

High-resolution Fourier transform spectrum of H₂S in the region of the second hexade

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Abstract

High-resolution Fourier transform infrared spectrum of H₂³²S was recorded and analyzed in the region of the second hexade $v = v_1 + \frac{1}{2}v_2 + v_3 = 2.5$. More than 1700 transitions were assigned to the $2v_1 + v_2$, $v_1 + v_2 + v_3$, $v_1 + 3v_2$, $3v_2 + v_3$, $5v_2$, and $v_2 + 2v_3$ bands with the maximum value of quantum number J equal to 18, 18, 13, 11, 13, and 9, respectively. The theoretical analysis was fulfilled with a Hamiltonian model which takes into account numerous resonance interactions between all the vibrational states in this polyad. By a least-square fitting, finally 505 upper energy levels were reproduced by 80 parameters with an rms deviation of 0.0019 cm^{-1} .

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1. Introduction

In the recent contributions [1,2], we presented results of analysis of the high-resolution Fourier transform spectrum of the H₂S molecule in the regions of the $v = v_1 + \frac{1}{2}v_2 + v_3 = 3$ and $v = 3.5$ polyads (7300–7900 and 8500–8900 cm^{-1} , respectively). In the present work, we will present the results of the high-resolution analysis of the H₂S spectrum in the longer wavelength region, namely, 5700–6650 cm^{-1} , where the $v = 2.5$ polyad is located.

Because the review of the earlier investigations of the H₂S spectra was made in [1], we will not repeat it here. As to the high-resolution spectroscopy study in the region which will be presented in this work, it was discussed without any details in [3]. As was mentioned in [3], transitions

of the five bands of this $v = 2.5$ polyad, $2v_1 + v_2$, $v_1 + v_2 + v_3$, $v_1 + 3v_2$, $3v_2 + v_3$, and $5v_2$, have been assigned with the maximum values of quantum numbers J equal to 8 for the first 4 bands and 12 for the last one. The values of the band centers were also presented. As will be shown in the following sections, the numbers of the obtained upper energy levels were much enlarged in present study compared with in [3]. The experimental details are given in Section 2. Theoretical background of the analysis is considered in Section 3. Description of the spectrum and assignments of the recorded transitions are given in Section 4. Section 5 presents the fitting results and discussion.

2. Experimental details

The hydrogen sulfide sample was purchased from Nanjing Special Gas Company with a stated purity of 99%. The sample was in natural abundance, but throughout this paper, the discussions will be constrained to the main

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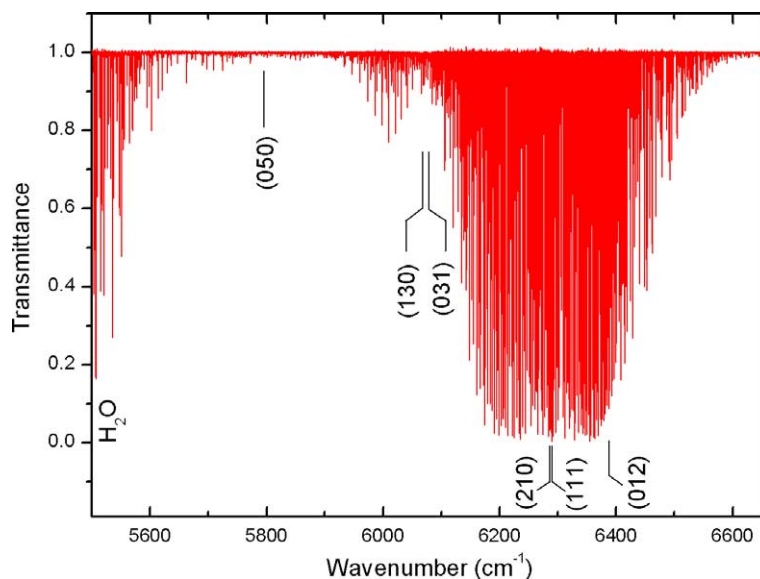


Fig. 1. Overview spectrum of H₂S in the 5500–6650 cm⁻¹ region. Experimental conditions: path length 105 m, gas pressure 2076 Pa.

isotope of this molecule, H₂³²S. The high-resolution spectra of H₂S in the 5000–6700 cm⁻¹ region were recorded with a Bruker IFS 120 HR Fourier transform spectrometer (Hefei, China) equipped with a path length adjustable multi-pass gas cell at room temperature. A tungsten source, a Ge detector and a CaF₂ beamsplitter were used. The unapodized spectral resolution was 0.015 cm⁻¹. The absorption path length was 105 m, and the pressure was 2076 Pa. Band-pass optical filters were applied in the measurements. An overview of the spectrum is presented in Fig. 1. The line positions were calibrated using H₂O lines listed in HITRAN [4] database. The accuracy of line positions of unblended and not-very-weak lines was estimated to be 0.002 cm⁻¹ or better.

3. Selection rules and the hamiltonian description

Since H₂S is an asymmetric top molecule with C_{2v} symmetry (the value of the asymmetry parameter is $\kappa \approx 0.532$), the vibrational states (210), (012), (130), (050) are the symmetric states and (111), (031) are antisymmetric. For this reason the selection rules are

$$\Delta J = 0, \pm 1; \Delta K_a = \pm(2n + 1); \Delta K_c = \pm(2m + 1) \quad (1)$$

for the $2v + v_2$, $v_1 + 3v_2$, $5v_2$, and $v_2 + 2v_3$ bands, and

$$\Delta J = 0, \pm 1; \Delta K_a = \pm 2n; \Delta K_c = \pm(2m + 1) \quad (2)$$

for the $v_1 + v_2 + v_3$ and $3v_2 + v_3$ bands. In Eqs. (1) and (2), n and $m = 0, 1, 2, \dots$. When $n = m = 0$, transitions are “allowed,” otherwise are so-called “forbidden” transitions.

Due to the presence of resonance interactions between all the states in this polyad, it is necessary to apply the effective Hamiltonian in the form

$$H^{v,-r} = \sum_{v,v'} H^{v,v'} |v\rangle \langle v'|$$

$$H^{v,v'} = \begin{vmatrix} 1 & 2 & 3 & 4 & 5 & 6 \\ W & D & F & - & C & - \\ D & W & - & - & C & C \\ F & - & W & F & C & C \\ - & - & F & W & - & C \\ C & C & C & - & W & F \\ - & C & C & C & F & W \end{vmatrix}. \quad (3)$$

Here $v, v' = 1, 2, \dots, 6$ and $|1\rangle = (210)$, $|2\rangle = (012)$, $|3\rangle = (130)$, $|4\rangle = (050)$, $|5\rangle = (111)$, and $|6\rangle = (031)$. W denotes the diagonal operator matrix elements of $H^{vv'}$; F and D denote the Fermi and Darling–Dennison-type interactions; C corresponds one of two Coriolis-type interactions, which connect the vibrational states $(v_1 v_2 v_3)$ and $(v_1 \pm 1 v_2 v_3 \mp 1)$, or $(v_1 v_2 v_3)$ and $(v_1 v_2 \pm 2 v_3 \mp 1)$. The diagonal blocks in expression (3) describe the rotational structures of isolated vibrational states and have the form of Watson’s operators [5], in A reduction and I' representation:

$$\begin{aligned} H^{vv} = & E^v + [A^v - \frac{1}{2}(B^v + C^v)]J_z^2 + \frac{1}{2}(B^v + C^v)J^2 \\ & + \frac{1}{2}(B^v - C^v)J_{xy}^2 - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v J^4 \\ & - \delta_K^v [J_z^2, J_{xy}^2]_{+} - 2\delta_J^v J_z^2 J_{xy}^2 + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 \\ & + H_{JK}^v J_z^2 J^4 + H_J^v J^6 + [J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J_z^2 J^2 + h_J^v J^4] \\ & + L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{JK}^v J_z^4 J^4 + L_{KJJ}^v J_z^2 J^6 + L_J^v J^8 \\ & + [J_{xy}^2, l_K^v J_z^6 + l_{KJ}^v J_z^4 J^2 + l_{KJ}^v J_z^2 J^4 + l_J^v J^6]_{+} + \dots \end{aligned} \quad (4)$$

The operators which describe Fermi-type interactions (Darling–Dennison interaction between the states (210) and (012), as well), are presented in the form of

$$\begin{aligned} H_F^{vv'} = & F^{vv'} + F_K^{vv'} J_z^2 + \dots + F_{xy}^{vv'} J_{xy}^2 + F_{xyK}^{vv'} [J_{xy}^2, J_z^2]_{+} \\ & + F_{xyJ}^{vv'} J_{xy}^2 J^2 + \dots \end{aligned} \quad (5)$$

The Coriolis-type interaction operators are in the following form:

$$\begin{aligned}
H_{C_y}^{v v'} = & 2(C\zeta^y)^{v v'} iJ_y + C_{yK}^{v v'} [iJ_y, J_z^2]_+ + C_{yJ}^{v v'} iJ_y J^2 \\
& + C_{yKK}^{v v'} [iJ_y, J_z^4]_+ + C_{yJK}^{v v'} [iJ_y, J_z^2 J^2]_+ + C_{yJJ}^{v v'} iJ_y J^4 \\
& + \dots + C_{xz}^{v v'} [J_x, J_z]_+ + C_{xzK}^{v v'} [[J_x, J_z]_+, J_z^2]_+ \\
& + C_{xzJ}^{v v'} [J_x, J_z]_+ J^2 + \dots + C_{xy}^{v v'} [iJ_y, J_{xy}^2]_+ + \dots \quad (6)
\end{aligned}$$

In the equations, $J_{xy}^2 = J_x^2 - J_y^2$ and $[A, B]_+ = AB + BA$.

4. Spectrum overview and assignments

Fig. 1 shows the overview spectra of the H₂S molecule in the region of the second hexade. The predicted band centers are also denoted in this figure. One can see the strong and overlapped “local mode” bands $2\nu_1 + \nu_2$ and $\nu_1 + \nu_2 + \nu_3$ of H₂³²S ((20⁺, 1) and (20⁻, 1) in the local mode notations). The *Q*, *P*, and *R* branches can be clearly seen. The $\nu_2 + 2\nu_3$ ((11, 1) in local mode notations) band is extremely weak and is covered by much stronger bands $2\nu_1 + \nu_2$ and $\nu_1 + \nu_2 + \nu_3$. The *P* branches of the bands $\nu_1 + 3\nu_2$ and $3\nu_2 + \nu_3$ ((10⁺, 3) and (10⁻, 3) in local mode notations) can be found very close to each other. The low frequency part of their *R* branches can be also recog-

Table 1
Ro-vibrational energy levels for the (111) and (210) states of H₂³²S (in cm⁻¹)^a

<i>J</i>	<i>K_a</i>	<i>K_c</i>	(111)			(210)			
			<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	
			1	2	3	4	5	6	7
0	0	0	6289.1741				6288.1456		-16
1	0	1	6302.5732	5	-1		6301.6566	3	-10
1	1	1	6304.0853	3	0		6303.1952		7
1	1	0	6308.5212		10		6307.4997	1	-3
2	0	2	6326.4474	4	15		6325.3755	4	-12
2	1	2	6326.6677	2	7		6325.6104	4	-7
2	1	1	6339.8775	9	6		6338.8980	8	-13
2	2	1	6344.1777	4	0		6343.2743	6	3
2	2	0	6347.4779	7	6		6346.4800	14	5
3	0	3	6358.8812	7	17		6357.8117	4	-8
3	1	3	6358.9015	11	-3		6357.8373	3	-5
3	1	2	6383.9454	8	9		6382.2641	7	5
3	2	2	6384.6153	6	-2		6382.9939	10	4
3	2	1	6395.8990	3	0		6394.9042	10	0
3	3	1	6404.3971	5	-3		6403.5482	9	15
3	3	0	6406.4846	3	-5		6405.5456	3	-1
4	0	4	6400.3069	10	9		6399.2100	7	12
4	1	4	6400.3091	7	14		6399.2100	7	-9
4	1	3	6435.4883	6	4		6434.3865	10	0
4	2	3	6435.6380	3	-2		6434.5552	4	-6
4	2	2	6458.0875	10	0		6457.2188	8	6
4	3	2	6462.0242	12	-14		6461.2993	5	5
4	3	1	6470.9123	10	-4		6469.9172	6	-3
4	4	1	6484.7728	5	-7		6484.0020	20	-15
4	4	0	6485.9173	19	-3		6485.0805		34
5	0	5	6450.7933	10	4		6449.6547	7	3
5	1	5	6450.7933	10	3		6449.6547	7	1
5	1	4	6496.1529	3	1		6495.0602	12	8
5	2	4	6496.1658	20	-17		6495.0791	4	12
5	2	3	6530.8513	12	-7		6529.3183	12	6
5	3	3	6531.2810	9	-7		6529.8148	6	13
5	3	2	6551.0954	5	5		6550.1437	7	-6
5	4	2	6558.9636	7	-17		6558.2651	9	-1
5	4	1	6565.2936	17	-2		6564.3333	10	-4
5	5	1	6585.2784	12	-15		6584.6137	2	21
5	5	0	6585.8442	8	-4		6585.1395	15	4
6	0	6	6510.3432	32	1		6509.1534	8	-2
6	1	6	6510.3432	32	1		6509.1534	8	-1
6	1	5	6565.7994	15	-2		6564.6704	7	10
6	2	5	6565.7994	15	-10		6564.6716	8	8
6	2	4	6610.6091	6	7		6609.5420	13	3
6	3	4	6610.6737	10	7		6609.6199	9	6
6	3	3	6642.6975	7	21		6641.9713	3	-1
6	4	3	6645.8529	7	-11		6645.2880	14	-11
6	4	2	6662.2629	8	3		6661.2457	8	-11
6	6	2	6675.4853		-22		6674.8337	8	0
6	6	1	6679.5085	10	5		6678.6334	5	-15
6	6	1	6705.8150	5	0		6705.2673	5	-4
6	6	0	6706.0714	13	17		6705.4533	18	-1
7	0	7	6578.9487	16	-4		6577.6988	10	0
7	1	7	6578.9487	16	-4		6577.6988	10	1
7	1	6	6644.4727	14	0		6643.2923	39	-23
7	2	6	6644.4727	14	5		6643.2923	39	-13
7	2	5	6699.3199	30	6		6698.2034	18	-4
7	3	5	6699.3233	14	-5		6698.2115		-4
7	3	4	6742.4733	11	6		6742.4662	17	-10
7	4	4	6743.6349	17	14		6743.5617	8	19
7	4	3	6772.8172	5	16		6771.9142	4	-1
7	5	3	6779.3686	7	-15		6778.7540	11	3
7	5	2	6791.9567	10	8		6790.9054	5	-12
7	6	2	6811.6114	10	-4		6811.0142	12	-1

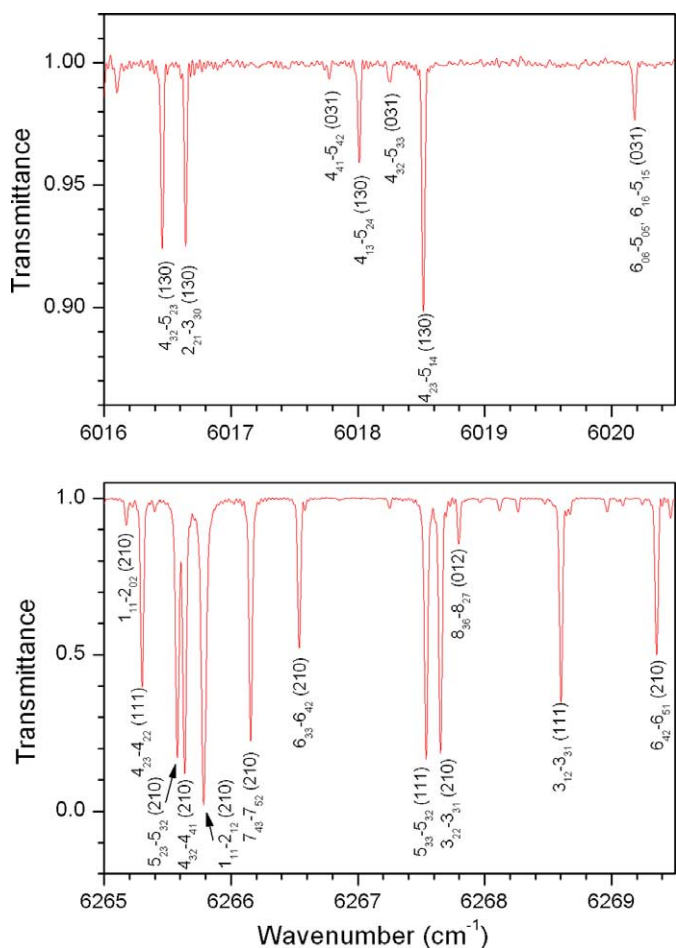


Fig. 2. Small portion of the spectrum of H₂S in the 6016–6020 and 6265–6269 cm⁻¹ regions. Assigned transition were denoted. Experimental conditions are the same as given in Fig. 1.

Table 1 (continued)

J	K _a	K _c	(111)			(210)		
			E	Δ	δ	E	Δ	δ
			1	2	3	4	5	6
7	6	1	6813.9010	8	-5	6813.1600	15	5
7	7	1	6846.2045	8	11	6845.7814	2	-31
7	7	0	6846.3240	5	5	6845.9224	11	19
8	0	8	6656.6017	16	2	6655.2801	6	-2
8	1	8	6656.6017	16	2	6655.2801	6	-2
8	1	7	6732.1692	8	-12	6730.9345	8	8
8	2	7	6732.1692	8	-9	6730.9345	8	11
8	2	6	6796.9799	16	9	6795.8205	11	26
8	3	6	6796.9799	16	-10	6795.8205	11	-4
8	3	5	6851.0536	11	11	6849.9452	33	-5
8	4	5	6851.0858	17	-14	6849.9877	10	-2
8	4	4	6895.4196	6	9	6891.3000	14	7
8	5	4	6894.9900	6	-13	6893.1287	10	10
8	5	3	6920.1795	6	4	6919.1063		-7
8	6	3	6931.8519	6	-25	6931.1898	2	24
8	6	2	6940.6648	8	4	6939.6335	11	0
8	7	2	6967.2965	9	31	6966.7485	9	-4
8	7	1	6968.4951	26	34	6967.8920	14	3
8	8	1	7006.2115	12	16	7005.9052	7	-37
8	8	0	7006.2700	35	9	7005.9859	3	-3
9	0	9	6743.2891	15	-2	6741.8863	3	-8
9	1	9	6743.2891	15	-2	6741.8863	3	-8
9	1	8	6828.8860	11	-11	6827.5823	15	-5
9	2	8	6828.8860	11	-11	6827.5823	15	-4
9	2	7	6903.6069	18	-4	6902.3886	38	-20
9	3	7	6903.6069	18	12	6902.3986	38	-7
9	3	6	6967.5786	21	18	6966.4382	19	16
9	4	6	6967.5786	21	-18	6966.4418	18	-42
9	4	5	7020.7480	17	-20	7019.4953	17	-16
9	5	5	7020.8224	12	15	7019.6151	11	2
9	5	4	7059.4356	7	4	7058.2722	23	4
9	6	4	7064.5816	13	-19	7062.7164	3	31
9	6	3	7085.0664	5	-40	7083.8538	4	-25
9	7	3	7103.3357	20	-25	7102.6010	13	24
9	7	2	7108.9141	19	-9	7107.9617	11	17
9	8	2	7142.4070	15	16	7141.8826	19	-37
9	8	1	7143.0041	16	-12	7142.5208	11	10
9	9	1	7185.6072	16	-7	7185.3239		-32
9	9	0	7185.5926	14	-36	7185.4030	23	54
10	0	10	6839.0055	12	15	6837.4862	9	5
10	1	10	6839.0055	12	15	6837.4862	9	5
10	1	9	6934.6125	4	-16	6933.2320	11	-30
10	2	9	6934.6125	4	-16	6933.2320	11	-29
10	2	8	7019.1200	12	-9	7017.9185	17	-1
10	3	8	7019.1200	12	-3	7017.9185	17	-24
10	3	7	7092.9622	9	7	7091.7686	8	3
10	4	7	7092.9594	14	42	7091.7686	8	3
10	4	6	7155.9407	22	55	7154.8048	47	-3
10	5	6				7154.8048	47	16
11	0	11	6942.1142	6	2	6943.7128	3	14
11	1	11	6942.1142	6	2	6943.7128	3	14
11	1	10	7049.2990	12	5	7047.8420	19	36
11	2	10	7049.2990	12	5	7047.8420	19	36
11	2	9	7143.8378	30	-49	7142.3264	15	-9
11	3	9	7143.8378	30	65	7142.3264	15	-5
11	3	8	7227.2414	13	-22	7225.9859	43	-5
11	4	8	7227.2414	13	21	7225.9859	43	46
11	4	7	7299.9180	10	-20	7298.7480	7	34
11	5	7	7299.9007		17	7298.7480	7	34
12	0	12	7057.4226	16	-5	7055.7103	5	10
12	1	12	7057.4226	16	-5	7055.7103	5	10
12	1	11	7173.0027	7	-3	7171.4355	4	4
12	2	11	7173.0027	7	-3	7171.4355	4	4

Table 1 (continued)

J	K _a	K _c	(111)			(210)		
			E	Δ	δ	E	Δ	δ
			1	2	3	4	5	6
12	2	10	7277.1841	16	3	7275.7579	25	1
12	3	10	7277.1841	16	4	7275.7579	25	-10
12	3	9	7370.2722	13	-10	7368.9918	19	7
12	4	9	7370.2722	13	21	7368.9918	19	-14
13	0	13	7180.1101	8	6	7178.2658	24	-13
13	1	13	7180.1101	8	6	7178.2658	24	-13
13	1	12	7305.6570	22	0	7303.9774	16	-10
13	2	12	7305.6570	22	0	7303.9774	16	-10
13	2	11	7419.5879	17	13	7418.0610	14	18
13	3	11	7419.5879	17	14	7418.0610	14	18
13	3	10	7522.2922	12	-4			
13	4	10	7522.2922	12	-4			
14	0	14	7311.7528	6	0	7309.7670	10	-20
14	1	14	7311.7528	6	0	7309.7670	10	-20
14	1	13	7447.2523	20	-5	7445.4513	14	-4
14	2	13	7447.2523	20	-5	7445.4513	14	-4
14	2	12	7570.8866	8	-2	7569.2531		0
14	3	12	7570.8866	8	-2	7569.2531		0
14	3	11	7683.1202	12	-5			
14	4	11	7683.1202	12	-5			
15	0	15	7452.3335	14	0	7450.2085		38
15	1	15	7452.3335	14	0	7450.2085		38
15	1	14	7597.7710	15	-4	7595.8345	15	-16
15	2	14	7597.7710	15	-4	7595.8345	15	-16
15	2	13	7731.0697	15	10			
15	3	13	7731.0697	15	10			
15	3	12	7852.7641	3	-5			
15	4	12	7852.7641	3	-5			
16	0	16	7601.8304	7	2	7599.5167		-60
16	1	16	7601.8304	7	2	7599.5167		-60
16	1	15	7757.1944	22	28	7755.1103	36	-8
16	2	15	7757.1944	22	28	7755.1103	36	-8
16	2	14	7900.1103	7	-21			
16	3	14	7900.1103	7	-21			
16	3	13	8031.2073	11	7			
16	4	13	8031.2073	11	7			
17	0	17	7760.2206	3	-4	7757.7273		-21
17	1	17	7760.2206	3	-4	7757.7273		-21
17	1	16						
17	2	16						
17	2	15	8077.9958	10	-77			
17	3	15	8077.9958	10	-77			
18	0	18	7927.4805		-47	7924.7900	8	9
18	1	18	7927.4805		-47	7924.7900	8	9

^a Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10⁻⁴ cm⁻¹; δ is the difference $E^{\text{exp}} - E^{\text{calc}}$, also in units of 10⁻⁴ cm⁻¹; Δ is not quoted when the energy value was obtained from only one transition (corresponding energies were used in the fit with the weight zero).

nized. The set of weak lines belonging to the 5ν₂ band can be seen near 5700–5800 cm⁻¹. From the figure, one can also get an idea about the relative strengths of all the bands in this polyad.

Assignments of the transitions were made with the Ground State Combination Differences method. The ground state energies were calculated on the base of parameters from [6]. As the result of the assignments, altogether more than 1700 transitions of H₂³²S were assigned. For

Table 2
 Experimental ro-vibrational term values for the (031), (130), and (050) vibrational states of the H₂³²S molecule (in cm⁻¹)^a

J	K _a	K _c	(031)			(130)			(050)		
			E	Δ	δ	E	Δ	δ	E	Δ	δ
		1	2	3	4	5	6	7	8	9	10
0	0	0	6077.5942		6	6074.5824		18			
1	0	1	6091.7020		28	6088.5909		-7	5811.8842		9
1	1	1	6093.3860	2	10	6090.4101	10	1			
1	1	0	6098.4771	5	17	6095.4961	6	-10	5819.9725	2	-19
2	0	2	6116.1259	8	0	6112.9293	8	5			
2	1	2	6116.4969	5	-2	6113.3528	6	-1	5837.6788	11	14
2	1	1	6131.7408	14	-13	6128.5799	13	-8			
2	2	1	6136.7985	12	-11	6134.0379	8	29	5861.8695		-59
2	2	0	6140.5498	2	10	6137.6880	5	7			
3	0	3	6149.1806	20	16	6145.8162	8	7	5870.7280	2	-2
3	1	3	6149.2355	15	-7	6145.8860	31	17			
3	1	2	6177.3481	9	-8	6174.0564	9	-3	5903.1172	20	4
3	2	2	6179.0912	11	3	6176.0316	7	-29			
3	2	1	6191.9843	2	-3	6188.7594	13	-19	5920.0373	10	38
3	3	1	6201.9710	11	2	6199.5280	15	19			
3	3	0	6204.3116		0	6201.7313	8	2	5935.8153	37	-19
4	0	4	6191.0851	13	0	6187.4687		-58	5912.9994		-44
4	1	4	6191.0916	4	-16	6187.4852	18	5	5913.0215	5	5
4	1	3	6231.6496	14	-2	6228.2777	10	8			
4	2	3	6232.0346	8	-8	6228.7382	12	-5	5960.7009	4	-1
4	2	2	6257.8802	6	-21	6254.4599	6	0			
4	3	2	6262.6456	16	19	6259.8005	42	-11	5996.8024	16	28
4	3	1	6272.6739	7	11	6269.4563		-12			
4	4	1	6288.8828	3	-17	6286.9027	15	0	6028.9210	25	24
4	4	0	6290.1498	14	-9	6288.0482	3	8			
5	0	5	6241.9500	20	-4	6238.0365	16	31	5964.0827		4
5	1	5	6241.9500	20	-16	6238.0365	16	15	5964.0827		-24
5	1	4	6294.3887	3	-12	6290.8197	5	2	6024.9994		-47
5	2	4	6294.4608	6	2	6290.9090	19	11			
5	2	3	6333.7343	21	16	6330.2287	12	15			
5	3	3	6335.1700	11	13	6331.9308	15	-19			
5	3	2	6357.6992		-12	6354.0585	13	9			
5	4	2	6367.2169	8	20	6364.6201	7	-5			
5	4	1	6374.2433		17	6371.1904	10	7			
5	5	1	6397.4354	6	-6	6396.0659		14			
5	5	0	6398.0556	2	-2	6396.6003	10	-9			
6	0	6	6301.7863	9	1	6297.5138	31	-7	6023.9957	5	7
6	1	6	6301.7863	9	1	6297.5138	31	-9	6023.9957	5	2
6	1	5	6365.9424	4	-3	6362.0960		8			
6	2	5	6365.9544	12	-7	6362.1100	26	-13	6098.6113	9	-28
6	2	4	6417.4776	6	-12	6413.8830	18	-17			
6	3	4	6417.8169	2	19	6414.3005	21	-20	6158.6793		-55
6	3	3	6454.5611		-67	6450.9139	5	30			
6	4	3	6458.5759		49	6455.5646		-32			
6	4	2	6476.9438	12	-8	6473.1473	18	-8			
6	6	2	6492.8380		18	6490.6093	24	9			
6	6	1	6497.2145	12	4	6494.5497	19	18			
6	6	1	6527.4103		5	6526.7905	2	-5			
6	6	0	6527.6962		4	6527.0284	8	0			
7	0	7	6370.5884	14	25	6365.9190	4	7	6092.7448	7	-2
7	1	7	6370.5884	14	24	6365.9190	4	2	6092.7448	7	-3
7	1	6	6446.4213		11	6442.2435	6	9	6180.9401		-33
7	2	6	6446.4213		-11	6442.2435	6	-23			
7	2	5	6509.6386		-67	6505.8282	6	7			
7	3	5	6509.7165	8	4	6505.9192		2			
7	3	4				6556.0155		-5			
7	4	4	6560.9112	13	1						
7	4	3				6589.8534	16	12			
7	5	3	6602.2397	23	24	6599.3339		-95			
7	5	2				6612.2566	32	-41			
7	6	2	6639.4689		-82						
7	6	1				6639.8452	15	13			

Table 2 (continued)

J	K_a	K_c	(031)			(130)			(050)		
			E	A	δ	E	A	δ	E	A	δ
		1	2	3	4	5	6	7	8	9	10
7	7	1	6678.4866		2	6678.7531		23			
7	7	0				6678.8511		−18			
8	0	8	6448.3423	8	12	6443.2402	8	2	6170.3292	20	−4
8	1	8	6448.3423	8	12	6443.2402	8	2	6170.3292	20	−4
8	1	7				6531.2922		26	6272.1331		25
8	2	7				6531.2922		26			
8	8	0	6850.3238		7						
9	0	9	6535.0415	14	0	6529.4718	6	−11	6256.7421		−19
9	1	9	6535.0415	14	0	6529.4718	6	−11	6256.7421		−19
9	1	8				6629.2452	3	−1			
9	2	8				6629.2452	3	−3			
9	8	1				6995.2285		−6			
9	9	1	7042.2957		6						
10	0	10	6630.6775	8	6	6624.6060		−22	6351.9842		19
10	1	10	6630.6775	8	6	6624.6060		−22	6351.9842		19
10	1	9				6736.1021		−13			
10	2	9				6736.1021		−13			
11	0	11	6735.2380		−8						
11	1	11	6735.2380		−8						
12	0	12				6841.5289		16	6568.9036		7
12	1	12				6841.5289		16	6568.9036		7
13	0	13				6963.2957		10	6690.5674		−24
13	1	13				6963.2957		10	6690.5674		−24

^a See footnote to Table 1.

Table 3

List of transitions belonging to the $\nu_2 + 2\nu_3$ band of H_2^{32}S

Upper level			Lower level			Line position in cm^{-1}	Transmittance in percent	Upper energy in cm^{-1}	Mean value in cm^{-1}	δ^a in 10^{-4}cm^{-1}
J'	K'_a	K'_c	J	K_a	k_c					
1			2			3	4	5	6	7
7	1	6	6	4	3	6381.1289	62.7	6740.4952	6740.4958	−9
			7	4	3	6253.2606	75.7	6740.4958		
			8	6	3	6094.0377	99.0	6740.4970		
7	4	4	7	5	3	6247.2596	94.3	6740.6282	6740.6256	3
			7	3	5	6325.1110	94.3	6740.6330		
8	2	6	7	3	5	6478.7821	99.2	6894.3042	6894.3036	−26
			8	5	3	6258.8936	90.9	6894.3019		
			7	7	1	6337.3980	98.3	6894.3046		
8	3	6	7	4	3	6404.9748	95.2	6892.2110	6892.2111	9
			8	4	5	6324.3288	63.6	6892.2105		
			9	4	5	6154.3507	66.9	6892.2116		
			7	2	5	6476.7342	79.1	6892.2115		
			9	2	7	6267.7989	85.1	6892.2119		
			7	6	1	6365.5574	93.8	6892.2108		
			8	6	3	6245.7522	93.0	6892.2116		
9	3	6	9	6	3	6090.9264	98.2	6892.2112	7065.0090	0
			8	4	5	6497.1278	87.0	7065.0096		
			9	4	5	6327.1461	84.0	7065.0070		
			10	4	7	6137.9073	90.1	7065.0095		
			8	6	3	6418.5535	95.3	7065.0129		
9	4	6	10	6	5	6250.5386	98.3	7065.0046	7066.0572	−5
			8	5	3	6430.6504	87.5	7066.0586		
			8	7	1	6384.3696	96.1	7066.0562		
			9	7	3	6247.3586	91.8	7066.0571		

^a The $\delta = E^{\text{exp}} - E^{\text{calc}}$ is the difference between the experimental value of upper energy from column 6 and corresponding value calculated with the parameters from Tables 5 and 7.

illustration, two small parts of the recorded spectrum with the assignments are shown in Fig. 2. Some relatively weaker unassigned lines in the figures can be due to H_2^{33}S . The obtained ro-vibrational energies of the states (210), (111), (130), (031), and (050) are given in Tables 1 and 2 together with the experimental uncertainties Δ . Since usually one upper ro-vibrational energy was determined from several transitions reaching the same upper level, Δ can be considered as an indication of the precision of the experimental line positions. In this case, the experimental accuracy of the line positions can be estimated as $0.0010\text{--}0.0020\text{ cm}^{-1}$ for unblended and not very weak lines. With the value of the quantum number J increases, the accuracy of line positions may decrease due to the decreasing in line strengths.

Table 3 presents the list of assigned transitions for the very weak band $\nu_2 + 2\nu_3$. Table 4 presents the statistical information on assigned transitions and derived levels of each band.

5. Determination of the ro-vibration parameters and discussion

The necessity of using the Hamiltonian in the form of Eq. (3) with a number of resonance interaction blocks leads to strong correlations between the parameters in the diagonal and nondiagonal blocks. In this case, the choice of physically suitable initial values for different kind parameters is very important. In present study, the initial values of

Table 4
Statistical information on the investigated bands of the H_2^{32}S molecule

Band	Center	Number of transitions	Number of levels	$J^{\text{max.}}$	$K_a^{\text{max.}}$
1	2	3	4	5	6
$2\nu_1 + \nu_2$	6288.1456	579	152	18	9
$\nu_1 + \nu_2 + \nu_3$	6289.1741	709	165	18	9
$\nu_2 + 2\nu_3$	6385.1381	24	6	9	4
$\nu_1 + 3\nu_2$	6074.5824	196	79	13	8
$3\nu_2 + \nu_3$	6077.5942	158	69	11	9
$5\nu_2$	5797.2372	57	34	13	4

Table 5
Spectroscopic parameters of the (210), (111), and (012) vibrational states of the H_2^{32}S molecule (in cm^{-1})^a

Parameter	(010) ^b	(210)	(111)	(012)
1	2	3	4	5
E	1182.576821	6272.881 (945)	6250.70906 (102)	6356.336 (239)
A	10.7220780	10.37214 (806)	10.45856 (342)	10.45391 (930)
B	9.2244497	8.96572 (645)	9.04397 (398)	9.01957 (189)
C	4.6688610	4.59355 (267)	4.61507 (308)	4.54698 (270)
$\Delta_K \times 10^3$	4.5579033	4.1116 (217)	4.5357 (111)	4.9135 (600)
$\Delta_{JK} \times 10^3$	-2.7348452	-2.6217148	-2.7071248	-2.7925348
$\Delta_J \times 10^3$	0.75614258	0.71789942	0.72273 (245)	0.78058540
$\delta_K \times 10^3$	-0.019544	-0.02330	-0.04392	-0.06454
$\delta_J \times 10^3$	0.3473094	0.336757	0.325390 (158)	0.352211
$H_K \times 10^6$	2.6294	2.7530	2.4300	2.1070
$H_{KJ} \times 10^6$	0.99673	0.92727	1.28097	1.63467
$H_{JK} \times 10^6$	-1.85037	-1.82803	-1.89524	-1.96245
$H_J \times 10^6$	0.374766	0.344374	0.352974	0.361574
$h_K \times 10^6$	2.12233	1.99135	2.04510	2.09885
$h_{JK} \times 10^6$	-0.62452	-0.63922	-0.66345	-0.68768
$h_J \times 10^6$	0.186968	0.164964	0.176244	0.187524
$L_K \times 10^9$	-9.9918	-6.8682	-5.1122	-3.3562
$L_{KKJ} \times 10^9$	12.641	7.523	5.308	3.093
$L_{KJ} \times 10^9$	-6.4092	-5.0620	-4.5142	-3.9664
$L_{KJJ} \times 10^9$	1.4788	1.3594	1.5801	1.8008
$L_J \times 10^9$	-0.21671	-0.21753	-0.21753	-0.21753
$l_K \times 10^9$	-4.3308	-6.2644	-4.6584	-3.0524
$l_{KJ} \times 10^9$	-0.5267	-0.5267	-0.5267	-0.5267
$l_{JK} \times 10^9$	0.47523	0.47523	0.47523	0.47523
$l_J \times 10^9$	-0.10858	-0.10858	-0.10858	-0.10858
$P_K \times 10^{12}$	16.806	16.806	16.806	16.806
$p_K \times 10^{12}$	11.616	11.616	11.616	11.616

^a Values in parentheses are the 1σ statistical confidence intervals. Values of parameters presented in columns 3–5 without confidence intervals were constrained at their initial values (see text, for details).

^b Reproduced from [7].

Table 6
Spectroscopic parameters of the (130), (031), and (050) vibrational states of the H₂³²S molecule (in cm⁻¹)^a

Parameter	(030) ^b	(130)	(031)	(050)
1	2	3	4	5
<i>E</i>	3513.79087	5992.281 (955)	6116.0567 (108)	5923.605 (955)
<i>A</i>	11.540152	11.3575 (136)	11.15087 (403)	12.3790 (156)
<i>B</i>	9.6863681	9.58319 (743)	9.58703 (340)	10.24670 (573)
<i>C</i>	4.5478783	4.43859 (345)	4.41038 (352)	4.42634 (269)
$\Delta_K \times 10^3$	6.94186	6.7958 (670)	6.8874067	10.7498 (595)
$\Delta_{JK} \times 10^3$	-3.97768	-3.9211148	-4.0065248	-5.667792
$\Delta_J \times 10^3$	1.037139	1.0180174	1.03759 (316)	1.40059
$\delta_K \times 10^3$	0.323995	0.322117	0.301497	0.779997
$\delta_J \times 10^3$	0.486891	0.481615	0.49691 (178)	0.672056
$H_K \times 10^6$	8.022	8.0838	7.7608	17.810647
$H_{KJ} \times 10^6$	-0.7639	-0.79863	-0.44493	-4.482468
$H_{JK} \times 10^6$	-2.9783	-2.96713	-3.03434	-4.790861
$H_J \times 10^6$	0.71176	0.696564	0.705164	1.249548
$h_K \times 10^6$	5.1642	5.09871	5.15246	9.877821
$h_{JK} \times 10^6$	-1.1669	-1.17425	-1.19848	-2.080000
$h_J \times 10^6$	0.35503	0.344028	0.355308	0.621793
$L_K \times 10^9$	-29.45	-27.8882	-26.1322	-59.426932
$L_{KKJ} \times 10^9$	27.259	24.7000	22.4850	36.956026
$L_{KJ} \times 10^9$	-7.5	-6.8264	-6.2786	2.841736
$L_{KJJ} \times 10^9$	2.5820	2.5223	2.7430	3.561581
$L_J \times 10^9$	-0.45511	-0.45552	-0.45552	-0.819964
$l_K \times 10^9$	-10.851	-11.8178	-10.2118	-15.472476
$l_{KJ} \times 10^9$	2.555	2.555	2.555	11.130947
$l_{JK} \times 10^9$	0.7	0.7	0.7	0.772407
$l_J \times 10^9$	-0.23	-0.23	-0.23	-0.416529

^a Values in parentheses are the 1 σ statistical confidence intervals. Values of parameters presented in columns 3–5 without confidence intervals were constrained at their initial values (see text for details).

^b Reproduced from [8].

Table 7
Parameters of resonance interactions between the states of the (*v* = 2.5) polyad of the H₂³²S molecule (in cm⁻¹)^{a,b}

Parameter	Value	Parameter	Value	Parameter	Value
<i>Fermi-type interaction</i>					
F^{1-2}	47.70	$F_J^{1-2} \times 10^2$	-0.823 (183)		
$F_{xy}^{1-2} \times 10^2$	-0.509 (185)	$F_{xyK}^{1-2} \times 10^4$	-0.4767 (745)	$F_{xyJ}^{1-2} \times 10^4$	0.2812 (137)
F^{1-3}	107.296 (985)	F_K^{1-3}	-0.33712 (665)	F_J^{1-3}	-0.06061 (212)
		F_{xy}^{1-3}	-0.02808 (214)		
F_K^{2-3}	0.21331 (805)	$F_{KK}^{2-3} \times 10^3$	0.5623 (493)		
F^{5-6}	81.60	F_K^{5-6}	-0.19883 (149)	F_J^{5-6}	-0.11022 (251)
		$F_{KK}^{5-6} \times 10^3$	0.3134 (104)		
$F_{xy}^{5-6} \times 10$	-0.67886 (914)	$F_{xyKK}^{5-6} \times 10^3$	-5.131 (672)	$F_{xyJ}^{5-6} \times 10^3$	6.354 (382)
		$F_{xyKK}^{5-6} \times 10^5$	-0.15056 (907)		
F^{3-4}	146.841 (796)	F_{3-4}^K	-0.4242 (105)	F_J^{3-4}	-0.13007 (449)
$F_{KK}^{3-4} \times 10^3$	1.1182 (541)	$F_{JK}^{3-4} \times 10^3$	-0.6152 (262)	F_{xy}^{3-4}	-0.14770 (553)
		$F_{xyKK}^{3-4} \times 10^5$	-0.1894 (167)		
<i>Coriolis-type interactions</i>					
$2(C_{\zeta}^{\nu})^{1-5}$	0.15105 (277)	$C_{yK}^{1-5} \times 10^2$	0.3674 (222)	$C_{yJ}^{1-5} \times 10^2$	0.5862 (521)
$C_{yKK}^{1-5} \times 10^4$	-0.1762 (126)	$C_{yJK}^{1-5} \times 10^4$	0.2612 (173)	C_{xz}^{1-5}	-0.23790 (256)
$C_{xzK}^{1-5} \times 10^3$	-0.2421 (116)	$C_{xzJ}^{1-5} \times 10^3$	-0.1419 (178)	$C_{xzJK}^{1-5} \times 10^6$	1.0959 (616)
$2(C_{\zeta}^{\nu})^{2-5}$	-0.150	$C_{yK}^{2-5} \times 10^3$	-5.874 (311)	$C_{yJ}^{2-5} \times 10^3$	-0.6684 (660)
C_{xz}^{2-5}	-0.11070 (216)	$C_{xzK}^{2-5} \times 10^3$	-0.08120 (926)	$C_{xzJ}^{2-5} \times 10^3$	0.4499 (168)
		$C_{xzJ}^{2-6} \times 10^3$	-0.3021 (253)		
$2(C_{\zeta}^{\nu})^{3-6}$	0.150	C_{xzJ}^{3-6}	-0.15734 (439)		
$2(C_{\zeta}^{\nu})^{4-6}$	-0.6460 (138)	$C_{yK}^{4-6} \times 10^3$	1.8249 (935)	$C_{yJ}^{4-6} \times 10^3$	-0.1972 (186)
C_{xz}^{4-6}	-0.12553 (784)	$C_{yJ}^{4-6} \times 10^3$	0.2417 (145)	$C_{xzJ}^{4-6} \times 10^3$	-0.5767 (448)
		$C_{xzK}^{4-6} \times 10^6$	1.262 (238)		

^a Values in parentheses are the 1 σ statistical confidence intervals.

^b Notations of superscripts (*v-v'*) at resonance interaction parameters correspond to notations in Eq. (3).

all rotational and centrifugal distortion parameters of the states (210), (111), (012), and (130), (031) have been estimated with the formula

$$P_n^{v_1 v_2 v_3} = P_n^{0v_2 0} + (P_n^{110} - P_n^{010})v_1 + (P_n^{011} - P_n^{010})v_3, \quad (7)$$

where P_n is one of the rotational or centrifugal distortion parameters. The ground state spectroscopic parameters have been taken from [6]. Corresponding parameters of the states (010), (030), and (100), (001) have been taken from [7,8], respectively. It should be mentioned that we used parameters of the states (010), (110), and (011) from [7,8], instead of those of the states (000), (100), and (001) from [6,10], because the set of parameters of [7,8] is more complete (compare Table 7 of [10] and Table 4 of [8]).

To estimate the initial values of rotational and centrifugal distortion parameters of the (050) state, we use the non-linear approximation with the formula

$$P_n^{0v_2 0} = P_n^{000} + \alpha_n v_2 + \beta_n v_2^2 + \gamma_n v_2^3, \quad (8)$$

where the notations for P_n values are the same as in Eq. (7). The values of coefficients P_n^{000} , α_n , β_n , and γ_n have been determined with a least-square fitting based on the values of corresponding parameters of the ground vibrational state [6], and of the states (010) [7], (020) [9], and (030) [8]. The initial values of the band centers and of the pure vibrational Darling–Dennison and Fermi interaction parameters have been taken from [3].

Upper ro-vibrational energy levels from Tables 1 and 2 were used in the fit procedure based on the Hamiltonian, Eqs. (3)–(6). All the input energy levels were used with weights proportional to $(1/\Delta^2)$, where Δ is the experimental uncertainty of corresponding energy value. For those upper levels obtained from only one transition, the energy values were not used in the fit (with weight zero).

As the result, altogether 80 fitted parameters were derived (33 parameters of the diagonal blocks and 47 resonance interaction parameters) which reproduce 505 initial upper energy levels with rms deviation of 0.0019 cm^{-1} . The obtained parameters are presented in Tables 5–7 together with their 1σ statistical confidence intervals. Parameters presented in Tables 5–7 without confidence intervals were constrained to their initial values as discussed above. Columns 2 of Tables 5 and 6 show, for comparison, the spectroscopic parameters of the (010) and (030) vibrational states which are reproduced from [7,8], respectively. One can see satisfactory correlations in the parameters of the states discussed in the present study,

not only among themselves, but also with the corresponding parameters of the ground and (020) vibrational states. The reproductive power of the derived parameters is illustrated by the $\delta = E^{\text{exp}} - E^{\text{calc}}$ values given in Tables 1–3.

It should be mentioned that the H_2S is one of the typical local mode molecules. The vibrational states discussed here, (210) and (111) ($(20^+, 1)$ and $(20^-, 1)$ in the local mode notations) belong to the second set of the local mode states $(v0^+, 1)/(v0^-, 1)$. And, in agreement with the local mode theory, the difference $\delta = v^{(v0^-, 1)} - v^{(v0^+, 1)}$ decreases from the value of 10.10261 cm^{-1} for the pair of states $(10^+, 1)/(10^-, 1)$ [8], to the value 1.02849 cm^{-1} for the states $(20^+, 1)$ and $(20^-, 1)$ discussed in present study, and then to 0.01593 cm^{-1} for the pair of states $(30^+, 1)/(30^-, 1)$ [2].

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