_1:on the basis of the basis D, correlating the $2s^22p^63s^23p^4$ electrons of S atom to account for the CV effect of the S_2.

basis E contains additional s and p bond functions [exponents (α(s) = 1.0 and α(p) = 0.6 relative to basis D

basis F adds only an s bond function to basis D.

basis G consists of the double-zeta (12s, 9p) set for sulfur contracted to [6s, 4p] with s and p bond functions (exponents α(s)= 1.0 and α (p) = 0.6).

Table S3.The error analysis for the Einstein coefficient A of the b-$X_{Ms=0}$ transition.

	Values	*Errors*
$\Delta E_{b\text{-}X(0,0)}/cm^{-1}$	7641 cm^{-1}	1.86 cm^{-1}
$C_{b,X}$	0.057467	0.000037i
A/s^{-1}	0.403824 s^{-1}	0.0003218 s^{-1}

Table S4. The theoretically inferred energy, Einstein coefficient and oscillator strength of the experimentally observable b-$X_{Ms=\pm1}$ band

v'-v''	$E(cm^{-1})$	$A(s^{-1})$	$f(a.u.)$
0-0	7640.75	0.403824	1.0413E-08
0-1	6936.95	0.302197	9.4536E-09
1-0	8281.40	0.514157	1.1286E-08
1-1	7577.60	0.393894	1.0327E-08
2-0	8925.67	0.643733	1.2164E-08
2-1	8221.86	0.503147	1.1205E-08
2-2	7523.10	0.385455	1.0252E-08
3-0	9560.64	0.791124	1.3029E-08
3-1	8856.84	0.628956	1.2070E-08
3-2	8158.07	0.491526	1.1118E-08
3-3	7463.83	0.376418	1.0172E-08
4-0	10191.61	0.958324	1.3889E-08
4-1	9487.81	0.773182	1.2930E-08
4-2	8789.04	0.614622	1.1978E-08
4-3	8094.81	0.480179	1.1032E-08
4-4	7405.11	0.367603	1.0092E-08
5-0	10818.75	1.146344	1.4744E-08
5-1	10114.95	1.146344	1.3785E-08
5-2	9416.18	0.936860	1.2832E-08
5-3	8721.94	0.755802	1.1886E-08
5-4	8032.25	0.600653	1.0946E-08
5-5	7348.49	0.469133	1.0014E-08
6-0	11439.27	0.359235	1.5589E-08
6-1	10735.46	1.120074	1.4630E-08
6-2	10036.70	0.915285	1.3678E-08
6-3	9342.46	0.738190	1.2732E-08
6-4	8652.77	0.586475	1.1792E-08
6-5	7969.01	0.458139	1.0860E-08
6-6	7292.73	0.351119	9.9385E-09
7-0	12052.70	1.585029	1.6425E-08
7-1	11348.90	1.323261	1.5466E-08
7-2	10650.13	1.093576	1.4514E-08
7-3	9955.90	0.893357	1.3568E-08
7-4	9266.21	0.720261	1.2628E-08
7-5	8582.45	0.572291	1.1696E-08
7-6	7906.16	0.447385	1.0774E-08
7-7	7236.98	0.343129	9.8625E-09
8-0	12656.75	1.835483	1.7248E-08
8-1	11952.95	1.545998	1.6289E-08
8-2	11254.18	1.290403	1.5337E-08

8-3	10559.94	1.066028	1.4391E-08
8-4	9870.25	0.870500	1.3451E-08
8-5	9186.49	0.701832	1.2519E-08
8-6	8510.21	0.557962	1.1598E-08
8-7	7841.03	0.436419	1.0686E-08
8-8	7177.36	0.334718	9.7812E-09
9-0	13251.97	2.106812	1.8060E-08
9-1	12548.17	1.788650	1.7101E-08
9-2	11849.40	1.506169	1.6148E-08
9-3	11155.17	1.256645	1.5202E-08
9-4	10465.48	1.037675	1.4262E-08
9-5	9781.72	0.847285	1.3330E-08
9-6	9105.43	0.683417	1.2409E-08
9-7	8436.26	0.543542	1.1497E-08
9-8	7772.59	0.425091	1.0592E-08
9-9	7113.89	0.325916	9.6947E-09

Table S5. The theoretically inferred energy, Einstein coefficient and oscillator strength of the experimentally observable a-$X_{Ms=\pm1}$ band

v'-v''	$E(cm^{-1})$	$A(s^{-1})$	$f(a.u.)$
0-0	4197.02	0.001386	1.1848E-10
1-0	4877.78	0.002176	1.3770E-10
2-0	5546.69	0.003200	1.5658E-10
2-1	4842.89	0.002130	1.3672E-10
3-0	6214.53	0.004501	1.7544E-10
3-1	5510.73	0.003138	1.5557E-10
3-2	4811.96	0.002089	1.3584E-10
4-0	6875.18	0.006094	1.9409E-10
4-1	6171.38	0.004408	1.7422E-10
4-2	5472.61	0.003074	1.5449E-10
4-3	4778.38	0.002046	1.3489E-10
5-0	7532.69	0.008015	2.1265E-10
5-1	6828.89	0.005972	1.9278E-10
5-2	6130.12	0.004320	1.7305E-10
5-3	5435.88	0.003012	1.5346E-10
5-4	4746.19	0.002005	1.3399E-10
6-0	8183.05	0.010276	2.3101E-10
6-1	7479.25	0.007846	2.1114E-10
6-2	6780.48	0.005846	1.9141E-10
6-3	6086.25	0.004228	1.7182E-10
6-4	5396.55	0.002947	1.5235E-10
6-5	4712.79	0.001963	1.3304E-10
7-0	8824.37	0.012886	2.4911E-10
7-1	8120.57	0.010042	2.2925E-10
7-2	7421.80	0.007666	2.0952E-10
7-3	6727.57	0.005710	1.8992E-10
7-4	6037.88	0.004128	1.7045E-10
7-5	5354.12	0.002878	1.5115E-10
7-6	4677.83	0.001920	1.3206E-10
8-0	9458.05	0.015866	2.6700E-10
8-1	8754.25	0.012581	2.4713E-10
8-2	8055.48	0.009803	2.2741E-10
8-3	7361.25	0.007480	2.0781E-10
8-4	6671.55	0.005569	1.8834E-10
8-5	5987.79	0.004026	1.6904E-10
8-6	5311.51	0.002810	1.4994E-10
8-7	4642.33	0.001876	1.3105E-10
9-0	10085.55	0.019238	2.8472E-10
9-1	9381.75	0.015485	2.6485E-10
9-2	8682.98	0.012276	2.4512E-10

9-3	7988.74	0.009561	2.2552E-10
9-4	7299.05	0.007292	2.0605E-10
9-5	6615.29	0.005429	1.8675E-10
9-6	5939.01	0.003928	1.6766E-10
9-7	5269.83	0.002744	1.4877E-10
9-8	4606.16	0.001833	1.3003E-10