

Vibrational spectrum of the H₂S molecule

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Parameters of the effective vibrational Hamiltonian of the H₂S molecule are derived using an extended experimental data set. The Darling–Dennison and weak Fermi-type resonance interactions were taken into account in the effective Hamiltonian. As a result of fitting to 52 experimental band origins, 25 vibrational constants were derived, which reproduce the initial data accurate to 0.03 cm⁻¹.

Introduction

Experimental and theoretical investigations of rotational-vibrational (RV) spectra of hydrogen sulfide attract continuous interest due to the fact that the H₂S molecule is close to the local-mode limit, which is characterized by a high degree of localization of stretching vibrations. Therefore, the RV spectrum of H₂S has an unusual character at high excitation of stretching vibrations. In particular, the rotational structure of the spectrum of a local-mode pair becomes similar to the structure of the spectrum of a C_s-type molecule, and the energy levels form four-fold clusters.^{1,2}

The reliable calculation of the vibrational spectrum allows us to follow the evolution of the local-mode effects in H₂S upon the increase of the excitation energy. It is also needed for assignment of experimental absorption spectra of hydrogen sulfide. The vibrational spectrum of the H₂S molecule has been simulated using various approaches in many papers, which are reviewed in Ref. 3.

In Refs. 3 and 4, the vibrational spectrum of H₂S was calculated based on the effective Hamiltonian proposed in Ref. 5. The parameters of the Hamiltonian were retrieved using all available experimental information. Meanwhile, new experimental data on centers of high-excited RV bands of H₂S were reported recently,^{6–9} which are presented in Table 1. As can be seen from Table 1, the error of prediction of new centers of H₂S RV bands from the data of Refs. 1, 10, and 11 achieves several reciprocal centimeters. Our previous calculation,³ based on the use of the most complete set of initial experimental

data, proved to be much better in prediction than the cited papers, but, as can be seen from Table 1, it also needs in correction.

Results and discussion

For simulation of the H₂S vibrational spectrum, we used, as before, the effective vibrational Hamiltonian⁵:

$$H = \sum_{i,j} H_{ij} |i\rangle \langle j|,$$

where

$$\begin{aligned} H_{ii} = & \sum_{\lambda} \omega_{\lambda} \left(v_{\lambda}^i + \frac{1}{2} \right) + \sum_{\lambda, \mu \geq \lambda} x_{\lambda\mu} \left(v_{\lambda}^i + \frac{1}{2} \right) \left(v_{\mu}^i + \frac{1}{2} \right) + \\ & + \sum_{\lambda, \mu \geq \lambda, \nu \geq \mu} y_{\lambda\mu\nu} \left(v_{\lambda}^i + \frac{1}{2} \right) \left(v_{\mu}^i + \frac{1}{2} \right) \left(v_{\nu}^i + \frac{1}{2} \right) + \\ & + \sum_{\lambda, \mu \geq \lambda, \nu \geq \mu, \eta \geq \nu} z_{\lambda\mu\nu\eta} \left(v_{\lambda}^i + \frac{1}{2} \right) \left(v_{\mu}^i + \frac{1}{2} \right) \left(v_{\nu}^i + \frac{1}{2} \right) \left(v_{\eta}^i + \frac{1}{2} \right) + \dots, \\ H_{ij} = & \left\{ \Gamma_{DD} + \gamma_2 \left(v_2 + \frac{1}{2} \right) \right\} \times \\ & \times \left\{ \left(v_1 + \frac{1}{2} \pm \frac{1}{2} \right) \left(v_1 + \frac{1}{2} \pm \frac{3}{2} \right) \left(v_3 + \frac{1}{2} \mp \frac{3}{2} \right) \left(v_3 + \frac{1}{2} \mp \frac{1}{2} \right) \right\}^{1/2}, \\ & |i\rangle = |v_1 v_2 v_3\rangle, \quad |j\rangle = |v_1 \pm 2 \ v_2 \ v_3 \mp 2\rangle, \\ H_{ij} = & F \left\{ \left(v_1 + \frac{1}{2} \pm \frac{1}{2} \right) \left(v_2 + \frac{1}{2} \mp \frac{1}{2} \right) \left(v_2 + \frac{1}{2} \mp \frac{3}{2} \right) \right\}^{1/2}, \\ & |i\rangle = |v_1 v_2 v_3\rangle, \quad |j\rangle = |v_1 \pm 1 \ v_2 \mp 2 \ v_3\rangle. \end{aligned}$$

Table 1. Accuracy of prediction of vibrational energy levels of H₂³²S molecule by different methods

v ₁ v ₂ v ₃	E _{exp} , cm ⁻¹	ΔE*, cm ⁻¹				
		this work	Ref. 3	Ref. 10	Ref. 1	Ref. 11
0 1 2	6385.299	0.008	0.122	-1.199	0.591	0.601
2 2 0	7419.916	-0.027	-0.083	-3.316	0.114	0.284
1 3 1	8539.561	-0.015	-0.133	-4.961	-0.631	-5.561
2 3 0	8539.925	0.016	-0.253	-5.361	0.005	-5.725
1 4 1	9647.167	0.012	-0.353	-7.267	-2.107	-16.567
2 2 1	9806.667	-0.004	-0.206	-2.267	-1.297	3.933
1 2 2	9806.733	0.05	-0.159	-2.333	-1.233	3.867

* ΔE = E_{exp} - E_{calc}

The set of parameters of the effective Hamiltonian obtained in Ref. 3 was taken as the initial approximation. The fitting incorporated 52 experimental vibrational energy levels, including seven new levels presented in Table 1. It should be noted that the vibrational energies of the states (012) and (230): 6385.299 and 8539.925 cm^{-1} , respectively, are not derived directly from the experiment, because the corresponding transitions $0_{00}-1_{11}$ were absent in the spectrum, but retrieved from fitting to the available experimental levels. These vibrational energies are determined accurate to 0.02 cm^{-1} .

To reconstruct the initial data with high accuracy (0.03 cm^{-1}), three additional (with respect to the set from Ref. 3) parameters were varied: Y_{112} , Y_{223} , and Z_{1222} , which are responsible for the anharmonic effects connected with excitation of the bending vibration. The complete set of the parameters of the vibrational Hamiltonian is given in Table 2.

The experimental and calculated energy levels are presented in Table 3 along with their vibrational assignment by the method of normal and local modes.

The 5th and 11th columns of Table 3 give the references to the papers, the experimental data are taken from. The experimental energy levels marked by asterisk correspond to the "dark" states and were not included in fitting. The deviation from the calculation for such levels achieves 3.3 cm^{-1} , and, in our opinion, the calculation is more accurate than the experimental vibrational energy, which is estimated roughly from individual RV energy levels or from the resonance interaction of the corresponding "dark" state with a "light" state.

The absorption spectrum of the hydrogen sulfide molecule in the range 8500–8900 cm^{-1} was analyzed in Ref. 12. The fitting to the observed RV energy levels yielded the spectroscopic parameters of six vibrational states, four of which were "dark." At the same time, in Ref. 12 no one experimental energy level for the "dark" states was determined. The initial values of the vibrational energies of the "dark" states were taken from Ref. 1. These values remained fixed for the states (310) and (013) (8877.73 and

Table 2. Parameters of the effective vibrational Hamiltonian of the H_2^{32}S molecule, cm^{-1}

Parameter	Value	Parameter	Value	Parameter	Value
ω_1	2719.936(240)	$y_{111} \cdot 10$	-1.539(420)	$z_{1111} \cdot 100$	2.921(370)
ω_2	1212.9385(710)	$y_{112} \cdot 10$	2.958(610)	$z_{1112} \cdot 100$	-8.02(100)
ω_3	2735.8186(810)	$y_{113} \cdot 10$	4.113(210)	$z_{1133} \cdot 10$	-1.2659(500)
		y_{123}	-1.0681(140)	$z_{1222} \cdot 1000$	-5.30(150)
x_{11}	-24.232(160)	$y_{133} \cdot 10$	8.373(400)	$z_{1333} \cdot 10$	-1.0892(560)
x_{12}	-17.591(110)	$y_{222} \cdot 100$	-6.124(260)	$z_{2333} \cdot 100$	-6.622(210)
x_{13}	-96.725(120)	$y_{223} \cdot 100$	8.57(110)		
x_{22}	-5.3411(240)			Γ_{DD}	-23.39195(320)
x_{23}	-21.1302(470)			$F \cdot 10$	5.670(320)
x_{33}	-24.4079(190)			$\gamma_2 \cdot 10$	-2.5634(300)

Note. 68% confidence intervals in the units of the last significant digit are given in parenthesis.

Table 3. Experimental and calculated vibrational energy levels of the H_2^{32}S molecule, cm^{-1}

Normal modes $v_1 v_2 v_3$	Local modes $mn \pm, v$	$E_{\text{calc.}}$ cm^{-1}	$E_{\text{exp.}}$ cm^{-1}	Ref.	Exp.– calc., $\text{cm}^{-1} \cdot 10^{-3}$	Normal modes $v_1 v_2 v_3$	Local modes $mn \pm, v$	$E_{\text{calc.}}$ cm^{-1}	$E_{\text{exp.}}$ cm^{-1}	Ref.	Exp.– calc., $\text{cm}^{-1} \cdot 10^{-3}$
1	2	3	4	5	6	7	8	9	10	11	12
0 1 0	00+,1	1182.562	1182.5770	14	14	0 3 1	10–,3	6077.594	6077.5954	4	2
0 2 0	00+,2	2353.951	2353.9644	4	14	2 1 0	20+,1	6288.178	6288.1462	4	-32
1 0 0	10+,0	2614.401	2614.4080	4	7	1 1 1	20–,1	6289.184	6289.1735	4	-10
0 0 1	10–,0	2628.421	2628.4551	4	34	0 1 2	11+,1	6385.291	6385.2990	7	8
0 3 0	00+,3	3513.783	3513.7900	4	7	0 6 0	00+,6	6920.104			
1 1 0	10+,1	3779.158	3779.1665	4	8	0 4 1	10–,4	7204.290			
0 1 1	10–,1	3789.276	3789.2688	4	-7	1 4 0	10+,4	7204.435			
0 4 0	00+,4	4661.674	4661.6770	4	3	2 2 0	20+,2	7419.943	7419.9160	8	-27
1 2 0	10+,2	4932.692	4932.6992	4	7	1 2 1	20–,2	7420.111	7420.0923	4	-19
0 2 1	10–,2	4939.127	4939.1044	4	-23	0 2 2	11+,2	7516.795			
2 0 0	20+,0	5144.979	5144.9862	4	7	1 0 2	30+,0	7576.432	7576.3816	4	-50
1 0 1	20–,0	5147.201	5147.2205	4	19	2 0 1	30–,0	7576.529	7576.5450	4	16
0 0 2	11+,0	5243.117	5243.1014	4	-16	3 0 0	21+,0	7752.211	7752.2644	4	53
0 5 0	00+,5	5797.243	5797.2350	4	-8	0 0 3	21–,0	7779.298	7779.3195	4	22
1 3 0	10+,3	6074.589	6074.5823	4	-7	0 7 0	00+,7	8029.877			

Table 3 continued

1	2	3	4	5	6	7	8	9	10	11	12
0 5 1	10-,5	8318.834				3 1 2	50+,1	13222.741		18	26
1 5 0	10+,5	8321.811				0 3 4	31+,3	13458.347			
1 3 1	20-,3	8539.576	8539.5610	9	-15	3 3 1	31-,3	13461.653			
2 3 0	20+,3	8539.909	8539.9250	9	16	4 3 0	22+,3	13556.618			
0 3 2	11+,3	8637.167	8637.1740	9	7	1 1 4	41+,1	13601.362			
1 1 2	30+,1	8697.147	8697.1420	4	-5	4 1 1	41-,1	13601.979			
2 1 1	30-,1	8697.170	8697.1550	4	-15	5 1 0	32+,1	13781.983			
3 1 0	21+,1	8878.383				0 1 5	32-,1	13802.386			
0 1 3	21-,1	8896.894				3 2 2	50+,2	14284.724	14284.7050	19	-19
0 6 1	10-,6	9420.842				2 2 3	50-,2	14284.728	14284.7050	19	-23
1 6 0	10+,6	9426.309				3 0 3	60-,0	14291.157	14291.1220	19	-35
1 4 1	20-,4	9647.155	9647.1670	6	12	4 0 2	60+,0	14291.161	14291.1220	19	-39
0 4 2	20+,4	9647.723				1 2 4	41+,2	14666.948			
2 4 0	11+,4	9745.927				4 2 1	41-,2	14667.503			
2 2 1	30-,2	9806.671	9806.6670	6	-4	1 0 5	51-,0	14761.726			
1 2 2	30+,2	9806.683	9806.7330	6	50	2 0 4	51+,0	14761.815			
3 0 1	40-,0	9911.033	9911.0230	4	-10	5 2 0	32+,2	14855.009			
2 0 2	40+,0	9911.062	9911.0230	4	-39	0 2 5	32-,2	14862.216			
3 2 0	21+,2	9993.536				6 0 0	42+,0	15041.462			
0 2 3	21-,2	10003.864				5 0 1	42-,0	15044.735			
0 0 4	31+,0	10188.329	10188.3010	4	-28	0 0 6	33+,0	15144.776			
1 0 3	31-,0	10194.455	10194.4480	4	-7	3 3 2	50+,3	15334.423			
4 0 0	22+,0	10292.272				2 3 3	50-,3	15334.431			
1 5 1	20-,5	10742.441				3 1 3	60-,1	15339.782			
0 5 2	20+,5	10743.032				4 1 2	60+,1	15339.784			
2 5 0	11+,5	10842.595				1 3 4	41+,3	15721.005			
2 3 1	30-,3	10904.618	10905.790*	15		4 3 1	41-,3	15721.308			
1 3 2	30+,3	10904.640	10905.790*	15		1 1 5	51-,1	15812.776			
3 1 1	40-,1	11008.661	11008.6840	15	23	2 1 4	51+,1	15812.886			
2 1 2	40+,1	11008.689	11008.6840	15	-5	0 3 5	32-,3	15911.614			
3 3 0	21+,3	11097.163	11097.1610	15	-2	5 3 0	32+,3	15916.667			
0 3 3	21-,3	11099.793	11102.215*	15		6 1 0	42+,1	16095.653			
0 1 4	31+,1	11290.469				5 1 1	42-,1	16098.937			
1 1 3	31-,1	11294.451				0 1 6	33+,1	16194.038			
4 1 0	22+,1	11390.260				4 0 3	70-,0	16334.153	16334.1620	3	9
2 4 1	30-,4	11990.601				3 0 4	70+,0	16334.157	16334.1620	3	5
1 4 2	30+,4	11990.629				3 2 3	60+,2	16378.263			
3 2 1	40-,2	12095.186				4 2 2	60-,2	16378.263			
2 2 2	40+,2	12095.213				1 2 5	51-,2	16852.727			
2 0 3	50-,0	12149.439	12149.4580	16	19	2 2 4	51+,2	16852.863			
3 0 2	50+,0	12149.442	12149.4580	16	16	2 0 5	61-,0	16901.492			
0 4 3	21-,4	12184.263				1 0 6	61+,0	16901.520			
3 4 0	21+,4	12188.777				0 2 6	42+,2	17136.605			
0 2 4	31+,2	12380.598				5 2 1	42-,2	17142.754			
1 2 3	31-,2	12383.672				6 2 0	33+,2	17235.363			
4 2 0	22+,2	12478.561	12481.847*	17		5 0 2	52+,0	17278.965			
1 0 4	41+,0	12524.616	12524.6280	17	12	6 0 1	52-,0	17280.152			
4 0 1	41-,0	12525.192	12525.2020	17	10	3 1 4	70+,1	17354.152			
5 0 0	32+,0	12698.191				4 1 3	70-,1	17354.152			
0 0 5	32-,0	12732.567				7 0 0	43+,0	17457.191			
1 3 3	40-,3	13170.187	13169.668*	18		0 0 7	43-,0	17483.180			
2 3 2	40+,3	13170.212	13169.668*	18		1 1 6	61-,1	17925.230			
2 1 3	50-,1	13222.733	13222.7670	18	34	2 1 5	61+,1	17925.230			

Note. Experimental energy levels obtained from the analysis of "dark" states and not included in fitting are marked by asterisk.

8898.66 cm^{-1} , respectively), and for the states (032) and (230) they were refined from the fitting and found to be 8629.940 and 8535.03 cm^{-1} , respectively. However, new estimates of the (032) and (230) vibrational energies from Ref. 12 deviate by up to 7 cm^{-1} from the values obtained in Refs. 1, 9 and in

this work, while the last three calculations are in a good agreement with each other, which suggests that the data of Ref. 12 are determined with serious errors, which are caused, certainly, by the absence of the experimental data for the high-excited (032) and (230) RV states in Ref. 12.

Conclusions

The parameters of the effective vibrational Hamiltonian obtained in this work allow the reconstruction of all available experimental data on the vibrational energy levels of the hydrogen sulfide molecule with a high accuracy of 0.03 cm^{-1} . The set of the experimental data used in this work is the most complete and accurate and can be recommended as initial information for simulation of the H_2S vibrational spectrum by other theoretical methods. The parameters obtained have been used to calculate the vibrational spectrum of the H_2S molecule in a wide spectral region. The analysis has shown that the accuracy of calculation of the vibrational spectrum of the hydrogen sulfide molecule based on the simple method of effective Hamiltonian is comparable with the accuracy achieved when using more general and cumbersome methods of retrieval of the potential energy surface.^{1,13}

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References

1. I.N. Kozin and P. Jensen, *J. Mol. Spectrosc.* **163**, 482–509 (1994).
2. M.S. Child, O.V. Naumenko, M.A. Smirnov, and L.R. Brown, *Mol. Phys.* **92**, 885–893 (1997).
3. O. Naumenko and A. Campargue, *J. Mol. Spectrosc.* **210**, 224–232 (2001).
4. A. Bykov, O. Naumenko, M. Smirnov, L. Sinitsa, L.R. Brown, J. Crisp, and D. Crisp, *Can. J. Phys.* **72**, 989–1000 (1994).
5. A.D. Bykov, Yu.S. Makushkin, and O.N. Ulenikov, *J. Mol. Spectrosc.* **99**, 221–227 (1983).
6. Y. Ding, O. Naumenko, S.-M. Hu, Q. Zhu, E. Bertseva, and A. Campargue, *J. Mol. Spectrosc.* **217**, 222–238 (2003).
7. L.R. Brown, O.V. Naumenko, E.R. Polovtseva, and L.N. Sinitsa, *Proc. SPIE* **5311**, 59–67 (2003).
8. L.R. Brown, O.V. Naumenko, E.R. Polovtseva, and L.N. Sinitsa, *Proc. SPIE* **5396**, 42–48 (2003).
9. L.R. Brown, O.V. Naumenko, E.R. Polovtseva, and L.N. Sinitsa, *Proc. SPIE* **5743**, 1–7 (2004).
10. L. Halonen and T. Carrington, *J. Chem. Phys.* **88**, 4171–4185 (1988).
11. Y. Zheng and S. Ding, *J. Mol. Spectrosc.* **201**, 109–115 (2000).
12. O.N. Ulenikov, A.-W. Liu, E.S. Bekhtereva, S.V. Grebneva, W.-P. Deng, O.V. Gromova, and S.-M. Hu, *J. Mol. Spectrosc.* (2004) (in press).
13. V.I.G. Tyuterev, S.A. Tashkun, and D. Schwenke, *Chem. Phys. Lett.* **348**, 223–234 (2001).
14. O.N. Ulenikov, A.B. Malikova, M. Koivussaari, S. Alanko, and R. Anttila, *J. Mol. Spectrosc.* **176**, 229–235 (1996).
15. O. Naumenko and A. Campargue, *J. Mol. Spectrosc.* **209**, 242–253 (2001).
16. J.-M. Flaud, R. Großkloß, S.B. Rai, R. Stuber, W. Demtroder, D.A. Tate, L.-G. Wang, and Th.F. Gallagher, *J. Mol. Spectrosc.* **172**, 275–281 (1995).
17. O. Vahtinen, L. Biennier, A. Campargue, J.-M. Flaud, and L. Halonen, *J. Mol. Spectrosc.* **184**, 228–289 (1997).
18. A. Campargue and J.-M. Flaud, *J. Mol. Spectrosc.* **194**, 43–51 (1999).
19. J.-M. Flaud, O. Vahtinen, and A. Campargue, *J. Mol. Spectrosc.* **190**, 262–268 (1998).