THE ABSORPTION SPECTRA OF H_2S IN THE REGION OF 1.9 μm

O.V. Zotov, V.S. Makarov, O.V. Naumenko, A.D. Bykov

Institute of Atmospheric Optics
Siberian Branch of the Academy of Sciences of the USSR, Tomsk
Received August 26, 1991

The absorption spectrum of H_2S *molecule in the region from* 5050 *to* 5257 cm^{-1} *has been recorded with an* UFS–02 *Fourier spectrometer with the resolution of* 0.0098 cm^{-1}. *Theoretical analysis of the recorded spectrum allowed us to identify* 261 *lines of* $2\nu_1$ *and* $\nu_1 + \nu_3$ *bands. Also* 175 *rovibrational energy levels (up to* $J \le 14$ *and* $K_a \le 8$*) have been revealed, and rotational, centrifugal, and resonance constants of vibrational states* (200) *and* (101) *have been determined.*

Knowledge of the rovibrational structure of the H_2S absorption spectrum is important for detecting and evaluating the hydrogen sulfide concentration in the earth's atmosphere since it is a polluting gas. Reliable data on the parameters of the H_2S spectral lines are necessary when determining the potential function of this molecule and detecting H_2S in the atmospheres of planet–giants.

In recent years many studies[1–7] of the absorption spectra of H_2S and its isotope–substituted modifications have been published. A pure rotational spectrum (ground state) was studied in Refs. 1 and 2, the absorption band ν_2 – in Refs. 3 and 4, $2\nu_2$, ν_1 and ν_3 – in Ref. 5, $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$ – in Ref. 6, and $2\nu_1 + \nu_2$, $\nu_1 + \nu_2 + \nu_3$, and $\nu_2 + \nu_3$ – in Ref. 7.

Thus, the short–wave boundary of the studied spectral interval reaches 1.6 μm. However, we know that earlier the $H_2{}^{32}S$ spectra in the 1.9–μm region at high resolution have not been studied. The investigations of the H_2S absorption spectrum near 2 μm at low resolution were made by Allen and Plyler.[8] This paper revises the high–resolution spectrum of $H_2{}^{32}S$ in the $\nu_1 + \nu_3$ and $2\nu_1$ bands located near 1.9 μm. These are the strongest of the six bands from the first hexade of resonating states. The centers and strengths of the bands from the first hexade taken from Ref. 9 are given in Table I.

TABLE I. Centers and strengths of the H_2S *absorption bands near* 1.9 μm.

υ_1	υ_2	υ_3	Center, cm^{-1}	Strength, atm^{-1}·cm^{-2}
0	4	0	4703.7	$0.245\cdot10^{-2}$
1	2	0	4960.1	$0.638\cdot10^{-2}$
0	2	1	4960.1	$0.548\cdot10^{-1}$
2	0	0	5154.5	0.359
1	0	1	5155.5	0.611
0	0	2	5251.2	$0.365\cdot10^{-1}$

The basic characteristics of the spectrum are summarized in Table II. The spectrum was recorded with an UFS–02 Fourier spectrometer with a spectral resolution of 0.0098 cm^{-1} in the range between 5050 and 5257 cm^{-1}. Of 287 absorption lines revealed in the spectrum 261 were interpreted as belonging to transitions in the $\nu_1 + \nu_3$ and $2\nu_1$ bands. Table III presents the frequencies of the recorded lines (cm^{-1}) together with the measured absorption at the line peaks (in percent) and vibrational and rotational quantum numbers. The asterisk denotes the lines which are not accounted for when determining the energy levels.

TABLE II. Principal characteristics of the Fourier spectrum of H_2S.

Parameter	Value
Spectral range, cm^{-1}	5050–5257
Spectral resolution, cm^{-1}	0.0098
Optical path length, cm	1005
Pressure, Torr	22.1
Line center determination precision, cm^{-1}	higher than 0.005
Number of recorded lines	287

To identify the spectrum for the lines for $J \le 4$ we used the method for searching after the combination differences of the ground state. The lines with larger J were interpreted simultaneously with the solution of the inverse problem concerning the agreement between the experimental and calculated values of the line centers. Identification of the majority of lines was possible only due to good predictive calculations since the combination differences were absent.

After the lines were interpreted, 175 rotational energy levels for the vibrational states (101) and (200) (91 for the state (101) and 84 for (200)) were determined up to $J = 14$ and $K_a = 8$ (the spectroscopic constants for the ground state taken from Ref. 1 were used in this case). The values of the experimental energy levels are presented in Table IV, where $\Delta E = E_{\text{exp}} - E_{\text{calc}}$, and N stands for the number of lines using which the given energy level was found. As can be seen from Table IV a major part of the levels, in particular for $J > 7$, was determined using a single line which lowered somewhat the accuracy of these levels and made the solution of the inverse problem more difficult.

As shown in Refs. 1–3 and 5, the energy levels of the H_2S molecule can be calculated using the effective Hamiltonian

TABLE III. H_2S *absorption lines near* 1.9 mm

ν	S	$\upsilon_1\,\upsilon_2\,\upsilon_3$	J'	K'_a	K'_c	J''	K''_a	K''_c
5050.551	0.30	101	5	4	2	6	4	3
5051.824	0.15	101	9	0	9	9	2	8
		101	9	1	9	9	1	8
5052.007	0.15	200	10	2	8	10	3	7
5056.136	0.60	200	6	1	5	7	2	6
		200	6	2	5	7	1	6
5056.212	0.80	200	7	0	7	8	1	8
		200	7	1	7	8	0	8
5058.492	0.80*	101	6	2	5	7	2	6
		101	6	1	5	7	1	6
5058.702	0.90	101	7	1	7	8	1	8
		101	7	0	7	8	0	8
5058.940	0.50	101	5	2	3	6	2	4
5059.062	0.70	101	5	3	3	6	3	4
5059.421	0.20	101	9	1	8	9	3	7
		101	9	2	8	9	2	7
5060.571	0.70	101	4	3	1	5	3	2
5060.778	0.50	101	4	4	0	5	4	1
5061.336	0.20	200	8	1	8	8	2	7
		200	8	0	8	8	1	7
5063.899	0.20	101	8	0	8	8	2	7
		101	8	1	8	8	1	7
5066.040	0.40	200	4	2	2	5	3	3
5067.541	0.70	200	5	1	4	6	2	5
5067.597	0.80	200	6	1	6	7	0	7
		200	6	0	6	7	1	7
5068.648	0.30	101	4	2	2	5	2	3
5069.264	0.30	200	8	2	7	8	3	6
	*	200	8	1	7	8	2	6
5069.860	0.90	101	5	2	4	6	2	5
		101	5	1	4	6	1	5
5070.009	0.90	101	6	0	6	7	0	7
		101	6	1	6	7	1	7
5071.117	0.90	200	4	3	2	5	2	3
5071.746	0.20	101	8	1	7	8	3	6
	*	101	8	2	7	8	2	6
5075.235	0.60	200	3	2	1	4	3	2
5075.752	0.40	101	7	0	7	7	2	6
		101	7	1	7	7	1	6
5075.950	0.20*	101	9	4	6	9	4	5
5076.857	0.30	101	2	0	2	3	2	1
5078.447	0.30	101	3	3	0	4	3	1
5078.626	0.20	200	4	1	3	5	2	4
5078.726	0.70	200	5	0	5	6	1	6
		200	5	1	5	6	0	6
5078.793	0.50	200	4	2	3	5	1	4
5079.263	0.60	101	2	1	1	3	3	0
5079.850	0.10*	101	8	2	6	8	4	5
5080.971	0.80	101	4	1	3	5	1	4
5081.013	0.25	101	4	2	3	5	2	4
5081.081	0.80	101	5	1	5	6	1	6
		101	5	0	5	6	0	6
5083.895	0.30	101	7	1	6	7	3	5
		101	7	2	6	7	2	5
5084.962	0.30	200	6	1	6	6	2	5
	*	200	6	0	6	6	1	5
		200	9	4	5	9	5	4
5085.082	0.50	101	3	3	1	4	3	2
5086.305	0.30	200	2	2	0	3	3	1
5086.813	0.20	200	3	3	1	4	2	2
5087.379	0.50	101	6	0	6	6	2	5
	*	101	6	1	6	6	1	5
5088.949	0.70	200	3	1	2	4	2	3
5089.608	0.80	200	4	0	4	5	1	5
		200	4	1	4	5	0	5
5089.946	0.15	200	8	5	4	8	6	3
5090.516	0.15	200	7	2	5	7	3	4
5091.728	0.60	101	3	1	2	4	1	3
5091.919	0.90	101	4	1	4	5	1	5
		101	4	0	4	5	0	5
5092.227	0.70	101	3	2	2	4	2	3
5092.854	0.20	101	7	3	5	7	3	4
5095.695	0.40	101	6	1	5	6	3	4
5096.422	0.70*	200	5	1	5	5	2	4
5096.462	0.40*	200	5	0	5	5	1	4
	*	100	2	2	0	3	2	1
5098.262	0.30	200	2	1	1	3	2	2
5098.804	0.50*	101	5	1	5	5	1	4
5100.207	0.30							
5100.230	0.70	200	3	0	3	4	1	4
5100.247	0.40	200	3	1	3	4	0	4
5101.136	0.20	200	6	3	4	6	4	3
5101.157	0.15	200	1	1	1	2	2	0
5101.599	0.60	101	2	1	1	3	1	2
5102.517	1.00	101	3	0	3	4	0	4
		101	3	1	3	4	1	4
5103.398	0.40	101	6	2	4	6	4	3
5103.721	0.80	200	2	2	1	3	1	2
5104.292	0.40	101	2	2	1	3	2	2
5104.367	0.40	200	6	4	3	6	5	2

TABLE III (continued).

ν	S	$\upsilon_1 \upsilon_2 \upsilon_3$	J'	K'_a	K'_c	J''	K''_a	K''_c
5104.859	0.40	101	7	4	4	7	4	3
5105.802	0.30	200	5	1	4	5	2	3
5107.071	0.30	101	5	1	4	5	3	3
5107.538	0.30*	200	4	1	4	4	2	3
5107.892	0.20							
5108.118	0.60	101	5	2	4	5	2	3
5109.847	0.60	101	4	0	4	4	2	3
5110.491	0.40	200	2	0	2	3	1	3
5110.731	0.70	200	2	1	2	3	0	3
5112.102	0.15							
5112.804	0.80	101	2	0	2	3	0	3
5112.938	0.40	101	2	1	2	3	1	3
5114.807	0.15							
5114.883	0.50	101	1	1	0	2	1	1
5115.044	0.50	200	4	2	3	4	3	2
5116.328	0.30	101	4	2	2	4	4	1
5117.220	0.60	101	4	1	3	4	3	2
5117.632	0.40	200	5	2	3	5	3	2
5119.576	0.30	101	7	5	3	7	5	2
5119.982	0.20							
5120.074	0.70	200	1	0	1	2	1	2
5120.296	0.20	101	3	0	3	3	2	2
5120.462	0.60	101	5	3	3	5	3	2
5120.942	0.30	101	4	2	3	4	2	2
5121.644	0.50	101	3	1	3	3	1	2
5122.690	0.50	101	1	0	1	2	0	2
5122.898	0.15	200	3	2	2	3	3	1
5123.544	0.80	101	1	1	1	2	1	2
5123.680	0.15	200	5	3	2	5	4	1
5126.175	0.40	101	8	8	0	8	8	1
5126.989	0.30	200	2	1	2	2	2	1
5127.468	0.40	101	8	7	1	8	7	2
5128.705	0.50	101	7	6	2	7	6	1
5129.064	0.40	101	2	0	2	2	2	1
5129.901	0.20	200	0	0	0	1	1	1
5129.996	0.40	200	3	1	2	3	2	1
5130.559	0.80	101	7	7	1	7	7	0
5130.813	0.40	101	7	7	0	7	7	1
		200	2	0	2	2	1	1
5131.215	0.30	101	6	5	2	6	5	1
5131.814	0.30	200	3	2	1	3	3	0
5131.857	0.20							
5132.580	0.80	101	5	4	2	5	4	1
5133.131	0.50	101	4	3	2	4	3	1
5133.273	0.80*	101	2	1	2	2	1	1
	*	101	3	2	2	3	2	1
5133.481	0.70	101	0	0	0	1	0	1
5134.489	0.50	101	6	6	1	6	6	0
5135.040	0.80	101	6	6	0	6	6	1
5136.286	0.30	200	2	1	1	2	2	0
5137.738	0.90	101	5	5	1	5	5	0
5138.894	0.60	101	5	5	0	5	5	1
5138.993	0.50	200	1	0	1	1	1	0
5139.264	0.60	101	6	5	1	6	5	2
5140.160	0.80	101	4	4	1	4	4	0
5141.657	0.70	101	3	3	1	3	3	0
5142.318	0.80	101	2	2	1	2	2	0
5142.458	1.00*	101	1	1	1	1	1	0
	*	101	4	4	0	4	4	1
5143.517	0.30							
5145.017	0.30	101	5	4	1	5	4	2
5145.753	0.70	101	3	3	0	3	3	1
5148.463	0.50*	200	7	5	2	7	4	3
5148.685	0.80	101	2	2	0	2	2	1
5150.050	0.50	200	1	1	0	1	0	1
5150.505	0.20	200	2	2	0	2	1	1
5150.931	0.40	101	1	1	0	1	1	1
5151.613	0.50	200	3	3	0	3	2	1
5151.892	0.40*	101	6	4	2	6	4	3
		200	4	3	1	4	2	2
5152.806	0.20	200	6	4	2	6	3	3
5153.499	0.30	200	4	4	0	4	3	1
5154.144	0.60	200	3	2	1	3	1	2
5154.719	0.40							
5154.886	0.20	101	3	2	1	3	2	2
5154.940	0.40							
5155.156	0.30							
5155.887	0.50	200	5	5	0	5	4	1
5156.638	0.15	200	2	1	1	2	0	2
5157.674	0.50	200	5	3	2	5	2	3
5158.157	0.15	200	6	6	0	6	5	1
5158.355	0.20	101	2	1	1	2	1	2
5159.060	0.20							
5159.529	0.30	200	1	1	1	0	0	0
5160.146	0.40	200	7	4	3	7	3	4
5160.484	0.60	200	2	2	1	2	1	2
5160.711	0.30	101	1	0	1	0	0	0
5160.759	0.30	200	3	3	1	3	2	2
5161.191	0.60	200	4	4	1	4	3	2
5161.641	0.15	200	5	5	1	5	4	2

TABLE III (continued).

ν	S	$\upsilon_1\,\upsilon_2\,\upsilon_3$	J'	K'_a	K'_c	J''	K''_a	K''_c
5161.940	0.70	200	6	6	1	6	5	2
5162.291	0.30	200	4	2	2	4	1	3
5162.391	0.50	200	6	5	2	6	4	3
5163.995	0.20	101	3	3	1	3	1	2
5164.131	0.30	200	5	4	2	5	3	3
5165.729	0.20							
5165.947	0.40	200	3	1	2	3	0	3
5166.038	0.60							
5166.253	0.30							
5168.327	0.10							
5168.406	0.60	200	2	1	2	1	0	1
	*	101	3	1	2	3	1	3
5169.224	0.30	101	3	2	2	3	0	3
5169.311	0.40	101	2	1	2	1	1	1
5169.640	0.50	101	6	3	3	6	3	4
5170.952	0.20	101	8	4	4	8	4	5
5171.150	0.40	200	5	2	3	5	1	4
5173.715	0.15							
5173.991	0.30	101	5	3	3	5	1	4
5174.038	0.20	200	7	3	4	7	2	5
5174.132	0.20							
5174.834	0.10	200	4	2	3	4	1	4
5176.407	0.40	200	3	1	3	2	0	2
5176.617	0.10	101	7	4	4	7	2	5
5177.010	0.30	101	4	1	3	4	1	4
5177.183	0.50							
5177.279	0.80	101	2	1	1	1	1	0
5178.398	0.80	101	3	1	3	2	1	2
5178.669	0.60	101	3	0	3	2	0	2
5178.900	0.20	200	6	3	4	6	2	5
5181.162	0.20	101	6	2	4	6	2	5
5182.208	0.20	200	3	1	2	2	2	1
5182.806	0.20	200	5	1	4	5	0	5
	*	200	5	2	4	5	1	5
5184.494	0.30*	200	4	0	4	3	1	3
5184.528	0.60	200	4	1	4	3	0	3
5185.484	0.70	101	3	2	2	2	2	1
5186.041	0.15	200	7	3	5	7	2	6
		200	7	2	5	7	1	6
5186.801	0.60	101	4	1	4	3	1	3
5186.838	0.80	101	4	0	4	3	0	3
5187.097	0.40	200	3	2	2	2	1	1
5187.241	0.15							
5187.947	0.50							
5188.733	0.20	101	3	1	2	2	1	1
5190.102	0.15	101	2	2	0	1	0	1
5190.552	0.20*	200	6	2	5	6	1	6
	*	200	6	1	5	6	0	6
5191.877	0.15							
5192.494	0.90	200	5	0	5	4	1	4
		200	5	1	5	4	0	4
	*	200	4	1	3	3	2	2
5193.954	0.50	200	4	2	3	3	1	2
5194.857	0.90	101	5	1	5	4	1	4
		101	5	0	5	4	0	4
5194.884	0.30	101	4	2	3	3	2	2
5196.131	0.80	101	4	1	3	3	1	2
5198.467	0.30							
5200.217	0.70	200	6	0	6	5	1	5
		200	6	1	6	5	0	5
5200.436	0.20	101	4	3	2	3	3	1
5200.727	0.50	200	5	1	4	4	2	3
5201.015	0.20	200	5	2	4	4	1	3
5202.638	0.80	101	6	1	6	5	1	5
		101	6	0	6	5	0	5
5203.045	0.70	101	5	2	4	4	2	3
5203.316	0.60	101	5	1	4	4	1	3
5203.820	0.30	200	3	3	0	2	2	1
5204.619	0.80	101	4	2	2	3	2	1
5206.918	0.80	101	4	3	1	3	3	0
5207.400	0.15	200	5	2	3	4	3	2
5207.670	0.70	200	7	0	7	6	1	6
		200	7	1	7	6	0	6
5208.272	0.20	200	6	2	5	5	1	4
5210.155	0.80	101	7	1	7	6	1	6
		101	7	0	7	6	0	6
5210.235	0.70	101	5	3	3	4	3	2
5210.574	0.40	101	6	2	5	5	2	4
5210.624	0.70	101	6	1	5	5	1	4
5211.485	0.35	200	5	3	3	4	2	2
5213.517	0.35	101	5	2	3	4	2	2
5214.255	0.60	101	5	4	2	4	4	1
5214.855	0.70	200	8	0	8	7	1	7
		200	8	1	8	7	0	7
5215.357	0.60	200	7	1	6	6	2	5
	*	200	7	2	6	6	1	5
5217.421	0.70	101	8	1	8	7	1	7
		101	8	0	8	7	0	7
5217.771	0.60	200	4	4	1	3	3	0
		101	7	2	6	6	2	5

TABLE III (continued).

ν	S	$\upsilon_1\,\upsilon_2\,\upsilon_3$	J'	K'_a	K'_c	J''	K''_a	K''_c
		101	7	1	6	6	1	5
5218.396	0.30	101	6	3	4	5	3	3
5219.317	0.30	101	5	4	1	4	4	0
5219.420	0.70	101	6	2	4	5	2	3
5220.089	0.15							
5220.168	0.60	101	5	3	2	4	3	1
5221.768	0.60	200	9	0	9	8	1	8
		200	9	1	9	8	0	8
5222.210	0.30	200	8	1	7	7	2	6
		200	8	2	7	7	1	6
5223.246	0.20	200	7	2	5	6	3	4
5224.427	0.80	101	9	1	9	8	1	8
		101	9	0	9	8	0	8
5224.685	0.60	101	8	2	7	7	2	6
		101	8	1	7	7	1	6
5226.998	0.15	101	6	5	2	5	5	1
5228.410	0.60	200	10	0	10	9	1	9
		200	10	1	10	9	0	9
5228.510	0.70	200	6	4	3	5	3	2
5228.784	0.50	200	9	1	8	8	2	7
		200	9	2	8	8	1	7
5229.250	0.15	101	4	3	1	3	1	2
5229.821	0.15*	200	8	2	6	7	3	5
5229.854	0.30	200	8	3	6	7	2	5
5230.472	0.50	101	6	5	1	5	5	0
5231.176	0.40	101	10	1	10	9	1	9
		101	10	0	10	9	0	9
5231.345	0.70	101	9	2	8	8	2	7
		101	9	1	8	8	1	7
5232.214	0.15	101	8	3	6	7	3	5
5232.258	0.60	101	8	2	6	7	2	5
5232.726	0.70	101	7	4	4	6	4	3
5233.222	0.15	200	7	4	4	6	3	3
5234.769	0.40	200	11	0	11	10	1	10
		200	11	1	11	10	0	10
5235.092	0.40	200	10	1	9	9	2	8
		200	10	2	9	9	1	8
5236.042	0.25	200	9	2	7	8	3	6
5237.448	0.60	101	7	5	3	6	5	2
		200	8	3	5	7	4	4
5237.647	0.65	101	11	1	11	10	1	10
		101	11	0	11	10	0	10
5237.741	0.70	101	10	2	9	9	2	8
		101	10	1	9	9	1	8
5238.283	0.20*	200	8	4	5	7	3	4
5238.516	0.20*	101	9	3	7	8	3	6
	*	101	9	2	7	8	2	6
5238.782	0.50	101	7	6	2	6	6	1
5239.808	0.25	101	8	4	5	7	4	4
5240.614	0.60	101	8	3	5	7	3	4
5240.852	0.25	200	12	0	12	11	1	11
		200	12	1	12	11	0	11
5240.886	0.15	101	7	6	1	6	6	0
5241.109	0.25	200	11	1	10	10	2	9
		200	11	2	10	10	1	9
5242.001	0.20	200	10	2	8	9	3	7
		200	10	3	8	9	2	7
5245.778	0.20	101	7	5	2	6	5	1
	*	101	5	4	1	4	2	2
5245.936	0.40*	101	9	4	6	8	4	5
5246.663	0.20	200	13	1	13	12	0	12
		200	13	0	13	12	1	12
5246.868	0.20	200	12	1	11	11	2	10
		200	12	2	11	11	1	10
5249.184	0.40*	200	10	3	7	9	4	6
		200	10	4	7	9	3	6
5249.737	0.30*	101	12	2	11	11	2	10
	*	101	12	1	11	11	1	10
5249.820	0.40*	101	13	0	13	12	0	12
	*	101	13	1	13	12	1	12
5250.311	0.60*	101	11	3	9	10	3	8
	*	101	11	2	9	10	2	8
5251.596	0.20	101	8	4	4	7	4	3
5251.639	0.15*	101	10	4	7	9	4	6
5251.675	0.30*	101	10	3	7	9	3	6
5252.345	0.20*	101	5	5	0	4	3	1
5252.627	0.20*	200	5	3	2	4	2	3
5253.036	0.30	101	9	5	5	8	5	4
5253.152	0.30	200	6	6	1	5	5	0
5254.119	0.25							
5255.495	0.30	101	14	0	14	13	0	13
		101	14	1	14	13	1	13
5255.809	0.20							
5255.867	0.50	101	8	6	2	7	6	1
		101	12	3	10	11	3	9
		101	12	2	10	11	2	9
5257.026	0.30	200	10	5	6	9	4	5
5257.652	0.40	101	8	5	3	7	5	2

TABLE IV. Rovibrational energy levels of the states (101) *and* (200) *of* H_2S (cm^{-1}).

J	K_a	K_c	E_{101}	$\Delta E\cdot 10^4$	N	E_{200}	$\Delta E\cdot 10^4$	N
0	0	0	5147.2270	0	1	5144.9910	0	1
1	0	1	5160.7085	7	2	5158.3695	29	2
1	1	1	5161.8410	–28	1	5159.5270	–53	2
1	1	0	5166.0220	–20	2	5158.7960	20	1
2	0	2	5184.2260	–7	2	5181.9545	–19	2
2	1	2	5184.4020	0	2	5182.1523	–7	3
2	1	1	5196.6538	–27	1	5194.6540	–24	3
2	2	1	5200.6850	–27	3	5198.7790	21	2
2	2	0	5203.8470	–9	2	5201.6450	–51	2
3	0	3	5216.6873	36	3	5214.4070	29	1
3	1	3	5216.6963	–3	3	5214.4210	–5	2
3	1	2	5239.8705	32	2	5237.3677	–19	4
3	2	2	5240.6460	21	3	5238.2375	–37	2
3	2	1	5251.2780	32	1	5249.2023	–10	3
3	3	1	5259.0493	–12	3	5257.1495	–42	2
3	3	0	5261.0940	6	2	5258.9810	–16	2
4	0	4	5258.2630	–8	3	5255.9520	17	1
4	1	4	5258.2645	5	2	5255.9520	8	2
4	1	3	5291.1870	14	4	5288.8900	–14	1
4	2	3	5291.2776	17	3	5289.0105	–19	4
4	2	2	5311.9890	8	3	5310.4315	–36	2
4	3	2	5315.7775	–17	2	5314.4600	36	1
4	3	1	5324.3080	2	3	5322.2270	–72	1
4	4	1	5336.9620	–18	1	5335.1600	–2	2
4	4	0	5338.1150	29	1	5336.1470	–25	1
5	0	5	5309.0270	–15	2	5306.6710	22	2
5	1	5	5309.0300	15	2	5306.6680	–7	2
5	1	4	5351.4577	16	3	5349.1463	–28	4
5	2	4	5351.4620	35	3	5349.1550	–26	1
5	2	3	5383.8545	–47	2	5381.3680	–27	3
5	3	3	5384.2045	25	4	5381.8200	–50	1
5	3	2	5402.8160	–39	1	5401.0170	–25	2
5	4	2	5409.9165	12	3	5408.5230	30	2
5	4	1	5416.1210	–36	2	—	–	
5	5	1	5434.4150	–19	1	5432.7470	10	1
5	5	0	5434.9980	–12	1	5433.2240	4	1
6	0	6	5368.9800	25	3	5366.5635	35	2
6	1	6	5368.9800	25	2	5366.5633	33	3
6	1	5	5420.8416	32	3	5418.4880	7	1
6	2	5	5420.8380	8	1	5418.4880	9	2
6	2	4	5462.7637	16	3	—	–	
6	3	4	5462.7880	13	1	5460.5020	–50	2
6	3	3	5494.7860	–91	1	—	–	
6	4	3	—	–		5492.2495	23	2
6	4	2	—	–		5509.3210	104	1
6	5	2	5523.1020	9	2	5521.7570	25	1
6	5	1	5527.1485	–19	2	—	–	
6	6	1	5551.3350	–20	1	5549.8265	–24	2
6	6	0	5551.6150	13	1	5550.0440	73	1
7	0	7	5438.1040	18	3	5435.6170	14	2
7	1	7	5438.1040	18	3	5435.6165	9	2
7	1	6	5499.3650	–28	1	5496.9590	–2	1
7	2	6	5499.3725	50	2			
7	2	5	—	–		5548.3930	29	3
7	3	5	5550.7330	–15	1	5548.3930	35	1
7	3	4	—	–		5589.5150	–128	1

TABLE IV (continued).

J	K_a	K_c	E_{101}	$\Delta E \cdot 10^4$	N	E_{200}	$\Delta E \cdot 10^4$	N
7	4	4	5592.0933	27	3	5589.7370	36	1
7	4	3	–	–		5618.0250	110	1
7	5	3	5625.3320	38	2	–	–	
7	5	2	5637.6656	0	1			
7	6	2	5655.3575	–12	2			
7	6	1	5657.7330	28	1	–	–	
7	7	1	5687.5880	–4	1	–	–	
7	7	0	5687.7190	31	1	–	–	
8	0	8	5516.3915	–8	2	5513.8240	–7	1
8	1	8	5516.3915	–8	2	5513.8240	–7	1
8	1	7	5587.0395	6	2	5584.5620	10	1
8	2	7	5587.0370	–18	1	5584.5610	0	2
8	2	6	5647.7350	–59	1	–	–	
8	3	6	5647.7360	–24	1	5645.3310	38	1
8	3	5	5698.4930	7	1	5696.1170	–16	1
8	4	5	5698.4760	83	1	–	–	
8	4	4	5738.8320	0	2	–	–	
8	5	4	–	–		5736.4050	27	1
8	5	3	5763.4080	–17	1	–	–	
8	6	2	5782.5204	15	1			
8	7	2	–	–		5805.5190	32	1
8	7	1	5807.9320	–47	1	–	–	
8	8	0	5843.0400	–10	1	–	–	
9	0	9	5603.8360	4	2	5601.1750	–2	1
9	1	9	5603.8360	4	2	5601.1750	–2	1
9	1	8	5683.8370	–27	2	5681.2780	–25	1
9	2	8	5683.8365	–32	2	5681.2780	–25	1
9	2	7	–	–		5751.3390	–3	1
9	5	5	5863.7600	0	1	–	–	
10	0	10	5700.4220	35	1	5697.6560	30	1
10	1	10	5700.4220	35	1	5697.6560	30	1
10	1	9	5789.7550	–7	1	5787.1060	29	1
10	2	9	5789.7550	–7	1	5787.1060	29	1
10	2	8	–	–		5866.4150	29	1
10	3	8	–	–		5866.4140	21	1
10	4	7	–	–		5935.6720	–84	1
10	5	6	–	–		5994.8870	–49	1
11	0	11	5806.1190	–67	1	5803.2410	–17	1
11	1	11	5806.1190	–67	1	5803.2410	–17	1
11	1	10	–	–		5902.0050	–66	1
11	2	10	–	–		5902.0050	–66	1
12	0	12	–	–		5917.9240	–35	1
12	1	12	–	–		5917.9240	–35	1
12	1	11	6028.8640	–5	1	6025.9950	76	1
12	2	11	6028.8640	–5	1	6025.9950	76	1
12	2	10	6126.4630	12	1	–	–	
12	3	10	6126.4630	12	1	–	–	
13	0	13	6044.8470	29	1	6041.6900	7	1
13	1	13	6044.8470	29	1	6041.6900	7	1
14	0	14	6177.8163	–3	1	–	–	
14	1	14	6177.8163	–3	1	–	–	

$$H = \sum_{\upsilon,\upsilon'} |\upsilon > H^{\upsilon\upsilon'} <\upsilon'| \ , \qquad (1)$$

where $H^{\upsilon\upsilon}$ is the well–known rotational Watson–type Hamiltonian in the H representations, and the resonance terms $H^{\upsilon\upsilon'}$ (for $\upsilon \neq \upsilon'$) in our case have the form

$$H^{101,200} = C_y^{101,200}\, iJ_y + C_{xz}^{101,200}\, \{J_x, J_z\} \ , \qquad (2)$$

$$H^{101,002} = C_y^{101,002}\, iJ_y + C_{xz}^{101,002}\, \{J_x, J_z\} \ , \qquad (3)$$

$$H^{200,002} = F_{xy}^{200,002}\, J_{xy}^2 \ , \qquad (4)$$

$$J_{xy}^2 = J_x^2 - J_y^2 \ , \ \{A, B\} = AB + BA \ .$$

The Hamiltonian in the form of Eqs. (1) – (4) takes into account the Coriolis and Darling–Dennison resonances between the three vibrational states (200), (101), and (002). Strictly speaking the summation in Eq. (1) must also involve υ, υ' = (021), (040), (120), i.e., all the states entering into the first hexade. But since the centers of the bands $2\nu_2 + \nu_3$, $4\nu_2$, $\nu_1 + 2\nu_2$ are too far from the centers of the analyzed bands (see Table I), their effect is neglected.

The spectroscopic constants resulted from the fitting are given in Table V. Given in brackets are the 68% confidence intervals in units of the last significant digits. The constants without confidence intervals were not varied in the fitting. The rotational constants and the vibrational energy of the (002) state were previously calculated using the rovibrational and anharmonic parameters.[9]

TABLE V. Vibrational, centrifugal, and resonance constants of the states (101), (200), *and* (002) *of* H_2S (cm^{-1}).

Parameter	(101)	(200)	(002)
E	5147.2270	5144.9910	5241.86_7 (11)
A	9.98976_2 (29)	10.00766_2 (26)	9.859_4 (10)
B	8.80994_3 (22)	8.79814_7 (22)	8.85
C	4.606521_1 (30)	4.601367_9 (33)	4.62
$\Delta_k \cdot 10^3$	3.387_4 (15)	3.422_8 (12)	3.4
$\Delta_{jk} \cdot 10^3$	-2.0482_2 (81)	-2.0516_1 (88)	–1.9
$\Delta_j \cdot 10^4$	6.178_9 (15)	6.247_4 (18)	6.2
$\delta_k \cdot 10^4$	-0.978_0 (28)	-1.209_2 (37)	–1.0
$\delta_j \cdot 10^4$	2.7936_8 (81)	2.940_0 (10)	2.9
$H_k \cdot 10^6$	1.43_7 (14)	1.3	1.3
$C_{xz}^{101-200} = -0.27207_7$ (29)			
$C_{xz}^{101-002} \cdot 10^2 = -3.32_5$ (10)			
$F_{xy}^{200-002} \cdot 10^2 = 4.97_9$ (10)			

Note. Standard deviation $\sigma = 3.6 \cdot 10^{-3}$ for 175 levels.

We have managed to determine the values of E_v and the rotational constant A for (002) more accurately through the fitting owing to resonance interaction between the states (101), (200), and (002). The spectroscopic constants from Table V reconstruct 175 experimental energy levels with the average accuracy $3.6 \cdot 10^{-3}$ cm^{-1}. Analysis of the differences $\Delta = E_{exp} - E_{calc}$ shows that

$$|\Delta| \leq 0.002 \text{ for } 50.3\% \text{ levels}$$
$$0.002 < |\Delta| \leq 0.004 \text{ for } 35.8\% \text{ levels}$$
$$0.004 < |\Delta| \leq 0.006 \text{ for } 5.8\% \text{ levels}$$
$$0.006 < |\Delta| \leq 0.019 \text{ for } 8.1\% \text{ levels}$$

Thus, 86% of all levels are reconstructed with precision better than 0.004 cm^{-1}.

The values of spectroscopic constants for the vibrational states (101) and (200) are very close due to a local character of the stretching vibrations of H_2S. The resonance constants $C_{xz}^{101,200}$, $C_{xz}^{101,002}$, and $F_{xz}^{200,002}$ are in good agreement with values[7] for the vibrational states (111), (210), and (012). In our case it was impossible to determine the parameters C_y due to smaller, than those in Ref. 7, values of quantum numbers J and K_a of the experimental energy levels included into the fitting.

As shown in Ref. 7, the Coriolis and Darling–Dennison resonances are very strong for H_2S, and, as consequence, almost uniform mixing of the vibrational states (111), (200), and (012) is observed. We have concluded that such a situation is also observed for the states (101), (200), and (002), but the transitions to the levels (101) and (200) connected with (002) through a strong resonance were not observed in the experiment. Examples of resonance mixing between the states (101), (200), and (002) are presented in Table VI.

TABLE VI. Mixing coefficients of wave functions for some energy levels of the states (101), (200), *and* (002) *of* H_2S.

J	K_a	K_c	υ	E^{exp}	(101)	(200)	(002)
2	1	1	101	5196.653	0.819	0.180	0.00
2	2	1	200	5198.779	0.180	0.819	0.00
4	2	2	101	5311.989	0.567	0.432	0.00
5	3	2	101	5402.816	0.770	0.229	0.00
5	4	2	101	5409.916	0.872	0.127	0.00
5	4	2	200	5408.523	0.263	0.736	0.00
6	2	4	101	5462.763	0.975	0.006	0.018
6	3	4	101	5462.788	0.970	0.013	0.015
6	3	3	101	5494.786	0.710	0.288	0.00
6	4	3	101	5495.504	0.805	0.134	0.00
7	4	4	101	5592.093	0.920	0.058	0.020
8	4	4	101	5738.832	0.828	0.093	0.078

It should be pointed out in conclusion that the levels (101) and (200) for $J \geq 7$ can be perturbed due to interaction with the states (021) and (120) as it follows from the comparison of their energy spectra. It is this fact that may explain the large values of ΔE for some levels for $J \geq 7$.

REFERENCES

1. J.M. Flaud, C. Camy-Peyret and J.W.C. Johns, Can. J. Phys. **61**, 1462 (1983).
2. C. Camy-Peyret, J.M. Flaud, L. Lechuga–Fossat, and J.W.C. Johns, J. Mol. Spectrosc. **109**, 300 (1985).
3. L.L. Strow, J. Mol. Spectrosc. **97**, 9 (1983).
4. W.C. Lane, T.H. Edwards, J.R. Gillis, et al., J. Mol. Spectrosc. **111**, 320 (1985).
5. L. Lechuga–Fossat, J.M. Flaud, C. Camy–Peyret, and J.W.C. Johns, Can. J. Phys. **62**, 1889 (1984).
6. L.E. Snuder and T.H. Edwards, J. Mol. Spectrosc. **31**, 347 (1969).
7. L. Lechuga–Fossat, J.M. Flaud, C. Camy–Peyret, et al., Mol. Phys. **61**, 23 (1987).
8. H.C. Allen and E.K. Plyler, J. Mol. Spectrosc. **22**, 1104 (1954).
9. J. Senekowitsch, S. Carter, A. Zilch, et al., J. Chem. Phys. **90**, 783 (1989).