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Joint ro-vibrational analysis of the HDS high resolution infrared data

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Abstract

High resolution Fourier transform spectra of the HDS molecule were recorded and analyzed for the first time in the region of the bands $\nu_1 + 2\nu_2$ (3938.6 cm^{-1}), $\nu_1 + \nu_3$ (4522.6 cm^{-1}), $2\nu_2 + \nu_3$ (4638.8 cm^{-1}), $2\nu_1 + \nu_2$ (4767.7 cm^{-1}), $\nu_1 + \nu_2 + \nu_3$ (5525.2 cm^{-1}), $3\nu_1$ (5560.6 cm^{-1}), $\nu_1 + 2\nu_3$ (7047.2 cm^{-1}), and $2\nu_2 + 2\nu_3$ (7123.9 cm^{-1}). The ro-vibrational energies of the upper vibrational states of these bands together with the ro-vibrational energies of 12 other bands already studied at high resolution were used as inputs in a Global Fit analysis firstly described in [O.N. Ulenikov, G.A. Onopenko, H. Lin, J.-H. Zhang, Z.-Y. Zhou, Q.-S. Zhu, R.N. Tolchenov, J. Mol. Spectrosc. 189 (1998) 29–39]. In this case, the resonance interactions between the states ($v_1\ v_2\ v_3$) and ($v_1 \pm 2\ v_2 \mp 1\ v_3 \mp 1$) were taken into account. The resulting set of 143 parameters reproduces all the experimental data (2984 vibration–rotation energies of 20 vibrational states which correspond to about 9700 ro-vibrational transitions with $J^{\rm max.} = 23$) with accuracies comparable with the experimental uncertainties.

Keywords: Vibration–rotation spectra; HDS isotopic species; Fundamental bands; Spectroscopic parameters

1. Introduction

The present contribution is the continuation of our spectroscopic "global" high resolution analysis of the spectra of the hydrogen sulfide molecule. This method was first applied to the di-deuterated species [1] and since a general review of the high resolution spectroscopy studies on hydrogen sulfide has been presented in [1], we will give in this paper only the relevant information.

This investigation is dealing with the mono-deuterated, HDS, species whose spectra were studied earlier with high resolution on several occasions [2–8]. The pure rotational spectrum of the HDS molecule was discussed in [2]. The lowest ν_2 band was analyzed in Refs. [3,4]. Refs. [5] and [6] were devoted to the study of the bands $\nu_3/\nu_1 + \nu_2$ and $\nu_1/2\nu_1/\nu_2 + \nu_3$. Finally, sets of highly excited vibrational states, $2\nu_2$, $3\nu_2$ and $2\nu_3$, $3\nu_3$, $\nu_2 + 2\nu_3$, and $\nu_2 + 3\nu_3$, were investigated in [7,8], respectively. In this study we report (1) on the analysis of all the other bands corresponding to double or triple excitations of the vibrational quanta (with the exception of the $2\nu_1 + \nu_3$ band which is probably too weak to be observed in our spectra) and of the $2\nu_2 + 2\nu_3$ band and (2) on a global fit of all the available data (20 bands altogether). Experimental details are given in Section 2. Section 3 is devoted to a short theoretical background of the Global Fit method [1,9–11] applied to the HDS molecule. The results of the assignments of the newly analyzed bands are given in Section 4 and finally Section 5 reports on the results of the global fit.

2. Experimental details

The experimental details were already presented in Ref. [1] and we just give a simple description here. Deuterated

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hydrogen sulfide samples were synthesized with anhydrous sodium sulfide and deuterated phosphoric acid diluted in deuterated water. The isotope abundance of the synthesized sample was determined by a photoionization mass spectrum (PIMS) experiment which gives an $HD^{32}S$ abundance of 23.5%; 68.7% of $D_2^{32}S$ and small amounts of other isotopes are also found in the sample. The spectra in the 3850–8650 cm^{-1} region were measured with the Fourier Bruker IFS 120 HR spectrometer equipped with a path length adjustable multi-pass cell in Hefei. The experimental conditions in the different absorption regions have been listed in Table 1 of Ref. [1]. The line positions were calibrated with H_2O and CO_2 lines given by the HITRAN2004 database [12]. The accuracy of line positions of unblended and not-very-weak lines is estimated to be better than 0.001 cm^{-1} in the lower frequency part of the studied spectra and 0.002–0.003 cm^{-1} in the higher frequency region.

3. Theoretical background: Hamiltonian model

As in Ref. [1], we use an Effective Hamiltonian model for the description of the rotational structures of the polyads of interacting vibrational states:

$$H^{v-r} = \sum_{v,\tilde{v}} |v\rangle\langle\tilde{v}|H^{v\tilde{v}} \tag{1}$$

where $|v\rangle$ and $|\tilde{v}\rangle$ denote the different interacting vibrational states of a given polyad. H^{vv} denotes the diagonal operator matrix element, describing the rotational structure of a vibrational state $|v\rangle$. For the HDS-type molecules, the Watson's form, [13], of the operator H^{vv} in A reduction and I^r representation is suitable:

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

Here $J^2 = J_x^2 + J_y^2 + J_z^2$; $[A,B]_+$ denotes the anticommutator $(AB + BA)$.

Because the HDS molecule is an asymmetric top with a symmetry group isomorphous to the C_s point group, all its vibrational states are symmetric ones. As a consequence, any of the resonance interaction block $H^{vv'}(v \neq v')$ in the operator (1) can be written as a sum of two terms:

$$H^{vv'} = H^{vv'+} = H_F^{vv'} + H_C^{vv'}, \tag{3}$$

$H_F^{vv'}$ which describes resonance interactions of the pure vibrational Fermi type can be written as:

$$\begin{aligned} H_F^{vv'} = a^{vv'}\{ & F^{vv'} + F_K^{vv'} J_z^2 + F_J^{vv'} J^2 + F_{KK}^{vv'} J_z^4 + F_{KJ}^{vv'} J_z^2 J^2 \\ & + F_{JJ}^{vv'} J^4 + \cdots + F_{xy}^{vv'}(J_x^2 - J_y^2) + F_{xyK}^{vv'}[J_z^2, (J_x^2 - J_y^2)]_+ \\ & + F_{xyJ}^{vv'} J^2 (J_x^2 - J_y^2) + F_{xyKK}^{vv'}[J_z^4, (J_x^2 - J_y^2)]_+ \\ & + F_{xyKJ}^{vv'}[J_z^2 J^2, (J_x^2 - J_y^2)]_+ + F_{xyJJ}^{vv'} J^4 (J_x^2 - J_y^2) + \cdots\} \end{aligned} \tag{4}$$

$H_C^{vv'}$ which describes Coriolis-type interactions can be written as:

Table 1
Statistical information on the investigated bands of the HDS molecule

Band	Center, (cm^{-1})		Number of transitions	Number of levels	J^{max}	K_a^{max}	rms, (10^3 cm^{-1})	Ref.
	Calc. (14)	Exp.						
1	2	3	4	5	6	7	8	9
ν_2	1032.66	1032.71556	1400	229	22	10	0.4	[4]
ν_1	1902.71	1902.85624	1000	268	23	10	0.5	[6]
$2\nu_2$	2056.87	2056.96580	600	154	19	8	0.4	[7]
ν_3	2621.89	2621.45594	600	178	15	11	0.3	[5]
$\nu_1+\nu_2$	2924.88	2924.97773	900	185	22	9	0.4	[5]
$3\nu_2$	3071.97	3072.49232	400	112	18	6	0.3	[7]
$\nu_2+\nu_3$	3635.47	3634.33224	550	252	21	11	0.6	[6]
$2\nu_1$	3756.02	3756.32989	250	118	15	6	0.6	[6]
$\nu_1+2\nu_2$	3938.67	3938.63701	350	86	15	7	1.5	Present
$\nu_1+\nu_3$	4523.20	4522.65030	750	213	21	11	1.2	Present
$2\nu_2+\nu_3$	4640.64	4638.86437	300	109	19	10	1.6	Present
$2\nu_1+\nu_2$	4767.10	4767.69431	800	187	19	10	1.6	Present
$2\nu_3$	5147.97	5147.35539	900	236	23	11	1.2	[8]
$\nu_1+\nu_2+\nu_3$	5526.28	5525.26664	30	15	7	4	3.3	Present
$3\nu_1$	5559.95	5560.54225	30	13	8	1	3.3	Present
$\nu_2+2\nu_3$	6141.30	6139.73928	600	248	20	12	1.5	[8]
$\nu_1+2\nu_3$	7047.88	7047.15309	150	66	10	5	1.2	Present
$2\nu_2+2\nu_3$	7126.26	7123.89641	150	71	16	6	2.0	Present
$3\nu_3$	7578.22	7577.84009	500	128	20	6	1.5	[8]
$\nu_2+3\nu_3$	8550.18	8548.90007	200	116	17	6	2.6	[8]

$$\begin{aligned}H_C^{vv'} = b_y^{vv'}\{&C_y^{vv'} iJ_y + C_{yK}^{vv'}[iJ_y, J_z^2]_+ + C_{yJ}^{vv'} iJ_y J^2 + C_{yKK}^{vv'}[iJ_y, J_z^4]_+ \\ &+ C_{yJK}^{vv'}[iJ_y, J_z^2 J^2]_+ + C_{yJJ}^{vv'} iJ_y J^4 + \cdots\} \\ &+ b_{xz}^{vv'}\{C_{xz}^{vv'}(J_xJ_z + J_zJ_x) + C_{xzK}^{vv'}[(J_xJ_z + J_zJ_x), J_z^2]_+ \\ &+ C_{xzJ}^{vv'}(J_xJ_z + J_zJ_x)J^2 + C_{xzKK}^{vv'}[(J_xJ_z + J_zJ_x), J_z^4]_+ \\ &+ C_{xzJK}^{vv'}[(J_xJ_z + J_zJ_x), J_z^2]_+ J^2 \\ &+ C_{xzJJ}^{vv'}(J_xJ_z + J_zJ_x)J^4 + \cdots,\} \end{aligned} \tag{5}$$

The coefficients $a^{vv'}$, $b_y^{vv'}$, and $b_{xz}^{vv'}$ in Eqs. (4) and (5) depend on the considered interacting vibrational states. In our case, the analysis of the vibrational structure of the HDS molecule shows that the most likely resonance interactions exist between the states (v_1, v_2, v_3) and ($v_1 \pm 2$, $v_2 \mp 1$, $v_3 \mp 1$). In this case, the coefficients $a^{vv'}$, $b_y^{vv'}$, and $b_{xz}^{vv'}$ have the following vibrational dependence:

$$\begin{aligned} a^{v_1,v_2,v_3\ \ v_1\pm 2,v_2\mp 1,v_3\mp 1} &= b_{xz}^{v_1,v_2,v_3\ \ v_1\pm 2,v_2\mp 1,v_3\mp 1} \\ &= \mp b_y^{v_1,v_2,v_3\ \ v_1\pm 2,v_2\mp 1,v_3\mp 1} \\ &= \frac{1}{4}\sqrt{(2v_1+1\pm 1)(2v_1+1\pm 3)(2v_2+1\mp 1)(2v_3+1\mp 1)} \end{aligned} \tag{6}$$

As was discussed in Ref. [1], the spectroscopic parameters of the excited vibrational states of a normal polyatomic molecule should be only slightly different from the corresponding parameters of the ground vibrational state and can be expressed as a function of more fundamental spectroscopic quantities P^0, p^λ, etc., in the following form:

$$P^{v_1,v_2,\ldots,v_n} = P^0 + \sum_\lambda p^\lambda v_\lambda + \sum_{\lambda\mu \geqslant \lambda} p^{\lambda\mu} v_\lambda v_\mu + \cdots \tag{7}$$

Here n ($n = 3$ in our case) is the number of vibrational modes of a molecule; $P^{v_1,v_2,\ldots,v_n}$ denotes any individual spectroscopic parameter of the vibrational state (v_1, v_2, …, v_n) of the molecule (parameter of a diagonal block of the Hamiltonian (1)); P^0 is the corresponding parameter of the ground vibrational state; p^λ, $p^{\lambda\mu}$ are corrections accounting for the differences between the parameter values for the different vibrational states.

As far as the parameters $F_{\ldots}^{vv'}$ and $C_{\ldots}^{vv'}$ of the resonance blocks $H^{vv'}(v \neq v')$ are concerned, for HDS they have a similar form:

$$\begin{aligned} F_{\ldots}^{v_1,v_2,v_3\ \ v_1\pm 2,v_2\mp 1,v_3\mp 1} = F_{\ldots} &+ f_{\ldots}^1\left(v_1 + \frac{1}{2} \pm 1\right) \\ &+ f_{\ldots}^2\left(v_2 + \frac{1}{2} \mp \frac{1}{2}\right) \\ &+ f_{\ldots}^3\left(v_3 + \frac{1}{2} \mp \frac{1}{2}\right) + \cdots \end{aligned} \tag{8}$$

and

$$\begin{aligned} C_{\ldots}^{v_1,v_2,v_3\ \ v_1\pm 2,v_2\mp 1,v_3\mp 1} = C_{\ldots} &+ c_{\ldots}^1\left(v_1 + \frac{1}{2} \pm 1\right) \\ &+ c_{\ldots}^2\left(v_2 + \frac{1}{2} \mp \frac{1}{2}\right) \\ &+ c_{\ldots}^3\left(v_3 + \frac{1}{2} \mp \frac{1}{2}\right) + \cdots \end{aligned} \tag{9}$$

4. Assignments of transitions

Since the sample under study was a mixture of H_2S and of its deuterated and di-deuterated isotopic species, the bands of all three species can be found in the recorded spectra. In fact, because of strong differences in intensities of the

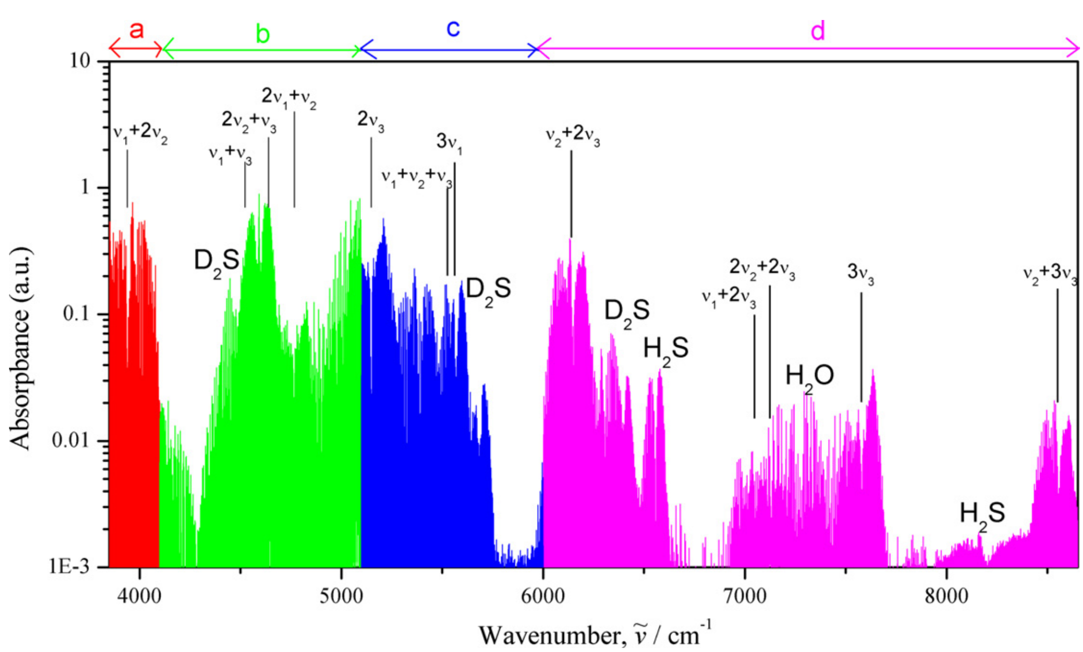

Fig. 1. Overview transmitted spectrum of the synthesized $HDS/D_2S/H_2S$ sample in the whole region 3850–8650 cm^{-1}. The band centers of HDS are marked. Experimental conditions: (a) 4445 Pa sample pressure, 87 m path length with 0.01 cm^{-1} unapodized resolution; (b) 8043 Pa sample pressure, 87 m path length with 0.008 cm^{-1} unapodized resolution; (c) 4445 Pa sample pressure, 105 m path length with 0.008 cm^{-1} unapodized resolution; (d) 8043 Pa sample pressure, 105 m path length with 0.016 cm^{-1} unapodized resolution.

different bands of hydrogen sulfide, the whole region was recorded into different parts, see Fig. 1. The corresponding experimental conditions are given in the caption to Fig. 1.

The molecular symmetry group of HDS is isomorphous to the C_s point group; as a consequence, the selection rules allow ro-vibrational transitions of the type

$$\Delta J = 0, \pm 1; \quad \Delta K_a = \pm(n); \quad \Delta K_c = \pm(2m+1) \tag{10}$$

for any of the ro-vibrational band of HDS. Here n and/or m equal to 0, 1, 2, ...

Assignments of the transitions were made with the Ground State Combination Differences method using ground state energies which were calculated using the parameters from Ref. [2]. Finally, we were able to assign more than 2550 transitions to the bands $\nu_1 + 2\nu_2$, $\nu_1 + \nu_3$, $2\nu_2 + \nu_3$, $2\nu_1 + \nu_2$, $\nu_1 + \nu_2 + \nu_3$, $3\nu_1$, $\nu_1 + 2\nu_3$, and $2\nu_2 + 2\nu_3$. Statistical information concerning the assigned bands and transitions is presented in Table 1 (see also [15]). As an illustration, two small parts of the recorded spectra are shown on Figs. 2 and 3.

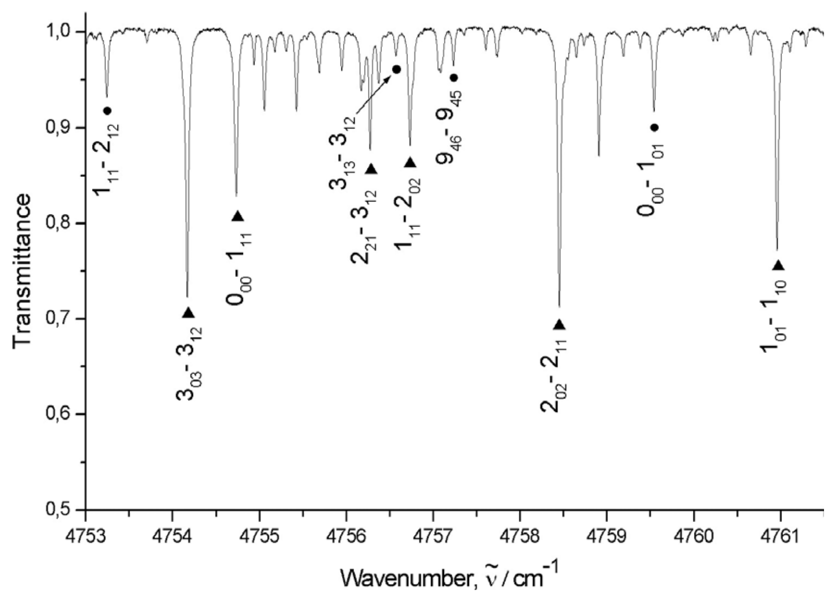

Fig. 2. Small portion of the high-resolution spectrum of HDS in the region of the band $2\nu_1 + \nu_2$. Lines belonging to the *b*- and *a*-type subbands are marked by dark triangles and dark circles, respectively. Weak unmarked lines belong to D_2S.

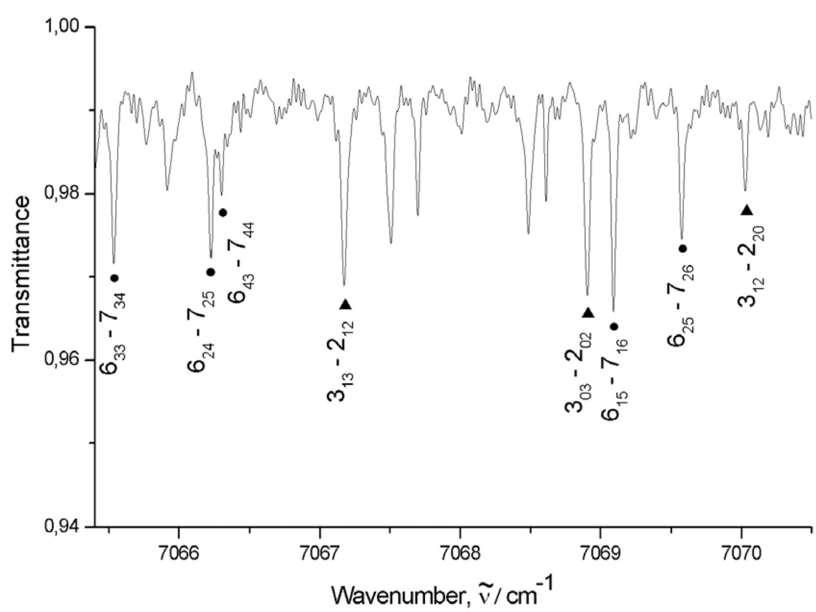

Fig. 3. Small portion of the high-resolution spectrum of HDS in the region of the weak bands $\nu_1 + 2\nu_3$ and $2\nu_2 + 2\nu_3$; lines are marked by dark triangles and dark circles, respectively. Unmarked lines belong likely to one of the D_2S bands: $2\nu_1 + 4\nu_2$ (7062 cm^{-1}, [14]), $\nu_1 + 4\nu_2 + \nu_3$ (7063 cm^{-1}, [14]), and/or $4\nu_2 + 2\nu_3$ (7114 cm^{-1}, [14]).

Table 2
Experimental ro-vibrational term values for some vibrational states of the HDS molecule (in cm^{-1})[a]

	(010)			(100)			(020)			(001)			(110)			(030)			(011)		
$J\ K_a\ K_c$	E	Δ	δ	E	Δ	δ	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	17	18	19	20	21	22
4 0 4	1109.59933	4	−21	1978.56415	5	9	2134.01402	4	11	2697.61732	8	5	3000.78618	11	−20	3149.75639	8	8	3710.59707	4	−21
4 1 4	1110.69016	2	−25	1979.76092	7	10	2135.10151	4	−2	2698.54985	9	6	3001.97487	12	−15	3150.84448	14	−7	3711.52008	15	−13
4 1 3	1128.55230	4	5	1995.85138	9	9	2154.22995	3	45	2715.44156	8	−3	3019.25224	9	−15	3171.30373	17	24	3729.63373	13	4
4 2 3	1138.11419	4	−2	2005.60931	8	9	2164.01871	7	8	2723.92569	6	0	3029.22535	9	−1	3181.34422	28	18	3738.28431	4	−3
4 2 2	1143.34098	4	13	2010.05819	3	4	2169.72374	3	33	2729.01131	3	3	3034.11071	17	−15	3187.55181	6	17	3743.85198	8	9
4 3 2	1168.84999	4	14	2035.22918	7	−4	2196.16540	6	−8	2752.05594	6	9	3060.17520	14	11	3214.99354	31	10	3767.68755	8	6
4 3 1	1169.26062	8	12	2035.54826	5	−5	2196.62788	9	2	2752.47498	7	−3	3060.53827	12	21	3215.51094	12	−17	3768.16265	18	8
4 4 1	1209.60489	7	38	2074.78525	8	−6	2238.67349	9	−14	2789.21684	4	−2	3101.39352	42	61	3259.37067	6	24	3806.40651		42
4 4 0	1209.61209	7	39	2074.79042	11	−5	2238.68190	6	−4	2789.22486		33	3101.39923	23	28	3259.38050		55	3806.41537	5	33
5 0 5	1145.36358	5	−19	2014.03765	10	10	2169.65985	3	2	2733.15050	5	12	3036.12047	8	−9	3185.30072	8	11	3745.99238	2	−13
5 1 5	1145.85844	4	−23	2014.60777	5	8	2170.14436	6	−3	2733.56335	12	22	3036.67573	10	−14	3185.77740	12	17	3746.39278	8	−4
5 1 4	1171.70462	5	16	2037.99563	7	0	2197.77505	8	47	2757.94638	6	3	3061.74484	9	−8	3215.28166	6	27	3772.48756	11	12
5 2 4	1178.20858	5	7	2044.87768	7	11	2204.34236		9	2763.60653	10	1	3068.68006	12	−9	3221.93004	6	7	3778.16809	16	7
5 2 3	1188.64384	5	24	2053.86752	4	2	2215.68291	14	51	2773.70004	6	8	3078.50440	9	−19	3234.21979	14	7	3789.16482	15	0
5 3 3	1210.70220	8	8	2075.98821	6	−4	2238.40640	10	−4	2793.45642	13	−2	3101.26617	8	4	3257.66319	26	1	3809.45410	12	17
5 3 2	1212.24378	4	16	2077.19759	7	1	2240.13576	6	3	2795.02162	6	−4	3102.63678	7	3	3259.59217	22	−8	3811.22031	17	26
5 4 2	1251.36360	5	22	2115.43878	9	−4	2280.81829	3	−14	2830.55017	6	5	3142.37515	16	34	3301.93976	13	7	3848.10753	2	17
5 4 1	1251.42721	4	22	2115.48452	5	−7	2280.89167	5	−19	2830.61785	10	−2	3142.42869	24	30				3848.18653	17	21
5 5 1	1303.63480		51	2166.21046	18	127	2335.31129		21	2878.21253	5	3	3195.25727		69						
5 5 0	1303.63546	7	41	2166.21135		−12	2335.31212	9	14	2878.21335	9	0	3195.25727	17	8						
6 0 6	1187.34503	3	−17	2055.72301	5	11	2211.45035	4	−3	2774.92465	10	−2	3077.59126	10	−2	3226.91789	11	0	3787.55658	10	−14
6 1 6	1187.55271	5	−18	2055.97436	19	17	2211.64995	7	−5	2775.09373	5	4	3077.83120	6	−3	3227.11084	15	0	3787.71728	17	−3
6 1 5	1221.72659	2	20	2087.08758	7	−4	2248.10176	5	36	2807.23060	12	2	3111.10120	5	−2	3265.95349	21	12	3822.02370	12	6
6 2 5	1225.61146	5	6	2091.39765	8	2	2251.95531	4	5	2810.52825	8	2	3115.36474	8	−3	3269.78945	14	7	3825.26696	10	11
6 2 4	1243.02983	7	30	2106.56867	20	−2	2270.80971	6	49	2827.28628	5	−1	3131.87083	13	−5	3290.14680		−29	3843.44533	11	16
6 3 4	1260.83691	7	12	2124.84778	9	3	2288.98973	3	−10	2843.03498	13	2	3150.50990	6	0	3308.74225		4	3859.45092	7	15
6 3 3	1264.96385	6	27	2128.13795	7	3	2293.59111	8	13	2847.18916	10	16	3154.21575	8	−1	3313.84476	8	−15	3864.10462	2	11
6 4 3	1301.70476	5	9	2164.42051	5	7	2331.64385	9	−21	2880.37188	12	0	3191.77023	16	3	3353.29727	15	22	3898.39141	5	7
6 4 2	1302.01253	8	6	2164.64310	6	0	2331.99851	5	−16	2880.69880	11	0	3192.03041	13	10	3353.70245	28	16	3898.77148	8	7
6 5 2	1353.54331	6	13	2214.81522	26	8	2385.65983	14	−8	2927.62959	9	−9	3244.23613	9	27	3409.62920	3	42	3947.58210	3	16
6 5 1	1353.55169	5	21	2214.82060	7	−8	2385.66956	13	−15	2927.63866	11	−26	3244.24278	24	26	3409.64070	10	47	3947.59309	11	10
6 6 1	1417.42732		36	2276.88380	29	−36	2452.23592	12	44	2985.90258	17	3	3308.86708	26	44	3479.06601	23	−36	4008.24990	38	51
6 6 0	1417.42737	2	34	2276.88380	29	−40	2452.23592	12	35	2985.90258	17	−5	3308.86708	26	38	3479.06601	23	−47	4008.24990	38	40
7 0 7	1235.60579	8	−21	2103.67262	5	7	2259.45304	3	−18	2822.99895	9	17	3125.25695	17	−11	3274.68136	16	3	3835.35344	6	8
7 1 7	1235.68832	3	−20	2103.77759	4	15	2259.53086	2	−18	2823.06445	5	12	3125.35522	16	0	3274.75530	13	9	3835.41442	23	7
7 1 6	1277.97692	6	18	2142.50965	7	0	2304.54565	6	18	2862.71378	4	5	3166.67376	8	9	3322.63312	19	9	3877.64680	12	20
7 2 6	1280.02864	5	11	2144.91035	5	−2	2306.54100	5	7	2864.40837	18	6	3168.99889	4	−2	3324.58249	18	0	3879.27698	24	32
7 2 5	1305.80229	7	34	2167.59552	11	0	2334.33215	5	40	2889.07568	11	−6	3193.57656	7	−1	3354.48168		−24	3905.92022	7	18
7 3 5	1319.01897	3	13	2181.62048	11	−6	2347.65415	6	−6	2900.55487	14	99	3207.69579	7	−3	3367.94139		7	3917.41282	6	12
7 3 4	1327.70635	6	30	2188.69132	4	0	2357.26665	4	17	2909.20559	8	−3	3215.59542	11	−7	3378.52533	3	−18	3927.02234	10	16
7 4 4	1360.65904	2	2	2221.76696	4	7	2391.17901	1	−32	2938.70402	15	−6	3249.61539	10	−3	3413.46912	24	3	3957.27649	2	0
7 4 3	1361.72403	7	0	2222.54469	3	6	2392.40154	6	−28	2939.82908	14	−10	3250.52074	15	0	3414.86075	72	−40	3958.57875	3	5
7 5 3	1412.02119	3	−9	2271.72843	8	3	2444.67781	2	−27	2985.52928	9	−9	3301.60960	7	4	3469.23835	19	0	4006.00048	10	−13
7 5 2	1412.07003	4	−12	2271.76109	27	−6	2444.73546	46	−27	2985.58360	3	−6	3301.64887	12	0	3469.30595	26	32	4006.06529	3	−17
7 6 2	1475.38384	8	−10	2333.35351	54	47	2510.67338	9	19	3043.31044	19	80	3365.74502	43	53	3538.02980	33	52	4066.12050	230	70
7 6 1	1475.38487	8	−4	2333.35351	54	−13	2510.67458	13	23	3043.31044	19	−33	3365.74502	43	−21	3538.02980	33	−86	4066.12050	230	−69

7 7 1	1550.87241	10	12	2406.71820	16	−48	2589.31319		51	3112.19913	21	−3	3442.11404	18	−17				4137.81844	11	63
7 7 0	1550.87241	10	11	2406.71820	16	−49	2589.31319		51	3112.19913	21	−4	3442.11404	18	−18				4137.81844	11	62
8 0 8	1290.18699	2	−16	2157.92705	1	23	2313.71088	2	−15	2877.40868	7	14	3179.16031	7	14	3328.63537	26	−5	3889.41942		−3
8 1 8	1290.21848	5	−12	2157.96905	5	19	2313.73996	3	−16	2877.43303	16	10	3179.19870	8	−1	3328.66255	15	3	3889.44180	20	14
8 1 7	1340.22608	5	11	2203.97244	3	−7	2366.89629	4	0	2924.22053	20	11	3228.18745	7	4	3385.12971	22	−3	3939.20442	14	25
8 2 7	1341.20793	3	12	2205.18505	7	−9	2367.83208	3	−5	2925.00953	2	0	3229.33679	10	7	3386.02663	30	−13	3939.94663	6	19
8 2 6	1376.08257	3	31	2236.21886	4	−7	2405.28530	3	15	2958.20195	19	−16	3262.81331	17	7	3426.16912	19	−53	3975.63666	16	−1
8 3 6	1384.93932	3	14	2246.05115	7	3	2414.05990	4	−12	2965.70651	9	−11	3272.54057	9	−10	3434.88909		−5	3983.00216	10	20
8 3 5	1400.25072	4	33	2258.77764	4	3	2430.87493	3	11	2980.79741	10	−3	3286.64017	14	−6	3453.27571		−16	3999.62529	7	1
8 4 5	1428.16943	5	2	2287.44822	2	9	2459.35370		−31	3005.47816		−12	3315.87016	12	−13	3482.37150	15	15	4024.67872	4	−7
8 4 4	1431.06972	3	9	2289.60040	3	10	2462.66216	4	−19	3008.51442	9	1	3318.36028	8	−14	3486.11609	24	24	4028.16639	6	−5
8 5 4	1479.16090	3	−21	2337.03023	6	16	2512.46565		−38	3051.99958	9	4	3367.46544	23	−13	3537.73473	17	−14	4073.09409	5	−28
8 5 3	1479.36597	5	−21	2337.16838	5	15	2512.70709		−39	3052.22665	2	0	3367.63096	18	−13				4073.36469	3	−27
8 6 3	1541.85428	5	−25	2398.07930	22	6	2577.72017	1	9	3109.14872	9	0	3430.96161	17	9				4132.51491	1	−46
8 6 2	1541.86094	7	−28	2398.08337	8	−3	2577.72825		10	3109.15627		−24	3430.96646	18	−18				4132.52478		−24
8 7 2	1616.77355	6	−11	2470.95965	27	−12	2655.72371	10	86	3177.50226	27	−19	3506.78832	53	16				4203.61509	19	0
8 7 1	1616.77365	6	−11	2470.95965	27	−18	2655.72371	10	74	3177.50226	27	−32	3506.78832	53	9				4203.61530	21	6
8 8 1	1703.84199	2	−28	2555.60955	32	−36	2746.38825	4	−39	3256.99895	9	−21	3594.87222	15	−85				4286.32342	3	31
8 8 0	1703.84199	2	−28	2555.60955	32	−36	2746.38825	4	−39	3256.99895	9	−21	3594.87222	15	−85				4286.32342	3	31

	(200)			(120)			(101)			(021)			(210)			(002)			(111)		
$J\ K_a\ K_c$	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
1	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
4 0 4	3830.97732	1	7	4014.5901	12	−6	4597.7711	1	−2	4715.2782	1	−12	4842.4342	11	5	5222.8821	2	−2			
4 1 4	3832.27952	2	−3	4015.7762	3	7	4598.7936	2	−5	4716.1959	13	−3	4843.7276	28	7	5223.6630	9	2			
4 1 3	3847.80369	15	−19	4034.2998	5	10	4615.1282	11	5	4735.5893	2	−3	4860.4147	5	0	5240.7900	5	2			
4 2 3	3857.96777		−18	4044.5089	0	−9	4624.0106	1	2	4744.4256	5	−4	4870.8026	6	−7	5248.4143	5	0			
4 2 2	3862.10389	10	−12	4049.8550	12	0	4628.7616	27	25	4750.5004		8	4875.3562	9	−4	5253.8361	11	2	5633.2261		50
4 3 2	3887.80544	14	−15	4076.8739	0	0	4652.3575	7	8	4775.1790	4	−6	4901.9688	4	0	5275.2827	16	0			
4 3 1	3888.08525	2	−22	4077.2849	11	8	4652.7263	28	3	4775.7182	16	36	4902.2874	10	−10	5275.7697	9	1	5658.0518	19	−2
4 4 1	3927.81298	28	−27	4119.8608	11	8	4689.9880	17	50				4943.6478	30	18	5310.5056	5	−3			
4 4 0	3927.81700		−55				4689.9880	17	−14				4943.6478	30	−32	5310.5167	12	12			
5 0 5	3866.02423	23	−2	4049.8006	4	12	4632.8852	7	−4	4750.5506		−8	4877.3368	3	2	5258.0412	3	−3			
5 1 5	3866.66330	16	7	4050.3425	10	−3	4633.3524	6	−2	4750.9406	1	−10	4877.9583	5	−4	5258.3711	6	2			
5 1 4	3889.28663	13	4	4077.1735	16	−5	4657.0013	5	0				4902.2373	12	13	5282.9746	2	0			
5 2 4	3896.60674	1	−14	4084.1788	12	−7	4663.0702	12	−16	4784.5416		−5	4909.6154	6	−3	5287.8696	6	−2			
5 2 3	3905.02656	11	0	4094.8818	3	18	4672.5676	10	−2	4796.4880		31	4918.8391	2	2	5298.5101	7	3	5677.6334	30	2
5 3 3	3927.82466		2	4118.3308	6	−14	4693.0173	2	4	4817.3482		−6	4942.2997	2	0	5316.5823	7	3			
5 3 2	3928.89110	7	6	4119.8760	12	4	4694.4049	6	−1	4819.3287	13	−4	4943.5132	11	0	5318.3806	7	1			
5 4 2	3967.71532		−23	4161.2043	1	0	4730.5594	10	12	4857.6564	11	−4	4983.8536	6	−11	5351.7684	7	−2			
5 4 1	3967.75347	20	−26	4161.2651	12	−13	4730.6161	12	11	4857.7453		−27	4983.8989	2	−7	5351.8529	9	−4	5737.8201		−25
5 5 1				4216.3286	7	2	4778.8339	5	−2	4909.3836	15	−3	5037.3413	25	4	5396.9208	4	8			
5 5 0				4216.3286	7	−6	4778.8339	11	−8				5037.3413	5	−1	5396.9214	8	2			
6 0 6	3907.20541	13	−3	4091.0685	12	−14	4674.1608	2	−3	4791.9206	4	−6	4918.2968	5	0	5299.3926	7	−1			
6 1 6	3907.49510	15	−40	4091.3017	3	14	4674.3595	7	12	4792.0741	7	−6	4918.5732	4	−3	5299.5213	5	0			
6 1 5	3937.70202	5	−17	4126.8254	22	−30	4705.6521	6	11	4828.6500	20	4	4950.9103	8	−7	5331.7532	4	−3	5710.0648	7	28

[a] Δ is experimental error in the value of energy level E (in last digits of E). The value of Δ is absent when the upper level was determined from a single transition; δ is the difference $E^{exp.} - E^{calc.}$ also in last digits of E.

(*continued on next page*)

Table 2 (*continued*)

	(200)			(120)			(101)			(021)			(210)			(002)			(111)		
$J\ K_a\ K_c$	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
1	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
6 2 5	3942.41628	8	15	4131.0680	17	84	4709.2992	6	2	4831.8510	5	6	4955.5768	9	0	5334.4699	5	−1	5713.6530	2	10
6 2 4	3956.72156	5	8	4148.9625	13	−11	4725.1728	8	−1	4851.5142	6	16	4971.1726	29	−76	5351.9569	9	−4			
6 3 4	3975.81417	14	27	4168.0028	16	17	4741.7329	10	20	4867.8056	13	−12	4990.6520	7	7	5366.0024	9	3	5747.7457	21	−22
6 3 3	3978.74184	6	−7	4172.1446	20	−45	4745.4546	3	−7	4872.9915	17	21	4993.9629	7	−2	5370.6932	6	2			
6 4 3	4015.78253	7	0	4211.0538	10	−13	4779.4577	7	3	4908.4476	11	1	5032.3072	7	−12	5401.5154	16	−11			
6 4 2	4015.96876	74	0	4211.3565	16	4	4779.7327	5	3	4908.8840	20	−14	5032.5265	17	−6	5401.9223	4	−2			
6 5 2	4066.78740		117	4265.7199	11	6	4827.3434		−3	4959.6870		22	5085.3968	7	13	5446.2533	25	10			
6 5 1	4066.79135		72	4265.7247	7	−25	4827.3498	12	−13	4959.6977		−2	5085.3976	28	−32	5446.2649	3	2			
6 6 1				4333.0679	9	1	4886.3658	23	0				5150.7656	10	3	5501.4589	1	5			
6 6 0				4333.0679	9	0	4886.3658	23	0				5150.7656	10	2	5501.4592	3	0			
7 0 7	3954.56843	28	42	4138.4670		2	4721.6540	3	3	4839.4566		−2	4965.3681	4	2	5346.9961	14	14			
7 1 7	3954.69299	10	28	4138.5583	1	−10	4721.7317	26	−8	4839.5144		5	4965.4842	3	−3	5347.0418	7	−5	5723.7188		131
7 1 6	3992.43978	1	0	4182.5842	8	−16	4760.4831	7	0	4884.4489	13	0	5005.7942	2	3	5386.5997	9	2			
7 2 6	3995.15080	6	8	4184.8480	7	2	4762.4226	6	0	4886.0260	9	18	5008.4203	9	−7	5387.9243	11	3			
7 2 5	4016.67822	22	−39	4211.4029	29	11	4785.9437	19	−4	4914.7284	11	15	5031.7941	9	−5	5413.4068	5	3			
7 3 5	4031.60763	14	8				4798.2855	11	−7	4926.2609	10	18	5046.8358	5	−2	5423.2751	7	0			
7 3 4	4037.97807		30	4234.4220		25	4806.1487	9	9	4936.8742	6	−6	5053.9828	5	−4	5432.8474	6	4			
7 4 4				4269.4475	3	−4	4836.7095	3	1	4967.9380	15	2	5089.0480	6	0	5459.7574	4	0			
7 4 3	4072.70827	1	22	4270.4945	22	23	4837.6634	8	12	4969.4326		7	5089.8131	4	0	5461.1394	6	0	5845.9678		−33
7 5 3	4122.63340		6	4323.5970	7	−13	4884.1644	21	−4	5018.6741	11	26	5141.6711	1	0	5504.0755	11	5			
7 5 2	4122.65939	7	3	4323.6440	10	−10	4884.2082	7	0				5141.7031	16	6	5504.1475	7	−2			
7 6 2	4185.00491	10	−17	4390.3938	18	13	4942.7203	15	11				5206.5692	7	−7	5558.7630	13	16			
7 6 1	4185.00491	10	−63	4390.3946	18	−4	4942.7203	13	3	5081.2656	11	8	5206.5701	3	−4	5558.7637	18	−8			
7 7 1				4469.9465	5	12	5012.4904	2	−4				5283.8133	12	15	5624.0369	7	5			
7 7 0				4469.9465	5	12	5012.4904	2	−4				5283.8133	12	15	5624.0371	5	7			
8 0 8	4008.15319		28				4775.4054	10	47	4893.1965		−2	5018.5944	8	11	5400.8811	10	19			
8 1 8	4008.20470	7	32				4775.4287	16	−23	4893.2174		4	5018.6400	17	−4	5400.8945	22	−16			
8 1 7	4053.17256	5	−15	4244.1883	3	11	4821.2766	15	5	4946.0969	3	5	5066.5686	10	5	5447.4118	4	1			
8 2 7	4054.58769		7	4245.2827	14	0	4822.2118	17	11				5067.9090	3	−4	5447.9970	7	0			
8 2 6	4084.23335	3	−22				4854.0833	9	−4	4985.0864		7	5099.9561	11	8	5481.9218	6	−2			
8 3 6	4094.97401		21	4290.9530	4	6	4862.4014	3	0	4992.3370		15	5110.5958	3	0	5488.0667	14	4			
8 3 5	4106.58930		16				4876.2958	2	5	5010.5617	1	20	5123.5165	8	4	5504.4409	10	−5			
8 4 5	4136.51395	10	61	4336.3325	15	12	4902.2643	5	3	5036.0285	6	15	5154.0477	7	0	5526.3947	13	4			
8 4 4	4138.33876		14	4339.1866	12	0	4904.8658	6	12	5040.0007	6	14	5156.1720	13	4	5530.0541	10	3			
8 5 4	4186.69637	11	26	4390.0666	7	52	4949.3816	7	3	5086.4485	6	17	5206.2508	1	1	5570.4769	10	−11			
8 5 3	4186.80621		0	4390.2570	20	−4	4949.5644	12	8				5206.3815	15	−19	5570.7802	5	2			
8 6 3				4456.1470	10	−1	5007.3340	23	5				5270.5409	9	−1	5624.5103	26	32			
8 6 2	4248.52396		−35	4456.1510	7	−4	5007.3362	7	−32				5270.5434	20	−15	5624.5168	25	−16			
8 7 2							5076.5956	6	3				5347.2650	15	−4	5689.2167	14	8			
8 7 1							5076.5956	9	2				5347.2656	11	1	5689.2164	8	3			
8 8 1							5157.1058	2	−7				5436.3566	4	5	5764.5520	9	4			
8 8 0							5157.1058	2	−7				5436.3566	4	5	5764.5520	8	4			
4 0 4				6215.3622	1	0	7121.6582	12	−4	7199.6625	9	19	7652.7000	12	−7	8623.8458	7	−5			
4 1 4	5635.5999	11	−4	6216.1315	4	2				7200.4210	10	−2	7653.3422	12	−10	8624.4753	15	−6			

	(300)			(012)			(102)			(022)			(003)			(013)		
J K_a K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
1	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61
4 1 3				6234.4937	0	2				7220.0782	13	14	7670.7006	23	0	8643.0823	10	−8
4 2 3				6242.2467	2	2	7147.1143	4	0	7227.9741	0	−2	7677.4812	35	0	8649.9564	8	21
4 2 2				6248.1790	1	0	7152.1845	10	−7	7234.4414	7	−15	7683.2617	6	−2	8656.2794	12	17
4 3 2				6270.3322	0	−2	7174.1976	10	−13	7257.3478	2	−9	7703.1043	7	2	8676.7394	10	6
4 3 1				6270.8838	4	−7	7174.6277	22	−5	7257.9688	6	−18	7703.6718	15	−5	8677.3837	10	3
4 4 1				6307.0188		−4							7736.3984	22	32	8711.4011		43
4 4 0				6307.0310		6							7736.4073	7	0	8711.4065		−45
5 0 5	5668.8045	14	16	6250.3797	8	10	7156.4037		0	7234.5511		18	7687.4752	29	−10	8658.4781	33	45
5 1 5				6250.6966	3	0	7156.7793	3	−1	7234.8579	9	7	7687.7335	20	−2	8658.7201	0	−1
5 1 4	5691.3728		79	6277.0169	1	3	7180.6730	13	9	7262.9738		21	7712.5323	15	10	8685.2373	13	−9
5 2 4				6281.9075	1	−1	7185.9583	10	7	7267.8670	21	−35	7716.6976	13	−4	8689.3785	7	3
5 2 3				6293.4927	0	2	7195.9850	8	−14	7280.4453	2	7	7727.9091	16	3	8701.5767	12	−22
5 3 3				6312.0113	1	−2	7214.7577	16	−5	7299.4460	3	5	7744.2990	4	−4	8718.3288	15	5
5 3 2				6314.0398	0	−2	7216.3587		25	7301.7178	12	−15	7746.3706	9	0	8720.6644	30	1
5 4 2				6348.6682	1	−4	7250.3964	1	−6				7777.5926	18	2	8753.0011	19	3
5 4 1				6348.7664	3	−9	7250.4645	9	−35	7337.7710		−19	7777.6996	5	5	8753.1270	30	15
5 5 1				6395.6694	16	−27							7820.2357	24	0	8797.3673	46	−7
5 5 0				6395.6726	22	−51							7820.2358	22	−15	8797.3705	8	7
6 0 6	5709.4777		−23	6291.5170	4	6	7197.2613	5	15	7275.4885		−6	7728.3958	25	14	8699.1736	3	0
6 1 6	5709.8163	12	20	6291.6374	4	2	7197.4120		7	7275.6022	20	−21	7728.4900	8	1	8699.2618	2	−11
6 1 5	5739.0906		18	6326.0285	0	3	7228.8412	12	−8	7312.2515	7	16	7760.7661	4	−1	8733.6857	22	13
6 2 5				6328.6833	3	0	7231.8728	5	−18	7314.8545	10	1	7762.9568	25	3	8735.8092	17	0
6 2 4				6347.6386	0	3	7248.4713		−11	7335.3423	11	4	7781.1852	5	7	8755.5533	11	−10
6 3 4				6361.8616	1	−1	7263.3185		−2				7793.5502	22	−3	8768.0224	19	14
6 3 3				6367.1106	1	0	7267.5368	15	−10				7798.8480	14	17	8773.9405	25	0
6 4 3				6398.9014	8	−3	7299.2160	16	−8	7388.4231	2	7	7827.2720	28	8	8803.1904	39	18
6 4 2				6399.3733	1	−2	7299.5584	3	−4				7827.7792	19	2	8803.7812	48	13
6 5 2				6445.4515	11	62	7344.5974	8	49				7869.4961	45	59			
6 5 1				6445.4547		−86							7869.5011	31	−59	8847.1051	46	−61
6 6 1				6502.8989	2	−4							7921.6311	31	−14	8901.3304	9	52
6 6 0				6502.8992	3	0										8901.3308	13	54
7 0 7	5756.2530		−31	6338.8401	22	3	7244.2843		−1	7322.5480	22	16	7775.5137	19	13	8746.0054	23	−8
7 1 7	5756.4037	17	−4	6338.8791	26	−2	7244.3427		4	7322.5847		−25	7775.5446	11	−13	8746.0369	5	1
7 1 6				6380.9976	0	4	7283.0543	3	3	7367.3800	12	16	7814.9496	11	−9	8787.9752	19	9
7 2 6				6382.2613	11	4	7284.5848	7	−15	7368.5926	13	13	7815.9598	17	8	8788.9281	12	−2
7 2 5				6409.7587	0	3	7308.9411	5	0	7398.1846	3	−8	7842.2321	19	9	8817.2521	11	15
7 3 5				6419.5848	4	0	7319.6393	6	0	7407.9899	1	−2	7850.5568	23	9	8825.4790	36	−21
7 3 4				6430.1978	3	0	7328.3700	12	−11	7419.6960	13	−9	7861.1272	17	16	8837.1831	4	−6
7 4 4				6457.7186	1	−5	7356.3750	43	5	7447.8674	15	−38	7885.4186	16	−22	8861.9385	21	−15
7 4 3				6459.3175	1	−4	7357.5500	12	22	7449.7042		−8	7887.1243	8	−5	8863.9099	32	−14
7 5 3				6503.8164	3	−4	7401.3248		−15				7927.2446	13	−15	8905.4279	29	30
7 5 2				6503.9033	3	−3	7401.3847		3				7927.3421	18	−22	8905.5325		−102
7 6 2				6560.6906	13	−3							7978.8395	14	−17	8959.0538	4	46
7 6 1				6560.6922	15	10							7978.8406	43	−20	8959.0554	31	32
7 7 1				6628.6010	1	2												

Line missing

Table 2 (continued)

J K_a K_c	(300)			(012)			(102)			(022)			(003)			(013)		
	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
1	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61
7 7 0				6628.6011	0	1												
8 0 8	5809.1719		−2	6392.3760	5	7	7297.5140	6	29	7375.7542	1	−6	7828.8587	12	13	8798.9976	10	−16
8 1 8				6392.3900	6	−14	7297.5394	1	26	7375.7684	13	−2	7828.8684	20	−2	8799.0104	8	12
8 1 7				6441.8502	5	5	7343.1621	6	23				7875.0562	20	14	8848.1035	24	−34
8 2 7				6442.3954	2	3	7343.8628	20	15				7875.4757	22	−3	8848.4962	30	8
8 2 6				6478.8290	4	0	7376.5208	2	−27				7910.0540	19	23	8885.5870	7	17
8 3 6				6484.8120	1	0	7383.4119	19	4	7473.7030	18	−17	7914.9523	19	2	8890.3093	13	−9
8 3 5				6502.8150	21	8				7493.4120	11	11	7932.6728	22	10	8909.7640	4	21
8 4 5				6525.0049	3	−2	7421.7934	3	−15	7515.8662	16	−7	7951.9097	15	10	8929.1004	8	27
8 4 4				6529.2016	1	−4	7424.9472		35	7520.6350		−44	7956.3202	14	3	8934.1535	45	54
8 5 4				6570.8763	1	−6				7563.6239		−28	7993.5915	21	−17	8972.4651	21	5
8 5 3				6571.2361	3	−6				7564.0513		1	7993.9986	16	8	8972.9544		60
8 6 3				6627.0298*						7622.0069		6	8044.5001	54	−32			
8 6 2				6627.0305*						7622.0239		9	8044.5133	47	−64			
8 7 2				6694.3020	2	−2												
8 7 1				6694.3022	1	−2												

(continued on next page)

5. Upper ro-vibrational energies of HDS and global fit

The upper ro-vibrational energy levels of the states (120), (101), (021), (210), (111), (300), (102), and (022) were determined by adding to the ground state energy levels [2] the observed transitions. Then, together with the upper ro-vibrational energies of the previously studied vibrational states (see Table 1), they were used as an input data in the Global Fit procedure discussed in the previous section. The whole list of upper ro-vibrational energies is given in Table S.I. of the Supplementary Materials [15], a small portion of these Table being given in Table 2. Values in columns 3, 6, 9, 12, 15, etc. of Tables 2 and S.I. are the experimental uncertainties Δ of the upper energy values. 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. The experimental accuracy is in general decreasing:

– when going towards high values of the J and K_a quantum numbers because of weaker line strengths,
– when going towards high frequencies both because of a decreasing instrumental resolution and because of weaker band strengths. Finally the number of upper ro-vibrational energies is 2984 with maximum value of the quantum numbers $J^{\max.} = 23$ and $K_a^{\max.} = 11$.

As in Ref. [1], all the spectroscopic parameters P^0, p_λ, $p_{\lambda\mu}$ of Eq. (7), and/or $F\ldots$, $f^1\ldots$, $f^2\ldots$, $f^3\ldots$, $C\ldots$, $c^1\ldots$,

Table 3
Vibrational parameters $E^{v_1v_2v_3}$ of the HDS molecule (in cm^{-1})

State	Band center, exp.	Band center, Ref. [14]
(010)	1032.71556(14)	1032.66
(100)	1902.85624(10)	1902.71
(020)	2056.96580(15)	2056.87
(001)	2621.45594(10)	2621.89
(110)	2924.97773(12)	2924.88
(030)	3072.49232(20)	3071.97
(011)	3634.33224(12)	3635.47
(200)	3756.32989(13)	3756.02
(120)	3938.63701(35)	3938.67
(101)	4522.65030(14)	4523.20
(021)	4638.86437(35)	4640.64
(210)	4767.69431(14)	4767.10
(002)	5147.35539(12)	5147.97
(111)	5525.26664(88)	5526.28
(300)	5560.54225(93)	5559.95
(012)	6139.73928(13)	6141.30
(201)	6375.04[a]	6375.04
(102)	7047.15309(34)	7047.88
(022)	7123.89641(44)	7126.26
(400)	7314.45[a]	7314.45
(211)	7367.00[a]	7367.00
(003)	7577.84009(15)	7578.22
(013)	8548.90007(26)	8550.18
(202)	8898.33[a]	8898.33

[a] Constrained to the value of band center from Ref. [14].

Table 4
Corrections to the rotational and centrifugal distortion parameters of the HDS molecule (in cm^{-1})[a]

Parameter	Value	Parameter	Value	Parameter	Value
$a^{1}\times 10$	−0.104900(128)	$c^{233}\times 10^{3}$	−0.01935(156)	$\delta_K^{112}\times 10^{6}$	−0.962(137)
$a^{2}\times 10$	2.659921(283)	$c^{333}\times 10^{3}$	−0.012690(924)	$\delta_K^{222}\times 10^{6}$	1.1811(986)
$a^{3}\times 10$	−2.881338(101)	$\Delta_K^{1}\times 10^{4}$	−0.07456(233)	$\delta_K^{233}\times 10^{6}$	−0.8839(805)
$a^{11}\times 10^{2}$	0.021946(478)	$\Delta_K^{2}\times 10^{4}$	0.62012(578)	$\delta_K^{333}\times 10^{6}$	−0.2744(481)
$a^{13}\times 10^{2}$	0.24201(450)	$\Delta_K^{3}\times 10^{4}$	−0.09414(194)	$\delta_J^{1}\times 10^{4}$	−0.0061782(268)
$a^{22}\times 10^{2}$	0.89707(221)	$\Delta_K^{12}\times 10^{5}$	−0.2377(201)	$\delta_J^{2}\times 10^{4}$	0.059401(409)
$a^{23}\times 10^{2}$	−1.08528(226)	$\Delta_K^{13}\times 10^{5}$	0.3654(170)	$\delta_J^{3}\times 10^{4}$	0.0044335(721)
$a^{33}\times 10^{2}$	0.066068(932)	$\Delta_K^{22}\times 10^{5}$	1.2949(353)	$\delta_J^{12}\times 10^{5}$	−0.03255(279)
$a^{112}\times 10^{3}$	−0.36158(564)	$\Delta_K^{23}\times 10^{5}$	−0.3837(329)	$\delta_J^{22}\times 10^{5}$	0.04126(418)
$a^{122}\times 10^{3}$	0.07114(788)	$\Delta_K^{112}\times 10^{6}$	−0.670(119)	$\delta_J^{23}\times 10^{5}$	0.02088(132)
$a^{133}\times 10^{3}$	−0.2183(411)	$\Delta_K^{233}\times 10^{6}$	−1.363(106)	$\delta_J^{122}\times 10^{6}$	0.1907(279)
$a^{222}\times 10^{3}$	0.31437(422)	$\Delta_{JK}^{1}\times 10^{4}$	−0.02305(100)	$\delta_J^{222}\times 10^{6}$	0.0682(102)
$a^{223}\times 10^{3}$	−0.6787(136)	$\Delta_{JK}^{2}\times 10^{4}$	0.74509(339)	$\delta_J^{233}\times 10^{6}$	0.01957(478)
$a^{233}\times 10^{3}$	−0.16062(720)	$\Delta_{JK}^{3}\times 10^{4}$	−0.04404(119)	$H_K^{1}\times 10^{6}$	−0.02043(202)
$a^{333}\times 10^{3}$	−0.04181(267)	$\Delta_{JK}^{13}\times 10^{5}$	−0.5331(750)	$H_K^{2}\times 10^{6}$	0.28656(796)
$b^{1}\times 10$	−0.9948924(377)	$\Delta_{JK}^{22}\times 10^{5}$	0.8751(236)	$H_K^{3}\times 10^{6}$	0.03166(196)
$b^{2}\times 10$	0.893061(214)	$\Delta_{JK}^{112}\times 10^{6}$	0.5000(721)	$H_K^{22}\times 10^{7}$	1.1254(626)
$b^{3}\times 10$	0.0031291(498)	$\Delta_{JK}^{133}\times 10^{6}$	5.964(766)	$H_K^{23}\times 10^{7}$	−0.4663(366)
$b^{11}\times 10^{2}$	0.005084(222)	$\Delta_{JK}^{223}\times 10^{6}$	−1.584(154)	$H_{KJ}^{1}\times 10^{6}$	0.00917(135)
$b^{12}\times 10^{2}$	−0.309792(513)	$\Delta_{JK}^{233}\times 10^{6}$	0.9741(680)	$H_{KJ}^{2}\times 10^{6}$	−0.34241(816)
$b^{22}\times 10^{2}$	0.29570(223)	$\Delta_J^{1}\times 10^{4}$	−0.009558(211)	$H_{KJ}^{3}\times 10^{6}$	−0.04647(211)
$b^{23}\times 10^{2}$	0.18770(106)	$\Delta_J^{2}\times 10^{4}$	0.114468(795)	$H_{KJ}^{22}\times 10^{7}$	−0.9447(664)
$b^{33}\times 10^{2}$	−0.000960(144)	$\Delta_J^{3}\times 10^{4}$	0.004373(162)	$H_{KJ}^{23}\times 10^{7}$	0.4764(325)
$b^{133}\times 10^{3}$	0.07898(370)	$\Delta_J^{12}\times 10^{5}$	−0.06591(547)	$H_{JK}^{2}\times 10^{6}$	0.12320(270)
$b^{222}\times 10^{3}$	0.12810(529)	$\Delta_J^{13}\times 10^{5}$	0.00557(105)	$H_{JK}^{3}\times 10^{6}$	0.011340(650)
$b^{223}\times 10^{3}$	0.04138(519)	$\Delta_J^{22}\times 10^{5}$	0.08416(819)	$H_{JK}^{22}\times 10^{7}$	0.4356(236)
$b^{233}\times 10^{3}$	0.09844(275)	$\Delta_J^{23}\times 10^{5}$	0.04334(172)	$H_J^{2}\times 10^{6}$	0.0029400(830)
$c^{1}\times 10$	−0.3872959(350)	$\Delta_J^{33}\times 10^{5}$	0.3490(370)	$h_K^{1}\times 10^{6}$	0.03368(371)
$c^{2}\times 10$	−0.3463424(438)	$\Delta_J^{122}\times 10^{6}$	0.3625(553)	$h_K^{2}\times 10^{6}$	0.45311(945)
$c^{3}\times 10$	−0.2883940(458)	$\Delta_J^{222}\times 10^{6}$	0.1216(199)	$h_K^{3}\times 10^{6}$	−0.02572(290)
$c^{11}\times 10^{2}$	−0.003463(200)	$\delta_K^{1}\times 10^{4}$	0.024595(616)	$h_K^{11}\times 10^{7}$	0.2145(346)
$c^{12}\times 10^{2}$	−0.05023(121)	$\delta_K^{2}\times 10^{4}$	1.60787(497)	$h_K^{22}\times 10^{7}$	1.0041(761)
$c^{13}\times 10^{2}$	0.023956(355)	$\delta_K^{3}\times 10^{4}$	−0.06410(222)	$h_K^{23}\times 10^{7}$	−0.8253(372)
$c^{22}\times 10^{2}$	0.016330(188)	$\delta_K^{12}\times 10^{5}$	0.2614(222)	$h_{JK}^{2}\times 10^{6}$	0.05716(147)
$c^{33}\times 10^{2}$	−0.034548(396)	$\delta_K^{13}\times 10^{5}$	0.1713(137)	$h_{JK}^{3}\times 10^{6}$	0.005134(387)
$c^{112}\times 10^{3}$	0.05923(306)	$\delta_K^{22}\times 10^{5}$	1.2915(482)	$h_{JK}^{22}\times 10^{7}$	0.1493(120)
$c^{122}\times 10^{3}$	−0.06807(974)	$\delta_K^{23}\times 10^{5}$	−0.2450(185)	$h_J^{2}\times 10^{6}$	0.0014459(423)
		$\delta_K^{33}\times 10^{5}$	0.1014(195)		

[a] Values in parentheses are 1σ standard errors.

$c^2\ldots$, $c^3\ldots$ of Eqs. (8) and (9), with the exception of the pure vibrational energies:

$$E^{v_1,v_2,v_3} = \sum_{\lambda} \tilde{\omega}_{\lambda} v_{\lambda} + \sum_{\lambda\mu \geqslant \lambda} x_{\lambda\mu} v_{\lambda} v_{\mu} + \cdots. \tag{11}$$

were fitted independently. All the vibrational energies E^{v_1,v_2,v_3} were fitted as separate values. In accordance with the discussion of Section 3, the "dark" vibrational states (201), (400), (211), and (202), were also included in the fitting procedure. In this case, the band centers of the

Table 5
Parameters of resonance interactions between vibrational states of the HDS molecule (in cm^{-1})[a]

Fermi type parameters $F_{\ldots}^{v_1,v_2,v_3\ v_1\pm 2,v_2\mp 1,v_3\mp 1}$					
		F_0	−0.68[b]		
$F_J\times 10^{2}$	0.16384(862)	$F_{xy}\times 10^{2}$	0.17704(610)	$F_{xyJ}\times 10^{5}$	0.1706(277)
Coriolis type parameters $C_{\ldots}^{v_1,v_2,v_3\ v_1\pm 2,v_2\mp 1,v_3\mp 1}$					
Parameter	Value	Parameter	Value	Parameter	Value
$C_y\times 10$	−0.5644(461)	$c_y^{2}\times 10$	−0.1165(178)	$c_y^{3}\times 10$	0.4546(234)
$c_{yK}^{3}\times 10^{3}$	−0.4437(256)	$C_{yJ}\times 10^{3}$	0.07571(790)	$C_{yJK}\times 10^{5}$	−0.2065(125)
$C_{xz}\times 10^{4}$	0.24204(981)	$C_{xzK}\times 10^{4}$	0.21295(766)		

[a] Values in parentheses are 1σ standard errors.
[b] Constrained to the value which was estimated on the basis of the intramolecular potential parameters from Ref. [16].

Table 6
Spectroscopic parameters of some vibrational states of the HDS molecules (in cm^{-1})

Parameter	(000)[a]	(100)	(200)	(300)	(400)	(001)	(002)
E		1902.85624	3756.32989	5560.54225	7314.45	2621.45594	5147.35539
A	9.75178112	9.74151058	9.73167896	9.72228626	9.71333248	9.46426619	9.17782176
B	4.93213844	4.83270004	4.73336332	4.63412828	4.53499492	4.93246095	4.93280266
C	3.22570284	3.18693862	3.14810514	3.10920240	3.0702304	3.19650527	3.16654060
$\Delta_K \times 10^3$	−0.377125	−0.384581	−0.392037	−0.399493	−0.406949	−0.386539	−0.395953
$\Delta_{JK} \times 10^3$	0.956467	0.954162	0.951857	0.949552	0.947247	0.952063	0.947659
$\Delta_J \times 10^3$	0.087209	0.0862532	0.0852974	0.0843416	0.0833858	0.0876812	0.0882232
$\delta_K \times 10^3$	0.648383	0.6508422	0.6533014	0.6557606	0.6582198	0.6427126	0.6374238
$\delta_J \times 10^3$	0.0284447	0.02782688	0.02720906	0.02659124	0.02597342	0.02888805	0.0293314
$H_K \times 10^6$	0.4191	0.39867	0.37824	0.35781	0.33738	0.45076	0.48242
$H_{KJ} \times 10^6$	−0.6773	−0.66813	−0.65896	−0.64979	−0.64062	−0.72377	−0.77024
$H_{JK} \times 10^6$	0.43313	0.43313	0.43313	0.43313	0.43313	0.44447	0.45581
$H_J \times 10^6$	0.002307	0.002307	0.002307	0.002307	0.002307	0.002307	0.002307
$h_K \times 10^6$	0.9932	1.04833	1.14636	1.28729	1.47112	0.96748	0.94176
$h_{JK} \times 10^6$	0.20978	0.20978	0.20978	0.20978	0.20978	0.214914	0.220048
$h_J \times 10^6$	0.001199	0.001199	0.001199	0.001199	0.001199	0.001199	0.001199
$L_K \times 10^9$	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655
$L_{KKJ} \times 10^9$	3.76	3.76	3.76	3.76	3.76	3.76	3.76
$L_{JK} \times 10^9$	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189
$L_{JJK} \times 10^9$	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201
$l_K \times 10^9$	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722
$l_{KJ} \times 10^9$	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479
$l_{JK} \times 10^9$	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656
$P_K \times 10^{12}$	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922
$p_K \times 10^{12}$	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43

Parameter	(003)	(101)	(201)	(102)	(202)	(010)	(020)
E	7577.84009	4522.65030	6375.04	7047.15309	8898.33	1032.71556	2056.96580
A	8.89219697	9.45619745	9.44856763	9.17151822	9.16565360	10.02705829	10.32216308
B	4.93316357	4.83310153	4.73384379	4.83368018	4.73465938	5.02452964	5.12360344
C	3.13573269	3.15798061	3.11938669	3.12825550	3.08990114	3.1912319	3.15708756
$\Delta_K \times 10^3$	−0.405367	−0.390341	−0.394143	−0.396101	−0.396887	−0.302164	−0.201305
$\Delta_{JK} \times 10^3$	0.943255	0.950391	0.948719	0.958548	0.969437	1.039727	1.140489
$\Delta_J \times 10^3$	0.088835	0.0867811	0.085881	0.0873788	0.0865344	0.099619	0.1144418
$\delta_K \times 10^3$	0.6308702	0.6468848	0.6510570	0.6433090	0.6491942	0.8232661	1.0310658
$\delta_J \times 10^3$	0.02977475	0.02827023	0.02765241	0.02871358	0.02809576	0.0348656	0.0425209
$H_K \times 10^6$	0.51408	0.43033	0.40990	0.46199	0.44156	0.81820	1.44238
$H_{KJ} \times 10^6$	−0.81671	−0.71460	−0.70543	−0.76107	−0.75190	−1.11418	−1.74000
$H_{JK} \times 10^6$	0.46715	0.44447	0.44447	0.45581	0.45581	0.59989	0.85377
$H_J \times 10^6$	0.02307	0.002307	0.002307	0.002307	0.002307	0.005247	0.008187
$h_K \times 10^6$	0.91604	1.02261	1.112064	0.99689	1.09492	1.54672	2.30106
$h_{JK} \times 10^6$	0.225182	0.214914	0.214914	0.220048	0.220048	0.28187	0.38382
$h_J \times 10^6$	0.001199	0.001199	0.001199	0.001199	0.001199	0.0026449	0.0040908
$L_K \times 10^9$	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655
$L_{KKJ} \times 10^9$	3.76	3.76	3.76	3.76	3.76	3.76	3.76
$L_{JK} \times 10^9$	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189
$L_{JJK} \times 10^9$	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201
$l_K \times 10^9$	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722
$l_{KJ} \times 10^9$	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479
$l_{JK} \times 10^9$	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656	0.0656
$P_K \times 10^{12}$	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922
$p_K \times 10^{12}$	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43

Parameter	(030)	(011)	(012)	(013)	(110)	(210)	(310)
E	3072.49232	3634.33224	6139.73928	8548.890007	2924.97773	4767.69431	6559.34
A	10.63898171	9.72785124	9.42939345	9.13143406	10.01649731	10.00565209	9.99452263
B	5.23012844	5.02686897	5.02942438	5.03219587	4.92199332	4.81955868	4.71722572
C	3.12326982	3.16201498	3.13199226	3.10108760	3.15195654	3.11273038	3.07355342
$\Delta_K \times 10^3$	−0.074548	−0.316778	−0.334118	−0.354184	−0.312667	−0.324510	−0.3376930
$\Delta_{JK} \times 10^3$	1.258753	1.0347133	1.0316482	1.0305317	1.0379220	1.0371172	1.0373123
$\Delta_J \times 10^3$	0.1324070	0.1005246	0.1015000	0.1025452	0.0983666	0.0971142	0.0958618
$\delta_K \times 10^3$	1.2788687	0.8139153	0.8038713	0.7904482	0.8273773	0.8295645	0.8298277
$\delta_J \times 10^3$	0.0518198	0.03550469	0.03624818	0.03699818	0.03408628	0.03330696	0.03252764
$H_K \times 10^6$	2.29164	0.80323	0.78826	0.77329	0.79777	0.77734	0.75691

Table 6 (*continued*)

Parameter	(000)[a]	(100)	(200)	(300)	(400)	(001)	(002)
$H_{KJ}\times 10^6$	−2.55476	−1.11301	−1.11184	−1.11067	−1.10501	−1.09584	−1.08667
$H_{JK}\times 10^6$	1.19477	0.61123	0.62257	0.63391	0.59989	0.59989	0.59989
$H_J\times 10^6$	0.011127	0.005247	0.005247	0.005247	0.005247	0.005247	0.005247
$h_K\times 10^6$	3.25622	1.43847	1.33022	1.22197	1.60185	1.69988	1.84081
$h_{JK}\times 10^6$	0.51563	0.287004	0.292138	0.297272	0.28187	0.28187	0.28187
$h_J\times 10^6$	0.0055367	0.0026449	0.0026449	0.0026449	0.0026449	0.0026449	0.0026449
$L_K\times 10^9$	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655
$L_{KKJ}\times 10^9$	3.76	3.76	3.76	3.76	3.76	3.76	3.76
$L_{JK}\times 10^9$	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189
$L_{JJK}\times 10^9$	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201
$l_K\times 10^9$	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722
$l_{KJ}\times 10^9$	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479
$l_{JK}\times 10^9$	0.0656	0.0656	0.0656	0.0656	−0.0656	−0.0656	−0.0656
$P_K\times 10^{12}$	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922	0.2292
$p_K\times 10^{12}$	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43
Parameter	(120)	(220)	(021)	(022)	(111)	(121)	(211)
E	3938.63701	5769.88	4638.86437	7123.89641	5525.26664	6251.02181	7367.00
A	10.31145394	10.29973740	10.00990651	9.69807796	9.71949206	10.00139917	9.71084864
B	5.01796920	4.91243664	5.12804235	5.13289422	4.92441163	5.02248709	4.82205597
C	3.11716492	3.07740994	3.12785129	3.09777052	3.12297918	3.08816821	3.08399258
$\Delta_K\times 10^3$	−0.214855	−0.231085	−0.221119	−0.246385	−0.323627	−0.231015	−0.331816
$\Delta_{JK}\times 10^3$	1.1391841	1.1398793	1.1316976	1.1268034	1.0335413	1.1310257	1.0333695
$\Delta_J\times 10^3$	0.1136178	0.1127938	0.1157808	0.1171896	0.0993279	0.1150125	0.0981312
$\delta_K\times 10^3$	1.036829	1.0387442	1.0187276	1.0032354	0.8200860	1.0262068	0.8239862
$\delta_J\times 10^3$	0.04196148	0.04140206	0.04342099	0.04439936	0.0347580	0.04286157	0.03397868
$H_K\times 10^6$	1.42195	1.40152	1.38078	1.31918	0.78280	1.36035	0.76237
$H_{KJ}\times 10^6$	−1.73083	−1.72166	−1.69119	−1.64238	−1.10384	−1.68202	−1.09467
$H_{JK}\times 10^6$	0.85377	0.85377	0.86511	0.87645	0.61123	0.86511	0.61123
$H_J\times 10^6$	0.008187	0.008187	0.008187	0.008187	0.005247	0.008187	0.005247
$h_K\times 10^6$	2.35619	2.45422	2.11028	1.91950	1.49736	2.16541	1.59163
$h_{JK}\times 10^6$	0.38382	0.38382	0.388954	0.394088	0.287004	0.388954	0.287004
$h_J\times 10^6$	0.0040908	0.0040908	0.0040908	0.0040908	0.0026449	0.0040908	0.0026449
$L_K\times 10^9$	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655	−2.655
$L_{KKJ}\times 10^9$	3.76	3.76	3.76	3.76	3.76	3.76	3.76
$L_{JK}\times 10^9$	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189	−1.189
$L_{JJK}\times 10^9$	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201	−0.1201
$l_K\times 10^9$	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722	−1.722
$l_{KJ}\times 10^9$	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479	−0.479
$l_{JK}\times 10^9$	−0.0656	−0.0656	−0.0656	−0.0656	−0.0656	0.0656	0.0656
$P_K\times 10^{12}$	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922	0.2922
$p_K\times 10^{12}$	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43	−6.43

[a] From Ref. [2].

"dark" states were constrained to the theoretically estimated values from Ref. [14].

Since the fit procedure was a weighted one, the weights of the energy levels introduced in the fit were taken proportional to $1/\Delta^2$, where the Δs are the experimental uncertainties of energies given in columns 3, 6, 9, 12, 15, etc., of Table 2 (Table S.I. of the Supplementary Materials).

As a result of the fit, 143 parameters were obtained (132 v-diagonal parameters and 11 resonance interaction parameters). They are presented in Tables 3–5 together with their 1σ statistical confidence intervals. In this case the lowest order Fermi-type parameter was estimated on the basis of intramolecular potential parameters from Ref. [16] and was not varied in the fit. Two remarks concerning the parameters obtained from the fit should be made here. Firstly, it is obvious that the total number, 143, of fitted parameters is considerably smaller than a summed up number of parameters which would be needed for an analogous description of all ro-vibrational energies in the framework of traditional Effective Hamiltonian model, Refs. [17,18]. The second remark deals with the physical meaning of the Global Fit parameters. In general indeed, as can be seen from Tables 4 and 5, their values are decreasing with respect to their order of magnitude in the expansion given in Eq. (7). Also it is satisfactory to notice that they reproduce quite nicely the observed energy levels (see δ in Tables 2 and S.I. of the Supplementary Materials) and that they allowed one to perform rather accurate predictions.

As shown by the analysis the resonance scheme for the HDS molecule is simpler than for D_2S [1] allowing one to reproduce satisfactorily the HDS energy levels with only seven interaction parameters.

Finally, since it can be interesting for the reader to make comparison with other set of parameters, we have gathered in Table 6 the "classical" effective parameters the values of which have been derived from the Global Fit parameters of Table 4.

6. Conclusion

Following our Global Fit analysis of the D_2S rotation–vibration spectra [1], this study present a thorough ro-vibrational analysis of eight vibrational bands recorded for the first time ($v_1 + 2v_2$, $v_1 + v_3$, $2v_2 + v_3$, $2v_1 + v_2$, $v_1 + v_2 + v_3$, $3v_1$, $v_1 + 2v_3$, and $2v_2 + 2v_3$) as well as a Global Fit of the 20 available vibrational states of the HDS molecule. The set of 143 parameters derived from the fit of experimental data (2984 vibration–rotation energies with $J^{max.} = 23$) allows one to reproduce them to within their experimental uncertainties.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spetroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

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