Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Spectroscopy 226 (2004) 57–70

Journal of
MOLECULAR
SPECTROSCOPY

www.elsevier.com/locate/jms

On the study of high-resolution rovibrational spectrum of H_2S in the region of 7300–7900 cm^{-1}

O.N. Ulenikov,[a,b] A.-W. Liu,[a] E.S. Bekhtereva,[a,b] O.V. Gromova,[b]
L.-Y. Hao,[a] and S.-M. Hu[a,*]

[a] *Laboratory of Bond Selective Chemistry, University of Science and Technology of China, Hefei 230026, PR China*
[b] *Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk 634050, Russia*

Received 27 January 2004; in revised form 8 March 2004
Available online 16 April 2004

Abstract

High-resolution Fourier transform infrared spectrum of H_2S was recorded and analyzed in the region of the $v = v_1 + v_2/2 + v_3 = 3$ poliad. Experimental transitions were assigned to the $3\nu_1, 2\nu_1 + \nu_3, \nu_1 + 2\nu_3, 3\nu_3, 2\nu_1 + 2\nu_2$, and $\nu_1 + 2\nu_2 + \nu_3$ bands with the maximum value of quantum number J equal to 11, 14, 10, 11, 8, and 11, respectively. The theoretical analysis was fulfilled with the Hamiltonian model which takes into account numerous resonance interactions between all the mentioned vibrational states. The *rms* deviation of the reproduction of 510 upper energy levels (derived from more than 1550 transitions) with 75 parameters was 0.0022 cm^{-1}.

Keywords: Vibration–rotation spectra; H_2S molecule; Resonance interactions; Spectroscopic parameters

1. Introduction

As one of the lightest triatomic and local-mode molecule, hydrogen sulfide attracts great spectroscopic interest. Both the local mode properties, and the conditions of their destruction can be analyzed in the rovibrational spectra of H_2S. As a consequence, numerous spectroscopic studies have been carried out on this molecule (see, for example, [1–18]), beginning at the low frequency microwave region [1], up to visible transitions in the highly excited stretching bands $(70^{\pm}, 0)$ observed by the sensitive intra-cavity laser absorption spectroscopy, [18]. The ground vibrational state was analyzed in [1–5]. The lowest five poliads of interacting vibrational states, with $v = v_1 + v_2/2 + v_3$, $v = 0.5$, 1, 1.5, 2, 2.5, were discussed in [6–11], respectively. Highly excited stretching local mode states $v = 4$, 4.5, 5, 6, 7 were considered in [12–18]. Moreover, the band centers of some additional infrared bands were discussed in [18]. The experimental results were reproduced well by quantum mechanics calculations on the structure of the rotation–vibration energy levels (see, for example, [19–22]). As to the bands of the $v = 3$ poliad which will be discussed in the present contribution, they have been mentioned in [10] on the discussion of the vibrational band centers. To the best of our knowledge, the rotational analysis of this poliad has not been fully carried out yet, if exclude the analysis with J up to 7 or 8 mentioned only in [10].

In this paper, we present the results of the high-resolution analysis of the spectral region where the absorption bands of the $v = 3$ poliad are located. Experimental details are reported in Section 2. Theoretical background of the analysis is considered in Section 3. Description of the spectrum and assignments of the recorded transitions are presented in Section 4. Sections 5 and 6 present the results of the fit of derived upper energies and discussion.

2. Experimental details

The H_2S sample was purchased from Nanjing Special Gas Company (China) with a stated purity of 99%. The spectra of H_2S in the 1–2 μm region were recorded with

---

[*] Corresponding author. Fax: +86-551-3602969.
E-mail addresses: Ulenikov@phys.tsu.ru (O.N. Ulenikov), smhu@ustc.edu.cn (S.-M. Hu).

doi:10.1016/j.jms.2004.03.014

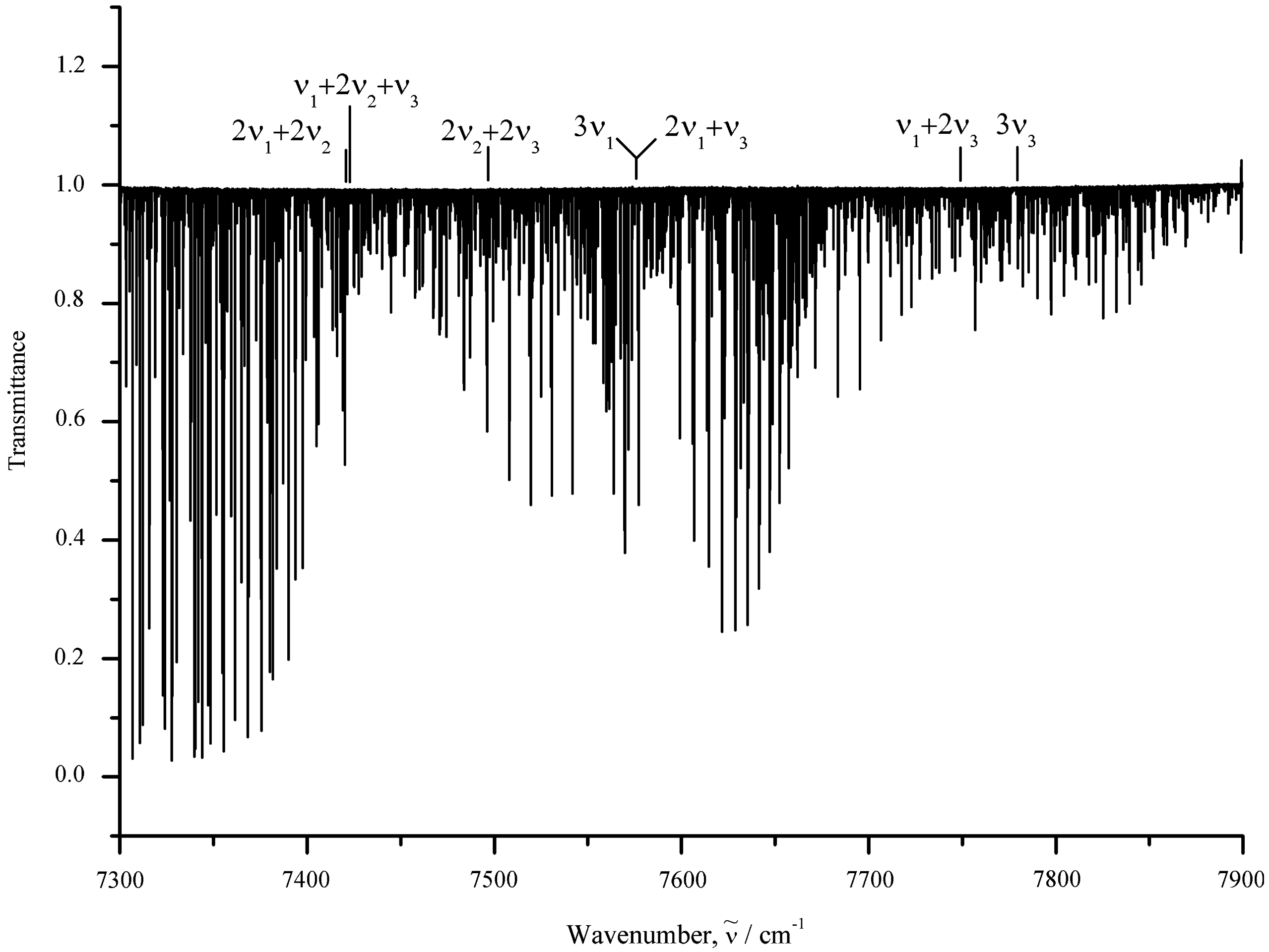

Fig. 1. Survey spectrum of H_2S molecule in the region of 7000–7990 cm^{-1}. Centers of bands located in this region are denoted. Strong lines belonging to the water vapor can be seen in the left side of the figure. Experimental conditions: absorption path length, 105 m; sample pressure, 2076 Pa; instrumental resolution, 0.015 cm^{-1}; room temperature.

a Bruker IFS 120 HR Fourier transform spectrometer (FTS) equipped with a path length adjustable multi-pass gas cell at room temperature. The unapodized resolution was 0.015 cm^{-1}. The absorption path length and the gas pressure were 105 m and 2076 Pa, respectively. A tungsten source, a Ge detector and a CaF_2 beam-splitter were applied. The line positions were calibrated using those of $^{12}C^{16}O_2$ and H_2O listed in HITRAN database. The absolute accuracy of line positions of unblended and not-very-weak lines was estimated to be 0.002 cm^{-1} or better. An overview of the spectrum is presented in Fig. 1. Some parts of the high-resolution spectrum are presented in Figs. 3–5.

3. Theoretical background

The H_2S molecule is an asymmetric top of the C_{2v} symmetry with the value of the asymmetry parameter $\kappa \simeq 0.532$. Its three fundamental bands ν_1, ν_2, and ν_3 are located at 2614.44, 1182.53, 2628.37 cm^{-1} and have the symmetries A_1, A_1, and B_2, respectively. As a consequence,

(a) the selection rules are in the H_2S molecule:

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

for the bands with even v_3, and

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

for the bands with odd v_3. Here $n, m = 0, 1, 2, \ldots$;

(b) the vibrational states with the fixed value of quantum number v ($v = v_1 + v_2/2 + v_3$) form so called poliads of interacting vibrational states. In this case, states in a same poliad can strongly perturb each other by Fermi (Darling-Dennison) and/or Coriolis type interactions. On this reason, the Hamiltonian used for analysis of experimental data should have the following form:

$$H^{v.-r.} = \sum_{v,v'} H^{vv'} |v\rangle\langle v'|, \tag{3}$$

where the summation is fulfilled in all vibrational states of a poliad. In our case, $v, v' = 1, \ldots, 7$, and it is denoted: $|1\rangle = (300, A_1)$, $|2\rangle = (220, A_1)$, $|3\rangle = (022, A_1)$, $|4\rangle = (102, A_1)$, $|5\rangle = (201, B_2)$, $|6\rangle = (121, B_2)$, $|7\rangle = (003, B_2)$.

For the convenience of the reader, diagram in Eq. (4) clarifies the structure of the matrix of effective Hamiltonian (3):

$$H^{vv'} = \begin{vmatrix} W & F & - & D & C & - & - \\ F & W & D & - & C & C & - \\ - & D & W & F & - & C & C \\ D & - & F & W & C & C & C \\ C & C & - & C & W & F & D \\ - & C & C & C & F & W & - \\ - & - & C & C & D & - & W \end{vmatrix}. \tag{4}$$

Here index W denotes the diagonal operator matrix elements $H^{vv'}$; F and D denote the Fermi and Darlig-Dennison type interactions; index 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 $(v_1 v_2 \pm 2 v_3 \mp 1)$. Strongly speaking, the vibrational states (140,A_1), (041,B_2), and (060,A_1) also should be added to the right-hand side of Eq. (3). However, as the analysis shows, on the one hand, the lines of these three bands are too weak to be recorded in our experiment. On the other hand, only a few of the rovibrational levels belonging to seven above mentioned vibrational states, derived from our experimental data, can be perturbed by the (140,A_1), (041,B_2), and (060,A_1) vibrational states. On this reason we omitted the (140,A_1), (041,B_2), and (060,A_1) states in Eq. (3).

The diagonal blocks H^{vv} in Eq. (3) have the form of usual Watson type operators, [23], in the A-reduction and I_r-representation, and they describe rotational structures of corresponding vibrational states:

$$\begin{aligned} H^{vv} = {} & E^v + \left[A^v - \frac{1}{2}(B^v + C^v)\right]J_z^2 + \frac{1}{2}(B^v + C^v)J^2 \\ & + \frac{1}{2}(B^v - C^v)J_{xy}^2 - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v J^4 \\ & - \delta_K^v [J_z^2, J_{xy}^2] - 2\delta_J^v J^2 J_{xy}^2 + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 \\ & + H_{JK}^v J_z^2 J^4 + H_J^v J^6 + [J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J^2 J_z^2 + h_J^v J^4] \\ & + L_K^v J_z^8 + L_{KKJ}^v J_z^6 J^2 + L_{JK}^v J_z^4 J^4 + L_{KJJ}^v J_z^2 J^6 + L_J^v J^8 \\ & + [J_{xy}^2, l_K^v J_z^6 + l_{KJ}^v J^2 J_z^4 + l_{JK}^v J^4 J_z^2 + l_J^v J^6] + P_K^v J_z^{10} \\ & + [J_{xy}^2, p_K^v J_z^8] + \cdots. \end{aligned} \tag{5}$$

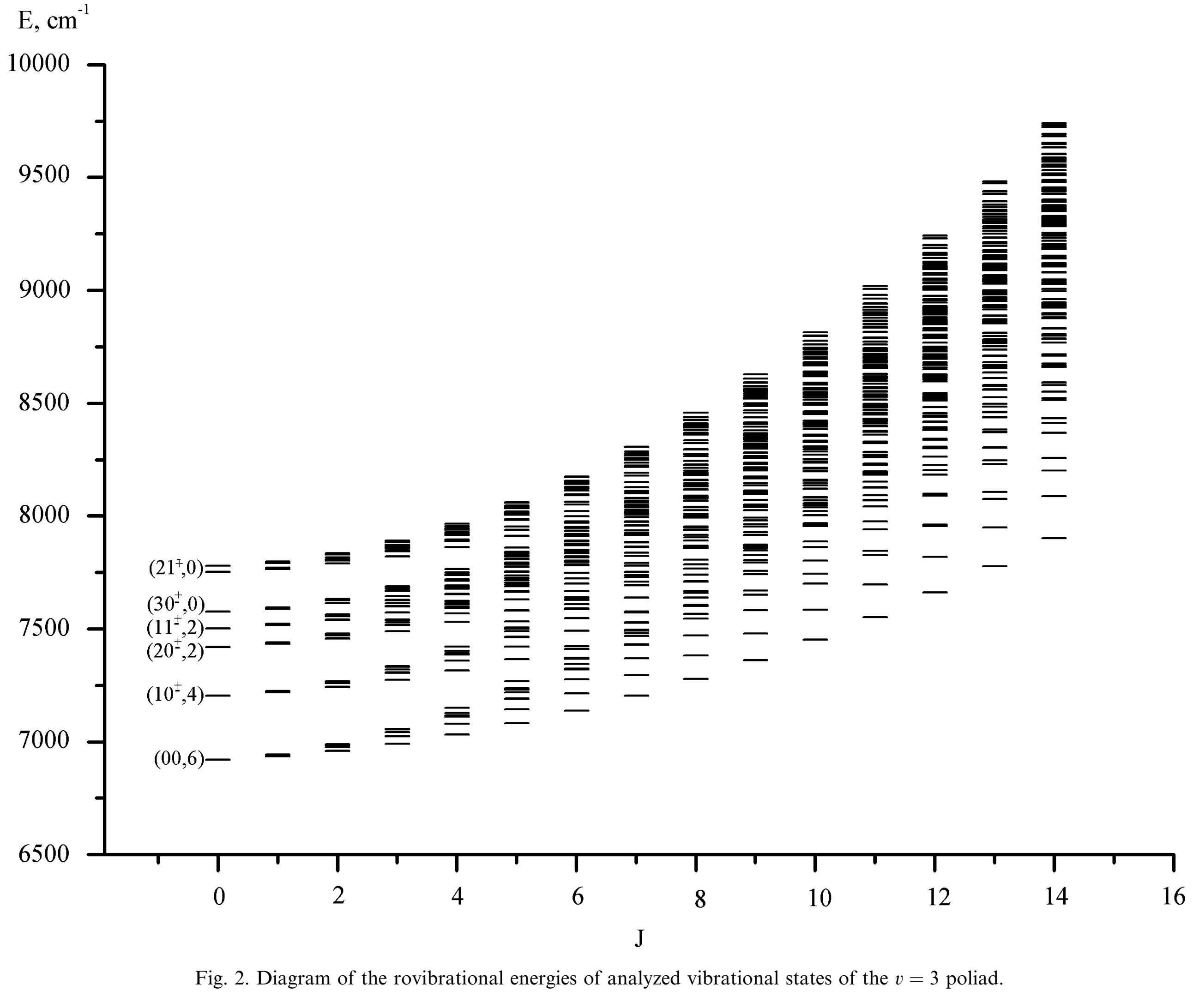

Fig. 2. Diagram of the rovibrational energies of analyzed vibrational states of the $v = 3$ poliad.

Non-diagonal operators $H^{vv'}$, $(v \neq v')$, describe resonance interactions between the states $|v\rangle$ and $|v'\rangle$. In this case, resonance interactions between the states of the same symmetry,are described by the Fermi type operators:

$$H_F^{vv'} = F^{vv'} + F_K^{vv'} J_z^2 + \cdots + F_{xy}^{vv'} J_{xy}^2 + F_{xyK}^{vv'} [J_{xy}^2, J_z^2]_+ + F_{xyJ}^{vv'} J_{xy}^2 J^2 + \cdots, \qquad (6)$$

where $J_{xy}^2 = J_x^2 - J_y^2$ and $J^2 = J_x^2 + J_y^2 + J_z^2$. Coriolis type non-diagonal operators $H^{vv'}$ describe resonance interactions between the states $|v\rangle$ and $|v'\rangle$ of different symmetries:

$$\begin{aligned} H_{C_y}^{vv'} &= 2(B\zeta^y)^{vv'} iJ_y + C_{yK}^{vv'}[iJ_y, J_z^2]_+ + C_{yJ}^{vv'} iJ_yJ^2 \\ &+ C_{yKK}^{vv'}[iJ_y, J_z^4]_+ + C_{yJK}^{vv'}[iJ_y, J_z^2J^2]_+ + C_{yJJ}^{vv'} iJ_yJ^4 \\ &+ \cdots + C_{xz}^{vv'}[J_x, J_z]_+ + C_{xzK}^{vv'}[[J_x, J_z]_+, J_z^2]_+ \\ &+ C_{xzJ}^{vv'}[J_x, J_z]_+ J^2 + \cdots + C_{yxy}^{vv'}[iJ_y, J_{xy}^2]_+ \cdots. \end{aligned} \qquad (7)$$

4. Description of the spectrum and assignment of transitions

As shown in Figs. 1 and 2 (the Fig. 2 shows the diagram of the rovibrational energies for all vibrational states of the considered poliad), the strongest pair of stretching $3\nu_1$ and $2\nu_1 + \nu_3$ bands ((3 0 0) and (2 0 1) in the normal mode notations, or $(30^+, 0)$ and $(30^-, 0)$ in the local mode notations) are totally overlapped and located about 176 and 203 cm^{-1} lower than the nearest weaker pair of stretching bands $\nu_1 + 2\nu_3$ and $3\nu_3$ ((1 0 2) and (0 0 3), or $(21^+, 0)$ and $(21^-, 0)$ in the normal and local mode notations, respectively). In its turn, three "bending doubly excited" bands of the considered poliad $(v_1 + v_2/2 + v_3) = 3$, namely, $2\nu_1 + 2\nu_2$, $\nu_1 + 2\nu_2 + \nu_3$, and $2\nu_2 + 2\nu_3$, are located about 156 and 60 cm^{-1} lower than the strongest $3\nu_1$ and $2\nu_1 + \nu_3$ bands. In this case, in accordance with the local mode theory, the first two bands, $2\nu_1 + 2\nu_2$ and $\nu_1 + 2\nu_2 + \nu_3$, construct the pair of close states $(20^+, 2)$ and $(20^-, 2)$. On this reason, and taking into account the values of rotational, A, B, and C parameters, one can expect that local perturbations of the rovibrational structures of the $(30^+, 0)$ and $(30^-, 0)$ states by the other vibrational states will appear for $J \geqslant 5 - 6$. Of course, strong resonance perturbations inside the "local mode" pairs, $(30^+, 0)/(30^-, 0)$, $(20^+, 2)/(20^-, 2)$ are presented beginning already with $J \geqslant 1$.

Assignments of the transitions were made with the Ground State Combination Differences method. In this case, the ground state energies were calculated on the

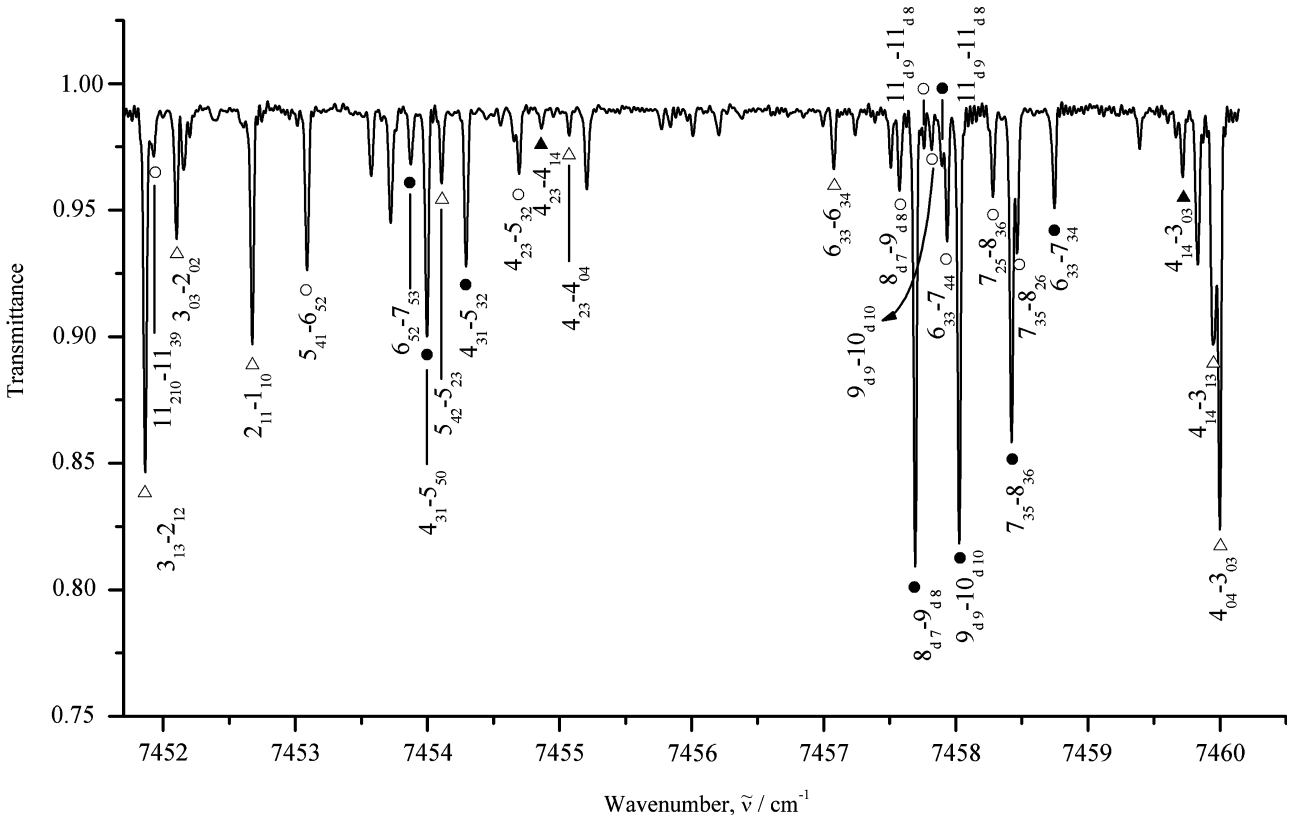

Fig. 3. A small part of the high-resolution spectrum of H$_2$S in the region of 7452–7460 cm^{-1}. The lines belonging to the bands $2\nu_1 + 2\nu_2$ (marked by dark triangle), $\nu_1 + 2\nu_2 + \nu_3$ (open triangle), $2\nu_1 + \nu_3$ (dark circle), and $3\nu_1$ (open circle) can be seen.

base of parameters from [3]. As the result of assignments, about 290, 350, 390, 270, and 210 transitions with $J^{\max} = 11$, 14, 10, 11, and 11 were assigned to the bands $3\nu_1$, $2\nu_1 + \nu_3$, $\nu_1 + 2\nu_3$, $3\nu_3$, and $\nu_1 + 2\nu_2 + \nu_3$, respectively (some examples of assigned transitions are shown in Figs. 3–5). Therefore rovibrational energies of the states (3 0 0), (2 0 1), (1 0 2), (0 0 3), and (1 2 1) ((30^+,0), (30^-,0), (21^+,0), (21^-,0), and (20^-,2) in the local mode notations) were obtained, which are presented in Table 1 together with their experimental uncertainties Δ given in $10^{-4}\,\mathrm{cm}^{-1}$. Since upper rovibrational energies were determined from several transitions reaching the same upper level, their uncertainties Δ can be considered as an indication of the precision of the experimental line positions. Thus the average experimental accuracy of the line positions can be estimated as 0.0010–$0.0030\,\mathrm{cm}^{-1}$ for unblended and not very weak lines. With increasing value of the quantum number J, the accuracy of line positions decrease due to the decreasing of line strengths.

The presence of resonance interactions allowed us to assign without doubt some tens transitions to the very weak band $2\nu_1 + 2\nu_2$. Positions and assignments of corresponding experimental transitions are listed in columns 1–3 of Table 2. Columns 4 gives the values of transmittances of transitions (see Table 3).

5. Determination of parameters

As was discussed above, the Hamiltonian (3) was used for further analysis and fit for the upper energy levels. In this case, the presence of numerous resonance interactions in (1) leads to necessity to have a physically suitable initial approximations for parameters of the Hamiltonian (1). In our case, it was made from the following assumptions:

(a) The centers of all seven considered bands were estimated on the base of Eqs. (21)–(26) from [24]. In this case, necessary for calculations values of parameters ω, x_m, and λ have been estimated from experimental values of the band centers, ν_1 and ν_3, from [8], $2\nu_1$, $\nu_1 + \nu_3$, $2\nu_3$, $\nu_1 + 2\nu_2$, and $2\nu_2 + \nu_3$, from [10], and $\nu_1 + 2\nu_2 + \nu_3$ from present study.

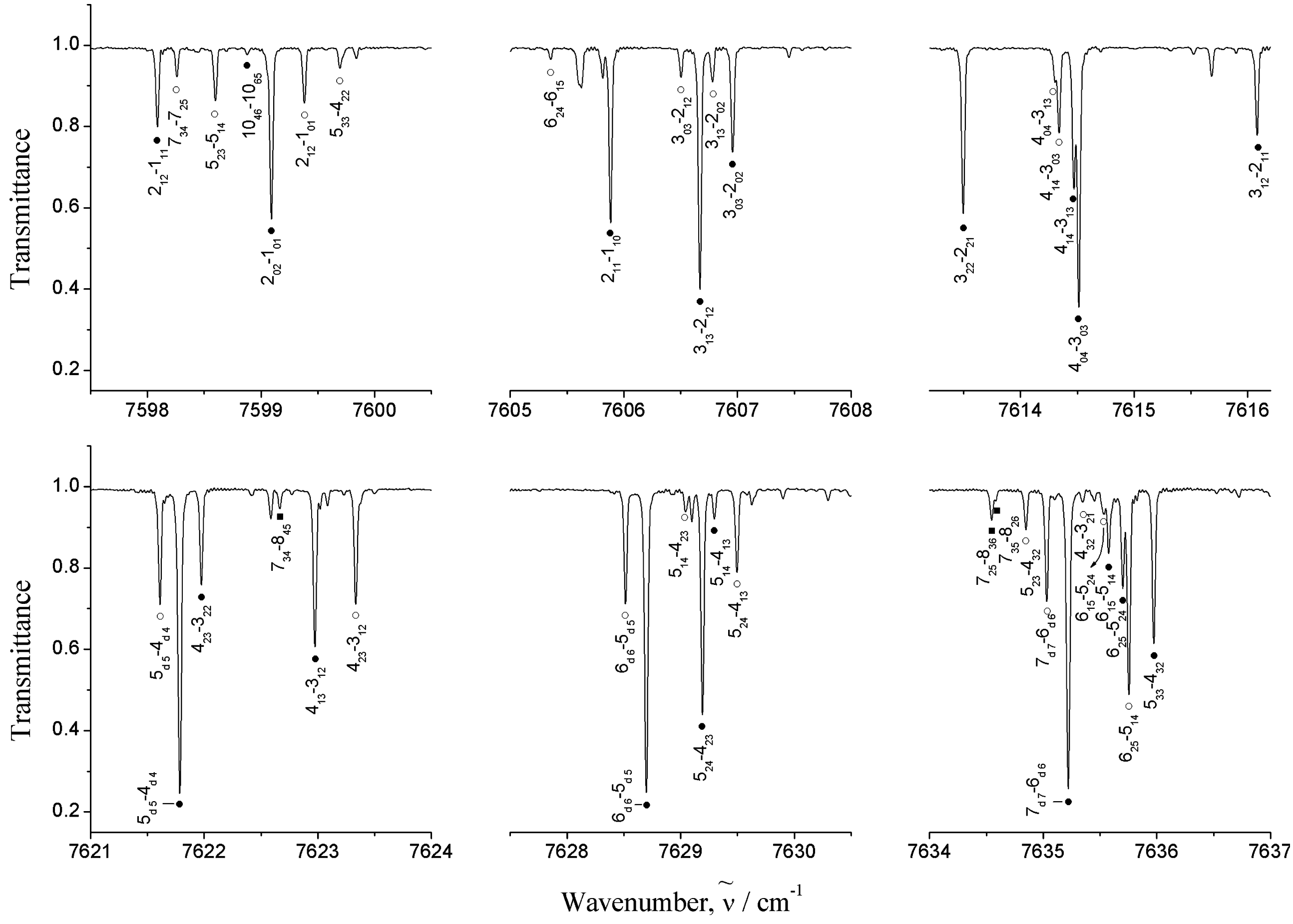

Fig. 4. Small parts of the high-resolution spectrum of H_2S in the region of R-branches of $2\nu_1 + \nu_3$ (marked by dark circle) and $3\nu_1$ (open circle). Parts of the spectrum were chosen to illustrate the behavior of the $[JK_a = dK_c = J] \leftarrow [J - 1K_a = d'K_c = J - 1]$ $(d, d' = 0$, and/or 1) doublets in the $2\nu_1 + \nu_3$ and $3\nu_1$ bands. Some lines belonging to the $\nu_1 + 2\nu_3$ band are marked by dark square.

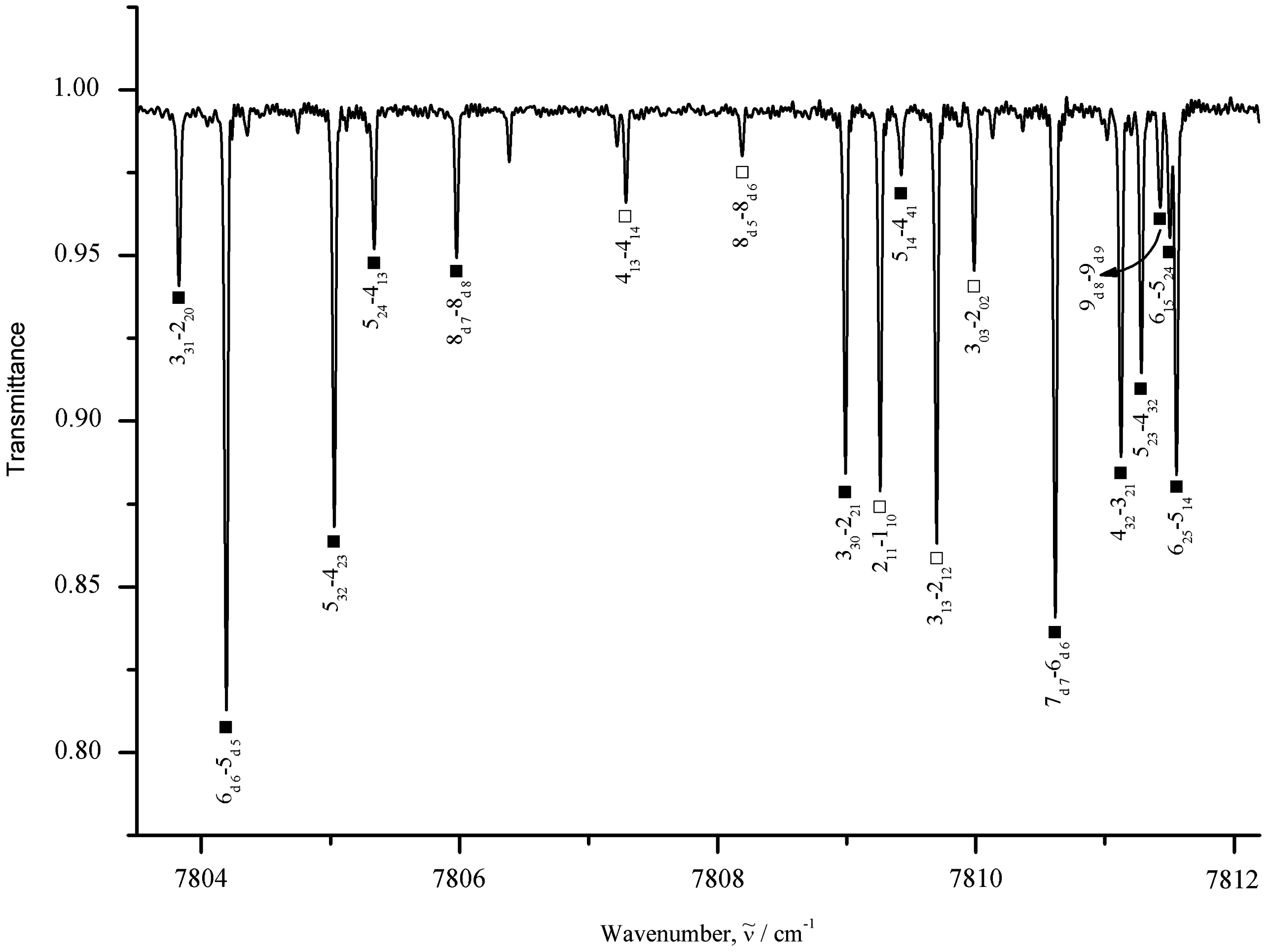

Fig. 5. Small portion of the $\nu_1 + \nu_2$ and $3\nu_3$ bands of H_2S in the region of the *R*-branch. Some transitions denoted by full square belong to the $\nu_1 + \nu_2$ band, and by open square—to the $3\nu_3$ band.

(b) All the pure vibrational resonance interaction parameters $F^{vv'}$ have been put as zero. This is physically suitable assumption which corresponds a fact that the effective Hamiltonian (3)–(7) can be constructed not only on the base of harmonic vibrational wavefunctions, but also, on the base of functions which are eigenfunctions of the total vibrational Hamiltonian of a molecule:

$$H_{\mathrm{vib.}} = \frac{1}{2}\sum_{\lambda}\omega_{\lambda}(p_{\lambda}^2 + q_{\lambda}^2) + \sum_{\lambda\leqslant\mu\leqslant\nu} k_{\lambda\mu\nu}q_{\lambda}q_{\mu}q_{\nu} + \sum_{\lambda\leqslant\mu\leqslant\nu\leqslant\xi} k_{\lambda\mu\nu\xi}q_{\lambda}q_{\mu}q_{\nu}q_{\xi} + \cdots + \frac{1}{2}\sum_{\alpha\beta}\mu_{\alpha\beta}(q)G_{\alpha}G_{\beta}. \tag{8}$$

(c) The initial values of the rotational *A*, *B*, and *C* parameters were extrapolated from the values of corresponding parameters of the (0 0 0), (1 0 0), (0 0 1), and (0 2 0) vibrational states from [3] and [8].

(d) The initial values of all centrifugal distortion parameters of the states (3 0 0), (2 0 1), (1 0 2), and (0 0 3) were fixed to the values of corresponding parameters of the ground vibrational state from [3]. Analogously, initial values of centrifugal distortion parameters of the (2 2 0), (1 2 1), and (0 2 2) states were fixed to the values of corresponding parameters of the (0 2 0) state from [8].

Upper rovibrational energy levels from Table 1 and experimental data from Table 2 were used then as an input to the fit procedure with the Hamiltonian, Eqs. (3)–(7). All the input energy levels were used with weights proportional to $(1/\Delta^2)$, where Δ are the experimental uncertainties of corresponding energy values. In this case, for the upper levels obtained from the only one transition, the weight was set to be zero.

As the result, the set of 75 fitted parameters was derived (54 parameters of the seven diagonal blocks and 21 resonance interaction parameters) which reproduce the 510 initial upper energy levels with *rms* deviation of $0.0022\,\mathrm{cm}^{-1}$. Obtained parameters are presented in Tables 4–6 together with their 1σ statistical confidential intervals. Parameters presented in Tables 4 and 5 without confidential intervals were constrained to their

Table 1
Experimental rovibrational term values for the (3 0 0), (2 0 1), (1 0 2), (0 0 3), and (1 2 1) vibrational states of the H_2S molecule (in cm^{-1})[a]

			(3 0 0)			(2 0 1)			(1 0 2)			(0 0 3)			(1 2 1)		
J	K_a	K_c	*E*	Δ	*δ*	*E*	Δ	*δ*	*E*	Δ	*δ*	*E*	Δ	*δ*	*E*	Δ	*δ*
	1		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0	0	0	7576.3808		−25	7576.5442		−24	7752.2638		0	7779.3201		−7	7420.0927		18
1	0	1	7589.5024	20	18	7589.6325	4	−11	7765.4608	2	10	7792.6388	9	6	7433.7578	21	−32
1	1	1	7590.8927		1	7591.0214	3	−13	7766.6498	16	6	7793.6326	3	3	7435.3352	2	−2
1	1	0	7594.8968	6	−2	7595.0577		−19	7770.7841	2	7	7797.8184	4	−3	7440.0330	5	−10
2	0	2	7612.7871		−8	7612.8400	7	−1	7788.6768	2	0	7815.9100	5	7	7457.6215	7	16
2	1	2	7613.1299	7	−13	7613.1810	6	5	7788.9048	25	−3	7816.1077	8	1	7457.9729	6	4
2	1	1	7625.1285	13	30	7625.2607	7	−2	7801.2900	25	−8	7828.6340	11	14	7472.0515	15	8
2	2	1	7629.2858	12	0	7629.4113	13	−10	7804.8482	7	−4	7831.6050	5	−9	7476.7569		−15
2	2	0	7632.1998	10	−10	7632.3587	5	−5	7807.9890	2	3	7834.9501	3	−3	7480.2086	12	−6
3	0	3	7644.8048	14	−15	7644.9756	12	−19	7820.6483	5	5	7848.0037	10	6	7490.1179	3	24
3	1	3	7644.7988	18	−1	7644.9685	8	−10	7820.6777	2	1	7847.9945	12	14	7490.1630	12	16
3	1	2	7667.1559	8	10	7667.2243	8	7	7843.3220	7	3	7870.7267	3	−3	7516.1161	27	2
3	2	2	7668.6041	26	−11	7668.6598	8	−3	7844.4109	3	−3	7871.6971	10	−17	7517.7430	10	−3
3	2	1	7678.7212	7	4	7678.8590	14	11	7855.1813	5	2	7882.7018	5	5	7529.6435	13	1
3	3	1	7686.9759	8	3	7687.0930	6	−18	7862.1966	8	−11	7888.5911	2	−18	7538.9643	17	8
3	3	0	7688.7605	15	7	7688.9058	7	−10	7864.1520	10	−2	7890.9556	16	−23	7541.1069	8	−12
4	0	4	7685.7677	15	−29	7685.9391	9	8	7861.5818	13	28	7889.1634	11	21	7531.4231	11	18
4	1	4	7685.7659	9	−14	7685.9369	19	−2	7861.5820	11	−5	7889.1634	11	21	7531.4249		−20
4	1	3	7718.0495	8	10	7718.0323	9	23	7894.0600	20	1	7921.4671	2	−8	7568.8740	18	16
4	2	3	7718.3920	14	0	7718.3697	15	6	7894.2633	5	2	7921.3920	6	−2	7569.2442	18	13
4	2	2	7738.8400	19	7	7738.9234	10	6	7915.5042	4	2	7943.2584	9	3	7593.1649	13	−15
4	3	2	7742.7169	8	3	7742.7700	13	5	7918.4923	9	1	7946.0610	7	−10	7597.5462	6	8
4	3	1	7750.5377	9	7	7750.6734	8	14	7927.4135	4	−1	7954.9870	3	2	7606.7950	15	−12
4	4	1	7764.0263	17	21	7764.1311	4	−7	7938.6745	12	−3	7964.5906	4	−34	7621.9718		−22
4	4	0	7764.9619	7	3	7765.0892	12	−1	7939.4384	2	−2	7966.0829	6	−16	7623.1230	22	1
5	0	5	7735.7884	21	−16	7735.9638	9	−3	7911.5404	12	−11	7939.4203	22	−4	7581.6612	25	22
5	1	5	7735.7884	21	−10	7735.9638	9	3	7911.5404	12	−11	7939.4203	22	−4	7581.6612	25	16
5	1	4	7777.4667	10	−2	7777.4382		−13	7953.4485	8	−1	7981.0437	21	−4	7630.1108	20	−3
5	2	4	7777.6389	8	−8	7777.6125	8	7	7953.4795	5	−1	7981.0437	21	1	7630.1623	15	3
5	2	3	7808.8158	7	9	7808.8097	9	−6	7985.2507	12	0	8012.8473	3	6	7666.4734	15	−18
5	3	3	7809.9621	8	2	7809.9429	12	11	7986.0250	10	−2	8012.6025	9	−7	7667.7935	11	5
5	3	2	7827.7794	5	4	7827.8790	15	0	8005.0831	1	3	8033.3298	4	−4	7688.6606	20	−7
5	4	2	7835.5449	5	−7	7835.5960	10	13	8011.1860	10	5	8033.5771	8	−7	7697.4522	8	10
5	4	1	7840.9739	5	5	7841.1013	8	31	8018.4704	7	−6	8045.7998	6	−10	7703.9300	24	30
5	5	1	7860.4476	2	−3	7860.5390	4	−3	8034.1047	6	−15	8059.5693	17	−18	7725.7360	20	16
5	5	0	7860.8894	6	6	7860.9928	4	3	8039.5988	13	2	8060.4296	11	7	7726.2859	6	−47
6	0	6	7794.8610	10	−6	7795.0430	5	4	7970.5376	1	−3	7998.7810	4	4	7640.8385	25	5
6	1	6	7794.8610	10	−5	7795.0430	5	5	7970.5376	1	−4	7998.7810	4	4	7640.8385	25	5
6	1	5	7845.7980	29	−14	7845.9718	13	−12	8021.7688	4	7	8049.6548	8	−1	7700.1009	13	−7
6	2	5	7845.7937	12	6	7845.9663	3	−2	8021.7725	14	−1	8049.6548	8	0	7700.1101		9
6	2	4	7887.1608	8	16	7886.8811	4	0	8063.2142	19	6	8090.8655	22	−9	7747.8697	14	68
6	3	4	7887.2347	19	1	7886.9505	20	−14	8063.3635	8	−3	8090.8655	22	11	7748.0645	11	17
6	3	3	7916.6054	18	−13	7916.6253	13	−15	8093.7713	2	−6	8121.7964	34	1	7782.2230	16	−72

Table 1 (*continued*)

			(3 0 0)			(2 0 1)			(1 0 2)			(0 0 3)			(1 2 1)		
J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
	1		2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
6	4	3	7919.6576	13	4	7919.6660	31	192	8095.9100	8	−1	8121.5915		−1	7785.7618	20	2
6	4	2	7934.1907	8	24	7934.3028	15	19	8112.1847	10	1	8140.9950	12	−8	7802.8083	20	10
6	5	2	7947.1798	27	18	7947.2399	18	202	8122.4773	8	2	8145.8839		2	7817.5165	9	1
6	5	1				7950.6254	16	96	8128.6889	8	−9	8155.9131	5	4	7821.5438	11	8
6	6	1	7976.1968	5	−7	7976.2680		−3	8147.8750	12	8	8173.4351		14	7850.1055		−56
6	6	0	7976.3902	13	−1	7976.4700	15	22	8152.8833	12	−1	8173.8983	5	−3	7850.3657	3	28
7	0	7	7862.9771	5	8	7863.1663	4	7	8038.5610	3	−2	8067.2338	5	6	7708.9507	5	−21
7	1	7	7862.9771	5	8	7863.1663	4	7	8038.5610	3	−2	8067.2338	5	6	7708.9507	5	−21
7	1	6	7923.1560	34	31	7923.3343	10	5	8099.0783	7	−6	8127.3265	21	−11	7778.9894	12	−6
7	2	6	7923.1522	7	−9	7923.3343	10	17	8099.0783	7	−13	8127.3265	21	−11	7778.9894	12	−16
7	2	5	7973.5788	10	−23	7973.5452	37	−11	8149.8459	8	5	8177.7520	2	−15	7837.4887	10	6
7	3	5	7973.7522	15	−27	7973.7185	12	−8	8149.8713		−3	8177.7527	2	−2	7837.5346	16	−15
7	3	4	8013.7387	6	−3	8013.6749	6	−18	8190.5481	12	−1	8218.3723	7	−3	7883.9116	7	1
7	4	4	8014.5758	10	−17	8014.5024	15	9	8191.0735	9	2	8218.3740	9	−6	7884.9349	29	70
7	4	3	8041.0490	10	11	8041.1073	22	10	8219.2015	3	−10	8247.9506	20	7			
7	5	3	8047.5017	20	−2	8047.4872	12	−64	8223.8900	7	9	8248.7201	19	3	7923.1510	9	−7
7	5	2	8058.4429	19	−19	8058.5778	22	1	8237.1468	13	0	8266.5700	9	−6	7936.0076		−9
7	6	2	8077.6675	20	9	8077.6950	5	−31	8252.1942	18	−9	8276.1155	15	2	7957.7446	13	−29
7	6	1	8079.4893	16	−14	8079.5633	23	−17	8258.0090	13	7	8278.5895		10	7959.9828		−29
7	7	1	8111.1565		−42	8111.2056	20	−17	8286.8217	23	7	8306.0391		29			
7	7	0	8111.2364	10	−47	8111.2922	10	12	8285.9114	10	21	8306.2803		4			
8	0	8	7940.1258	23	9	7940.3245	10	0	8115.6027	2	2	8144.7678	2	−7	7785.9946	9	4
8	1	8	7940.1258	23	9	7940.3245	10	0	8115.6027	2	2	8144.7678	2	−7	7785.9946	9	4
8	1	7	8009.5195	25	23	8009.7082	16	7	8185.3854	9	22	8214.0574	15	−7	7866.7828	14	−47
8	2	7	8009.5195	25	25	8009.7082	16	10	8185.3854	9	15	8214.0574	15	−7	7866.7828	14	−48
8	2	6	8069.0995	15	−26	8069.0966	33	22	8245.3678	8	23	8273.6258	14	11	.		
8	3	6	8069.2807	8	−6	8069.2751	25	21	8245.3701	22	2	8273.6258	14	13	7935.9361	25	4
8	3	5	8118.9405	13	−15	8118.7301	10	−50	8295.5175	8	4	8323.4863	13	20			
8	4	5	8119.0718	21	4	8118.8324	41	24	8295.6265	10	−2	8323.4822	10	−6			
8	4	4	8157.3044		−35	8157.2821	9	−8	8335.0037	15	−6	8363.2318	13	3			
8	5	4	8159.5557	12	3	8159.4950	7	21	8336.4715	13	9	8363.3025		−60			
8	5	3	8182.1309	3	−1	8182.2307	12	21	8361.3680	14	1	8391.0840	2	0			
8	6	3	8193.5567	3	6	8193.5522	18	2	8369.9227	3	4	8394.2201		23			
8	6	2	8201.0481		46	8201.1367	11	−99	8380.4644	1	6	8410.8421	5	−5			
8	7	2	8227.0127	19	−12	8227.0238	20	7	8399.7342	18	−4	8424.5094		57			
8	7	1	8227.9279		10	8227.9622	20	32	8406.3013		22	8426.3323	18	1			
8	8	1	8265.1776	5	8	8265.1940		−38	8438.3888	8	25	8457.1874		22			
8	8	0	8265.2116		25	8265.2300	9	−17	8438.1256	20	8	8457.3147		35			
9	0	9	8026.2895	11	−26	8026.4992	2	4	8201.6560	1	11	8231.3742	9	−7	7871.9524	7	12
9	1	9	8026.2895	11	−26	8026.4992	2	4	8201.6560	1	11	8231.3742	9	−7	7871.9524	7	12
9	1	8	8104.8742	10	−32	8105.0686	7	17	8280.6731	10	−16	8309.8348	13	−11	7963.4902	17	22
9	2	8	8104.8742	10	−32	8105.0686	7	17	8280.6731	10	−16	8309.8348	13	−11	7963.4902	17	22

9	2	7	8173.7762	11	−18				8349.8120		−28	8378.4931	4	−3			
9	3	7	8173.7789		−19							8378.4931	4	−1			
9	3	6	8232.4591	13	−7	8232.4140		−99	8409.1580	3	19	8437.4375	32	12			
9	4	6	8232.5982	12	10	8232.6345	12	−17				8437.4329		−21			
9	4	5	8281.1196		−31				8458.4584	10	13	8486.5732		−11			
9	5	5	8281.7378	10	−6	8281.6320	15	66	8458.8226	13	0	8486.5785	8	17			
9	5	4				8322.1371	2	1	8496.0355	14	−26	8525.0354		31			
9	6	4				8322.0870	35	0	8499.4539		3	8525.5331	31	−11			
9	6	3							8520.4408	8	−9						
9	7	3							8533.8661		6	8558.0344		−42			
9	7	2							8542.6195	17	25	8575.1926		−6			
9	8	2							8563.9141		11	8591.1531	6	−6			
9	8	1							8573.4359		−12	8592.2668		−50			
9	9	1							8609.1336		−18	8626.6472		−42			
9	9	0							8609.0395		−58	8626.7087		−77			
10	0	10	8121.4627	13	10	8121.6854	9	1	8296.7263	23	−4	8327.0370	3	−21	7966.8001	26	−113
10	1	10	8121.4627	13	10	8121.6854	9	1	8296.7263	23	−4	8327.0370	3	−21	7966.8001	26	−113
10	1	9	8209.2244	11	20	8209.4312		35	8384.9442	13	−80						
10	2	9	8209.2244	11	20	8209.4312		35	8384.9442	13	−80						
10	2	8				8287.1773	6	50									
10	3	8				8287.1773	6	50									
10	3	7	8354.8791	13	13	8355.0310	24	23									
10	4	7				8355.0190	35	1									
10	4	6				8413.1615	21	40									
11	0	11				8225.8639	34	−2				8431.7490	20	25	8070.5634	18	8
11	1	11				8225.8639	34	−2				8431.7490	20	25	8070.5634	18	8
11	1	10	8322.5253	4	−12	8322.7523	1	0							8183.5466	12	2
11	2	10	8322.5253	4	−12	8322.7523	1	0							8183.5466	12	2
11	2	9				8409.5421	5	4									
11	3	9				8409.5421	5	4									
12	0	12				8339.0148	2	−20									
12	1	12				8339.0148	2	−20									
12	1	11				8445.0282	1	0									
12	2	11				8445.0282	1	0									
13	0	13				8461.1238	4	−11									
13	1	13				8461.1238	4	−11									
13	1	12				8576.2355	12	6									
13	2	12				8576.2355	12	6									
14	0	14				8592.1694	1	11									
14	1	14				8592.1694	1	11									

[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 $E^{\mathrm{exp}} - E^{\mathrm{calc}}$, 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).

Table 2
List of transitions belonging to the $2\nu_1 + 2\nu_2$ band of H_2S

Upper			Lower			Line position (cm^{-1})	Transmitance (%)	Upper energy (cm^{-1})	Mean value (cm^{-1})	δ^{a} ($\times 10^4\ cm^{-1}$)
J'	K'_a	K'_c	J	K_a	K_c					
	1			2		3	4	5	6	7
2	1	2	1	0	1	7444.0361	95.1	7457.7824	7457.7819	−12
			2	2	1	7402.6213	97.5	7457.7829		
			3	0	3	7386.3562	95.8	7457.7805		
4	0	4	3	1	3	7459.6662	97.9	7531.1314	7531.1362	7
			5	1	5	7364.7967	97.7	7531.1409		
4	1	4	3	0	3	7459.7172	96.3	7531.1414	7531.1408	−6
			5	0	5	7364.7967	97.7	7531.1402		
4	2	3	3	1	2	7473.9844	91.5	7569.0407	7569.0424	−21
			4	1	4	7454.8634	98.2	7569.0410		
			4	3	2	7395.0782	95.5	7569.0454		
			5	1	4	7358.8253	92.9	7569.0426		
5	0/1	5	4	1	4	7467.1432	95.2	7581.3208	7581.3206	−2
			6	1/0	6	7353.3753	97.9	7581.3204		
6	0/1	6	5	1/0	5	7474.0969	95.3	7640.4407	7640.4402	6
			7	1/0	7	7341.4705	98.0	7640.4403		
6	1	5	5	2	4	7489.5094	98.1	7699.7742	7699.7736	−15
			6	4	2	7324.3421	94.8	7699.7730		
6	2	5	5	1	4	7489.5655	97.0	7699.7828	7699.7828	−5
6	3	4	6	2	5	7466.1199	98.0	7747.7222	7747.7239	30
			7	2	5	7332.2482	97.1	7747.7256		
7	0/1	7	6	1/0	6	7480.5448	96.0	7708.4898	7708.4890	14
			8	1	8	7329.0806	98.6	7708.4881		
7	1	6	6	2	5	7497.0060	96.9	7778.6083	7778.6072	−12
			7	0	7	7479.6362	98.3	7778.6059		
			8	2	7	7326.1126	98.3	7778.6073		
7	2	5	6	3	4	7512.0256	97.3	7837.1720	7837.1697	−15
			8	3	6	7321.8704	98.6	7837.1677		
			8	1	8	7457.7596	97.4	7837.1671		
8	0/1	8	7	1/0	7	7486.4850	96.8	7785.4547	7785.4547	0
8	1/2	7	7	2	6	7503.9919	97.1	7866.3448	7866.3428	10
			7	1	6	7503.9919	97.1	7866.3435		
			8	0/1	8	7486.9349	70.9	7866.3424		
			9	1/2	8	7314.3266	98.6	7866.3406		
8	3	6	7	2	5	7520.0932	97.9	7935.5706	7935.5695	−62
			9	2	7	7311.1554	98.7	7935.5684		
8	7	1	8	4	4	7510.8201	96.1	8119.3854	8119.3860	10
			7	2	6	7757.0379	83.7	8119.3907		
			9	2	8	7567.3679	97.3	8119.3819		

[a] The $\delta = E^{\exp.} - E^{\mathrm{calc.}}$ is the difference between the experimental value of upper energy from column 6 and corresponding value calculated with the parameters from Tables 4–6.

initial values as discussed above. Column 2 of Tables 4 and 5 shows, for comparison, spectroscopic parameters of the ground and (0 2 0) vibrational states which are reproduced from [3] and [8], respectively. One can see satisfactory correlations of the parameters of the states discussed in the present study among themselves, and the corresponding parameters of the ground and (0 2 0) vibrational states. The results achieved for $\delta = E^{\exp.} - E^{\mathrm{calc.}}$ are illustrated in columns 4, 7, 10, 13, and 16 of Table 1.

Table 3
Statistical information on the investigated bands of the H_2S molecule

Band	Center	Number of transitions	Number of levels	$J^{\max.}$	$K_a^{\max.}$
1	2	3	4	5	6
$3\nu_1$	7576.3833	290	97	11	8
$2\nu_1 + \nu_3$	7576.5466	350	115	14	8
$\nu_1 + 2\nu_3$	7752.2638	390	103	10	9
$3\nu_3$	7779.3208	270	103	11	9
$2\nu_1 + 2\nu_2$	7419.9184	37	16	8	7
$\nu_1 + 2\nu_2 + \nu_3$	7420.0930	210	76	11	6

6. Discussion

Both the local-mode behavior and the breakdown of local-mode might be evidenced in the H_2S molecule. On the one hand, one can expect that, H_2S, being the bright example of the local mode molecules, should show good

Table 4
Spectroscopic parameters of the (3 0 0), (2 0 1), (1 0 2), and (0 0 3) vibrational states of the H_2S molecule (in cm^{-1})[a]

	(0 0 0)[b]	(3 0 0)	(2 0 1)	(1 0 2)	(0 0 3)
E	–	7576.38334(82)	7576.54659(74)	7752.26383(67)	7779.32077(62)
A	10.3601594	9.799309(349)	9.797557(343)	9.8548746(753)	9.7463284(689)
B	9.0181358	8.716744(359)	8.717961(340)	8.6672220(754)	8.754137(756)
C	4.7307832	4.5412713(709)	4.5411692(251)	4.5319629(643)	4.5651725(323)
$\Delta_K \times 10^3$	3.70326	3.7130(128)	3.6623(136)	3.52894(238)	3.59583(323)
$\Delta_{JK} \times 10^3$	−2.28026	−2.3833(114)	−2.3239(117)	−2.20774(239)	−2.34502(323)
$\Delta_J \times 10^3$	0.652598	0.66219(163)	0.65651(140)	0.637457(720)	0.673472(614)
$\delta_K \times 10^3$	−0.132618	−0.19858(386)	−0.15693(385)	−0.124685(819)	−0.16176(125)
$\delta_J \times 10^3$	0.295517	0.293025(811)	0.295308(693)	0.289610(309)	0.306688(321)
$H_K \times 10^6$	1.3811	1.3811	1.3811	1.3811	1.3811
$H_{KJ} \times 10^6$	1.2592	1.2592	1.2592	1.2592	1.2592
$H_{JK} \times 10^6$	−1.5329	−1.5329	−1.5329	−1.5329	−1.5329
$H_J \times 10^6$	0.27098	0.27098	0.27098	0.27098	0.27098
$h_K \times 10^6$	1.229	1.229	1.229	1.229	1.229
$h_{JK} \times 10^6$	−0.48509	−0.48509	−0.48509	−0.48509	−0.48509
$h_J \times 10^6$	0.13541	0.13541	0.13541	0.13541	0.13541
$L_K \times 10^9$	−4.4878	−4.4878	−4.4878	−4.4878	−4.4878
$L_{KKJ} \times 10^9$	5.48	5.48	5.48	5.48	5.48
$L_{KJ} \times 10^9$	−3.319	−3.319	−3.319	−3.319	−3.319
$L_{KJJ} \times 10^9$	1.1843	1.1843	1.1843	1.1843	1.1843
$L_J \times 10^9$	−0.1395	−0.1395	−0.1395	−0.1395	−0.1395
$l_K \times 10^9$	−1.757	−1.757	−1.757	−1.757	−1.757
$l_{KJ} \times 10^9$	−0.301	−0.301	−0.301	−0.301	−0.301
$l_{JK} \times 10^9$	0.4051	0.4051	0.4051	0.4051	0.4051
$l_J \times 10^9$	−0.07044	−0.07044	−0.07044	−0.07044	−0.07044
$P_K \times 10^{12}$	3.67	3.67	3.67	3.67	3.67
$p_K \times 10^{12}$	4.01	4.01	4.01	4.01	4.01

[a] Values in parentheses are the 1σ statistical confidence intervals. Values of parameters presented in columns 3–6 without confidence intervals were constrained to the values of corresponding parameters of the ground vibrational state from column 2 and not fitted (see text, for details).

[b] Reproduced from [3].

Table 5
Spectroscopic parameters of the (2 2 0), (1 2 1), and (0 2 2) vibrational states of the H_2S molecule (in cm^{-1})[a]

	(0 2 0)[b]	(2 2 0)	(1 2 1)	(0 2 2)
E	2353.964684	7419.9184(34)	7420.09300(95)	7502.37(93)
A	10.11408795	10.70542(130)	10.696157(993)	11.3067(287)
B	9.44627863	9.243413(857)	9.249218(919)	9.244(121)
C	4.60765546	4.480125(168)	4.4826268(843)	4.4484(896)
$\Delta_K \times 10^3$	5.621785	5.4330(279)	5.2636(119)	5.621785
$\Delta_{JK} \times 10^3$	−3.290169	−3.3916(200)	−3.09704(739)	−3.290169
$\Delta_J \times 10^3$	0.880997	0.89768(231)	0.85767(138)	0.880997
$\delta_K \times 10^3$	0.122199	0.122199	0.122199	0.122199
$\delta_J \times 10^3$	0.40983	0.40983	0.40983	0.40983
$H_K \times 10^6$	4.55276	4.55276	4.55276	4.55276
$H_{KJ} \times 10^6$	0.49084	0.49084	0.49084	0.49084
$H_{JK} \times 10^6$	−2.317344	−2.317344	−2.317344	−2.317344
$H_J \times 10^6$	0.506367	0.506367	0.506367	0.506367
$h_K \times 10^6$	3.440503	3.440503	3.440503	3.440503
$h_{JK} \times 10^6$	−0.843633	−0.843633	−0.843633	−0.843633
$h_J \times 10^6$	0.2536025	0.2536025	0.2536025	0.2536025
$L_K \times 10^9$	−18.7187	−18.7187	−18.7187	−18.7187
$L_{KKJ} \times 10^9$	22.7863	22.7863	22.7863	22.7863
$L_{KJ} \times 10^9$	−10.3252	−10.3252	−10.3252	−10.3252
$L_{KJJ} \times 10^9$	2.38399	2.38399	2.38399	2.38399
$L_J \times 10^9$	−0.314052	−0.314052	−0.314052	−0.314052
$l_K \times 10^9$	−9.38637	−9.38637	−9.38637	−9.38637
$l_{KJ} \times 10^9$	–	–	–	–
$l_{JK} \times 10^9$	0.71741	0.71741	0.71741	0.71741
$l_J \times 10^9$	−0.1590498	−0.1590498	−0.1590498	−0.1590498
$P_K \times 10^{12}$	38.226	38.226	38.226	38.226
$p_K \times 10^{12}$	17.7738	17.7738	17.7738	17.7738

[a] Values in parentheses are the 1σ statistical confidence intervals. Values of parameters presented in columns 3–5 without confidence intervals were constrained to the values of corresponding parameters of the ground vibrational state from column 2 and not fitted (see text, for details).

[b] Reproduced from [8].

Table 6
Parameters of resonance interactions between the states of the $(v = 3)$ poliad of the H_2S molecule (in cm^{-1})[a,b]

Fermi type interaction					
		$F_{xy}^{1-3} \times 10^3$	0.12388(991)		
$F_{xy}^{1-4} \times 10$	−0.4331(433)	$F_{xyK}^{1-4} \times 10^3$	0.1743(499)	$F_{xyJ}^{1-4} \times 10^3$	0.5555(417)
$F_{xy}^{5-6} \times 10$	0.24733(953)	$F_{xyK}^{5-6} \times 10^3$	−0.2703(121)		
Coriolis type interactions					
$C_{y}^{1-5} \times 10^2$	−0.1889(158)	$C_{yK}^{1-5} \times 10^4$	−1.654(117)	$C_{yJ}^{1-5} \times 10^4$	0.839(118)
$C_{yJJ}^{1-5} \times 10^6$	0.2262(622)	C_{xz}^{1-5}	−0.433523(414)		
$C_{xz}^{2-5} \times 10^4$	0.5619(321)				
$C_{yK}^{1-6} \times 10^3$	−0.7692(818)	$C_{yJ}^{1-6} \times 10^3$	3.418(167)		
$C_{y}^{2-6} \times 10$	−0.11408(132)	$C_{yJJ}^{2-6} \times 10^5$	0.1409(117)	C_{xz}^{2-6}	−0.30748(243)
$C_{yxy}^{2-6} \times 10^5$	0.3932(350)				
C_{xz}^{4-7}	−0.1413599(712)	$C_{xzK}^{4-7} \times 10^5$	−0.4472(830)	$C_{xzJ}^{4-7} \times 10^5$	1.075(112)

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

[b] Notations of superscripts $(v - v')$ at resonance interaction parameters correspond notations in the right-hand side of Eq. (3).

local mode behavior for the reasons that, the mass of the central S atom is considerably larger than the masses of H atoms; equilibrium value of the inter-bond angle is very close to $\pi/2$; and vibrational interactions between the stretching and bending modes are weak. On the other hand, being a light molecule, with large values of all spectroscopic parameters, rotationally dependent resonance interaction existing not only inside "local mode" pairs, but also between different pairs, an appearance of local perturbations which will destroy the exact local mode behavior, can be also expected in this molecule.

Comparison of the results of the present study with earlier investigations of the high-resolution spectra of H_2S molecule definitely confirm the local mode behavior of the $(v0^+,0)/(v0^-,0)$ pair of vibrational states. In particular, as is seen from Table 7, The difference between the bands centers in the pair of states $(v0^+,0)$ and $(v0^-,0)$ is decreasing from $10.10282\,\text{cm}^{-1}$ for $v = 1$ to 0 for $v = 4$. Analogously, the value of the Coriolis parameter iC_y is decreasing from $-0.10118\,\text{cm}^{-1}$ for $v = 1$ to 0 for $v = 4$. The values of the C_{xz} parameters are considerably larger than the values of iC_y for all the pairs of states $(v0^+,0)$ and $(v0^-,0)$, which also indicates the local mode tendency. Moreover, in accordance with the general vibration–rotational theory, [25], the main parts of the C_{xz} parameter for the states $(v\,0\,0)$ and $(v-1\,0\,1)$ (in normal mode notations, which correspond the $(v0^+,0)$ and $(v0^-,0)$ states, in local mode notations) can be estimated by the expression

$$C_{xz} = \text{const} \times v^{1/2}. \tag{9}$$

If take into account Eq. (9), one can see that the absolute values of the C_{xz} parameter in Table 7 (C_{xy} for the $(40^+,0)/(40^-,0)$ pair, [12]) correlate with each other for all mentioned pairs of states. However, one can find that the signs of C_{xz} parameters for the pairs of states $(v0^+,0)/(v0^-,0)$ $(v = 1, 2, 3)$, is different with that of the states $(40^+,0)/(40^-,0)$. Actually, as it follows the general vibration–rotational theory, [25], ambiguities in signs of some spectroscopic parameters, Coriolis parameters in particular, are caused by ambiguities in a choice of the phase coefficients of so-called transformation coefficients $l_{N\alpha\lambda}$. It is known also that the simultaneous change of signs of all Coriolis type parameters in the effective Hamiltonian Eqs. (3)–(7) does not change the results of diagonalization of the Hamiltonian matrix. From this point of view, results of the fit for the states (3 0 1) and (2 0 2) ((3 0 1) and (4 0 0) in our notations), see the second column of Table 2 in [12], must be exactly the same, either in plus or minus sign of the C_{xy} parameter.

Table 7
Some spectroscopic parameters of the H_2S molecule (in cm^{-1})

$(v0^+,0)/(v0^-,0)$			
Parameter	v	Value	Ref.
iC_y	1	−0.10118	[9]
	2		
	3	−0.001889	[Present]
	4	0.0	[12]
C_{xz}	1	−0.1546236	[9]
	2		
	3	−0.433523	[Present]
	4	0.4914878	[12]
$\delta_{\text{vib.}}$[a]	1	10.10282	[9]
	2		
	3	0.1633	[Present]
	4	0.0	[12]

[a] The $\delta_{\text{vib.}} = \nu^{(v0^-,0)}$ - $\nu^{(v0^+,0)}$.

It is also interesting to compare the results obtained for the bands centers in the present study and in some earlier investigations. Table 8 shows the results of such comparison. Our results are presented in column 4. Columns 5, 6, 7, and 8 give the values of corresponding band centers derived from experimental data [10], purely quantum mechanical calculations with the MORBID program system [20], MORBID combined with a so-called EKE (Exact Kinetic Energy) approach

Table 8
Bands centers of the ($v = 3$) poliad of the H_2S molecule (in cm^{-1})

Band	State		Value				
	NMN[a]	LMN[a]	Our	Ref. [10]	Ref. [20]	Ref. [21]	Ref. [19]
1	2	3	4	5	6	7	8
$3\nu_1$	(3 0 0)	$(30^+, 0)$	7576.3833	7576.381	7576.45	7576.42	7589.4
$2\nu_1 + \nu_3$	(2 0 1)	$(30^-, 0)$	7576.5466	7576.545	7576.42	7576.48	7589.4
$\nu_1 + 2\nu_3$	(1 0 2)	$(21^+, 0)$	7752.2638	7752.264	7752.40	7752.65	7768.4
$3\nu_3$	(0 0 3)	$(21^-, 0)$	7779.3208	7779.319	7779.60	7779.80	7789.4
$2\nu_1 + 2\nu_2$	(2 2 0)	$(20^+, 2)$	7419.9184	—	7420.03	—	7451.5
$\nu_1 + 2\nu_2 + \nu_3$	(1 2 1)	$(20^-, 2)$	7420.0930	7420.092	7419.92	7419.64	7452.1
$2\nu_2 + 2\nu_3$	(0 2 2)	$(11, 2)$	7502.37	—	7517.74	7515.90[b]	7546.9

[a] Abbreviation NMN is "normal mode notation", LMN is "local mode notation."

[b] P. Jensen and O. Polyansky, private communication.

[21], and ab initio three-dimensional potential energy surface, respectively. One can see good correlations between the data of columns 4–6 with the exception of the center of the last band, $2\nu_2 + 2\nu_3$. In this case, this band was not discussed in [10]; ab initio result gives considerably larger value compared with other two ones. The difference between the MORBID result, [20,21], and our estimation is about 13–15 cm^{-1}, while it is difficult to tell exactly which results is better. On the one hand, the MORBID calculations, [20,21], were based on the limited number of experimental data. In this case, as the analogous MORBID calculations for the H_2Se molecule has shown, [26], the increasing of the number of input data (especially, for excited bending states) can produce perceptible changes of the final potential surface, and, as the consequence, of the predicted band centers. On the other hand, we clearly understand that the state (0 2 2) was a "dark" state in our analysis. So, it is more suitable to consider its parameters derived from the fit (the last column of Table 5), as "fitted" parameters only, without attaching their values with large physical importance.

If one will fit rovibrational energy values with $J \leqslant 5$ of the lowest stretching local mode states $(30^+, 0)$ and $(30^-, 0)$ separately without taking into account any interactions with other vibrational states in this poliad, a small *rms* value of 0.0009 cm^{-1} can be derived. In this case, as a full coincidence with the local mode theory, the values of all rotational parameters and centrifugal distortion coefficients are close to each other for the vibrational states, $(30^+, 0)$ and $(30^-, 0)$. However, beginning with $J = 6$, the rotational structures of the $(30^+, 0)$ and $(30^-, 0)$ states begin to be locally perturbed by the (0 2 2) ($(11^+, 2)$ in local mode notations) vibrational state. Then, resonance interactions among the pairs $(30^\pm, 0)$, $(20^\pm, 2)$, and $(21^\pm, 0)$, begin to play an important role for the states with $J \geqslant 8 - 9$. As the result, numerous of different resonance interactions should be taken into account, which destroy the local mode picture of the rotational structure of the $(30^+, 0)$ and $(30^-, 0)$ states. As the consequence, spectroscopic parameters of the same name come to be more different from each other in the final fit when energy levels with $J \geqslant 8 - 9$ are used in the fitting.

7. Conclusion

High-resolution Fourier transform spectrum of the H_2S molecule was studied in the region of 7300–7900 cm^{-1}. More than 1550 observed transitions yielded 97, 115, 103, 103, 76, and 16 upper state rovibrational energies of the states (3 0 0), (2 0 1), (1 0 2), (0 0 3), (1 2 1), and (2 2 0), respectively. These energies were fitted using a Watson-type Hamiltonian, A-reduction, I^r representation, taking into account resonance interactions. The derived 54 diagonal and 21 resonance interaction parameters reproduce the rovibrational energy levels with *rms* deviation of 0.0022 cm^{-1}.

Acknowledgments

This work was jointly supported by the National Project for the Development of Key Fundamental Sciences in China, the National Natural Science Foundation of China (20103007, 50121202, 20210102154), and the Chinese Academy of Science. O. N. Ulenikov and E. Bekhtereva thank University of Science and Technology of China for guest professorship in 2003–2004 years.

References

[1] S.P. Belov, K.M.T. Yamada, G. Winnewisser, L. Poteau, R. Bocquet, J. Demaison, O. Polyansky, M.Yu. Tretyakov, J. Mol. Spectrosc. 173 (1995) 380–390.

[2] K.M.T. Yamada, S. Klee, J. Mol. Spectrosc. 166 (1994) 395–405.

[3] J.-M. Flaud, C. Camy-Peyret, J.W.C. Johns, Can. J. Phys. 61 (1983) 1462–1473.

[4] A.V. Burenin, T.M. Fevralskikh, A.A. Melnikov, S.M. Shapin, J. Mol. Spectrosc. 109 (1985) 1–7.

[5] J.R. Gillis, T.H. Edwards, J. Mol. Spectrosc. 85 (1981) 55–73.

[6] O.N. Ulenikov, A.B. Malikova, M. Koivusaari, S. Alanko, R. Anttila, J. Mol. Spectrosc. 176 (1996) 229–235.

[7] L. Lechuga-Fossat, J.-M. Flaud, C. Camy-Peyret, J.W.C. Johns, Can. J. Phys. 62 (1984) 1889–1923.

[8] L.R. Brown, J.A. Crisp, D. Crisp, O.V. Naumenko, M.A. Smirnov, L.N. Sinitsa, A. Perrin, J. Mol. Spectrosc. 188 (1998) 148–174.

[9] O.N. Ulenikov, G.A. Onopenko, M. Koivusaari, S. Alanko, R. Anttila, J. Mol. Spectrosc. 176 (1996) 236–250.

[10] A.D. Bykov, O.V. Naumenko, M.A. Smirnov, L.N. Sinitsa, L.R. Brown, J. Crisp, D. Crisp, Can. J. Phys. 72 (1994) 989–1000.

[11] L. Lechuga-Fossat, J.-M. Flaud, C. Camy-Peyret, P. Arcas, M. Cnisenier, Mol. Phys. 61 (1987) 23–32.

[12] M.S. Child, O.V. Naumenko, M.A. Smirnov, L.R. Brown, Mol. Phys. 92 (1997) 885–893.

[13] Y. Ding, O. Naumenko, S.-M. Hu, Q.S. Zhu, E. Bertseva, A. Campargue, J. Mol. Spectrosc. 217 (2003) 222–238.

[14] O. Naumenko, A. Campargue, J. Mol. Spectrosc. 209 (2001) 242–253.

[15] J.-M. Flaud, R. Großkloß, S.B. Rai, R. Stuber, W. Demtröder, D.A. Tate, L.-G. Wang, Th.F. Gallagher, J. Mol. Spectrosc. 172 (1995) 275–281.

[16] O. Vaittinen, L. Biennier, A. Campargue, J.-M. Flaud, L. Halonen, J. Mol. Spectrosc. 184 (1997) 288–299.

[17] J.-M. Flaud, O. Vaittinen, A. Campargue, J. Mol. Spectrosc. 190 (1998) 262–268.

[18] O. Naumenko, A. Campargue, J. Mol. Spectrosc. 210 (2001) 224–232.

[19] J. Senekowitsch, S. Carter, A. Zilch, J. Chem. Phys. 90 (1989) 783–794.

[20] I.N. Kozin, Per Jensen, J. Mol. Spectrosc. 163 (1994) 483–509.

[21] O.L. Polyansky, Per Jensen, J. Tennyson, J. Mol. Spectrosc. 178 (1996) 184–188.

[22] Per Jensen, Mol. Phys. 98 (2000) 23–32.

[23] J.K.G. Watson, J. Chem. Phys. 46 (1967) 1935–1949.

[24] I.M. Mills, A.G. Robiette, Mol. Phys. 56 (1985) 743–765.

[25] D. Papousek, M.R. Aliev, Molecular Vibration-Rotation Spectra, Elsevier, Amsterdam, Oxford, New York, 1982.

[26] O.N. Ulenikov, E.S. Bekhtereva, N.A. Sanzharov, Per Jensen, A refined potential energy function for the electronic ground state of H_2Se, J. Mol. Spectrosc. (accepted).