

## Global fit of the high-resolution infrared spectrum of D<sub>2</sub>S

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### Abstract

High-resolution Fourier-transform spectra of the D<sub>2</sub>S molecule in the regions of polyads of interacting vibrational states  $v = 3/2, 2, 5/2, 3$  and  $7/2$  ( $v = v_1 + v_2/2 + v_3$ ) were recorded for the first time with a Bruker IFS 120 Fourier-transform interferometer and analysed. A global fit of all currently available rotation–vibration energies has been made for 22 vibrational states of the D<sub>2</sub>S molecule. The resulting set of 231 parameters reproduces all the initial experimental data (about 3670 vibration–rotation energies which correspond to more than 9700 ro-vibrational transitions with  $J^{\max} = 25$ ) with accuracies close to the experimental uncertainties.

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### 1. Introduction

The high-resolution spectroscopy of the hydrogen sulfide molecule and of its different isotopic species is of great interest for a number of reasons. On the one hand, the study of its spectra is important for terrestrial atmospheric pollutant measurements and for the investigation of physics and chemistry in the atmospheres of planets (like Venus) and interstellar medium [1]. On the other hand, the hydrogen sulfide molecule is of interest from a theoretical point of view because it is one of the lightest asymmetric top molecules. As a consequence, numerous spectroscopic effects and peculiarities which are inherent to asymmetric tops should be particularly pronounced in its spectra. An additional interest in the spectroscopic study of hydrogen sulfide arises from the fact that it can be considered as a local mode molecule, and both the local mode properties and the conditions of their breakdown can

be analyzed in the stretching fundamentals and their overtones. So, the hydrogen sulfide molecule can be considered as a good “touchstone” to test the various methods used in chemical physics to produce a potential energy surface (PES), dipole moment surface (DMS), and to simulate the experimental spectra (see, e.g. Refs. [2–9]).

Whenever it is desirable to obtain as complete as possible spectroscopic information on a target molecule, the study of the isotopic varieties of this molecule is an efficient mean to gather valuable additional information, in particular concerning intramolecular dynamics. The larger the mass ratio of the isotopically labelled variety with regard to the reference “mother” molecule is, the more pronounced are the apparent isotopic effects on the spectrum and on the ro-vibrational energy pattern. Also the larger the variety of isotopic substitution is, the larger is the number of effects which can be detected and studied in detail. Accordingly, the study of deuterated species of a molecule is the most efficient one because the ratio  $(m_D - m_H)/m_H$  is the largest one for stable isotopes. Moreover, deuterated species are usually available by feasible synthetic routes. All the above-mentioned reasons clearly suggest that a

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high-resolution spectroscopic study of the di-deuterated species of hydrogen sulfide is of great interest.

The  $D_2S$  molecule has been the subject of many experimental studies, see, e.g. [10–20]. However, only a few of studies were devoted to the analysis of its high-resolution spectra in the infrared region. In particular, the rotational structure of the ground vibrational state of  $D_2S$  was obtained in [18]. The three fundamentals  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  (they belong to the  $v = 1/2$  and  $v = 1$  polyads, where  $v = \nu_1 + \nu_2/2 + \nu_3$ ) were experimentally recorded and analysed in [17,19]. Two lowest combinational bands  $\nu_1 + \nu_2$  and  $\nu_2 + \nu_3$ , belonged to the third polyad  $v = 3/2$ , were discussed in [20]. Up to now there were no high-resolution spectroscopic information about higher vibrational bands of the  $D_2S$  molecule.

In this paper, we present the results of the first high-resolution spectroscopic study of the four polyads of strongly interacting vibrational states  $v = 2$  (states (200), (101), (002), and (021)),  $v = 5/2$  (states (210), (111), (012), (130), and (031)),  $v = 3$  (states (300), (201), (102), (003), and (121)),  $v = 7/2$  (states (310) and (211)). Additionally we were able (a) to experimentally record and analyse the earlier unstudied band  $3\nu_3$  belonging to the polyad  $v = 3/2$  and (b) to improve considerably the spectroscopic information about the bands  $\nu_1 + \nu_2$  and  $\nu_2 + \nu_3$  also belonging to the polyad  $v = 3/2$ . Details of our experimental study and results of assignments of experimental transitions are presented in Sections 2 and 4, respectively.

The first step on the way to extract some physical information from high-resolution infrared spectra is to fit the experimental energy levels (or experimental line positions) derived from the recorded spectra and to determine sets of parameters characterizing a molecule under study. For this purpose modern high-resolution molecular spectroscopy usually used the so-called effective Hamiltonian models which allows one to describe correctly the separate polyads of interacting states with a set of spectroscopic parameters, such as, band centers, rotational, numerous centrifugal distortion, resonance interaction, etc., effective constants. However, usually a set of parameters of a given polyad is valid for this polyad only and cannot be easily extrapolated to other polyads of the same molecule. For this reason, when the number of experimentally known vibrational bands of a molecule is large (in particular, in our study the number of bands under study is 22), the total number of such effective spectroscopic parameters becomes large. In this situation it is then advisable to use a different model than the usual effective Hamiltonian model in order to considerably reduce the number of parameters necessary for description of the whole set of experimental data. Such a method (Global Fit) was discussed previously in Ref. [21] and successfully applied to the description of the ro-vibrational structures of the  $H_2Se$  [21] and  $HDSe$  [22,23] ro-vibrational spectra. In the present study, given the large number of analyzed bands, it proves useful and adequate to use Global Fit procedure the theoretical basis of which is described in Section 3. Section 5 presents the results of a fit and discussion.

## 2. Experimental details

The deuterated hydrogen sulfide sample was synthesized with diluted phosphoric acid and sodium sulfide. The phosphoric acid-d3 (85% solution in  $D_2O$ , >99% D atom, from Fluka Chemical) was further diluted with deuterated water (99.8%, from PeKing Chemical Industry, Ltd.). Anhydrous sodium sulfide (99.9%) was purchased from Acr̄os Organics. The synthesized gas was collected and purified with low temperature distillations. The spectra were recorded with a Bruker IFS 120HR Fourier-transform spectrometer equipped with a path length adjustable multi-pass gas cell, a tungsten source and a  $CaF_2$  beam-splitter. The cell was operated at room temperature ( $297 \pm 1$  K), stabilized by an air-conditioning system. The pressure was measured by a capacitance manometer of 133 hPa full-scale range with an overall accuracy of 0.5%.

The spectra were recorded in the region of 2000–9000  $cm^{-1}$ . The whole region was divided into some parts which are marked by different colors on Fig. 1. Corresponding experimental conditions for any such separate part are given in the caption to Fig. 1. Since the sample was a mixture of hydrogen sulfide, deuterated, and di-deuterated species, the bands of  $D_2S$  and  $HDS$  and  $H_2S$  can be found in the recorded spectra. Because of the wide spectral range and the large range of absorption line intensities, different experimental conditions were used in the measurements as listed in Table 1. In most measurements which were mainly devoted to an accurate determination of the line positions, optical filters were applied to increase both the signal-noise-ratio and the resolution. The isotope abundance of the synthesized samples had been given as:  $H_2^{32}S$  3.0%,  $HD^{32}S$  23.5%,  $D_2^{32}S$  68.7%,  $D_2^{33}S$  0.5%,  $HD^{34}S$  1.0%, and  $D_2^{34}S$  3.0% by a photoionization mass spectrum (PIMS) experiment at the National Synchrotron Radiation Laboratory (Hefei, China). The line positions were calibrated with the  $H_2O$  and  $CO_2$  lines given by the HITRAN2004 database [24]. The accuracy of line positions of unblended and strong enough lines is estimated to be better than 0.001  $cm^{-1}$  in the lower frequency ( $\sim 2000$ – $2500$   $cm^{-1}$ ) part of the studied spectra decreasing up to 0.002–0.003  $cm^{-1}$  in the higher frequency ( $\sim 6000$ – $7000$   $cm^{-1}$ ) part of the spectra. Some extracts of the high-resolution spectra belonging to different studied polyads are given in Figs. 2–6 showing the quality of the experimental spectra.

## 3. Theoretical background: Hamiltonian model

If one assumes that the rotational structures of the interacting vibrational bands belonging to a given polyad can be correctly described by a set of band centers, rotational, centrifugal distortion, and resonance interaction parameters the Hamiltonian of a polyad of interacting vibrational states can be written as

$$H^{v,-r} = \sum_{v,\bar{v}} |v\rangle \langle \bar{v} | H^{v\bar{v}}. \quad (1)$$

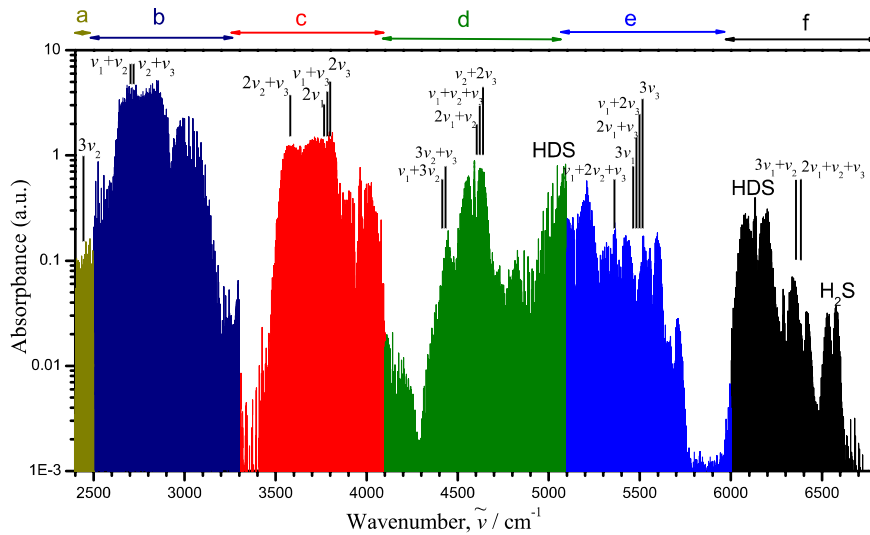


Fig. 1. Overview transmitted spectrum of the synthesized HDS/D<sub>2</sub>S/H<sub>2</sub>S sample in the whole region 2500–9000 cm<sup>-1</sup>. Band centers of D<sub>2</sub>S are marked. Experimental conditions: (a) 4445 Pa sample pressure, 51 m path length with 0.008 cm<sup>-1</sup> unapodized resolution; (b) 4445 Pa sample pressure, 87 m path length with 0.01 cm<sup>-1</sup> unapodized resolution; (c) 8043 Pa sample pressure, 87 m path length with 0.008 cm<sup>-1</sup> unapodized resolution; (d) 4445 Pa sample pressure, 105 m path length with 0.008 cm<sup>-1</sup> unapodized resolution; (e) 8043 Pa sample pressure, 105 m path length with 0.016 cm<sup>-1</sup> unapodized resolution.

Table 1

Experimental conditions used to record the Fourier-transform absorption spectra of the synthesized sample

Region (cm <sup>-1</sup> )	Gas pressure (Pa)	Detector	Path length (m)	Number of scans	Resolution (cm <sup>-1</sup> )
2500–3300	482	InSb	15	2789	0.008
2500–3300	4445	InSb	51	2785	0.008
3200–4200	4445	InSb	15	2751	0.012
3200–4200	4445	InSb	87	2768	0.010
4000–5200	4445	InSb	15	2726	0.008
4000–5200	8043	InSb	87	1343	0.008
4000–5200	2997	InSb	51	1507	0.008
4900–6400	4445	Ge	105	2055	0.008
2000–9000	1883	InSb	69	2532	0.016
5000–9000	8043	Ge	105	2954	0.016

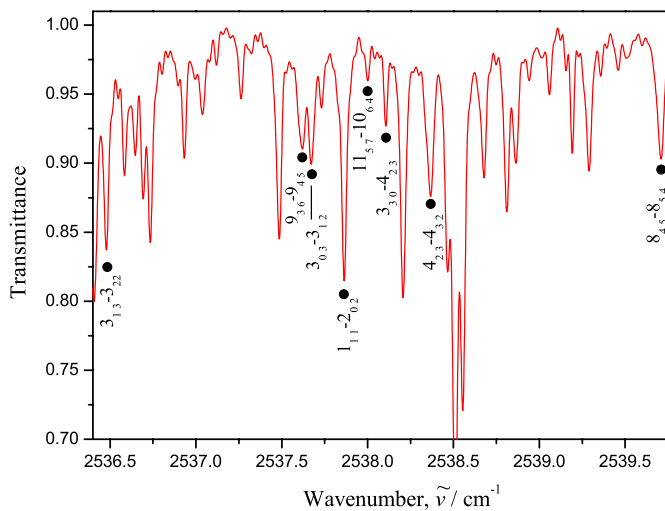


Fig. 2. Small portion of the D<sub>2</sub>S spectrum in the region of the 3ν<sub>2</sub> band. Lines of the 3ν<sub>2</sub> band are marked by dark circles. Unmarked lines belong to other hydrogen sulfide species. Experimental conditions: absorption path length, 87 m; sample pressure, 8043 Pa; instrumental resolution, 0.016 cm<sup>-1</sup>; room temperature.

Here  $|v\rangle$  and  $|\tilde{v}\rangle$  denote the different interacting vibrational states of a polyad.  $H^{vv}$  is the  $v$ -diagonal operator, describing the rotational structure of vibrational state  $|v\rangle$ . Usually,  $H^{vv}$  is a Watson's type Hamiltonian [25]. In the  $A$  reduction and  $I'$  representation one gets:

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

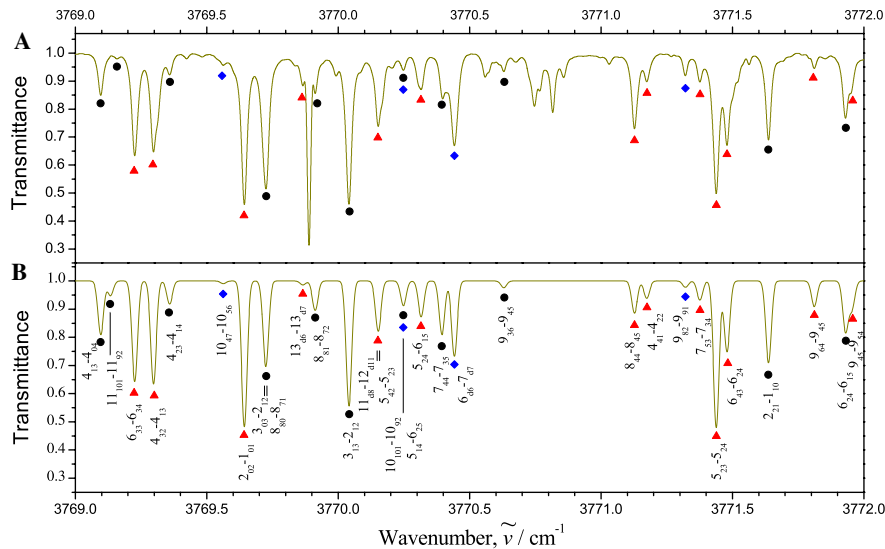


Fig. 3. Small portion (A, experimental; B, simulated) of the high-resolution spectrum of  $D_2S$  in the region of the  $v = 2$  polyad. Lines belonging to the  $2\nu_1$ ,  $\nu_1 + \nu_3$  and  $2\nu_3$  bands are marked by dark circles, dark triangles and dark diamonds, respectively. Unmarked lines belong to other hydrogen sulfide species. Experimental conditions: absorption path length, 15 m; sample pressure, 4445 Pa; instrumental resolution,  $0.012 \text{ cm}^{-1}$ ; room temperature.

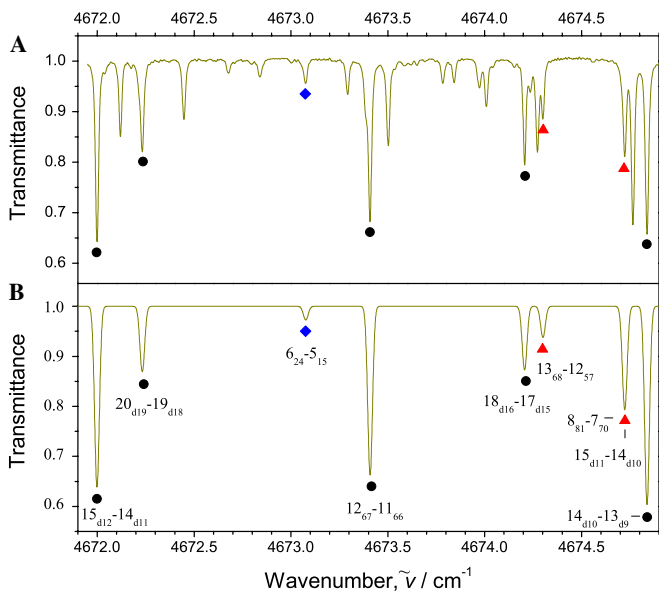


Fig. 4. Small portion of the  $D_2S$  spectrum in the region of the  $v = 5/2$  polyad (A, experimental; B, simulated). Lines of the  $\nu_1 + \nu_2 + \nu_3$ ,  $\nu_2 + 2\nu_3$  and  $2\nu_1 + \nu_2$  bands are marked by dark circles, dark diamonds, and dark triangles, respectively. Unmarked lines belong to other hydrogen sulfide species. Experimental conditions: absorption path length, 51 m; sample pressure, 4445 Pa; instrumental resolution,  $0.008 \text{ cm}^{-1}$ ; room temperature.

The non- $v$ -diagonal operators  $H^{v\tilde{v}}$  ( $v \neq \tilde{v}$ ) describe different types of resonance interactions. When the symmetries of states  $|v\rangle$  and  $|\tilde{v}\rangle$  are the same,  $H^{v\tilde{v}}$  describe vibrational resonances (Fermi or Darling–Dennison for example)

$$H_F^{v\tilde{v}} = a^{v\tilde{v}} \left\{ F^{v\tilde{v}} + F_K^{v\tilde{v}} J_z^2 + F_J^{v\tilde{v}} J^2 + F_{KK}^{v\tilde{v}} J_z^4 + F_{KJ}^{v\tilde{v}} J_z^2 J^2 + F_{JJ}^{v\tilde{v}} J^4 + \dots + F_{xy}^{v\tilde{v}} (J_x^2 - J_y^2) + F_{xyK}^{v\tilde{v}} \left[ J_z^2, (J_x^2 - J_y^2) \right] + F_{xyJ}^{v\tilde{v}} J^2 (J_x^2 - J_y^2) + F_{xyKK}^{v\tilde{v}} \left[ J_z^4, (J_x^2 - J_y^2) \right] + F_{xyKJ}^{v\tilde{v}} \left[ J_z^2 J^2, (J_x^2 - J_y^2) \right] + F_{xyJJ}^{v\tilde{v}} J^4 (J_x^2 - J_y^2) + \dots \right\}. \quad (3)$$

If the symmetries of the states  $|v\rangle$  and  $|\tilde{v}\rangle$  are different,  $H^{v\tilde{v}}$  describes Coriolis-type interaction

$$H_C^{v\tilde{v}} = b_y^{v\tilde{v}} \left\{ C_y^{v\tilde{v}} iJ_y + C_{yK}^{v\tilde{v}} [iJ_y, J_z^2] + C_{yJ}^{v\tilde{v}} iJ_y J^2 + C_{yKK}^{v\tilde{v}} [iJ_y, J_z^4] + C_{yJK}^{v\tilde{v}} [iJ_y, J_z^2 J^2] + C_{yJL}^{v\tilde{v}} iJ_y J^4 + \dots \right\} + b_{xz}^{v\tilde{v}} \left\{ C_{xz}^{v\tilde{v}} (J_x J_z + J_z J_x) + C_{xzK}^{v\tilde{v}} [(J_x J_z + J_z J_x), J_z^2] + C_{xzJ}^{v\tilde{v}} (J_x J_z + J_z J_x) J^2 + C_{xzKK}^{v\tilde{v}} [(J_x J_z + J_z J_x), J_z^4] + C_{xzJK}^{v\tilde{v}} [(J_x J_z + J_z J_x), J_z^2] J^2 + C_{xzJJ}^{v\tilde{v}} (J_x J_z + J_z J_x) J^4 + \dots \right\}. \quad (4)$$

In Eqs. (2)–(4)  $J^2 = J_x^2 + J_y^2 + J_z^2$ ;  $[A, B]_+$  denotes the anti-commutator ( $AB + BA$ ). In accordance with the general principles of vibration–rotation theory [26,27], 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. Moreover, it is possible to show that any individual parameter  $P$  of any diagonal block  $H^{v\tilde{v}}$  of a “normal” polyatomic (three-atoms in our case) molecule can be expressed as a function of the more fundamental spectroscopic quantities  $P^0$ ,  $p^\lambda$ , etc., in the following form:

$$P^{v_1, v_2, \dots, v_n} = P^0 + \sum_{\lambda} p^\lambda v_\lambda + \sum_{\lambda\mu \geq \lambda} p^{\lambda\mu} v_\lambda v_\mu + \dots \quad (5)$$

Here  $n$  ( $n = 3$  in our case) is the number of vibrational modes of the molecule;  $P^{v_1, v_2, \dots, v_n}$  denotes an individual spectroscopic parameter of the vibrational state ( $v_1, v_2, \dots, v_n$ ) of the molecule;  $P^0$  is the corresponding parameter of the ground vibrational states;  $p^\lambda$ ,  $p^{\lambda\mu}$  are the corrections accounting for the differences between the parameter values for the different vibrational states. In accordance with the general principles of vibration–rotation theory, see, e.g. [27], the order of magnitude relation

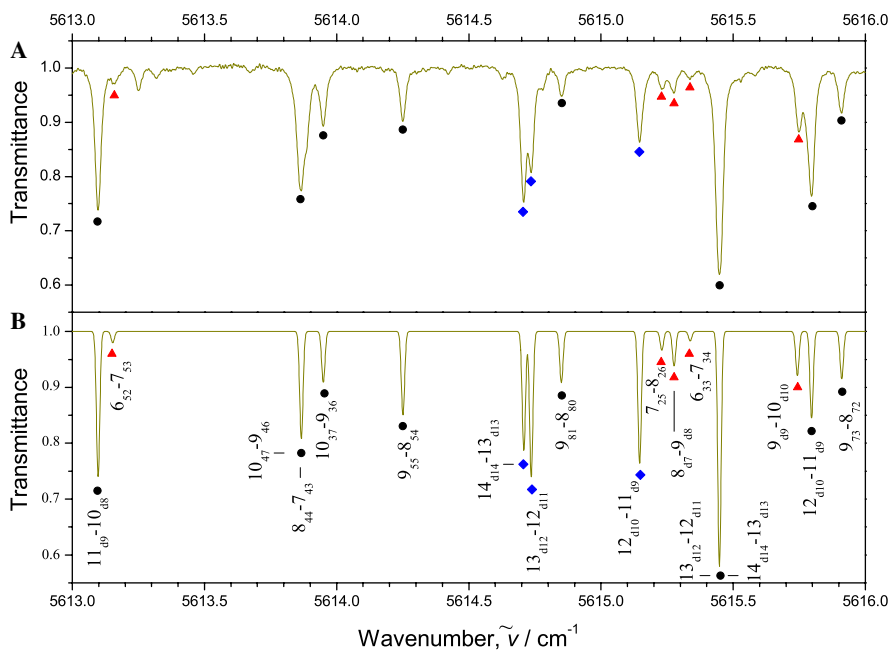


Fig. 5. Small portion of the  $D_2S$  spectrum in the region of the  $v = 3$  polyad (A, experimental; B, simulated). Lines of the  $2\nu_1 + \nu_3$ ,  $3\nu_1$  and  $3\nu_3$  bands are marked by dark circles, dark diamonds, and dark triangles, respectively. Experimental conditions: absorption path length, 105 m; sample pressure, 4445 Pa; instrumental resolution,  $0.008 \text{ cm}^{-1}$ ; room temperature.

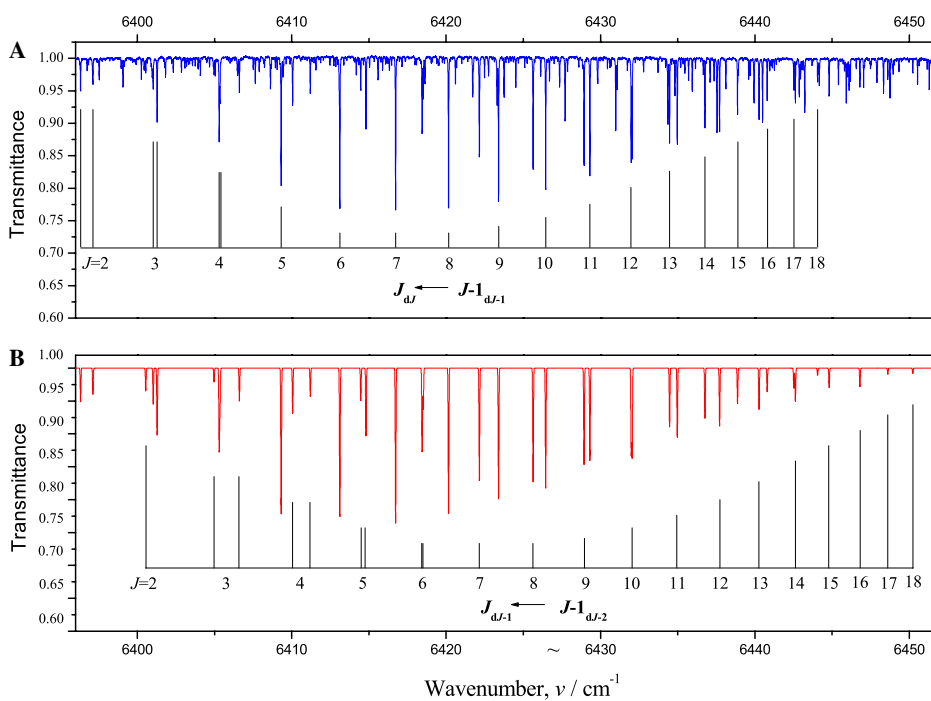


Fig. 6. Illustration of the  $D_2S$  experimental (upper trace A) spectrum in the region of the  $v = 7/2$  polyad. Two sets of transitions of the  $2\nu_1 + \nu_2 + \nu_3$  band are simulated (lower trace B) and marked. Experimental conditions: absorption path length, 105 m; sample pressure, 4445 Pa; instrumental resolution,  $0.015 \text{ cm}^{-1}$ ; room temperature.

$$|p^0| \gg |p^1| \gg |p^{2\mu}| \gg |p^{2\mu\nu}| \gg \dots \quad (6)$$

should be fulfilled for “normal” molecules.

In the same way as the  $v$ -diagonal parameters, the parameters describing the resonance interactions can be

expressed as functions of more fundamental parameters. Namely, for  $XY_2$  ( $C_{2v}$ -symmetry) molecules, which we discuss in the present contribution, the pure vibrational resonance interactions are divided into two types: Fermi-type resonances which characterize interactions between the

states  $|i\rangle = (v_1, v_2, v_3)$  and  $|j\rangle = (v_1 \pm 1, v_2 \mp 2, v_3)$  and Darling–Dennison resonances which characterize interactions between the states  $|i\rangle = (v_1, v_2, v_3)$  and  $|j\rangle = (v_1 \pm 2, v_2, v_3 \mp 2)$ . The rotational dependencies of the resonance operators of both types is determined by Eq. (3), and the values of the coefficients  $a^{vv'}$  are given by the relation

$$a^{v_1, v_2, v_3 \ v_1 \pm 2, v_2, v_3 \mp 2} = \frac{1}{4} \{ (2v_1 + 1 \pm 1)(2v_1 + 1 \pm 3)(2v_3 + 1 \mp 1)(2v_3 + 1 \mp 3) \}^{1/2} \quad (7)$$

for Darling–Dennison interactions, and by the relation

$$a^{v_1, v_2, v_3 \ v_1 \pm 1, v_2 \mp 2, v_3} = \frac{1}{8^{1/2}} \{ (2v_1 + 1 \pm 1)(2v_2 + 1 \mp 1)(2v_2 + 1 \mp 3) \}^{1/2} \quad (8)$$

for Fermi interactions. Also the  $F^{vv'}$  parameters of Eq. (3) can be expressed as functions of more fundamental spectroscopic quantities. Namely

$$F_{\dots}^{v_1, v_2, v_3 \ v_1 \pm 2, v_2, v_3 \mp 2} = F_{\dots} + f_{\dots}^1 (v_1 + \frac{1}{2} \pm 1) + f_{\dots}^2 (v_2 + \frac{1}{2}) + f_{\dots}^3 (v_3 + \frac{1}{2} \mp 1) + \dots \quad (9)$$

and

$$F_{\dots}^{v_1, v_2, v_3 \ v_1 \pm 1, v_2 \mp 2, v_3} = \tilde{F}_{\dots} + \tilde{f}_{\dots}^1 (v_1 + \frac{1}{2} \pm \frac{1}{2}) + \tilde{f}_{\dots}^2 (v_2 + \frac{1}{2} \mp 1) + \tilde{f}_{\dots}^3 (v_3 + \frac{1}{2}) + \dots \quad (10)$$

for the Darling–Dennison and Fermi resonance interactions, respectively.

Analogously to the vibrational Darling–Dennison and Fermi type interactions, the Coriolis parameters  $C_{\dots}^{vv'}$  (Eq. (4)) can be expressed as functions of more fundamental constants

$$C_{\dots}^{v_1, v_2, v_3 \ v_1 \pm 1, v_2, v_3 \mp 1} = C_{\dots} + c_{\dots}^1 (v_1 + \frac{1}{2} \pm \frac{1}{2}) + c_{\dots}^2 (v_2 + \frac{1}{2}) + c_{\dots}^3 (v_3 + \frac{1}{2} \mp \frac{1}{2}) + \dots \quad (11)$$

and

$$C_{\dots}^{v_1, v_2, v_3 \ v_1, v_2 \pm 2, v_3 \mp 1} = \tilde{C}_{\dots} + \tilde{c}_{\dots}^1 (v_1 + \frac{1}{2}) + \tilde{c}_{\dots}^2 (v_2 + \frac{1}{2} \pm 1) + \tilde{c}_{\dots}^3 (v_3 + \frac{1}{2} \mp \frac{1}{2}) + \dots \quad (12)$$

for the Coriolis interactions between the pair of states  $(v_1, v_2, v_3)/(v_1 \pm 1, v_2, v_3 \mp 1)$  and  $(v_1, v_2, v_3)/(v_1, v_2 \pm 2, v_3 \mp 1)$ , respectively. In these cases, the coefficients  $b^{vv'}$  in Eq. (4) are determined by the formulas

$$b_{xz}^{v_1, v_2, v_3 \ v_1 \pm 1, v_2, v_3 \mp 1} = \mp b_y^{v_1, v_2, v_3 \ v_1 \pm 1, v_2, v_3 \mp 1} = \frac{1}{2} \{ (2v_1 + 1 \pm 1)(2v_3 + 1 \mp 1) \}^{1/2} \quad (13)$$

and

$$b_{xz}^{v_1, v_2, v_3 \ v_1, v_2 \pm 2, v_3 \mp 1} = \mp b_y^{v_1, v_2, v_3 \ v_1, v_2 \pm 2, v_3 \mp 1} = \frac{1}{8^{1/2}} \{ (2v_2 + 1 \mp 1)(2v_2 + 1 \mp 3) \times (2v_3 + 1 \mp 1) \}^{1/2}. \quad (14)$$

#### 4. Assignments of transitions

Since the molecular symmetry group of  $D_2S$  is isomorphous to the  $C_{2v}$  point group, the selection rules allow ro-vibrational transitions of the  $b$ -type

$$\begin{aligned} \Delta J &= 0, \pm 1; & \Delta K_a &= \pm(2n + 1); \\ \Delta K_c &= \pm(2m + 1) \end{aligned} \quad (15)$$

Table 2  
Statistical information on the investigated bands of the  $D_2S$  molecule

Band	Center ( $\text{cm}^{-1}$ )		Number of transitions	Number of levels	$J^{\max}$	$K_a^{\max}$	rms, $10^3 \text{ cm}^{-1}$
	Calc. [29]	Exp.					
1	2	3	4	5	6	7	8
$v_2$	855.42	855.40416	786	351	23	17	0.41
$v_1$	1895.85	1896.43154	663	352	25	16	0.76
$v_3$	1910.13	1910.18375	367	258	20	13	0.57
$3v_2$	2549.40	2549.07336	402	137	19	8	1.5
$v_1 + v_2$	2742.34	2742.66570	1156	302	21	10	1.1
$v_2 + v_3$	2754.71	2754.45192	1032	298	21	11	1.1
$2v_2 + v_3$	3593.85	3593.12888	221	109	18	6	1.3
$2v_1$	3752.80	3753.470	668	224	19	10	1.3
$v_1 + v_3$	3756.61	3757.45948	779	237	22	11	1.2
$2v_3$	3808.79	3809.154	162	55	18	6	2.5
$v_1 + 3v_2$	4418.52	4417.95894	95	46	15	5	1.3
$3v_2 + v_3$	4427.16	4426.08293	85	48	13	3	1.6
$2v_1 + v_2$	4588.87	4589.226	623	192	19	9	1.5
$v_1 + v_2 + v_3$	4591.73	4592.18104	843	264	24	10	1.5
$v_2 + 2v_3$	4643.56	4643.477	8	5	6	2	7.0
$v_1 + 2v_2 + v_3$	5421.41	5421.3007	179	91	15	6	2.7
$3v_1$	5559.15	5560.15	227	112	20	7	2.4
$2v_1 + v_3$	5559.57	5560.74	533	194	20	10	1.9
$v_1 + 2v_3$	5645.49	5647.13	119	47	12	3	4.1
$3v_3$	5672.74	5672.89	197	99	15	8	3.8
$3v_1 + v_2$	6383.88	6384.63	165	95	18	5	2.5
$2v_1 + v_2 + v_3$	6384.12	6384.99	428	148	19	8	1.3

<sup>a</sup> Data in column 3 correspond to ones from column 3 of Table 4.

for the bands  $kv_1 + lv_2 + sv_3$  with  $k$  and  $l$  arbitrary and  $s$  even. For the bands  $kv_1 + lv_2 + sv_3$  with  $k$  and  $l$  arbitrary and  $s$  odd, the selection rules lead to ro-vibrational transitions of the  $a$ -type

$$\Delta J = 0, \pm 1; \quad \Delta K_a = \pm 2n; \quad \Delta K_c = \pm(2m + 1). \quad (16)$$

In Eqs. (15) and (16)  $n$  and/or  $m$  are integers.

The assignments of the transitions were performed using the Ground State Combination Differences method. The ground state energies were calculated on the base of the parameters from Table 2 of Ref. [18]. As the result of the assignments, altogether more than 9300 transitions were assigned for the bands of the five studied polyads of interacting vibrational states. Statistical information concerning the assigned bands and transitions is presented in Table 2 and as illustration portions of recorded spectra in each polyad are shown in Figs. 2–6 with the assignments of lines. The assigned transitions were then used for the determination of the upper ro-vibrational energy levels of the states (030), (110), (011), (200), (101), (002), (021), (210), (111), (012), (031), (130), (300), (201), (102), (003), (121), (310), and (112). Small fragments of the obtained upper energy levels with  $4 \leq J \leq 9$  are shown in Table 3. The whole obtained results are given in Table S.I of the Supplementary Materials [28]. Values denoted as  $\Delta$  in columns 9, 12, 15, etc., of Tables 3 and S.I are the experimental uncertainties of the obtained upper energy values. Since usually one upper ro-vibrational energy is determined from several transitions reaching the same upper level,  $\Delta$  can be considered as an indication of the precision of the experimental line positions. The experimental accuracy is decreasing both with an increase of the values of the quantum numbers  $J$  and  $K_a$  because of decreasing line strengths, and with an increase of the frequency region because of a decreasing instrumental resolution, increasing linewidths, and decreasing bandstrengths.

## 5. Global rotational–vibrational fit and discussion

The Hamiltonian as defined in Section 3 was used in the “Global Fit” analysis of the ro-vibrational energies of all available vibrational bands of the D<sub>2</sub>S molecule. The ground state rotational parameters of the diagonal blocks (rotational constants and centrifugal distortion coefficients) were not fitted but were fixed to their corresponding values of Ref. [18].

As was discussed in Ref. [21], the pure vibrational parameters appearing in Eq. (5) (in our case  $P^0 \equiv 0$ ;  $p^\lambda \equiv \tilde{\omega}_\lambda = \omega_\lambda + x_{\lambda\lambda} + 1/2 \sum_{\mu \neq \lambda} x_{\lambda\mu}$ ;  $p^{\lambda\mu} = x_{\lambda\mu}$ , ...) are considerably larger than the rotational and centrifugal distortion parameters. This means that any attempt to calculate the pure vibrational energies with the same accuracy than the rotational terms will need an extremely large number of high order terms in the vibrational series

$$E^{v_1, v_2, v_3} = \sum_{\lambda} \tilde{\omega}_\lambda v_\lambda + \sum_{\lambda\mu \geq \lambda} x_{\lambda\mu} v_\lambda v_\mu + \dots \quad (17)$$

For this reason, in the fit procedure we fitted directly the vibrational energies.

The 3664 energy levels of the 22 vibrational states (they correspond to more than 9700 infrared transitions which have been used in their determination) mentioned in Table 2 were used as input data in the fit procedure. In this case, presence of numerous and strong resonance interactions both between the observed vibrational states and between the observed and “dark” states led to the necessity of a correct estimation of the vibrational energy values of the “dark” states. As one can see from the comparison of values in columns 2 and 3 of Table 2, the predictions of the band centers from Ref. [29] are more than satisfactory. So, predicted values of the band centers from [29] were used as the initial data in the fit both for studied and “dark” vibrational bands.

The weights of the energy levels introduced in the fit were taken proportional to  $1/\Delta^2$ , where the  $\Delta$ s are the experimental uncertainties of energies given in columns 9, 12, 15, etc., of Table 3 (Table S.I of the Supplementary Materials). As the result of the fit a set of 231 parameters were obtained. These are given in Tables 4–6. Values in parentheses following the parameters values in Tables 4–6 are the  $1\sigma$  statistical confidence intervals. The vibrational energies  $E^{v_1, v_2, v_3}$  which are presented in Table 4 without confidence intervals were constrained to values which correspond to the values of band centers predicted in Ref. [29]. The set of 231 parameters reproduce the values of the 3664 experimental energy levels with the RMS deviations given in column 8 of Table 2. A comparison of these RMS with the values of the  $\Delta$ s given in Table 3 shows the quality of the fit since the RMS values are close to the experimental uncertainties.

One more remarks should be made here concerning the main part  $F^{v_1, v_2, v_3}_{v_1 \pm 1, v_2 \mp 2, v_3}$  of a Fermi-type interaction between the states  $(v_1, v_2, v_3)$  and  $(v_1 \pm 1, v_2 \mp 2, v_3)$ . It is known, [27], that a strength of this interaction is determined by a value of ratio  $f = |k_{122}/(\omega_1 - 2\omega_2)|$ . When the value of this ratio is close to 1, the resonance interaction is really strong, and non-zero  $F$ -parameters appeared in a corresponding resonance block. However, when  $f$  is considerably smaller than 1, corresponding effects can be “transferred” from nondiagonal blocks of the effective Hamiltonian, Eq. (1), to diagonal blocks. In this case, the  $F^{v_1, v_2, v_3}_{v_1 \pm 1, v_2 \mp 2, v_3}$ -values in resonance blocks can be fixed to zero. In real fits of experimental data the last situation is appeared as a strong correlations between the  $F$ -parameters of non-diagonal blocks and vibrational  $E$ -parameters of diagonal blocks. Just such situation was realized in our analysis. On that reason values of all  $F$ -parameters were fixed to zero.

From the parameters of Tables 4–6 it is possible to calculate the effective spectroscopic constants of any vibrational state (including the “dark” ones). The corresponding effective spectroscopic parameters are collected in Table 7 for all the studied vibrational bands of

Table 3  
Experimental ro-vibrational term values for some vibrational states of the D<sub>2</sub>S molecule (in cm<sup>-1</sup>)<sup>a,b</sup>

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	(010)		(100)		(001)		(030)			(110)		
			<i>E</i>	$\delta$	<i>E</i>	$\delta$	<i>E</i>	$\delta$	<i>E</i>	$\Delta$	$\delta$	<i>E</i>	$\Delta$	$\delta$
	1		2	3	4	5	6	7	8	9	10	11	12	13
4	0	4	914.31360	0	1954.64892	-30	1968.58047	36	2608.1247	—	17	2800.9220	* 1	2
4	1	4	914.32294	5	1954.65676	-38	1968.58529	36	2608.1360	10	16	2800.9303	5	-1
4	1	3	932.32512	-5	1971.67221	-6	1985.56757	11	2627.8988	12	-13	2818.7698	* 2	1
4	2	3	932.70308	3	1972.00959	3	1985.76449	17	2628.3465	28	1	2819.1333	* 4	1
4	2	2	943.47596	-14	1982.23690	11	1996.22297	-24	2640.0884	5	-12	2829.8238	* 0	-1
4	3	2	946.95713	9	1985.43941	37	1999.68696	10	2644.0677	2	10	2833.2313	* 2	2
4	3	1	950.54244	-3	1988.98456	28	2002.83722	-28	2647.9182	2	-2	2836.8689	* 1	3
4	4	1	960.49558	4			2011.59166	2	2659.0892	13	-6	2846.4783	* 2	0
4	4	0	960.82320	-2	1998.01609	64			2659.4336	8	4	2847.2761	5	7
5	0	5			1981.28847	20	1995.31889	90	2634.7764	8	-4	2827.4602	—	0
5	1	5	941.15570	-25	1981.28847	-9	1995.31889	26	2634.7764	8	-22	2827.4620	—	6
5	1	4	964.59591	-1	2003.43179	-4	2017.37962	9	2660.5357	12	0	2850.6839	* 3	-1
5	2	4	964.67654	-1	2003.50101	-1	2017.42181	6	2660.6341	6	2	2850.7593	* 3	1
5	2	3	981.74791	-17	2019.67495	-3	2033.67531	-21	2679.3059	—	-7	2867.6905	* 1	-1
5	3	3	983.10510	2	2020.89113	19	2034.45213	-2	2680.8982	4	-8	2868.9980	* 0	1
5	3	2	991.86918	-23	2029.27448	20	2043.39857	-68	2690.3705	3	-30	2877.7280	* 2	-1
5	4	2	998.55323	15	2035.39694	59			2697.9718	8	-11	2884.2134	* 3	4
5	4	1	1000.69377	4	2037.82404	32	2052.07532	-34	2700.2345	15	-5	2886.6044	* 2	6
5	5	1	1014.78444	-9	2050.00222	53	2063.91159	-5	2715.9985	7	5	2900.8299	3	-1
5	5	0	1014.91385	-4	2051.40072	17	2064.05521	-5	2716.1308	6	-5	2900.8042	1	0
6	0	6	972.82718	11	2012.74770	-74	2026.89940	41	2666.1723	7	0	2858.7753	* 5	2
6	1	6	972.82718	-9	2012.74770	90	2026.89932	25	2666.1723	7	-2	2858.7753	* 5	0
6	1	5	1001.56332	-1	2039.88841	-27	2053.92858	2	2697.7581	15	-2	2887.2420	* 3	-1
6	2	5	1001.57853	1			2053.93550	9	2697.7780	—	5	2887.2553	* 0	-4
6	2	4	1024.50811	-13	2061.59127	-13	2075.59295	-28	2722.9169	11	-4	2909.9831	* 1	-1
6	3	4	1024.88614	-2	2061.91631	14	2075.79498	-23	2723.3757	5	5	2910.3364	* 3	-2
6	3	3	1040.24478	-31	2076.53063	0	2090.72043	-38	2740.0660	11	2	2925.5942	* 0	-5
6	4	3	1043.64759	11	2079.58915	29	2092.95707	-27	2744.0246	22	1	2928.8692	* 1	1
6	4	2	1050.10635	-13	2085.90215	12	2100.26566	-38	2750.9220	21	12	2935.4007	* 1	0
6	5	2	1060.86012	29	2095.55158	56	2108.93894	-11	2763.0892	18	9	2945.3475	* 0	3
6	5	1	1061.95211	21	2097.40316	36	2110.04702	-16	2764.2205	8	-1	2947.3627	* 1	5
6	6	1	1080.08467	-20	2114.46008	30	2126.84085	-5	2784.4283	13	-3	2965.3636	2	-2
6	6	0	1080.13233	-38	2114.42546	33	2126.89640	-5	2784.4781	2	9	2965.3819	* 1	-1
7	0	7	1009.33212	-4	2049.02939	-97	2063.32306	25	2702.3114	3	2	2894.8677	* 1	7
7	1	7	1009.33212	-7	2049.02939	-99	2063.32306	24	2702.3114	3	2	2894.8677	* 1	0
7	1	6	1043.32426	3	2081.13063	-43	2095.29094	19	2739.6801	3	0	2928.5397	* 1	-3
7	2	6	1043.32688	-5	2081.13252	-60	2095.29160	-15	2739.6830	7	-6	2928.5421	* 1	-2
7	2	5	1071.69738	-10	2107.95140	-16	2122.01773	-19	2770.8163	2	-2	2956.6523	* 2	-2
7	3	5	1071.78441	-5	2108.02228	-1	2122.05769	-14	2770.9249	8	-6	2956.7304	* 1	-1
7	3	4	1093.69491	-23	2128.80669	-1	2142.94405	-36	2794.8483	12	7	2978.4724	10	0
7	4	4	1094.93610	6	2129.88052	11	2143.63861	-33	2796.3404	9	12	2979.6374	* 1	1
7	4	3	1107.82161	-36	2142.23789	-1	2156.69837	-56	2810.2083	7	-16	2992.4865	* 2	-4
7	5	3	1114.47892	29	2148.19861	48	2161.49582	-56	2817.8866	12	-1	2998.8178	* 1	3
7	5	2	1118.68463	8	2152.62577	23	2164.97523	-16	2822.3027	10	29	3003.3646	* 0	3
7	6	2	1133.98785	45	2168.26742	-5	2179.62296	-13	2839.5218	3	2	3019.0941	* 2	3
7	6	1	1134.47964	35	2167.80124	44	2180.16883	0	2840.0241	14	17	3019.2529	3	0
7	7	1	1156.34879	-72	2188.23040	-4						3040.8710	* 3	-11
7	7	0	1156.36611	-40	2188.23012	3			2864.3276	10	0	3040.8795	* 1	-13
8	0	8	1050.66781	4	2090.13094	-98	2104.58693	6	2743.1925	10	4	2935.7359	* 1	0
8	1	8	1050.66781	4	2090.13094	-98	2104.58693	6	2743.1925	10	4	2935.7359	* 1	0
8	1	7	1089.90183	16			2141.48120	12	2786.3299	12	-1	2974.6000	* 1	1
8	2	7	1089.90183	-30			2141.48109	-13	2786.3299	12	-7	2974.6000	* 1	-3
8	2	6	1123.55599	-1	2158.98438	-32	2173.16177	-14	2823.2712	5	-2	3007.9405	* 1	-2
8	3	6	1123.57413	-10	2158.99842	-19	2173.16864	-18	2823.2961	12	10	3007.9561	* 2	-2
8	3	5	1151.33237	-15	2185.27960	-12	2199.41271	-18	2853.6801	21	13	3035.4745	* 3	-4
8	4	5	1151.68312	-2	2185.56732	7	2199.57822	-29	2854.1132	—	-19	3035.7912	* 1	0
8	4	4	1171.76309	-36	2204.70983	-11	2219.10816	59	2875.8840	5	9	3055.7570	* 2	-3
8	5	4	1174.88418	16	2207.42895	31	2220.99342	-58	2879.5900	11	-16	3058.6925	* 2	5
8	5	3	1184.81175	-28	2217.12154	4	2232.06151	-38	2890.1375	4	0	3068.7144	* 2	1
8	6	3	1195.76592	32	2226.66684	22	2240.17662	-48	2902.6636	12	-11	3082.1384	* 1	-1
8	6	2	1198.14721	29	2229.96172	39	2242.61320	-55	2905.1110	16	-7	3082.1642	* 1	4
8	7	2	1217.98611	44	2248.98774	30	2260.75562	14				3102.0789	* 2	-1
8	7	1	1218.18967	36	2248.98531	47	2260.99517	0				3102.1861	* 3	-1
8	8	1	1243.49953	-65	2272.64911	-51						3127.1824	—	-17
8	8	0	1243.50529	-79	2272.65015	-59						3127.1863	—	-11

<sup>a</sup>  $\Delta$  is experimental error in the value of energy level  $E$  (in last digits of  $E$ ). The value of  $\Delta$  is absent when the upper level was determined from a single transition.  $\delta$  is the difference  $E^{\text{exp}} - E^{\text{calc}}$  also in last digits of  $E$ .

<sup>b</sup> Energy levels marked by asterisk were taken from Ref. [20].



Table 3 (continued)

J	K <sub>a</sub>	K <sub>c</sub>	(011)			(021)			(200)			(101)		
			E	$\Delta$	$\delta$	E	$\Delta$	$\delta$	E	$\Delta$	$\delta$	E	$\Delta$	$\delta$
			14	15	16	17	18	19	20	21	22	23	24	25
4	0	4	2812.8755	* —	−3	3651.6023	48	8	3811.1222	2	−2	3815.1854	6	4
4	1	4	2812.8814	* —	−2	3651.6087	1	2	3811.1282	—	5	3815.1879	7	−6
4	1	3	2830.6911	* 3	1	3670.2790	2	4	3827.9708	3	−3	3832.0265	7	1
4	2	3	2830.9583	* 1	0	3670.5894	2	1	3828.2421	6	0	3832.2424	2	2
4	2	2	2841.8478	* 1	4	3681.9573	15	−2	3838.4434	2	−5	3842.9203	4	−18
4	3	2	2844.7226	* 1	−6	3685.1737	4	−18	3841.1169	14	1	3845.3530	9	0
4	3	1	2848.9086	* 2	5				3844.9975	10	2	3848.8219	1	1
4	4	1	2858.0609	* 2	−5	3699.0653	15	16	3854.2746	—	−7	3857.8898	7	−6
4	4	0	2858.4193	* 2	−4	3699.4317	1	−1	3854.5289	2	−7	3858.2316	23	1
5	0	5	2839.5071	—	2	3678.1330	40	−2	3837.5048	—	−9	3841.6104	2	−2
5	1	5	2839.5075	—	−2	3678.1330	40	11	3837.5057	11	−5	3841.6104	2	1
5	1	4	2862.6505	* 2	−1	3702.4032	3	4	3859.3963	7	8	3863.4627	6	2
5	2	4	2862.7020	* 1	1	3702.4610	10	−18	3859.4419	2	0	3863.4936	5	2
5	2	3	2879.7194	* 1	1	3720.2744	4	12	3875.5147	9	−12	3879.6845	3	−8
5	3	3	2880.7161	* 1	0	3721.4128	22	−7	3876.4967	2	9	3880.4860	3	5
5	3	2	2889.9223	* 2	3	3731.0145	8	−36	3884.9825	15	−6	3888.5521	6	12
5	4	2	2895.7036	4	−7	3737.2054	9	−8	3891.5259	9	2	3894.7113	1	−3
5	4	1	2897.8438	* 2	−3	3739.5253	18	1	3893.1565	2	−6	3896.8741	3	−2
5	5	1	2911.5555	13	0	3753.7953	6	−9	3906.2395	1	−4	3909.7287	3	4
5	5	0	2911.7018	8	−6	3753.9444	2	−16	3906.3389	4	−7	3909.8688	12	8
6	0	6	2870.9355	* 6	−2	3709.4147	15	2	3868.6655	9	−4	3872.8221	6	−3
6	1	6	2870.9355	* 6	−1	3709.4147	15	4	3868.6655	9	−4	3872.8221	6	−3
6	1	5	2899.2934	* 0	1	3739.1569	8		3895.4836	16	2	3899.5879	3	0
6	2	5	2899.3018	* 0	1	3739.1664	22	2	3895.4906	7	8	3899.5908	14	−1
6	2	4	2922.0039	* 0	2	3762.9538	5	16	3916.9687	8	0	3921.0478	8	6
6	3	4	2922.2489	* 1	1	3763.2384	16	13	3917.1926	6	1	3921.2008	1	−4
6	3	3	2937.8255	4	1	3779.4974	9	12	3931.8110	11	4	3936.5114	6	−13
6	4	3	2940.4587	* 2	0	3782.4314	8	−2	3934.1026	4	20	3938.4197	4	0
6	4	2	2948.1462	* 0	7	3788.8960		34	3940.9753	8	−6	3944.6707	2	4
6	5	2	2957.2042	* 2	−2	3800.0229	10	6	3951.1112	4	−4	3954.3083	2	−1
6	5	1	2958.3937	* 1	−3	3801.2549		4	3952.0380	15	2	3955.4652	1	−2
6	6	1	2975.8891	* 1	−6	3819.6172		21	3968.7632	15	−15	3972.0839	5	10
6	6	0	2975.9448	2	−12				3968.7959	7	1	3972.1297	10	0
7	0	7	2907.1620	* 2	0	3745.4487	—	−6	3904.6034	8	10	3908.8207	4	−1
7	1	7	2907.1620	* 2	0	3745.4487	—	−6	3904.6034	8	10	3908.8207	4	−1
7	1	6	2940.7024	* 2	2	3780.6295	8	−9	3936.3189	10	6	3940.4737	6	−4
7	2	6	2940.7038	* 7	3	3780.6295	8	6	3936.3189	10	−12	3940.4737	6	−3
7	2	5	2968.7271	* 0	2	3810.0036	5	15	3962.8576	4	−1	3966.9598	4	1
7	3	5	2968.7760	* 1	1	3810.0659	—	51	3962.8950	2	7	3966.9788	4	9
7	3	4	2990.6337	* 2	1	3832.9250	5	22	3983.5350	7	−2	3987.7193	5	−5
7	4	4	2991.4667	* 1	2	3833.8832	13	16	3984.2930	10	−3	3988.2684	3	8
7	4	3	3005.0419	* 2	5				3996.8225	10	4	4000.0912	8	9
7	5	3	3010.3770	* 1	0	3853.8184		2	4003.5673	2	−5	4006.2264	5	−1
7	5	2	3014.6043	* 2	4	3858.3597	6	−21	4006.9001	4	−1	4010.4995	7	−1
7	6	2	3029.3419	* -	−2	3873.7234	5	0	4021.1760	5	4	4024.2364	5	2
7	6	1	3029.9055	* 3	−6	3874.2983	5	−2	4021.6088	5	0	4024.7864	8	−2
7	7	1	3051.0196	* 1	−5				4041.8019	6	0	4044.9210	—	7
7	7	0	3051.0405	* 1	−5							4044.9461	1	2
8	0	8	2948.1835	4	0	3786.2342	2	−5	3945.3130	3	1	3949.6031	4	1
8	1	8	2948.1835	4	0	3786.2342	2	−5	3945.3130	3	1	3949.6031	4	1
8	1	7	2986.8950	* 1	2	3826.8404	8	−2	3981.9155	12	−1	3986.1331	7	−1
8	2	7	2986.8950	* 1	4	3826.8404	8	0	3981.9155	12	−2	3986.1331	7	−1
8	2	6	3020.1155	* 8	3	3861.6629	10	8	4013.3501	8	0	4017.5075	8	−2
8	3	6	3020.1241	* 0	1	3861.6730	11	1	4013.3561	16	10	4017.5075	8	5
8	3	5	3047.6171	* 1	0	3890.4616		14	4039.5100	8	1	4043.5872	8	4
8	4	5	3047.8195	* 1	1	3890.7010	3	10	4039.6400	28	−10	4043.6652	5	4
8	4	4	3068.1972	* 2	0	3911.9570	30	−3	4058.6899	8	9	4063.3986	8	3
8	5	4	3070.3989	* 1	2	3914.4461	9	11	4060.5354	5	18	4064.7873	3	9
8	5	3	3078.5017	* -	4				4070.8742	8	39	4074.4239	10	−9
8	6	3	3090.6245	* 1	4				4081.2926	7	−8	4084.0507	7	−1
8	6	2	3093.2221	* 2	2				4083.2694	11	12	4086.6048	4	−2
8	7	2	3112.1709	* 0	0				4101.6776	4	3	4104.5439	2	17
8	7	1	3112.4149	* 0	−1				4101.8882	4	4	4104.7912	2	13
8	8	1	3136.8722	—	3				4125.2777	2	10	4128.2162	—	−16
8	8	0	3136.8798	—	5				4125.2952	20	−3			

(continued on next page)

Table 3 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	(002)			(130)			(031)			(210)		
			<i>E</i>	<i>A</i>	<i>δ</i>	<i>E</i>	<i>A</i>	<i>δ</i>	<i>E</i>	<i>A</i>	<i>δ</i>	<i>E</i>	<i>A</i>	<i>δ</i>
	1		26	27	28	29	30	31	32	33	34	35	36	37
4	0	4				4476.3620	20	8				4646.9242		12
4	1	4				4476.3735		19	4484.6346	12	−18	4646.9286		0
4	1	3	3883.7997	—	41	4495.9671	15	10				4664.5905	5	−5
4	2	3	3884.0768	10	−35				4504.5533	19	1	4664.8777	10	−1
4	2	2				4508.0567	13	3				4675.5497	12	3
4	3	2										4677.9823	2	8
4	3	1	3900.7610	17	12							4682.4277	11	1
4	4	1										4692.1547	8	−2
4	4	0				4527.2730	2	5				4692.4475	7	1
5	0	5				4502.7169	8	−1	4511.0656	42	−1	4673.2106	17	3
5	1	5				4502.7169	8	0	4511.0656	42	10	4673.2106	17	−4
5	1	4	3915.3014	4	−24				4536.5146	21	12	4696.1685	5	−6
5	2	4	3915.3572	21	−33	4528.3329	19	−10				4696.2182	2	−5
5	2	3							4555.2190	8	32	4713.0490	2	−10
5	3	3	3932.4603	2	−42				4556.4831	5	−4	4714.0698	1	1
5	3	2										4722.9515	2	−5
5	4	2										4729.6288	3	0
5	4	1	3948.7964	10	57							4731.5505	7	−7
5	5	1				4583.3130	15	−12				4745.2848	2	2
5	5	0										4745.3981	8	5
6	0	6				4533.7610	6	1	4542.2066	11	−8	4704.2310	6	−2
6	1	6	3924.7856		31	4533.7610	6	−1	4542.2066	11	−7	4704.2310	6	−2
6	1	5	3951.4510	15	−7	4565.0592	8	9				4732.3605	17	−2
6	2	5	3951.5163	17	1	4565.0748		−3	4573.4072	24	−7	4732.3675	1	−1
6	2	4	3972.9548		38							4754.8720	9	−10
6	3	4	3973.2277		44									
6	3	3										4770.3841	6	−10
6	4	3										4774.4247	13	−2
6	4	2										4779.9871	9	−9
6	5	2										4790.5636	2	5
6	5	1										4791.5526	6	−9
6	6	1										4809.1950	3	20
6	6	0										4809.1156	14	21
7	0	7				4569.4935	9	−10	4578.0564		−12	4739.9857	1	1
7	1	7				4569.4935	9	−10	4578.0564		−12	4739.9857	1	1
7	1	6				4606.5230	60	28	4614.9496		−32	4773.2551	8	−1
7	2	6	3992.5256	22	4	4606.5230	60	−17	4614.9496		−13	4773.2551	8	−8
7	2	5							4645.7314	7	17	4801.0613	9	2
7	3	5	4018.9960	24	4							4801.1019	8	4
7	3	4										4822.6965	3	−18
7	4	4										4823.4968	10	−17
7	4	3										4836.5744	9	−22
7	5	3										4843.3410	3	7
7	5	2										4847.1553	29	19
7	6	2										4862.1161	6	6
7	6	1										4862.5771	6	−3
7	7	1										4883.8281	4	10
7	7	0										4883.8583		36
8	0	8				4609.9167	14	2	4618.6146	19	10	4780.4712	4	1
8	1	8				4609.9167	14	2	4618.6146	19	10	4780.4712	4	1
8	1	7	4038.0149	20	5	4652.6558	12	−12	4661.2018		11	4818.8694	4	−2
8	2	7	4038.0359	5	−13	4652.6558	12	−17	4661.2018		14	4818.8694	4	−3
8	2	6										4851.8235	25	5
8	3	6							4697.7033	16	−10	4851.8235	25	−50
8	3	5										4879.1308	14	3
8	4	5										4879.2996		42
8	4	4										4899.2140	15	−4
8	5	4										4903.1064	8	−15
8	5	3										4911.9659	5	0
8	6	3										4922.7761	10	1
8	6	2										4924.9807	6	8
8	7	2										4944.2998	1	16
8	7	1										4944.5240	11	8
8	8	1										4969.0962		27
8	8	0										4969.1216		33

Table 3 (continued)

J	K <sub>a</sub>	K <sub>c</sub>	(111)			(012)			(121)			(300)		
			E	Δ	δ	E	Δ	δ	E	Δ	δ	E	Δ	δ
	1		38	39	40	41	42	43	44	45	46	47	48	49
4	0	4	4649.9383		-3				5479.1128	18	9	5617.2630	13	26
4	1	4	4649.9428	1	0				5479.1159	3	-10	5617.2640	18	26
4	1	3	4667.6046	2	2				5497.6368		2	5633.9086	3	9
4	2	3	4667.8473	4	4				5497.9043	12	-32	5634.0524	2	0
4	2	2	4679.4164	1	2							5644.1897	—	-3
4	3	2	4681.6499	3	-2				5512.4278	2	-9	5647.3731	—	6
4	3	1	4685.2785	5	0				5516.2056	16	5	5650.6422	—	17
4	4	1	4694.8047	4	-21				5526.2418		44	5659.7287	—	-7
4	4	0	4695.1546	1	-17				5526.5930		-20	5660.0250	26	-24
5	0	5	4676.2610	2	1				5505.3363	7	-6	5643.4052	45	36
5	1	5	4676.2610	2	4				5505.3363	7	-1	5643.4052	45	38
5	1	4	4699.1874	4	2				5529.3840	16	18	5665.0160	2	29
5	2	4	4699.2240	6	-1				5529.4271	16	10	5665.0261	—	24
5	2	3	4716.2113	3	1				5547.2731	20	12	5680.9081	—	1
5	3	3	4717.0866	8	4				5548.1906	20	-43	5682.2333	4	5
5	3	2	4725.7046	3	6				5557.2688	11	-11			
5	4	2	4732.0611	2	-11				5563.9450		1	5696.2808	4	21
5	4	1	4734.2965	3	-3				5566.2482	11	16	5698.2387	6	34
5	5	1	4747.8130	16	11				5580.4743		32	5711.1207	—	12
5	5	0	4747.9530	3	-14							5711.2353	—	-14
6	0	6	4707.3248	6	3				5536.2576	7	-6	5674.2778	17	-15
6	1	6	4707.3248	6	3				5536.2576	7	-6	5674.2778	17	-14
6	1	5	4735.4093	6	8				5565.7184	11	22	5700.7432	—	10
6	2	5	4735.4125	5	-1				5565.7218	2	1	5700.7405	15	14
6	2	4	4757.8589	7	-65	4758.8946	11	-10	5589.3716	—	-79	5721.9785	20	-3
6	3	4	4758.0328	15	-3				5589.5655	—	-52	5722.0341	15	-4
6	3	3	4772.4985	3	4									
6	4	3	4776.2287	1	-2				5608.6045	22	-8	5739.6309	6	15
6	4	2	4782.7782	1	3				5615.4183	10	-1	5745.5378	20	-28
6	5	2	4792.9293	4	-16				5626.1455	13	-10	5755.3301	2	2
6	5	1	4794.1105	2	-11				5627.3497	—	4	5756.3291	—	-6
6	6	1	4811.5652	9	-1				5645.6964	—	21	5772.9404	13	-11
6	6	0	4811.6239	3	4				5645.7502	9	-6	5772.9843	—	-4
7	0	7	4743.1310	4	7				5571.8777	7	2	5709.8936	—	13
7	1	7	4743.1310	4	7				5571.8777	7	2	5709.8936	—	13
7	1	6	4776.3452	6	3				5606.7150	34	-45	5741.1835	3	-6
7	2	6	4776.3452	6	6				5606.7150	34	-40	5741.1835	3	4
7	2	5	4804.1127	15	8				5635.8278	—	35	5767.3545	—	-59
7	3	5	4804.1371	3	6				5635.8562	—	-5	5767.3517	25	15
7	3	4	4825.8218	9	-32									
7	4	4	4826.4512	8	-37							5789.0251	15	-3
7	4	3	4839.1733	3	2									
7	5	3	4845.4423	8	-9							5806.8095	5	9
7	5	2	4849.8561	4	-1									
7	6	2	4864.3515	11	-6							5824.6274	10	12
7	6	1	4864.9055	5	-7							5825.0795	25	18
7	7	1	4886.0201	13	0							5845.1648	18	37
7	7	0	4886.0447	7	4							5845.1797	—	31
8	0	8	4783.6758	2	3				5612.1915	3	-6	5750.2389	—	12
8	1	8	4783.6758	2	3				5612.1915	3	-6	5750.2389	—	12
8	1	7	4822.0095	5	-3				5652.4060	20	-12	5786.3496	12	-4
8	2	7	4822.0095	5	-3				5652.4060	20	-12	5786.3496	12	-1
8	2	6	4854.9109	13	-13				5686.8997	26	-13			
8	3	6	4854.9109	13	6				5686.8997	26	22			
8	3	5	4882.2100	5	6									
8	4	5	4882.3161	13	17									
8	4	4	4900.9946	9	-3									
8	5	4	4904.5370	20	-16									
8	5	3	4914.7048	5	0									
8	6	3	4924.8688	5	-13									
8	6	2	4927.4713	2	-8									
8	7	2	4946.3692	9	-6									
8	7	1	4946.6172	8	7									
8	8	1	4971.1190	10	20									
8	8	0	4971.1196	4	-6									

(continued on next page)



Table 3 (continued)

J	K <sub>a</sub>	K <sub>c</sub>	(310)			(211)		
			E	A	δ	E	A	δ
			59	60	61	62	63	64
4	0	4	6441.7697	19	-19	6442.1439	3	-5
4	1	4	6441.7697	19	-32	6442.1454	2	-1
4	1	3	6459.2231	2	-3	6459.7204	25	13
4	2	3	6459.3543	8	-15	6459.8425	14	1
4	2	2	6469.9960	11	-10	6470.2970	13	9
4	3	2	6473.3240	—	-27	6473.5878	10	2
4	3	1	6476.7812	8	10	6477.1168	6	5
4	4	1	6486.3282	15	-18	6486.6305	10	2
4	4	0	6486.6428	7	-29	6486.9585	11	0
5	0	5	6467.8146	40	7	6468.1920	43	6
5	1	5	6467.8146	40	9	6468.1920	43	3
5	1	4	—	—	—	6490.8660	6	-1
5	2	4	6490.4984	2	-21	6490.8780	9	16
5	2	3	6507.1188	9	-5	6508.4402	8	15
5	3	3	6507.3196	11	-6	6508.6069	10	-33
5	3	2	6516.8688	—	-7	6517.1836	10	4
5	4	2	6523.2557	7	-5	6523.5072	26	0
5	4	1	6525.3231	3	-3	6525.6380	4	6
5	5	1	6538.8546	21	-19	6539.1350	12	-3
5	5	0	6538.9786	2	-24	6539.2666	12	4
6	0	6	6498.5494	2	2	6498.9333	4	2
6	1	6	6498.5494	2	3	6498.9333	4	1
6	1	5	6526.3163	15	-1	6526.6922	8	0
6	2	5	6526.3163	15	19	6526.6910	6	13
6	2	4	6548.5644	2	-13	6548.6216	2	-2
6	3	4	6549.0715	10	-11	6549.1187	6	8
6	3	3	6563.7905	—	-10	6564.0320	11	13
6	4	3	6567.0266	11	23	6567.2028	7	3
6	4	2	—	—	—	6573.5766	30	-6
6	5	2	6583.5446	—	19	6583.7776	11	-10
6	5	1	6584.6005	5	8	6584.8783	15	-8
6	6	1	—	—	—	6602.2931	—	-2
6	6	0	—	—	—	6602.3427	17	5
7	0	7	6533.9764	—	0	6534.3684	9	5
7	1	7	6533.9764	—	0	6534.3684	9	5
7	1	6	6566.8124	7	-9	6567.1948	16	7
7	2	6	6566.8124	7	10	6567.1948	16	-4
7	2	5	6594.2580	—	26	6594.6449	18	-13
7	3	5	6594.2576	7	-57	6594.6367	7	15
7	3	4	6615.6154	20	-3	6616.8248	8	15
7	4	4	6615.7269	6	9	6616.9026	6	14
7	4	3	6629.2490	—	-14	6629.5223	8	-1
7	5	3	—	—	—	6635.7434	4	4
7	5	2	—	—	—	6639.9436	2	3
7	6	2	—	—	—	6654.5064	15	3
7	6	1	—	—	—	6655.0085	8	-3
7	7	1	—	—	—	6676.0641	—	8
7	7	0	—	—	—	6676.0804	2	-5
8	0	8	6574.0930	1	1	6574.4934	5	1
8	1	8	6574.0930	1	1	6574.4934	5	1
8	1	7	6611.9913	2	1	6612.3807	12	2
8	2	7	6611.9913	2	4	6612.3807	12	-1
8	2	6	6644.5084	5	-7	6644.8909	1	1
8	3	6	6644.5049	2	21	6644.8852	6	12
8	3	5	6671.4527	—	-19	6671.9453	8	-1
8	4	5	6671.4478	—	22	6671.9288	5	25
8	4	4	—	—	—	6691.4196	3	-1
8	5	4	—	—	—	6694.2819	11	3
8	5	3	—	—	—	6704.1004	23	-8
8	6	3	—	—	—	6714.3822	8	-4
8	6	2	—	—	—	6716.7949	9	2
8	7	2	—	—	—	6735.7430	3	-14
8	7	1	—	—	—	6735.9507	17	-18
8	8	1	—	—	—	—	—	—
8	8	0	—	—	—	6760.3845	12	41

Table 4  
Vibrational parameters  $E^{v_1 v_2 v_3}$  of the D<sub>2</sub>S molecule (in cm<sup>-1</sup>)

State	$E^{v_1 v_2 v_3}$	Band center, exp.	Band center, Ref. [29]
(010)	855.40416(20)	855.40416	855.42
(100)	1896.43154(21)	1896.43154	1895.85
(001)	1910.18375(23)	1910.18375	1910.13
(030)	2549.07336(39)	2549.07336	2549.40
(110)	2742.66570(22)	2742.66570	2742.34
(011)	2754.45192(23)	2754.45192	2754.71
(120)	3583.36	3583.36 <sup>a</sup>	3583.36
(021)	3593.12888(35)	3593.12888	3593.85
(200)	3768.024(25)	3753.470	3752.80
(101)	3757.45948(28)	3757.45948	3756.61
(002)	3794.600(25)	3809.154	3808.79
(130)	4417.95894(55)	4417.95894	4418.52
(031)	4426.08293(70)	4426.08293	4427.16
(210)	4605.218(19)	4589.226	4588.87
(111)	4592.18432(90)	4592.18104	4591.73
(012)	4627.485(19)	4643.477	4643.56
(220)	5436.07	5419.40 <sup>a</sup>	5419.40
(121)	5421.30072(36)	5421.3007	5419.40
(022)	5456.36	5473.03 <sup>a</sup>	5473.03
(300)	5610.02(33)	5560.15	5559.57
(201)	5580.98(15)	5560.74	5559.15
(102)	5597.26(13)	5647.13	5645.49
(003)	5652.65(15)	5672.89	5672.74
(310)	6438.17(14)	6384.63	6384.12
(211)	6406.28(15)	6384.99	6383.88
(112)	6419.94(13)	6473.48	6472.09
(013)	6474.27(15)	6495.56	6493.01

<sup>a</sup> Constrained to the value of band center from Ref. [29].

the D<sub>2</sub>S molecule. The ground state parameters from [18] are also reproduced for convenience.

It should be noted that the number of 231 fitted parameters determined in the present “Global Fit” is considerably smaller than the number of, at least, 550–600 parameters which would be needed for an analogously accurate calculation of the values of the rotation–vibration energies of 22 strongly interacted vibrational states using the traditional Effective Hamiltonian model. In this respect it is important to note that in the traditional Effective Hamiltonian method the presence of numerous ambiguities and correlations between the parameters of Hamiltonians of separate polyads leads very often to the appearance of physically unsuitable values of some parameters. At the same time, the “Global Fit” method used in the present study is “free” from such problems. Moreover, the “Global Fit” procedure presents also the advantage to better estimate the dark state constants.

## 6. Conclusion

Using high-resolution Fourier-transform spectra an extended analysis of the D<sub>2</sub>S absorption spectrum has been carried out and the corresponding experimental energy levels have then been satisfactorily extracted using a “Global Fit” method.

Table 5  
Corrections to the rotational and centrifugal distortion parameters of the D<sub>2</sub>S molecule (in cm<sup>-1</sup>)<sup>a</sup>

Parameter	Value	Parameter	Value	Parameter	Value
$a^1 \times 10$	-0.523446(968)	$\Delta_{KJ}^{11} \times 10^5$	-0.617(109)	$H_{JK}^{333} \times 10^6$	0.1129(133)
$a^2 \times 10$	1.301948(819)	$\Delta_{KJ}^{12} \times 10^5$	-0.1711(373)	$H_{JK}^{22} \times 10^6$	0.03611(375)
$a^3 \times 10$	-0.964882(908)	$\Delta_{KJ}^{22} \times 10^5$	1.8458(725)	$H_{JK}^{12} \times 10^6$	-0.04230(405)
$a^{11} \times 10^3$	-5.5055(968)	$\Delta_{KJ}^{23} \times 10^5$	-0.6002(689)	$H_{JK}^{112} \times 10^6$	-0.008622(685)
$a^{12} \times 10^3$	-0.2957(486)	$\Delta_{KJ}^{33} \times 10^5$	-0.4073(550)	$H_{JK}^{122} \times 10^6$	0.002929(645)
$a^{13} \times 10^3$	-3.565(196)	$\Delta_{JK}^1 \times 10^4$	0.15341(835)	$H_{JK}^{123} \times 10^6$	-0.00921(125)
$a^{22} \times 10^3$	2.842(101)	$\Delta_{JK}^2 \times 10^4$	-0.67233(518)	$H_{JK}^{133} \times 10^6$	-0.02018(309)
$a^{23} \times 10^3$	-3.0133(655)	$\Delta_{JK}^3 \times 10^4$	-0.16334(387)	$H_{JK}^{333} \times 10^6$	-0.01850(172)
$a^{33} \times 10^3$	11.895(290)	$\Delta_{JK}^1 \times 10^5$	0.4200(663)	$H_J \times 10^6$	0.002308(177)
$a^{111} \times 10^3$	1.1963(434)	$\Delta_{JK}^{13} \times 10^5$	0.642(145)	$H_J^3 \times 10^6$	-0.009248(520)
$a^{112} \times 10^3$	-1.2408(310)	$\Delta_{JK}^{22} \times 10^5$	-1.0108(365)	$H_J^{12} \times 10^6$	0.001488(245)
$a^{113} \times 10^3$	0.7095(986)	$\Delta_{JK}^{133} \times 10^6$	-4.80(126)	$H_J^{22} \times 10^6$	0.007342(179)
$a^{122} \times 10^3$	-1.558(115)	$\Delta_J^2 \times 10^4$	0.154108(749)	$H_J^{33} \times 10^6$	0.012057(693)
$a^{222} \times 10^3$	0.3014(248)	$\Delta_J^3 \times 10^4$	0.04341(108)	$H_J^{111} \times 10^6$	-0.0009986(741)
$a^{223} \times 10^3$	-0.0629(249)	$\Delta_J^{11} \times 10^5$	-0.1886(107)	$H_J^{112} \times 10^6$	0.000756(113)
$a^{233} \times 10^3$	-1.2141(422)	$\Delta_J^{22} \times 10^5$	0.1213(434)	$H_J^{113} \times 10^6$	-0.005014(500)
$a^{333} \times 10^3$	-2.6733(773)	$\Delta_J^{33} \times 10^5$	0.04261(753)	$H_J^{123} \times 10^6$	0.001787(290)
$b^1 \times 10$	-0.434193(914)	$\Delta_J^{111} \times 10^6$	0.98455(986)	$h_K^2 \times 10^6$	0.2644(596)
$b^2 \times 10$	0.720885(177)	$\delta_K^2 \times 10^4$	0.21440(224)	$h_K^3 \times 10^6$	0.1668(109)
$b^3 \times 10$	-0.247355(188)	$\delta_K^3 \times 10^5$	0.1677(222)	$h_K^{12} \times 10^6$	-0.04729(370)
$b^{11} \times 10^3$	-4.281(118)	$\delta_K^{12} \times 10^6$	-0.3499(640)	$h_K^{13} \times 10^6$	-0.2508(792)
$b^{12} \times 10^3$	0.5156(208)	$\delta_K^{13} \times 10^6$	-13.457(543)	$h_K^{22} \times 10^6$	0.01755(364)
$b^{13} \times 10^3$	3.2405(321)	$\delta_K^{33} \times 10^6$	15.357(549)	$h_K^{23} \times 10^6$	-0.1566(101)
$b^{22} \times 10^3$	1.95122(829)	$\delta_J^2 \times 10^4$	0.077748(376)	$h_K^{222} \times 10^6$	0.0644(196)
$b^{111} \times 10^3$	0.9971(324)	$\delta_J^3 \times 10^4$	0.015389(561)	$h_{JK}^3 \times 10^6$	-0.02026(530)
$b^{112} \times 10^3$	-0.2128(157)	$\delta_J^{13} \times 10^5$	0.03601(350)	$h_{JK}^{11} \times 10^6$	-0.001884(468)
$b^{122} \times 10^3$	0.04672(925)	$\delta_J^{23} \times 10^5$	1.0660(231)	$h_{JK}^{33} \times 10^6$	0.02659(727)
$b^{123} \times 10^3$	0.1646(127)	$\delta_J^{111} \times 10^6$	0.2625(181)	$h_{JK}^{122} \times 10^6$	0.004089(343)

Table 5 (continued)

Parameter	Value	Parameter	Value	Parameter	Value
$b^{223} \times 10^3$	-0.0606(125)	$H_K^2 \times 10^6$	-0.808(220)	$h_{JK}^{222} \times 10^6$	-0.001872(506)
$b^{233} \times 10^3$	0.8271(149)	$H_K^{11} \times 10^6$	-0.7484(622)	$h_{JK}^{333} \times 10^6$	-0.01245(222)
$c^1 \times 10$	-0.302909(756)	$H_K^{13} \times 10^6$	-0.04807(387)	$h_J^{11} \times 10^6$	0.0005724(758)
$c^2 \times 10$	-0.2276404(539)	$H_K^{22} \times 10^6$	0.19781(727)	$h_J^{22} \times 10^6$	0.0037029(898)
$c^3 \times 10$	-0.150387(776)	$H_K^{23} \times 10^6$	1.232(293)	$h_J^{23} \times 10^6$	0.0005466(620)
$c^{11} \times 10^3$	2.2872(740)	$H_K^{33} \times 10^6$	-0.1516(139)	$h_J^{112} \times 10^6$	0.0008609(531)
$c^{12} \times 10^3$	0.30978(364)	$H_K^{33} \times 10^6$	0.9737(775)	$h_J^{113} \times 10^6$	-0.002304(255)
$c^{13} \times 10^3$	-1.1780(315)	$H_K^{222} \times 10^6$	-0.2987(731)	$h_J^{123} \times 10^6$	0.001250(142)
$c^{22} \times 10^3$	0.02706(223)	$H_K^{233} \times 10^6$	0.04316(583)	$h_J^{233} \times 10^6$	-0.0004124(611)
$c^{23} \times 10^3$	-0.20245(515)	$H_K^{333} \times 10^6$	-0.2000(203)	$h_J^{333} \times 10^6$	0.0013610(926)
$c^{33} \times 10^3$	-2.1075(754)	$H_{KJ}^2 \times 10^6$	0.321(104)	$L_K^2 \times 10^9$	-0.1777(144)
$c^{113} \times 10^3$	4.839(150)	$H_{KJ}^3 \times 10^6$	0.4731(383)	$L_{KKJ}^1 \times 10^9$	0.03691(613)
$c^{123} \times 10^3$	0.07716(438)	$H_{KJ}^{11} \times 10^6$	0.02132(279)	$L_{KKJ}^2 \times 10^9$	0.1876(160)
$c^{133} \times 10^3$	-4.499(141)	$H_{KJ}^{22} \times 10^6$	-0.523(164)	$L_{KJJ}^1 \times 10^9$	-0.01009(133)
$c^{223} \times 10^3$	-0.01270(159)	$H_{KJ}^{23} \times 10^6$	0.04620(758)	$L_{KJJ}^2 \times 10^9$	-0.03492(270)
$\Delta_K^1 \times 10^4$	-0.1430(125)	$H_{KJ}^{33} \times 10^6$	-0.5742(482)	$I_K^2 \times 10^9$	-0.09388(709)
$\Delta_K^2 \times 10^4$	1.353272(929)	$H_{KJ}^{222} \times 10^6$	0.1381(418)	$I_{JK}^2 \times 10^9$	-0.01581(133)

<sup>a</sup> Values in parentheses are 1σ standard errors.

Table 6

Parameters of resonance interactions between vibrational states of the D<sub>2</sub>S molecule (in cm<sup>-1</sup>)<sup>a</sup>

Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
Darling–Dennison type parameters $F^{v_1, v_2, v_3} \quad v_1 \pm 2, v_2, v_3 \mp 2$							
$F^0$	11.5621(396)	$f^1$	-0.1848(112)	$f^2$	-0.13480(297)	$f^3$	-0.2175(324)
$F_K^0$	—	$f_K^1 \times 10^2$	-0.28566(623)	$f_K^2 \times 10^2$	0.12383(238)	$f_K^3 \times 10^2$	0.15821(856)
$F_J^0 \times 10^2$	0.14368(513)	$f_J^1 \times 10^2$	0.09295(337)	$f_J^2$	—	$f_J^3 \times 10^2$	-0.14561(369)
$F_{KK}^0 \times 10^4$	-0.8308(319)	$f_{KK}^1 \times 10^4$	0.24163(865)	$f_{KK}^2$	—	$f_{KK}^3 \times 10^4$	0.2765(113)
$F_{JK}^0 \times 10^4$	0.5123(219)	$f_{JK}^1 \times 10^4$	-0.18392(544)	$f_{JK}^2$	—	$f_{JK}^3 \times 10^4$	-0.16931(948)
$F_{JJ}^0 \times 10^4$	-0.04191(192)	$f_{JJ}^1 \times 10^4$	0.018429(810)	$f_{JJ}^2 \times 10^4$	0.001641(225)	$f_{JJ}^3 \times 10^4$	0.011058(554)
$F_{xy}^0 \times 10^2$	0.27230(546)	$f_{xy}^1 \times 10^2$	-0.12439(324)	$f_{xy}^2 \times 10^2$	-0.016042(754)	$f_{xy}^3 \times 10^2$	0.07732(357)
$F_{xyK}^0 \times 10^4$	0.15608(779)	$f_{xyK}^1$	—	$f_{xyK}^2$	—	$f_{xyK}^3 \times 10^4$	-0.11240(468)
$F_{xyJ}^0$	—	$f_{xyJ}^1 \times 10^4$	0.011144(678)	$f_{xyJ}^2$	—	$f_{xyJ}^3$	—
$F_{xyKK}^0$	—	$f_{xyKK}^1$	—	$f_{xyKK}^2$	—	$f_{xyKK}^3 \times 10^7$	0.1335(153)
$F_{xyJK}^0 \times 10^7$	-0.2342(322)	$f_{xyJK}^1 \times 10^7$	-0.0511(128)	$f_{xyJK}^2$	—	$f_{xyJK}^3 \times 10^7$	0.1092(133)
$F_{xyJJ}^0 \times 10^7$	-0.02491(153)	$f_{xyJJ}^1$	—	$f_{xyJJ}^2$	—	$f_{xyJJ}^3$	—
Coriolis type parameters $C^{v_1, v_2, v_3} \quad v_1 \pm 1, v_2, v_3 \mp 1$							
$C^0 \times 10$	-0.7911(325)	$c^1 \times 10$	0.09082(823)	$c^2 \times 10$	0.06742(448)	$c^3 \times 10$	0.2308(122)
$C_K^0 \times 10^3$	1.0080(300)	$c_K^1 \times 10^3$	-0.2701(108)	$c_K^2$	—	$c_K^3 \times 10^3$	-0.2988(162)
$C_J^0 \times 10^3$	-0.3187(178)	$c_J^1 \times 10^3$	0.12011(496)	$c_J^2$	—	$c_J^3 \times 10^3$	0.1566(821)
$C_{KK}^0 \times 10^5$	-1.2459(316)	$c_{KK}^1 \times 10^5$	0.6743(152)	$c_{KK}^2$	—	$c_{KK}^3 \times 10^5$	0.5601(169)
$C_{JK}^0 \times 10^5$	0.5923(175)	$c_{JK}^1 \times 10^5$	-0.3161(816)	$c_{JK}^2$	—	$c_{JK}^3 \times 10^5$	-0.29664(859)
$C_{JJ}^0$	—	$c_{JJ}^1$	—	$c_{JJ}^2 \times 10^5$	-0.007126(613)	$c_{JK}^3 \times 10^5$	-0.001748(747)
$C_{xz}^0 \times 10$	-0.67726(156)	$c_{xz}^1 \times 10$	0.024842(821)	$c_{xz}^2 \times 10$	-0.023460(371)	$c_{xz}^3$	—
$C_{xzK}^0 \times 10^4$	0.1027(115)	$c_{xzK}^1 \times 10^4$	0.03207(722)	$c_{xzK}^2$	—	$c_{xzK}^3 \times 10^4$	0.03638(872)
$C_{xzJ}^0 \times 10^4$	0.2183(142)	$c_{xzJ}^1 \times 10^4$	0.07390(843)	$c_{xzJ}^2$	—	$c_{xzJ}^3 \times 10^4$	-0.03036(663)
$C_{xzKK}^0 \times 10^7$	-0.3025(355)	$c_{xzKK}^1 \times 10^7$	0.2243(354)	$c_{xzKK}^2$	—	$c_{xzKK}^3$	—
$C_{xzJK}^0 \times 10^7$	-0.6492(737)	$c_{xzJK}^1$	—	$c_{xzJK}^2 \times 10^7$	-0.0519(194)	$c_{xzJK}^3 \times 10^7$	0.7842(531)
$C_{xzJJ}^0 \times 10^7$	-1.1828(765)	$c_{xzJJ}^1 \times 10^7$	-0.99637(789)	$c_{xzJJ}^2 \times 10^7$	0.2968(317)	$c_{xzKK}^3$	1.484(102)
Coriolis type parameters $C^{v_1, v_2, v_3} \quad v_1, v_2 \pm 2, v_3 \mp 1$							
$C_{xz}^0$	—	$c_{xz}^1 \times 10^3$	-0.3398(459)	$c_{xz}^2$	—	$c_{xz}^3$	—
$C_{xzK}^0$	—	$c_{xzK}^1 \times 10^4$	0.2019(368)	$c_{xzK}^2$	—	$c_{xzK}^3$	—
$C_{xzJ}^0 \times 10^5$	-0.2279(209)	$c_{xzJ}^1$	—	$c_{xzJ}^2$	—	$c_{xzJ}^3 \times 10^5$	-0.2755 (129)





Table 7 (continued)

Parameter	(011)	(012)	(120)	(021)	(030)	(130)	(031)
<i>E</i>	2754.45226	4628.11299	3583.36	3593.12707	2549.0726	4417.95784	4426.08087
<i>A</i>	5.53346027	5.44722547	5.70549767	5.66987477	5.91597907	5.85331357	5.81546427
<i>B</i>	4.56268158	4.54036678	4.61868202	4.64126904	4.74643734	4.70106302	4.72363774
<i>C</i>	2.40407998	2.38250363	2.37137433	2.38115657	2.37612973	2.34905537	2.35826188
$\Delta_K \times 10^3$	1.1136848	1.0954638	1.2905690	1.2983840	1.5420782	1.5164752	1.5199992
$\Delta_{JK} \times 10^3$	-0.6560405	-0.6723745	-0.7261225	-0.7535975	-0.8550365	-0.8438955	-0.8713705
$\Delta_J \times 10^3$	0.1824213	0.1880406	0.1985275	0.2041960	0.2254462	0.2245448	0.2302133
$\delta_K \times 10^3$	0.0004955	0.0004955	0.0262667	0.0269665	0.0567915	0.0557418	0.0567915
$\delta_J \times 10^3$	0.0823359	0.0838748	0.0920323	0.0933087	0.1048746	0.1051371	0.1064135
$H_K \times 10^6$	0.25044	1.00102	1.08261	0.9391	0.80748	0.75931	0.50736
$H_{KJ} \times 10^6$	0.13026	-0.28274	-0.18772	-0.10484	0.12086	0.14218	0.27126
$H_{JK} \times 10^6$	-0.206251	-0.335751	-0.284069	-0.297041	-0.453931	-0.453436	-0.472431
$H_J \times 10^6$	0.042743	0.069666	0.067758	0.064769	0.098670	0.106712	0.101479
$h_K \times 10^6$	0.26488	-0.02057	0.19993	0.24523	0.43393	0.43393	0.49678
$h_{JK} \times 10^6$	-0.06254	-0.09018	-0.05505	-0.07564	-0.10509	-0.07018	-0.11121
$h_J \times 10^6$	0.0214389	0.0302753	0.0333466	0.0326818	0.0495669	0.052722	0.051331
$L_K \times 10^9$	-0.508	-0.508	-0.6857	-0.6857	-0.8634	-0.8634	-0.8634
$L_{KKJ} \times 10^9$	0.6142	0.6142	0.8387	0.8018	0.9894	1.0263	0.9894
$L_{JK} \times 10^9$	-0.2663	-0.2663	-0.2663	-0.2663	-0.2663	-0.2663	-0.2663
$L_{JJK} \times 10^9$	0.04652	0.04652	0.00151	0.0116	-0.02332	-0.03341	-0.02332
$L_J \times 10^9$	-0.009532	-0.009532	-0.009532	-0.009532	-0.009532	-0.009532	-0.009532
$l_K \times 10^9$	-0.2317	-0.2317	-0.3256	-0.3256	-0.4194	-0.4194	-0.4194
$l_{KJ} \times 10^9$	-0.0343	-0.0343	-0.0343	-0.0343	-0.0343	-0.0343	-0.0343
$l_{JK} \times 10^9$	0.01142	0.01142	-0.00439	-0.00439	-0.0202	-0.0202	-0.0202
$l_J \times 10^9$	-0.004783	-0.004783	-0.004783	-0.004783	-0.004783	-0.004783	-0.004783
$P_K \times 10^{12}$	0.559	0.559	0.559	0.559	0.559	0.559	0.559
$P_{KKKJ} \times 10^{12}$	-0.873	-0.873	-0.873	-0.873	-0.873	-0.873	-0.873
$P_{KKJJ} \times 10^{12}$	0.353	0.353	0.353	0.353	0.353	0.353	0.353
$p_K \times 10^{12}$	0.2049	0.2049	0.2049	0.2049	0.2049	0.2049	0.2049

<sup>a</sup> From Ref. [18].

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## Appendix A. Supplementary data

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

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