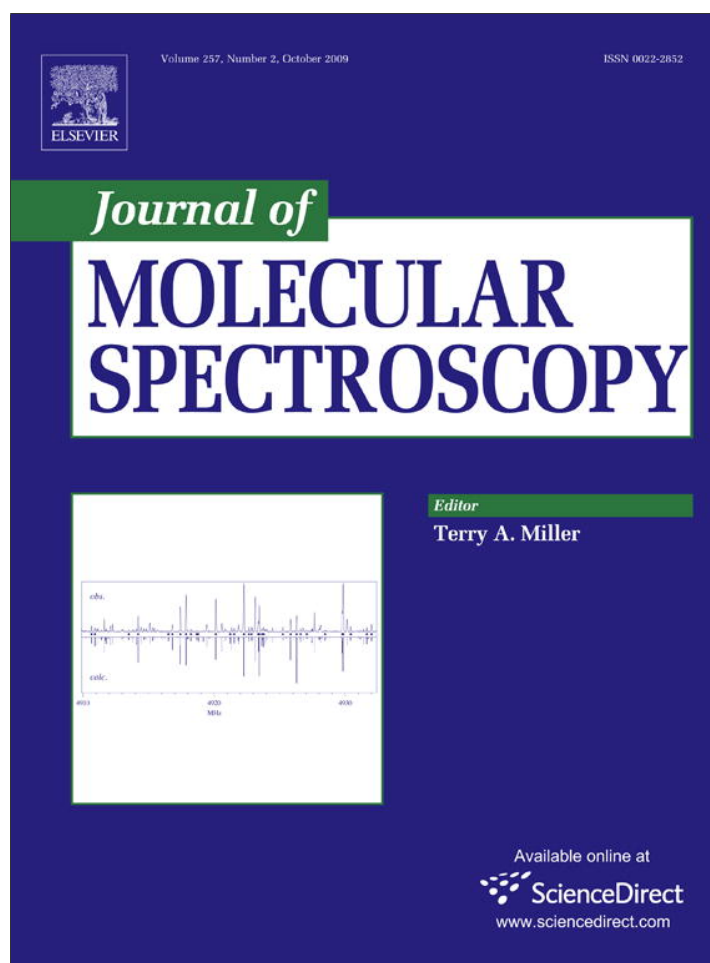


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

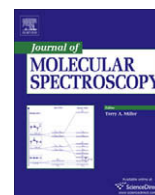
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Journal of Molecular Spectroscopy

journal homepage: www.elsevier.com/locate/jmsOn the high resolution spectroscopy and intramolecular potential function of SO₂O.N. Ulenikov^{a,*}, E.S. Bekhtereva^a, S. Alanko^b, V.-M. Horneman^b, O.V. Gromova^c, C. Leroy^c^aLaboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk 634050, Russia^bDepartment of Physical Sciences, University of Oulu, P.O. Box 3000, FIN-90014, Finland^cInstitut Carnot de Bourgogne-UMR 5209 CNRS, Université de Bourgogne B.P. 47870, F-21078 Dijon Cedex, France

ARTICLE INFO

Article history:

Received 7 May 2009

In revised form 17 July 2009

Available online 25 July 2009

Keywords:

Sulfur dioxide

High-resolution spectra

Spectroscopic parameters

Potential function

ABSTRACT

Two weak stretching bands, $\nu_1 + 3\nu_3$ and $3\nu_1 + \nu_3$, of the sulfur dioxide molecule have been recorded at high resolution and analyzed for the first time with using a Fourier transform Bruker IFS-120 HR interferometer. About 1000 transitions with $J^{max} = 51$, $K_a^{max} = 16$, and 900 transitions with $J^{max} = 53$, $K_a^{max} = 16$ have been assigned to the bands $\nu_1 + 3\nu_3$ and $3\nu_1 + \nu_3$, respectively. Analysis of the recorded spectra was made using the model of isolated vibrational states. Parameters obtained from the fit reproduce the initial experimental ro-vibrational energies with the rms deviation of 0.0006 and 0.0012 cm⁻¹ for the bands, $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$, respectively. The problem of determination of the intramolecular potential function of SO₂ is discussed.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Sulfur dioxide is a molecule that is well known for its important role in environmental chemistry. In particular, sulfur dioxide is one of the major air pollutants released in the atmosphere as a result of volcanic eruptions and of fuel combustion in human activities; it contributes to the generation of smog and constitutes a serious health hazard for the respiratory system, etc. For this reason, spectra of SO₂ have been a subject of intense study for a long time (see, e.g., Refs. [1–34]). In this communication, we continue our recent study, Ref. [35], of the high resolution stretching bands of the SO₂ molecule. The subject of the study is two very weak bands, $\nu_1 + 3\nu_3$ and $3\nu_1 + \nu_3$, that correspond to the fourfold excitations of stretching vibrational quanta and that have not been studied earlier with high resolution.

2. Experimental details

The experimental measurements for this research were performed in the laboratory of infrared spectroscopy of Oulu using a Bruker IFS-120 HR Fourier spectrometer. The SO₂ sample, obtained from Sigma–Aldrich Inc. with a purity of 99.9%, was in a multiple path White cell [36] at a pressure of 630 Pa. The absorption path length was 154 m and the cell contained two 6 mm thick potassium bromide windows. A tungsten source, a quartz beam splitter, and an indium antimonide semiconductor detector were used. Optical band-pass filters were used to limit the total radiation

intensity. The instrumental resolution due to the aperture broadening and the maximum optical path difference in the interferometer was better than 0.007 cm⁻¹ giving, together with the Doppler and pressure broadening, a final spectral resolution of about 0.01 cm⁻¹. The total registration time was more than 48 h in order to get reasonable signal to noise ratio for the weak bands $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$. The spectrum was calibrated with 56 water lines [37]. The reference values were corrected by a factor of 0.999999917 as given in Ref. [38].

3. Description of the spectrum and assignment of transitions

Experimentally recorded spectra of the $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$ bands are shown in the upper parts of Figs. 1 and 2 (Figs. 1I and 2I, respectively). In both cases, all three (P-, Q-, and R-) branches are clearly pronounced. In this case, contrary to the wide P- and R-branches of the parallel-type bands (see, e.g., survey spectrum of the $3\nu_1$ band in Fig. 1 of Ref. [35]), the R-branches of the perpendicular bands, $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$, are considerably more narrow than the corresponding P-branches. As an illustration of the quality of experimentally recorded spectra, Figs. 3I and 4I present small portions of the high resolution spectra in both regions.

Assignments of the transitions have been made on the basis of the Ground State Combination Differences (GSCD) method. Rotational energies necessary for realization of the GSCD procedure have been calculated by using the ground state parameters from Ref. [29]. As a result of the assignments of about 1900 transitions, we were able to obtain 479 and 471 upper ro-vibrational energies for the states (301) and (103), respectively. The list of obtained “experimental” upper energies for both vibrational states, (301)

* Corresponding author. Fax: +7 049 20 24 39 2581.

E-mail addresses: Ulenikov@phys.tsu.ru, ulenikov@mail.ru (O.N. Ulenikov).

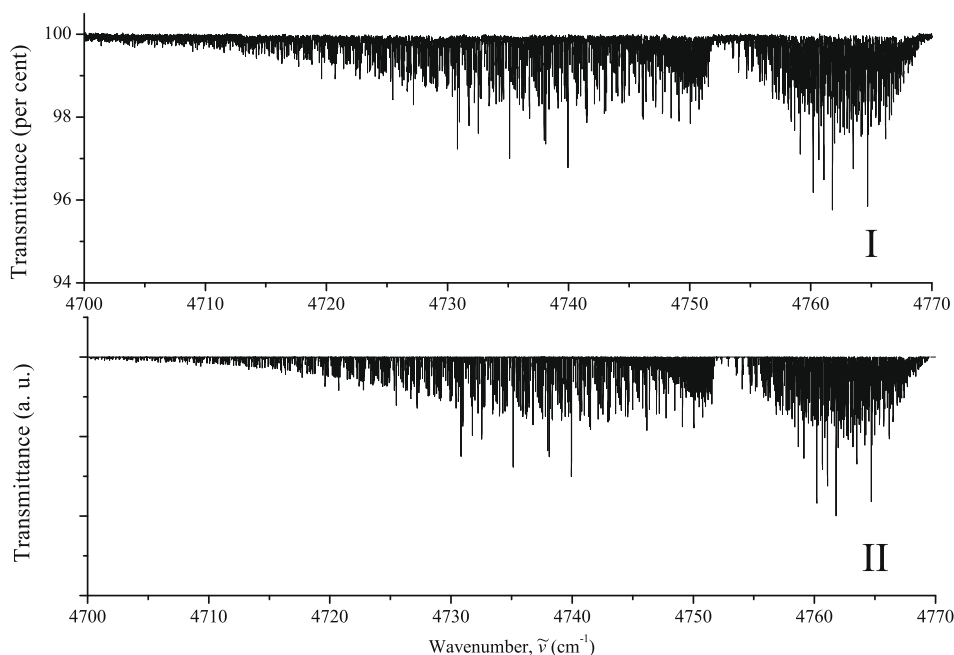


Fig. 1. Survey spectrum of SO₂ in the region of the band $3\nu_1 + \nu_3$: (I) is the experimentally recorded spectrum; (II) is the simulated spectrum (relative intensities have been calculated with only one dipole moment parameter in accordance with the theory from Ref. [39]).

and (103), is presented in Tables 1 and 2, respectively, together with their experimental uncertainties, Δ . As seen from Tables 1 and 2, only ro-vibrational states with odd values of the sum, $K_a + K_c$, of quantum numbers, K_a and K_c , are observed for the vibrational states of the B_1 symmetry. This is a consequence of the nuclear spin statistics of the SO₂ molecule.

4. Hamiltonian model and determination of parameters

As was discussed in many publications (see, Refs. [25–28,35], etc.), the presence of local resonance interactions is distinct to

the high resolution spectra of the SO₂ molecule. As shown by the analysis, however, in our case the Hamiltonian model of isolated vibrational state is suitable for the study. The reason is that both bands discussed in the present paper are very weak. As a consequence, transitions with a combination of high enough values of quantum numbers J and K_a , that correspond an appearance of local resonance interactions, are not seen in our experimental spectrum. As confirmation of the above point, we refer to Fig. 4 of Ref. [35]. In that figure, one can see that for the pair of states, (300)/(220), which is very similar to the pairs of states, (301)/(221) and (103)/(023), studied in the present paper, strong local

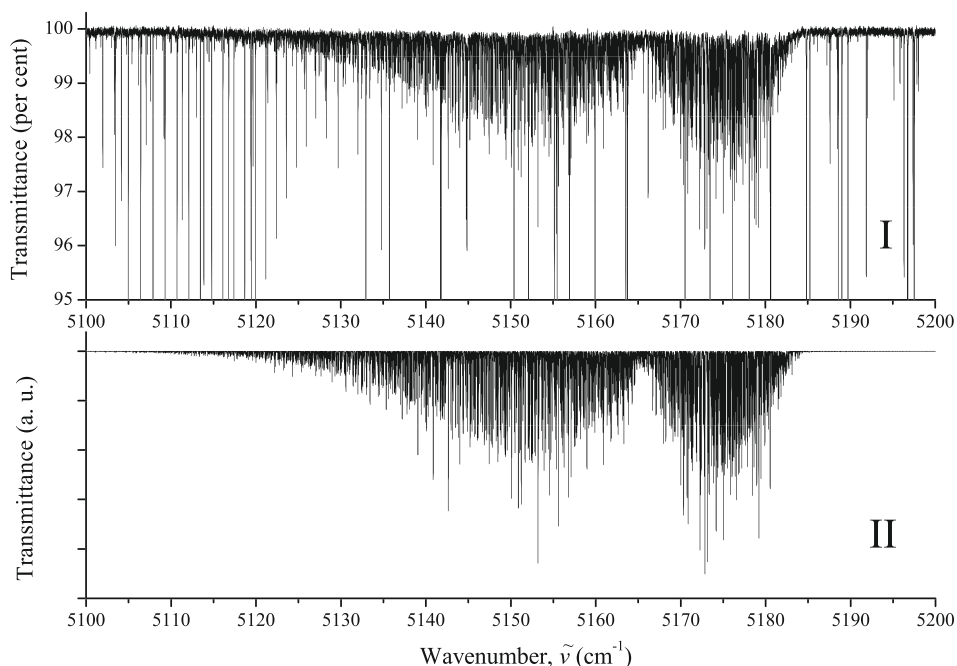


Fig. 2. Survey spectrum of SO₂ in the region of the band $\nu_1 + 3\nu_3$: (I) is the experimentally recorded spectrum; (II) is the simulated spectrum (relative intensities have been calculated with only one dipole moment parameter in accordance with the theory from Ref. [39]).

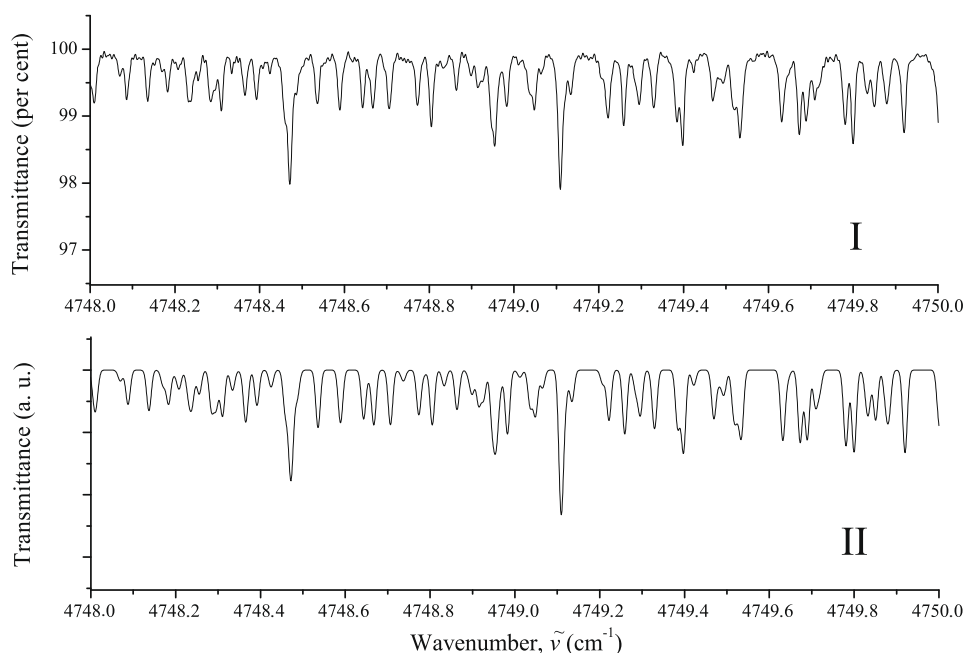


Fig. 3. Small portion of the recorded high resolution spectrum of the SO₂ molecule in the region of the $3\nu_1 + \nu_3$ absorption band: (I) is the experimentally recorded spectrum; (II) is the simulated spectrum (one dipole moment parameter was used for estimation of relative intensities).

resonance interactions can be seen for the set of states with $K_a = 13$ and J more than 40. Similarly, in our analysis we were not able to assign transitions with analogous combinations of quantum numbers J and K_a , both for (301), and (103) states (see Tables 1 and 2 below).

Continuing from the above discussion, both studied states, (301) and (103), were analyzed with the Watson Hamiltonian in A reduction and I' representation, [40],

$$\begin{aligned}
 H^{\nu\nu} = & E^{\nu} + \left[A^{\nu} - \frac{1}{2}(B^{\nu} + C^{\nu}) \right] J_z^2 + \frac{1}{2}(B^{\nu} + C^{\nu}) J^2 + \frac{1}{2}(B^{\nu} - C^{\nu}) J_{xy}^2 \\
 & - \Delta_K^{\nu} J_z^4 - \Delta_{JK}^{\nu} J_z^2 J^2 - \Delta_J^{\nu} J^4 - \delta_K^{\nu} [J_z^2, J_{xy}^2]_{+} - 2\delta_J^{\nu} J^2 J_{xy}^2 + H_{KJ}^{\nu} J_z^6 \\
 & + H_{KJ}^{\nu} J_z^4 J^2 + H_{JK}^{\nu} J_z^2 J^4 + H_J^{\nu} J^6 + [h_K^{\nu} J_z^4 + h_{JK}^{\nu} J_z^2 J^2 + h_J^{\nu} J^4, J_{xy}^2]_{+} \\
 & + L_K^{\nu} J_z^8 + L_{KKJ}^{\nu} J_z^6 J^2 + L_{JK}^{\nu} J_z^4 J^4 + L_{JJ}^{\nu} J_z^2 J^6 + L_J^{\nu} J^8 \\
 & + [l_K^{\nu} J_z^6 + l_{KJ}^{\nu} J_z^4 J^2 + l_{JK}^{\nu} J_z^2 J^4 + l_J^{\nu} J^6, J_{xy}^2]_{+} + P_{KJ}^{\nu} J_z^{10} + P_{KKJ}^{\nu} J_z^8 J^2 \\
 & + P_{KJ}^{\nu} J_z^6 J^4 + P_{JK}^{\nu} J_z^4 J^6 + \dots + S_{KJ}^{\nu} J_z^{12} + S_{KKJ}^{\nu} J_z^{10} J^2 + \dots \quad (1)
 \end{aligned}$$

Here J_{α} ($\alpha = x, y, z$) are the components of the angular momentum operator defined in the molecule-fixed coordinate system, $J_{xy}^2 = J_x^2 - J_y^2$, and $[\dots]_{+}$ denotes anticommutator.

The initial values of the parameters in Hamiltonian (1) were estimated in the following way: Band centers were estimated with the use of parameters of intramolecular potential function from Section 5 of the present paper. Effective rotational parameters were predicted in two ways. On the one hand, calculations with the parameters of the potential function from Section 5 were performed. On the other hand, the data (vibration-rotation coefficients, α_{λ}^{ν} and $\gamma_{\lambda\mu}^{\nu}$) from Ref. [26] were used.¹ To estimate the values of centrifugal distortion coefficients, Δ_K , Δ_{JK} , δ_K , H_K , and H_{KJ} , we performed a linear extrapolation of the values of the corresponding parameters of the states (010), (020), (100), (200), (001), (002), (003), (101), (201), (110), (210), (011), and (111) (see, Refs. [20–33]). All other centrifugal distortion coefficients have been constrained to the corresponding ground state values from Ref.

[29]. The estimated values are shown in columns 2 and 4 of Table 3. For convenience of the reader, column 4 of Table 4 presents the values of the ground state parameters from Ref. [29].

As the second step of analysis, the fit of the Hamiltonian parameters was made with the experimental ro-vibrational energies (479 and 471 energies for the states (301) and (103), respectively) from Tables 1 and 2. As the result, the set of 18 fitted parameters was determined and are presented in Table 4 together with their 1σ statistical confidence intervals. The parameters, which are given in Table 4 without confidence intervals, have been constrained to the values estimated by the procedure discussed above, or to the values of corresponding parameters of the ground vibrational state. The *rms* deviation of the fit is 0.0006 and 0.0012 cm⁻¹ for the bands, $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$, respectively, and it correlates satisfactorily with the experimental uncertainties. To illustrate the quality of experimental data and the results of the fit, the list of energy values, $E^{\text{exp.}}$ in cm⁻¹, is presented in column 2 of Tables 1 and 2 together with associated experimental uncertainties Δ in columns 3 and $\delta = (E^{\text{exp.}} - E^{\text{calc.}})$ in columns 4. The values of $E^{\text{calc.}}$ have been calculated using the parameters from Table 4. A good correlation can be seen between experimental and calculated values. As additional confirmations of correctness of the assignments and fit, we note:

- A good correlation between the predicted values and those obtained from the fit of spectroscopic parameters. As can be seen from columns 2, 3, and 4, 5 of Table 3, there are only minor differences between the two sets of parameters.
- A good correlation between experimentally recorded (upper parts of Figs. 1–4) and simulated (lower parts of Figs. 1–4) spectra. In this case, the simulated spectra were constructed on the basis of data from Table 4 with two dipole moment parameters (one parameter for one band that allows one to estimate relative intensities of lines presented in simulated spectra). In this case, the relative intensities of lines were calculated in the model of asymmetric top molecule with the using of general formulas from Ref. [39].

¹ As was expected, both results are very close.

Table 1
Experimental ro-vibrational term values for the (301) vibrational state of the SO₂ molecule (in cm⁻¹).^a

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
1	0	1	4752.3443		12
2	2	1	4760.3773		-4
3	0	3	4755.4689	4	5
3	1	2	4757.3186	3	-3
3	2	1	4762.2615	3	-3
4	1	4	4759.4223	3	2
4	2	3	4764.7604	1	1
4	3	2	4773.2370	5	-11
4	4	1	4785.0931		5
5	0	5	4761.0702	5	-8
5	1	4	4763.1717	2	0
5	2	3	4767.9265		-6
5	3	2	4776.3730	7	-3
5	4	1	4788.2256	2	-8
5	5	0	4803.4556		-1
6	1	6	4766.0221		-2
6	2	5	4771.6400	11	-9
6	3	4	4780.1362	2	4
6	4	3	4791.9877	2	0
6	5	2	4807.2177	6	12
6	6	1	4825.8116	3	0
7	0	7	4769.1127	2	-2
7	1	6	4771.6116	4	2
7	2	5	4776.1516	2	-1
7	3	4	4784.5306	3	0
7	4	3	4796.3768	2	-2
7	5	2	4811.6045	12	-2
7	6	1	4830.2005	6	10
7	7	0	4852.1481		-9
8	1	8	4775.0065	2	1
8	2	7	4781.0115	4	2
8	3	6	4789.5480	4	-3
8	4	5	4801.3945	4	-2
8	5	4	4816.6206	8	0
8	6	3	4835.2149	6	1
8	7	2	4857.1636	10	-7
8	8	1	4882.4554		2
9	0	9	4779.5458	1	1
9	1	8	4782.6209	7	7
9	2	7	4786.9738	3	-2
9	3	6	4795.2132	4	4
9	4	5	4807.0416		2
9	5	4	4822.2642	3	-2
9	6	3	4840.8576	8	0
9	7	2	4862.8075	2	5
9	8	1	4888.0982		0
9	9	0	4916.7158	2	3
10	1	10	4786.3618	3	0
10	2	9	4792.8602	3	-1
10	3	8	4801.4792	5	-4
10	4	7	4813.3171	2	-2
10	5	6	4828.5371	7	4
10	6	5	4847.1287	4	4
10	7	4	4869.0776	4	3
10	8	3	4894.3692	6	5
10	9	2	4922.9862		-3
10	10	1	4954.9134		1
11	0	11	4792.3216	2	3
11	1	10	4796.1729	2	2
11	2	9	4800.4282	2	-2
11	3	8	4808.4347	3	-5
11	4	7	4820.2241		-4
11	5	6	4835.4364	9	-13
11	6	5	4854.0272	7	1
11	7	4	4875.9755	6	3
11	8	3	4901.2668	2	2
11	9	2	4929.8853	2	3
11	10	1	4961.8132		4
11	11	0	4997.0306		0
12	1	12	4800.0754	3	2
12	2	11	4807.1737		-3
12	3	10	4815.9319	4	1

^a In Table 1, Δ is the experimental uncertainty of the energy value, equal to one standard error in units of 10^{-4} cm⁻¹; δ is the difference $E^{exp.} - E^{calc.}$, also in units of 10^{-4} cm⁻¹. When the Δ -value is absent, corresponding energy level was determined from the only transition.

Table 1 (continued)

J	K_a	K_c	E	Δ	δ
1			2	3	4
12	4	9	4827.7605	5	2
12	5	8	4842.9678	9	-2
12	6	7	4861.5545	3	3
12	7	6	4883.5005	6	-5
12	8	5	4908.7928	7	6
12	9	4	4937.4112	3	2
12	10	3	4969.3393	6	-4
12	11	2	5004.5585	3	-2
12	12	1	5043.0462		-11
13	0	13	4807.4040		1
13	1	12	4812.2342	5	4
13	2	11	4816.5338	4	-1
13	3	10	4824.2207	4	4
13	4	9	4835.9335	7	6
13	5	8	4851.1270		-11
13	6	7	4869.7098	4	-2
13	7	6	4891.6557	4	7
13	8	5	4916.9452	6	-4
13	9	4	4945.5650	2	3
13	10	3	4977.4940	5	-2
13	11	2	5012.7152		7
13	12	1	5051.2045		-2
13	13	0	5092.9408		-14
14	1	14	4816.1335	6	0
14	2	13	4823.9359	2	-2
14	3	12	4832.9044	3	0
14	4	11	4844.7282	6	-9
14	5	10	4859.9182		-1
14	6	9	4878.4951	3	3
14	7	8	4900.4375	2	2
14	8	7	4925.7270	4	1
14	9	6	4954.3457	8	-4
14	10	5	4986.2759		-4
14	11	4	5021.4983		5
14	12	3	5059.9897		1
14	13	2	5101.7283		-8
14	14	1	5146.6925	8	2
15	0	15	4824.7747	1	0
15	1	14	4830.7583		-1
15	2	13	4835.2877	1	-1
15	3	12	4842.5988	4	5
15	4	11	4854.1760	18	8
15	5	10	4869.3394	1	-2
15	6	9	4887.9087	10	-3
15	7	8	4909.8485	4	4
15	8	7	4935.1368	5	5
15	9	6	4963.7552	8	-1
15	10	5	4995.6858	5	-3
15	11	4	5030.9082	3	-7
15	13	2	5111.1430		-10
15	15	0	5204.2732		-1
16	1	16	4834.5252		-1
16	2	15	4843.1285		0
16	3	14	4852.3932	4	-1
16	4	13	4864.2285	11	-4
16	5	12	4879.3919	2	2
16	6	11	4897.9528	12	-2
16	7	10	4919.8882		4
16	8	9	4945.1744	3	3
16	9	8	4973.7918	10	-7
16	10	7	5005.7237	5	0
16	11	6	5040.9478	6	3
16	12	5	5079.4430		4
16	14	3	5166.1557		16
16	16	1	5265.6592	14	-2
17	0	17	4844.4290	2	0
17	1	16	4851.6929	4	-2
17	2	15	4856.6673	2	-12
17	3	14	4863.6049	4	-3
17	4	13	4874.9643	10	10
17	6	11	4908.6275		4
17	7	10	4930.5567	2	1
17	8	9	4955.8401	7	-2

(continued on next page)

Table 1 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
17	9	8	4984.4585	5	7
17	10	7	5016.3893	1	1
17	11	6	5051.6141	8	1
17	14	3	5176.8275		7
17	15	2	5224.9970		7
18	1	18	4855.2411		-4
18	2	17	4864.7320	2	2
18	3	16	4874.3896	2	-2
18	4	15	4886.2636	6	-5
18	5	14	4901.3934	1	2
18	6	13	4919.9309	8	-10
18	7	12	4941.8554	8	6
18	8	11	4967.1354		2
18	9	10	4995.7509	4	-4
18	10	9	5027.6830		3
18	11	8	5062.9083	5	-1
18	12	7	5101.4065	3	-1
18	13	6	5143.1546	2	3
18	14	5	5188.1284		12
18	15	4	5236.2988		-9
18	16	3	5287.6443		-4
19	0	19	4866.3690		0
19	1	18	4874.9825	2	0
19	2	17	4880.6417		6
19	3	16	4887.2761	3	1
19	4	15	4898.3135	1	-1
19	5	14	4913.3472	2	2
19	6	13	4931.8678	2	0
19	7	12	4953.7828		1
19	8	11	4979.0590	10	0
19	9	10	5007.6728	8	-5
19	10	9	5039.6044		1
19	11	8	5074.8302	3	-4
19	12	7	5113.3305	8	2
19	13	6	5155.0803		2
19	15	4	5248.2323		13
19	16	3	5299.5799		5
20	1	20	4878.2747	3	2
20	2	19	4888.7266		0
20	3	18	4898.8814		0
20	4	17	4910.8375	1	0
20	5	16	4925.9281	2	2
20	6	15	4944.4363	6	11
20	7	14	4966.3405	7	-3
20	8	13	4991.6121	1	1
20	9	12	5020.2233	9	-5
20	10	11	5052.1542		2
20	11	10	5087.3812	3	3
20	12	9	5125.8821		2
20	13	8	5167.6342	4	5
20	14	7	5212.6116	4	-1
21	0	21	4890.5986		-2
21	1	20	4900.5792		1
21	2	19	4907.1609	1	0
21	3	18	4913.6350	5	-8
21	4	17	4924.2476	1	-4
21	5	16	4939.1564	2	4
21	6	15	4957.6346	10	-5
21	7	14	4979.5287	5	-5
21	8	13	5004.7940	10	-3
21	9	12	5033.4030	2	-1
21	10	11	5065.3321		0
21	12	9	5139.0611	3	-2
21	13	8	5180.8150	5	-1
21	14	7	5225.7954	8	-4
21	15	6	5273.9764		-9
22	1	22	4903.6196	7	5
22	2	21	4915.0940	2	0
22	3	20	4925.8515	19	-2
22	4	19	4937.9498	9	5
22	5	18	4953.0009	4	-3
22	6	17	4971.4667	5	-4
22	7	16	4993.3483	4	-1
22	8	15	5018.6060	4	-3
22	9	14	5047.2106	5	-6

Table 1 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
22	10	13	5079.1385	5	-1
22	11	12	5114.3654		-1
22	13	10	5194.6246	8	2
22	14	9	5239.6074		-2
23	0	23	4917.1221	3	-1
23	1	22	4928.4512		-4
23	2	21	4936.1747		-2
23	3	20	4942.6870	5	1
23	4	19	4952.7953		3
23	5	18	4967.5136	1	0
23	6	17	4985.9334	4	-1
23	7	16	5007.7985	8	-4
23	8	15	5033.0488	4	6
23	9	14	5061.6481	4	-3
23	10	13	5093.5738		1
23	12	11	5167.3045		3
23	13	10	5209.0619		3
24	1	24	4931.2718	7	5
24	2	23	4943.8170		0
24	3	22	4955.2820	3	5
24	4	21	4967.5960	1	-3
24	5	20	4982.6187	5	4
24	7	18	5022.8813		5
24	8	17	5048.1210		8
24	9	16	5076.7152	2	3
24	10	15	5108.6374	6	0
24	11	14	5143.8632	4	1
24	12	13	5182.3678		1
24	13	12	5224.1270		3
25	0	25	4945.9418	2	-2
25	1	24	4958.5862		-4
25	2	23	4967.6237	3	1
25	3	22	4974.4140	5	0
25	4	21	4983.9895	11	5
25	5	20	4998.4317	3	1
25	6	19	5016.7674		-6
25	7	18	5038.5953		4
25	8	17	5063.8231	2	4
25	9	16	5092.4114	6	6
25	11	14	5159.5555		11
25	12	13	5198.0601		8
25	13	12	5239.8213		15
26	1	26	4961.2286	2	0
26	2	25	4974.8817	11	10
26	3	24	4987.1489	6	-6
26	4	23	4999.7704	5	-5
26	5	22	5014.7838	7	4
26	6	21	5033.1342	4	-3
26	7	20	5054.9418		5
26	8	19	5080.1560	2	1
26	9	18	5108.7364	3	0
26	11	16	5175.8751		10
26	12	15	5214.3793		2
27	0	27	4977.0588	6	-8
27	1	26	4990.9837		1
27	2	25	5001.4446		3
27	3	24	5008.7807	7	7
27	4	23	5017.8656		0
27	5	22	5031.9254	2	-2
27	6	21	5050.1444	3	-3
27	7	20	5071.9204	5	-4
27	8	19	5097.1195		-7
27	9	18	5125.6925	5	6
27	10	17	5157.6021		0
27	11	16	5192.8227	1	2
27	12	15	5231.3269		-1
27	13	14	5273.0897	3	-2
28	1	28	4993.4889		-1
28	2	27	5008.2729	1	-1
28	3	26	5021.4337		-1
28	4	25	5034.4620	3	2
28	5	24	5049.4995		2
28	6	23	5067.7795	4	-2

(continued on next page)

Table 1 (continued)

J	K_a	K_c	E	Δ	δ
1			2	3	4
28	7	22	5089.5331	2	-2
28	8	21	5114.7160	2	1
28	9	20	5143.2777	2	2
28	11	18	5210.3995	2	0
28	12	17	5248.9030	7	-3
28	13	16	5290.6663	4	-7
29	0	29	5010.4765	9	6
29	1	28	5025.6489		2
29	2	27	5037.5790	3	-2
29	3	26	5045.7356	10	0
29	4	25	5054.4539	2	-3
29	5	24	5068.0150		-10
29	6	23	5086.0710	6	2
29	7	22	5107.7806	3	1
29	8	21	5132.9438	5	4
29	9	20	5161.4939		4
29	10	19	5193.3911		-1
29	11	18	5228.6058	2	5
29	12	17	5267.1081		2
30	1	30	5028.0512	2	1
30	2	29	5043.9840	1	-1
30	3	28	5058.1128	12	5
30	4	27	5071.6532	2	-1
30	5	26	5086.7659	6	-5
30	6	25	5104.9726	2	-2
30	7	24	5126.6611	6	1
30	8	23	5151.8036	8	7
30	9	22	5180.3397		-3
30	10	21	5212.2307		7
30	11	20	5247.4398		-2
30	13	18	5327.7063		10
31	0	31	5046.1919	6	6
31	1	30	5062.5890	4	-3
31	3	28	5085.2222	4	-2
31	4	27	5093.7676	6	-3
31	5	26	5106.7299	3	4
31	6	25	5124.5553		3
31	7	24	5146.1782		-2
31	8	23	5171.2958	8	9
31	9	22	5199.8171	3	-2
31	10	21	5231.6988		2
31	11	20	5266.9023		-13
31	13	18	5347.1667		0
32	1	32	5064.9136		-2
32	3	30	5097.1636	5	-8
32	4	29	5111.3264	5	1
32	5	28	5126.5825	5	2
32	6	27	5144.7190	12	6
32	7	26	5166.3284	1	0
32	8	25	5191.4213	13	16
32	9	24	5219.9248		-10
32	10	23	5251.7969		-1
32	12	21	5325.4918		-6
32	13	20	5367.2570	8	8
33	0	33	5084.2051	4	-4
33	1	32	5101.8117	5	-2
33	2	31	5116.6337	3	3
33	3	30	5127.1756	9	4
33	4	29	5135.7964	10	-9
33	6	27	5165.6083	1	-1
33	7	26	5187.1176		-17
33	8	25	5212.1784	3	5
33	9	24	5240.6657		2
33	10	23	5272.5254		-1
33	11	22	5307.7177		-6
33	12	21	5346.2114		3
33	13	20	5387.9754		16
34	1	34	5104.0771	8	10
34	2	33	5122.3354		-6
34	3	32	5138.5711		-4
34	4	31	5153.4591		1
34	5	30	5168.9412	13	8
34	6	29	5187.0203	4	-1
34	7	28	5208.5397	10	-3
34	8	27	5233.5691		-3

Table 1 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
34	9	26	5262.0358	6	-11
34	10	25	5293.8846		3
34	12	23	5367.5586	3	3
34	13	22	5409.3195		-2
35	0	35	5124.5176	9	-6
35	1	34	5143.3214	2	2
35	2	33	5159.5190		-7
35	3	32	5171.5258	10	8
35	4	31	5180.5101	9	-8
35	5	30	5192.1579	5	0
35	6	29	5209.2430	15	-24
35	7	28	5230.6098	10	9
35	8	27	5255.5954	4	-1
35	9	26	5284.0392		-10
35	10	25	5315.8728		-7
35	12	23	5389.5347		3
36	1	36	5145.5375	8	3
36	2	35	5164.9674	4	-3
36	3	34	5182.3169	7	-7
36	4	33	5198.0281		1
36	5	32	5213.8297		-7
36	6	31	5231.8813	3	-3
36	8	29	5278.2552		-2
36	9	28	5306.6757		1
36	10	27	5338.4899		-35
37	0	37	5167.1291	2	2
37	1	36	5187.1205	1	1
37	2	35	5204.6483	11	8
37	3	34	5218.2046	6	-4
37	4	33	5227.8591	12	-2
37	5	32	5238.9417	4	2
37	6	31	5255.4851		4
37	7	30	5276.6538	6	0
37	8	29	5301.5511		-3
37	9	28	5329.9440		1
37	10	27	5361.7442		1
38	1	38	5189.2957	9	-6
38	2	37	5209.8996	5	6
38	3	36	5228.3893	4	1
38	4	35	5245.0089	16	-12
38	5	34	5261.2374	5	-2
38	6	33	5279.3009	11	-17
38	7	32	5300.6137	8	-4
38	8	31	5325.4823	16	11
38	9	30	5353.8441	4	-2
38	10	29	5385.6246		-12
39	0	39	5212.0370	3	0
39	1	38	5233.2112	8	-2
39	2	37	5252.0251	19	-9
39	3	36	5267.1587	6	5
39	4	35	5277.7813	2	0
39	5	34	5288.4703	2	-3
39	6	33	5304.3502	4	-2
39	10	29	5410.1389		1
40	1	40	5235.3529		3
40	2	39	5257.1284		4
40	3	38	5276.7773		12
40	4	37	5294.3829	11	13
40	5	36	5311.1433	8	-5
40	6	35	5329.2810	4	-5
40	7	34	5350.4860		7
40	9	32	5403.5460		4
40	10	31	5435.2827		-6
41	0	41	5259.2427	11	10
41	1	40	5281.5948		-1
41	2	39	5301.6664		10
41	3	38	5318.3450		-4
41	4	37	5330.2068		-9
41	5	36	5340.7476	8	10
41	8	33	5401.0945		2
41	10	31	5461.0599		4
42	1	42	5283.7056	3	4
42	2	41	5306.6529	6	-3

(continued on next page)

Table 1 (continued)

J	K_a	K_c	E	Δ	δ
1			2	3	4
42	3	40	5327.4705	10	6
42	5	38	5363.5274		-2
42	8	35	5427.5674		1
42	10	33	5487.4671		-5
43	0	43	5308.7415	6	-7
43	1	42	5332.2720	7	7
43	2	41	5353.5743		-1
43	3	40	5371.7467	18	-9
43	4	39	5385.0633	13	-10
43	5	38	5395.7463	3	-9
43	6	37	5410.0844		-7
43	7	36	5430.2093		-23
43	10	33	5514.5082	2	3
44	1	44	5334.3531		-1
44	2	43	5358.4732	9	0
44	3	42	5380.4657	19	4
44	4	41	5400.2092	14	-4
44	5	40	5418.3654		2
44	7	38	5457.9127		-14
45	0	45	5360.5376		-1
45	1	44	5385.2396	5	-8
45	2	43	5407.7580	7	-10
45	4	41	5442.2776	8	10
45	6	39	5467.0235		1
46	1	46	5387.2952	6	-6
46	2	45	5412.5871	2	2
46	3	44	5435.7570	3	-4
46	6	41	5494.4916		-4
47	0	47	5414.6281	6	8
47	2	45	5464.2261		24
47	4	43	5501.7781		14
48	1	48	5442.5328		7
48	2	47	5468.9926	5	-7
49	0	49	5471.0089		-11
49	1	48	5498.0552	5	3
51	0	51	5529.6871		23
53	0	53	5590.6517		9

5. On the intramolecular potential function of SO₂

In this section, we briefly consider the problem of determining the intramolecular potential function of the SO₂ molecule. In this respect, it is necessary to mark two points. On the one hand, there is a set of publications (see, e.g., Ref. [41], and references cited therein), where qualitative peculiarities of the potential energy surface of the SO₂ molecule have been carefully discussed in a wide spectral region (up to dissociation limit). Unfortunately, the use of this information for numerical calculations of the characteristics of high resolution spectra (such, for example, as band centers, rotational, resonance interaction, and other spectroscopic parameters) is very complicated. On the other hand, studies have been made (see, Ref. [42], and references cited therein) where highly accurate quantitative information about parameters of the intramolecular potential function of the SO₂ molecule was presented. In particular, as is seen from Ref. [42], the potential parameters from that paper give very good prediction of, at least, values of the centers of the bands of the ³²SO₂ isotopic species. However, we have found that, even those accurate results can be improved on the basis of the modern experimental information about both the pure vibrational and ro-vibrational spectra.

To realize this, we used an approach discussed recently in Ref. [43]. We will not repeat here details of the calculation scheme from Ref. [43] and give only the form of the used potential function:

$$V = V^{(2)} + V^{(3)} + V^{(4)}, \quad (2)$$

where

$$V^{(2)} = \frac{1}{2}f_{rr}(\Delta r_1^2 + \Delta r_2^2) + f_{rr'}\Delta r_1\Delta r_2 + f_{r\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha + \frac{1}{2}f_{\alpha\alpha}\Delta\alpha^2; \quad (3)$$

$$V^{(3)} = \frac{1}{6}f_{rrr}(\Delta r_1^3 + \Delta r_2^3) + \frac{1}{2}f_{rrr'}(\Delta r_1^2\Delta r_2 + \Delta r_2^2\Delta r_1) + \frac{1}{2}f_{rr\alpha}(\Delta r_1^2 + \Delta r_2^2)\Delta\alpha + f_{rr'\alpha}\Delta r_1\Delta r_2\Delta\alpha + \frac{1}{2}f_{r\alpha\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha^2 + \frac{1}{6}f_{\alpha\alpha\alpha}\Delta\alpha^3; \quad (4)$$

and

$$V^{(4)} = \frac{1}{24}f_{rrrr}(\Delta r_1^4 + \Delta r_2^4) + \frac{1}{6}f_{rrr'}(\Delta r_1^3\Delta r_2 + \Delta r_2^3\Delta r_1) + \frac{1}{4}f_{rrr'r'}(\Delta r_1^2\Delta r_2^2) + \frac{1}{6}f_{rrr\alpha}(\Delta r_1^3 + \Delta r_2^3)\Delta\alpha + f_{rrr'\alpha}(\Delta r_1 + \Delta r_2)\Delta r_1\Delta r_2\Delta\alpha + \frac{1}{2}f_{rr\alpha\alpha}(\Delta r_1^2 + \Delta r_2^2)\Delta\alpha^2 + \frac{1}{2}f_{rr'\alpha\alpha}\Delta r_1\Delta r_2\Delta\alpha^2 + \frac{1}{6}f_{r\alpha\alpha\alpha}(\Delta r_1 + \Delta r_2)\Delta\alpha^3 + \frac{1}{24}f_{\alpha\alpha\alpha\alpha}\Delta\alpha^4. \quad (5)$$

Here, Δr_1 and Δr_2 denote the changes of the bonds S–O₍₁₎ and S–O₍₂₎, respectively; $\Delta\alpha$ denotes the change of the inter-bond angle; f_{\dots} are the parameters of the intramolecular potential function.

In the framework of the procedure discussed in Ref. [43], the transformation is determined from curvilinear coordinates, Δr_1 ,

Table 2Experimental ro-vibrational term values for the (103) vibrational state of the SO₂ molecule (in cm⁻¹).^a

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
1	0	1	5165.4790		4
1	1	0	5167.1559	7	-4
2	1	2	5168.3104		-9
2	2	1	5173.3430	3	-5
3	0	3	5168.6113	1	-3
3	1	2	5170.4199	3	-2
3	2	1	5175.2329	15	3
3	3	0	5183.4861		4
4	1	4	5172.5265	5	-2
4	2	3	5177.7380	11	9
4	3	2	5185.9994	3	1
4	4	1	5197.5512		-6
5	0	5	5174.2272	1	0
5	1	4	5176.2883	11	-2
5	2	3	5180.9138	18	4
5	3	2	5189.1426	5	0
5	4	1	5200.6941	7	3
5	5	0	5215.5353		-5
6	1	6	5179.1412	4	-8
6	2	5	5184.6357	16	8
6	3	4	5192.9149	3	0
6	4	3	5204.4639		-10
6	5	2	5219.3070	4	7
6	6	1	5237.4293		2
7	0	7	5182.2858	1	-1
7	1	6	5184.7497	2	-3
7	2	5	5189.1607	10	-13
7	3	4	5197.3219	3	5
7	4	3	5208.8647	10	-10
7	5	2	5223.7065	8	5
7	6	1	5241.8289	10	4
7	7	0	5263.2218		3
8	1	8	5188.1454		-6
8	2	7	5194.0279	5	-4
8	3	6	5202.3524	13	3
8	4	5	5213.8957	13	-7
8	5	4	5228.7348	13	-2
8	6	3	5246.8569	5	-1
8	7	2	5268.2499		-2
8	8	1	5292.9025	12	15
9	0	9	5192.7374	5	-5
9	1	8	5195.7857	4	-5
9	2	7	5200.0171	10	-5
9	3	6	5208.0314	9	-11
9	4	5	5219.5582	12	1
9	5	4	5234.3933	15	-4
9	6	3	5252.5157	19	10
9	7	2	5273.9081	6	3
9	8	1	5298.5600	23	9
9	9	0	5326.4549	8	10
10	1	10	5199.5254	4	-5
10	2	9	5205.9052	7	-4
10	3	8	5214.3143	2	-4
10	4	7	5225.8506	1	1
10	5	6	5240.6821	6	-4
10	6	5	5258.8024	12	4
10	7	4	5280.1954	5	7
10	8	3	5304.8474	8	11
10	9	2	5332.7442	17	23
10	10	1	5363.8617		-30
11	0	11	5205.5348	2	2
11	1	10	5209.3704	4	1
11	2	9	5213.5147	1	-2
11	3	8	5221.2914	5	-5
11	4	7	5232.7763	18	1
11	5	6	5247.6024		6
11	6	5	5265.7186	19	-4
11	7	4	5287.1115	3	6
11	8	3	5311.7625	9	-3
11	9	2	5339.6607	12	17
11	10	1	5370.7800		-30

(continued on next page)

^a See footnote to Table 1.

Table 2 (continued)

J	K_a	K_c	E	Δ	δ
1			2	3	4
11	11	0	5405.1179	2	14
12	1	12	5213.2673	4	-4
12	2	11	5220.2526	5	2
12	3	10	5228.8042	11	-7
12	4	9	5240.3327	8	7
12	5	8	5255.1523	4	3
12	6	7	5273.2666	4	6
12	7	6	5294.6570	2	2
12	8	5	5319.3091		6
12	9	4	5347.2064	12	10
12	10	3	5378.3277	12	-28
12	12	1	5450.1907		0
13	0	13	5220.6409	2	2
13	1	12	5225.4643	12	-12
13	2	11	5229.6711	13	-2
13	3	10	5237.1236	6	3
13	4	9	5248.5249	23	-20
13	5	8	5263.3340		2
13	6	7	5281.4437	5	2
13	7	6	5302.8326	3	2
13	8	5	5327.4838	2	0
13	9	4	5355.3820	8	8
13	10	3	5386.5046	17	-28
13	11	2	5420.8438	6	-1
13	12	1	5458.3729		18
13	13	0	5499.0687		12
14	1	14	5229.3586	2	0
14	2	13	5237.0525	13	7
14	3	12	5245.8225	9	6
14	4	11	5257.3464	4	0
14	5	10	5272.1477	5	3
14	6	9	5290.2519	11	2
14	7	8	5311.6385	5	3
14	8	7	5336.2890	3	3
14	9	6	5364.1883	12	19
14	10	5	5395.3112	17	-24
14	11	4	5429.6522	19	5
14	12	3	5467.1808	9	0
14	13	2	5507.8791	2	-5
14	14	1	5551.7245		-9
15	0	15	5238.0390	1	1
15	1	14	5244.0234	9	-13
15	2	13	5248.4813	7	-5
15	3	12	5255.5595	6	9
15	4	11	5266.8204	4	10
15	5	10	5281.5942	3	1
15	6	9	5299.6918	11	7
15	7	8	5321.0737	8	-5
15	8	7	5345.7243	2	8
15	9	6	5373.6231	15	20
15	10	5	5404.7463	16	-29
15	11	4	5439.0889	19	0
15	12	3	5476.6205		5
15	13	2	5517.3210	18	-3
15	14	1	5561.1675		-24
15	15	0	5608.1404		-15
16	1	16	5247.7875	4	5
16	2	15	5256.2855	12	6
16	3	14	5265.3608		1
16	4	13	5276.8994		4
16	5	12	5291.6726		-7
16	6	11	5309.7619	3	-1
16	7	10	5331.1407	3	-1
16	8	9	5355.7877	16	-6
16	9	8	5383.6872	7	16
16	10	7	5414.8112	18	-32
16	11	6	5449.1559	4	4
16	12	5	5486.6892	7	5
16	13	4	5527.3933	8	8
16	14	3	5571.2437		-4
16	15	2	5618.2186	3	-7
16	16	1	5668.2902		-28
17	0	17	5257.7255	1	0
17	1	16	5264.9924		-1
17	2	15	5269.9220		-7

Table 2 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
17	3	14	5276.6344		-4
17	5	12	5302.3878	2	-1
17	6	11	5320.4650	2	2
17	7	10	5341.8387	3	4
17	8	9	5366.4839	1	6
17	9	8	5394.3819	17	20
17	10	7	5425.5063	20	-29
17	11	6	5459.8521	8	4
17	12	5	5497.3863		-6
17	13	4	5538.0950	10	17
17	14	3	5581.9462		-17
17	15	2	5628.9267		1
17	16	1	5679.0023		-18
18	1	18	5268.5439	1	3
18	2	17	5277.9320	1	-2
18	3	16	5287.4127		5
18	4	15	5298.9940		-2
18	5	14	5313.7350	6	5
18	6	13	5331.8002	5	1
18	7	12	5353.1670	2	0
18	8	11	5377.8094	2	7
18	9	10	5405.7067	22	25
18	10	9	5436.8300	23	-38
18	11	8	5471.1769	7	-6
18	12	7	5508.7146	6	-1
18	13	6	5549.4238	18	1
18	14	5	5593.2820	2	6
18	15	4	5640.2633	3	-4
19	0	19	5279.7032		1
19	1	18	5288.3128	3	8
19	2	17	5293.9560	4	-5
19	3	16	5300.3858	4	-11
19	4	15	5311.0852	2	2
19	5	14	5325.7213	2	-1
19	6	13	5343.7686		2
19	7	12	5365.1283		11
19	8	11	5389.7654	3	5
19	9	10	5417.6596	6	9
19	10	9	5448.7850	24	-31
19	11	8	5483.1317	17	-13
19	12	7	5520.6730	12	9
19	13	6	5561.3838	3	1
19	14	5	5605.2452	4	6
19	15	4	5652.2313		8
19	16	3	5702.3140	19	-21
20	1	20	5291.6212	1	0
20	2	19	5301.9746		11
20	3	18	5311.9626		-2
20	4	17	5323.6345	1	0
20	5	16	5338.3364	1	-1
20	6	15	5356.3704	6	5
20	7	14	5377.7198	6	6
20	8	13	5402.3519	7	1
20	9	12	5430.2448	16	13
20	10	11	5461.3701	15	-24
20	12	9	5533.2599		7
20	13	8	5573.9737	10	4
20	16	5	5714.9166		-4
21	0	21	5303.9762	2	1
21	1	20	5313.9386	5	-4
21	2	19	5320.5361		0
21	3	18	5326.8366		-5
21	4	17	5337.0986	1	-3
21	5	16	5351.6024	2	0
21	6	15	5369.6063	6	4
21	7	14	5390.9437	1	3
21	8	13	5415.5696		-5
21	9	12	5443.4596	18	8
21	11	10	5508.9341	5	9
21	12	9	5546.4758	4	-1
21	13	8	5587.1934	4	8
21	14	7	5631.0610	8	10
21	15	6	5678.0550		14

(continued on next page)

Table 2 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
21	16	5	5728.1506		28
22	1	22	5317.0143	4	-3
22	2	21	5328.3901	2	1
22	3	20	5338.9952	2	0
22	4	19	5350.8200	3	3
22	5	18	5365.4845	5	-2
22	6	17	5383.4756	2	-1
22	7	16	5404.8005	1	2
22	8	15	5429.4185	15	-11
22	9	14	5457.3062	21	15
22	10	13	5488.4284		-32
22	11	12	5522.7781	11	-1
22	12	11	5560.3233	2	9
22	13	10	5601.0424	1	8
22	14	9	5644.9136	6	14
23	0	23	5330.5483		2
23	1	22	5341.8427	3	3
23	2	21	5349.6059	1	-3
23	3	20	5355.9871	11	9
23	4	19	5365.7377		-8
23	5	18	5380.0410	5	4
23	6	17	5397.9820	6	-1
23	7	16	5419.2904	5	2
23	8	15	5443.9027	20	18
23	9	14	5471.7829	14	14
23	10	13	5502.9037	22	-28
23	11	12	5537.2532	5	1
23	12	11	5574.7992	5	5
23	13	10	5615.5213	8	10
24	1	24	5344.7205	3	3
24	2	23	5357.1640	4	-3
24	3	22	5368.4896	2	1
24	4	21	5380.5462	6	7
24	5	20	5395.1844		1
24	6	19	5413.1231	12	10
24	7	18	5434.4134		0
24	8	17	5459.0154	4	12
24	9	16	5486.8908	13	15
24	10	15	5518.0094	20	-25
24	11	14	5552.3588	6	7
24	12	13	5589.9052	7	4
24	13	12	5630.6310	18	23
24	14	11	5674.5076		18
25	0	25	5359.4219	2	1
25	1	24	5372.0117	5	-3
25	2	23	5381.1040	5	-7
25	3	22	5387.8117	4	-7
25	4	21	5397.0386	14	-9
25	5	20	5411.0481	5	-7
25	6	19	5428.9020		-3
25	7	18	5450.1713	1	6
25	8	17	5474.7607	5	10
25	9	16	5502.6297		13
25	10	15	5533.7452	21	-27
25	11	14	5568.0933	11	0
25	13	12	5646.3683	20	14
25	14	11	5690.2488	12	16
26	1	26	5374.7350	6	-3
26	2	25	5388.2825	3	5
26	3	24	5400.4237	2	2
26	4	23	5412.8038	2	0
26	5	22	5427.4395	2	0
26	6	21	5445.3138		-2
26	7	20	5466.5622		1
26	8	19	5491.1381		3
26	9	18	5519.0006	11	16
26	10	17	5550.1110	26	-37
26	11	16	5584.4586		-2
26	12	15	5622.0057		-12
26	14	13	5706.6203		21
27	0	27	5390.5990	3	4
27	1	26	5404.4491		-4
27	2	25	5414.9674		-5
27	3	24	5422.2749	1	-5
27	4	23	5431.0384	10	5

Table 2 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
27	5	22	5444.6435	1	-3
27	6	21	5462.3730	4	1
27	7	20	5483.5888	3	1
27	8	19	5508.1497		8
27	11	16	5601.4548	3	2
27	12	15	5639.0025		-4
27	13	14	5679.7335	6	8
28	1	28	5407.0583		1
28	3	26	5434.7745	3	-2
28	4	25	5447.5813	3	-4
28	5	24	5462.2521	3	-5
28	6	23	5480.0569		4
28	7	22	5501.2499	8	-2
28	8	21	5525.7938		7
28	9	20	5553.6357	5	3
28	10	19	5584.7382	23	-28
28	11	18	5619.0820	8	11
28	12	17	5656.6310		20
28	13	16	5697.3619		16
29	0	29	5424.0788	36	-3
29	1	28	5439.1606		-8
29	2	27	5451.1412		22
29	3	26	5459.3231		6
29	4	25	5467.7603	2	-5
29	5	24	5480.8478	2	-2
29	6	23	5498.4021		5
29	7	22	5519.5490		7
29	8	21	5544.0725	10	15
29	9	20	5571.9034	12	16
29	10	19	5602.9976		-33
29	11	18	5637.3383	11	6
29	12	17	5674.8866		13
30	1	30	5441.6875		-4
30	2	29	5457.5023	11	0
30	3	28	5471.5194	9	-14
30	4	27	5484.8624	2	-1
30	5	26	5499.6233	1	-2
30	6	25	5517.3551	3	3
30	7	24	5538.4827	13	12
30	8	23	5562.9838		9
30	9	22	5590.8019	10	13
30	10	21	5621.8893		-28
30	11	20	5656.2252	5	-1
31	0	31	5459.8645	15	9
31	1	30	5476.1562	7	7
31	2	29	5489.5765	5	-3
31	3	28	5498.8919	4	-2
31	4	27	5507.2168	11	2
31	5	26	5519.6896		-2
31	6	25	5536.9969		-8
31	7	24	5558.0540	2	0
31	8	23	5582.5300	7	8
31	9	22	5610.3333		13
31	10	21	5641.4128	20	-22
31	11	20	5675.7438	6	2
32	1	32	5478.6218	12	-3
32	2	31	5495.5894	14	7
32	3	30	5510.6415	3	3
32	4	29	5524.6263		6
32	5	28	5539.5487	4	1
32	6	27	5557.2136	12	0
32	7	26	5578.2617		12
32	8	25	5602.7108	6	7
32	9	24	5630.4981	15	17
32	10	23	5661.5662		-33
32	11	22	5695.8928	8	-1
33	0	33	5497.9520	11	1
33	1	32	5515.4375	10	-2
33	2	31	5530.2601	13	-4
33	3	30	5540.9157	7	-4
33	4	29	5549.3901		2
33	5	28	5561.2032	2	-4
33	6	27	5578.1734	2	-1

(continued on next page)

Table 2 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
33	7	26	5599.1116		6
33	8	25	5623.5265	3	1
33	9	24	5651.2957		17
33	11	24	5716.6740	5	9
34	1	34	5517.8608		-3
34	2	33	5535.9842		-11
34	3	32	5552.1174		1
34	4	31	5566.8485	3	-2
34	5	30	5582.0206		2
34	6	29	5599.6354	10	-13
34	7	28	5620.5931		12
34	8	27	5644.9776	9	-4
34	9	26	5672.7263		12
34	10	25	5703.7717	20	-29
35	0	35	5538.3420	25	-26
35	1	34	5557.0139		12
35	2	33	5573.1853		-8
35	3	32	5585.3252	14	11
35	4	31	5594.2422	4	-7
35	5	30	5605.4254	7	-4
35	6	29	5621.9450		3
35	7	28	5642.7244	5	-9
35	8	27	5667.0634		-28
35	9	26	5694.7917	12	17
36	1	36	5559.4043	3	6
36	2	35	5578.6889	4	3
36	3	34	5595.9337	3	0
36	4	33	5611.5073	3	-2
36	5	32	5627.0282	25	11
36	7	30	5665.4813	8	11
36	8	29	5689.7907	2	7
36	9	28	5717.4899		9
36	10	27	5748.5055	22	-34
37	0	37	5581.0376	10	-5
37	1	36	5600.8830	6	-2
37	3	34	5632.0496	3	1
37	4	33	5641.7220	20	7
37	5	32	5652.3867	8	-12
37	6	31	5668.3322	6	3
37	7	30	5688.9042	4	1
37	8	29	5713.1543		20
37	9	28	5740.8229	14	5
37	10	27	5771.8221		-28
38	1	38	5603.2497		7
38	2	37	5623.6967	6	7
38	3	36	5642.0763		-12
38	4	35	5658.5776	10	-2
38	5	34	5674.5528	7	4
38	6	33	5692.1826	8	2
38	7	32	5712.9294		-7
38	8	31	5737.1497	4	-2
38	9	30	5764.7906	7	1
39	0	39	5626.0351	17	5
39	1	38	5647.0502		-5
39	2	37	5665.7931		-2
39	3	36	5681.0386	7	-3
39	4	35	5691.7586	6	-10
39	5	34	5702.1052	12	-12
39	6	33	5717.3611	6	-3
39	7	32	5737.6556		-5
39	8	31	5761.7881	12	-7
39	10	29	5820.3538		-23
40	1	40	5649.3989		27
40	2	39	5671.0061		6
40	3	38	5690.5392	4	3
40	4	37	5708.0364		1
40	5	36	5724.5771		4
40	6	35	5742.3032		13
40	7	34	5762.9460	7	1
40	8	33	5787.0627	25	12
41	0	41	5673.3293	23	-33
41	1	40	5695.5172	9	12
41	2	39	5715.4946	12	-4
41	3	38	5732.2586		0
41	4	37	5744.2833	13	-18

Table 2 (continued)

<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ
1			2	3	4
41	6	35	5769.0664		8
41	7	34	5788.9936		12
42	1	42	5697.8445		0
42	2	41	5720.6156	4	-2
42	3	40	5741.3104	2	1
42	4	39	5759.8615	18	-3
42	5	38	5777.0776		4
42	6	37	5794.9768		-13
42	7	36	5815.5317		9
43	0	43	5722.9306		-5
43	1	42	5746.2788	4	-3
43	2	41	5767.4741	10	7
43	3	40	5785.6965	13	7
43	4	39	5799.2240		26
43	5	38	5809.7653		13
43	6	37	5823.4812		7
44	1	44	5748.5940		11
44	2	43	5772.5258	9	3
44	4	41	5814.0371	14	17
44	6	39	5850.1998		-4
45	0	45	5774.8303	7	10
45	1	44	5799.3400	9	1
45	2	43	5821.7346		4
46	2	45	5826.7337	1	2
47	0	47	5829.0280	13	17
47	1	46	5854.6970	7	-8
47	2	45	5878.2810	9	-2
48	2	47	5883.2403	12	14
49	0	49	5885.5202	5	-8
49	2	47	5937.1162		-5
51	0	51	5944.3125		0

Δr_2 , and $\Delta \alpha$ to a new set of stretching Morse-type coordinates, $y_1 = 1 - \exp(-aR_1)$ and $y_3 = 1 - \exp(-aR_3)$, and bending-type coordinate, R_2 . In this case, the general number of new potential parameters is the same as the number of parameters in Eqs. (2)–(4) plus one extra parameter, a , in the exponent of the Morse-type coordinates $y_N = 1 - \exp(-aR_N)$ ($N = 1$ or 3). It is possible to show

that the mentioned extra parameter, a , depends strongly on the value of dissociation energy of a molecule. In our case of the SO_2 molecule, the “experimental” dissociation energy (122 kcal/mol $\approx 42\,700\text{ cm}^{-1}$) was obtained from Ref. [44]. The value $a = 2.471\text{ \AA}^{-1}$ (see below) correctly corresponds to this value of the dissociation energy.

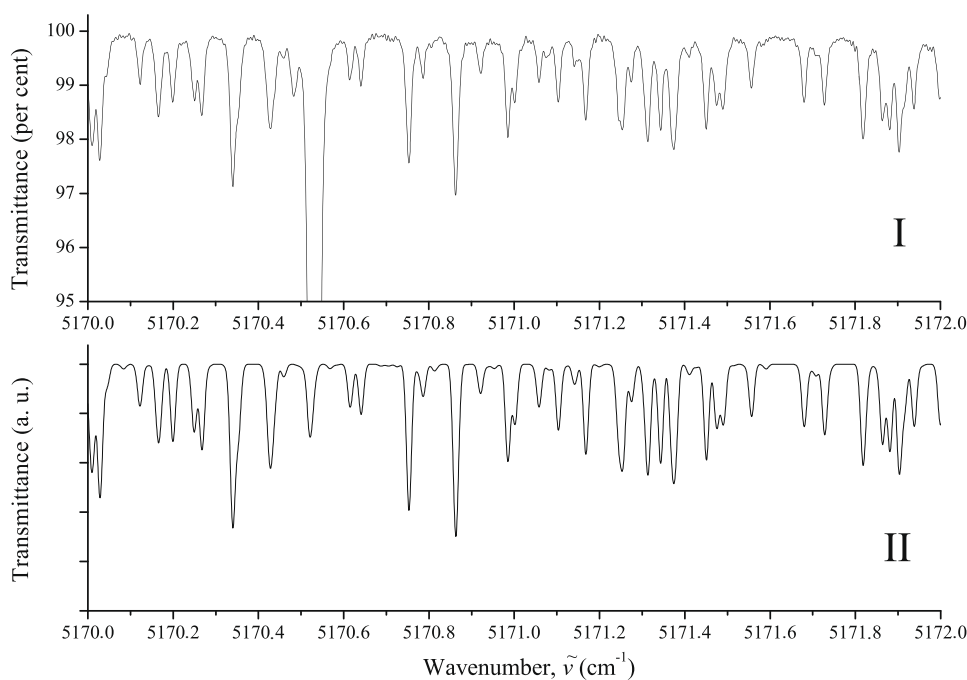


Fig. 4. Small portion of the recorded high resolution spectrum of the SO_2 molecule in the region of the $\nu_1 + 3\nu_3$ absorption band: (I) is the experimentally recorded spectrum; (II) is the simulated spectrum (one dipole moment parameter was used for estimation of relative intensities).

Table 3
Estimated spectroscopic parameters of the (301) and (103) states of the SO₂ molecule (in cm⁻¹).^a

Parameter	(301)		(103)	
	Pred. 2	Fit. 3	Pred. 4	Fit. 5
<i>E</i> / <i>v</i>	4751.900 ^c	4751.7169(14)	5164.643 ^c	5164.8508(18)
<i>A</i>	2.0099	2.008999(315)	1.9663	1.966545(364)
<i>B</i>	0.3380	0.3380517(381)	0.3390	0.339021(597)
<i>C</i>	0.2853	0.2881267(268)	0.2878	0.2887454(365)
$\Delta_K \times 10^4$	0.8875	0.8872(374)	0.8353	0.8381(599)
$\Delta_{JK} \times 10^5$	-0.3663	-0.3798(254)	-0.4272	-0.4350(285)
$\Delta_J \times 10^6$	0.220549 ^b	0.22123(920)	0.220549 ^b	0.2275(164)
$\delta_K \times 10^6$	1.0198	1.0198	0.7532	0.7532
$\delta_J \times 10^7$	0.5674232 ^b	0.5711(301)	0.5674232 ^b	0.5883(648)
$H_K \times 10^7$	0.1332	0.1293(112)	0.1174	0.1242(180)
$H_{KJ} \times 10^9$	-0.8076	-0.8076	-0.5929	-0.5929

^a Values presented in columns 2 and 4 have been theoretically estimated (see text for details). Values in columns 3 and 5 were obtained from the fit (see, for more details, Table 4). In this case, corresponding 1 σ statistical confidence interval for fitted parameter is given also. Parameters presented in columns 3 and 5 without confidence intervals have been constrained to the predicted ones.

^b Constrained to the value from the ground vibrational state.

^c This is the value of the band center calculated with the parameters of the intramolecular potential function from Section 5.

The above mentioned “highly accurate results of analysis of high resolution SO₂ spectra” used in the present study as the initial data determining the parameters of the potential function, Eqs. (2)–(5), consisted of: (a) ro-vibrational energies with $J \leq 4$ of the states (100), (001), and (010) from Refs. [20] and [29], and (b) high accuracy values of the centers of the bands, ν_1 , ν_3 , $2\nu_1$,

$\nu_1 + \nu_3$, $2\nu_3$, $3\nu_1$, $2\nu_1 + \nu_3$, $\nu_1 + 2\nu_3$, $3\nu_3$, ν_2 , $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, $2\nu_1 + \nu_2$, $\nu_1 + \nu_2 + \nu_3$, $2\nu_2$, $2\nu_2 + \nu_3$, $\nu_1 + 3\nu_2$, and $\nu_1 + 3\nu_2 + \nu_3$ from Refs. [20–29]. In the fit of the parameters of the potential function, Eqs. (2)–(5), the values of all band centers used have been taken with the same weights equal to 1. As for the ro-vibrational energies, they have been used with the weight 1000. In this case, the

Table 4
Spectroscopic parameters of the (301), (103), and (000) vibrational states of the SO₂ molecule (in cm⁻¹).^a

Parameter	(301)	(103)	(000) ^b
	2	3	4
<i>E</i>	4751.7169(14)	5164.8508(18)	
<i>A</i>	2.008999(315)	1.966545(364)	2.02735433
<i>B</i>	0.3380517(381)	0.339021(597)	0.3441739084
<i>C</i>	0.2881267(268)	0.2887454(365)	0.293526529
$\Delta_K \times 10^4$	0.8872(374)	0.8381(599)	0.8640369
$\Delta_{JK} \times 10^5$	-0.3798(254)	-0.4350(285)	-0.3901187
$\Delta_J \times 10^6$	0.22123(920)	0.2275(164)	0.220549
$\delta_K \times 10^6$	1.0198 ^c	0.7532 ^c	0.846284
$\delta_J \times 10^7$	0.5711(301)	0.5883(648)	0.5674232
$H_K \times 10^7$	0.1293(112)	0.1242(180)	0.12375
$H_{KJ} \times 10^9$	-0.8076 ^c	-0.5929 ^c	-0.64936
$H_{JK} \times 10^{11}$	0.116 ^d	0.116 ^d	0.116
$H_J \times 10^{12}$	0.37589 ^d	0.37589 ^d	0.37589
$h_K \times 10^9$	0.5670 ^d	0.5670 ^d	0.5670
$h_{JK} \times 10^{12}$	-0.23 ^d	-0.23 ^d	-0.23
$h_J \times 10^{12}$	0.1829 ^d	0.1829 ^d	0.1829
$L_K \times 10^{11}$	-0.265 ^d	-0.265 ^d	-0.265
$L_{KKJ} \times 10^{12}$	0.180 ^d	0.180 ^d	0.180
$L_{JK} \times 10^{13}$	-0.109 ^d	-0.109 ^d	-0.109
$L_{JJK} \times 10^{17}$	-0.88 ^d	-0.88 ^d	-0.88
$L_J \times 10^{17}$	-0.116 ^d	-0.116 ^d	-0.116
$l_K \times 10^{12}$	-0.32 ^d	-0.32 ^d	-0.32
$l_{KJ} \times 10^{14}$	0.27 ^d	0.27 ^d	0.27
$l_{JK} \times 10^{17}$	-0.2 ^d	-0.2 ^d	-0.2
$l_J \times 10^{18}$	-0.597 ^d	-0.597 ^d	-0.597
$P_K \times 10^{15}$	0.649 ^d	0.649 ^d	0.649
$P_{KKJ} \times 10^{16}$	-0.394 ^d	-0.394 ^d	-0.394
$P_{KJ} \times 10^{18}$	-0.703 ^d	-0.703 ^d	-0.703
$P_{JK} \times 10^{19}$	0.778 ^d	0.778 ^d	0.778
$S_K \times 10^{18}$	-0.12 ^d	-0.12 ^d	-0.12
$S_{KJ} \times 10^{20}$	0.70 ^d	0.70 ^d	0.70

^a Values in parentheses are 1 σ confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to the predicted values (see text, for details), or to the values of corresponding parameters of the ground vibrational state.

^b Recalculated from Table 3 of Ref. [29]. Number of kept digits in the values of parameters corresponds the number of digits in the initial values from Ref. [29].

^c Constrained to the predicted values (see text, for details).

^d Constrained to the values of corresponding parameters of the ground vibrational state from the column 4.

fit of the ro-vibrational energies was made in the following manner. For three considered bands, ν_1 , ν_2 , and ν_3 , values of the band centers and of all centrifugal distortion coefficients were constrained to their “experimental” values from Refs. [20] and [29]. Rotational parameters $A \equiv B_z$, $B \equiv B_x$, and $C \equiv B_y$ were presented as sums of two terms $B_\beta^{\nu_\lambda} = B_\beta^{gr} - \alpha_\lambda^\beta$ ($\beta = x, y, z$; $\lambda = 1, 2, 3$). The ground state rotational parameters, B_β^{gr} , were constrained to the values of parameters from Ref. [29], and the rotational–vibrational coefficients, α_λ^β , were considered as functions of the potential parameters, f_{\dots} .

As the result of the fit, a set of 13 parameters of the potential function was obtained, which is presented in Table 5 and reproduces the initial 53 data with the following accuracy: 17 band centers are reproduced with the *rms* deviation 0.152 cm^{-1} (the values of the centers of the bands, $3\nu_1 + \nu_3$ and $\nu_1 + 3\nu_3$, were not used in the fit because their values, 4751.900 cm^{-1} and 5164.643 cm^{-1} , presented in column 3 of Table 6 are considered as the predictions); 36 initial ro-vibrational energies are reproduced with the *rms* deviation 0.00052 cm^{-1} . It should be also mentioned that the value of the dissociation energy, calculated from the parameters from Table 5, is 42699 cm^{-1} , which is close to the experimental value, 42700 cm^{-1} .

In Table 6 (column 4) we present results of calculations, with the parameters from Table 5, of the vibrational energies that were used in the fit as the initial data (the lasts are given in column 2 of Table 6). One can see good correlations between the energy values of columns 2 and 4.

Because the parameters of the potential function in Eqs. (2)–(5) are isotopically invariant, it is interesting to check a prediction possibility of data from Table 5 with the isotopic species different from the $^{32}\text{SO}_2$ one. We used parameters from Table 5 for estimation of the centers of the bands of the $^{34}\text{SO}_2$ isotopic species that have been analyzed earlier with high accuracy in Refs. [45] and [46] in this prediction study. Column 4 of Table 7 presents the result of such prediction. For comparison, column 2 gives corresponding experimental values from Refs. [45,46]. One can see good correlation between two sets of data.

We also note two points that allow us to speak about certain improvements of the potential parameters from Ref. [42] (at the present time, data from Ref. [42] can be considered as the numerically mostly correct, at least, near the equilibrium configuration).

Table 5
Potential energy parameters for the SO_2 molecule.^a

Parameter	Value
1	2
$a/\text{\AA}^{-1}$	2.471
$f_{rr}/\text{aJ \AA}^{-2}$	10.390(34)
$f_{rr'}/\text{aJ \AA}^{-2}$	0.067(31)
$f_{rzz}/\text{aJ \AA}^{-1}$	0.423(64)
f_{zz}/aJ	1.6516(52)
$f_{rrr}/\text{aJ \AA}^{-3}$	-72.66(43)
$f_{rrr'}/\text{aJ \AA}^{-3}$	-1.81(25)
$f_{rrzz}/\text{aJ \AA}^{-2}$	-2.90(61)
$f_{rr'z}/\text{aJ \AA}^{-2}$	-1.488(95)
f_{zzzz}/aJ	-3.248(84)
f_{zzzz}/aJ	-2.688(98)
$f_{rrrr}/\text{aJ \AA}^{-4}$	419.3(79)
$f_{rrrrz}/\text{aJ \AA}^{-2}$	7.3(18)
f_{zzzzz}/aJ	10.1(16)
$r_e/\text{\AA}^b$	1.431
α_e/deg^b	119.3

^a Uncertainties in parentheses are one standard errors.

^b Constrained to the value from Ref. [42].

Table 6
Band centers of the SO_2 molecule (in cm^{-1}).

Band	Exp.	Ref.	Calc.
1	2	3	4
ν_2	517.8726	[29]	517.832
$2\nu_2$	1035.1264	[25]	1035.009
ν_1	1151.7130	[25]	1151.673
ν_3	1362.0603	[25]	1362.088
$\nu_1 + \nu_2$	1666.3348	[22]	1666.438
$\nu_2 + \nu_3$	1875.7975	[22]	1875.755
$2\nu_1$	2295.8083	[22]	2295.661
$2\nu_2 + \nu_3$	2388.9155	[23]	2388.667
$\nu_1 + \nu_3$	2499.8700	[27]	2499.945
$\nu_1 + 3\nu_2$	2693.6348	[30]	2693.852
$2\nu_3$	2713.3826	[30]	2713.487
$2\nu_1 + \nu_2$	2807.1890	[22]	2807.335
$\nu_1 + \nu_2 + \nu_3$	3010.3178	[22]	3010.523
$3\nu_1$	3432.2877	[35]	3431.986
$2\nu_1 + \nu_3$	3629.7619	[27]	3629.856
$\nu_1 + 3\nu_2 + \nu_3$	4029.3903	[26]	4029.247
$3\nu_3$	4054.0012	[26]	4054.084
$3\nu_1 + \nu_3$	4751.7169		4751.900 ^a
$\nu_1 + 3\nu_3$	5164.8507		5164.643 ^a

^a Prediction; experimental value was not used in the fit.

Table 7
Band centers of the $^{34}\text{SO}_2$ molecule (in cm^{-1}).

Band	Exp.	Ref.	Calc.
1	2	3	4
ν_2	513.538709	[45]	513.91
$2\nu_2$	1026.455469	[45]	1026.94
ν_1	1144.478633	[45]	1144.91
ν_3	1345.094641	[45]	1344.93
$3\nu_2$	1538.720198	[46]	1539.49
$\nu_1 + \nu_2$	1654.829004	[45]	1655.88
$\nu_2 + \nu_3$	1854.610452	[45]	1854.88
$\nu_1 + \nu_3$	2475.828004	[46]	2475.98
$2\nu_3$	2679.800919	[46]	2679.42
$\nu_1 + \nu_2 + \nu_3$	2982.118600	[46]	2982.81
$2\nu_1 + \nu_3$	3598.773915	[46]	3599.50

First, Table 8 presents values of the lowest ($J \leq 4$) ro-vibrational energies for the three fundamental bands of the $^{32}\text{SO}_2$ molecule (calculations have been made on the scheme discussed above). Experimental values are shown in columns 2, 5, and 8. Other columns give the values, $\Delta = (E^{exp.} - E^{calc.}) \times 10^3 \text{ cm}^{-1}$, the difference between experimental and calculated values. In this case, calculations were made with the parameters from Table 5 (columns 3, 6, and 9), and from Ref. [42] (columns 4, 7, and 10), respectively. A correspondence between our calculated and experimental data is considerably better than between experimental energies and energies calculated with the parameters from [42]. In general, for the presented energy values, the *rms* deviation in our case is about 15 times better than the *rms* deviation of data calculated with the parameters from Ref. [42]. This fact indicates an improvement of the cubic f_{\dots} parameters. As the second illustration, the value of the dissociation energy will be discussed. In our case, it was fit to the experimental value and is 42699 cm^{-1} (the experimental value from Ref. [44] is about 42700 cm^{-1}). At the same time, parameters from Ref. [42] give the value 49740 cm^{-1} that is far from the experimental one. In our opinion, it indicates an improvement of the value of a -parameter in the above mentioned $y_1 = 1 - \exp(-aR_1)$ and $y_3 = 1 - \exp(-aR_3)$ coordinates. The presented discussion gives us possibility to hope that the potential parameters obtained in the present section are eligible for the using in SO_2 spectroscopy.

Table 8
Ro-vibrational term values for the (010), (100), and (001) vibrational state of the SO₂ molecule (in cm⁻¹).^a

			(100)			(010)			(001)		
1			2	3	4	5	6	7	8	9	10
<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ_1	Δ_2	<i>E</i>	Δ_1	Δ_2	<i>E</i>	Δ_1	Δ_2
0	0	0	1151.71299			517.87243			1362.06061		
1	0	1							1362.69613	0.07	0.05
1	1	1	1154.03349	-0.11	0.11	520.23193	-0.28	1.81			
1	1	0							1364.41029	0.09	-0.26
2	0	2	1153.61575	-0.08	-0.43	519.78304	-0.23	-1.54			
2	1	2							1365.58002	0.00	-0.47
2	1	1	1155.40354	0.26	0.19	521.60894	0.63	1.66			
2	2	1							1370.72152	0.05	-1.41
2	2	0	1160.46126	0.01	0.95	526.77572	0.14	0.86			
3	0	3							1365.86761	0.02	-0.15
3	1	3	1157.07996	-0.77	-1.04	523.28938	-1.80	-1.80			
3	1	2							1367.71321	0.13	-0.28
3	2	2	1162.36408	-0.08		528.68642	-0.21				
3	2	1							1372.63359	0.05	-1.50
3	3	1	1170.91505	0.01	2.21	537.42097	0.06	19.80			
3	3	0							1381.06809	0.04	-3.24
4	0	4	1158.04251	-0.39	-1.52	524.22797	-1.0	-5.34			
4	1	4							1369.84813	-0.18	-0.97
4	1	3	1160.01926	0.75	0.22	526.24600	1.75	-0.45			
4	2	3							1375.16885	0.00	-1.66
4	2	2	1164.91844	-0.05	0.06	531.25148	-0.16	5.31			
4	3	2							1383.61228	0.01	-3.38
4	3	1	1173.45605	0.06	1.66	539.97252	-0.17	17.80			
4	4	1							1395.41860	0.03	-5.79
4	4	0	1185.41720	0.03	4.01	552.19000	0.15	35.54			

^a In Table 8 Δ is the difference ($E^{exp.} - E^{calc.}$) $\times 10^{-3}$ cm⁻¹, where $E^{calc.}$ is a value of the rotational energy calculated with the parameters of the potential function of the present paper (columns 3, 6, 9) and of Ref. [42] (column 4, 7, 10), respectively.

Acknowledgments

Part of the work benefited from the joint PICS grant of CNRS (France) and RFBR (Russia), 4221 N 0000211752a; from the grant of the President of the Russian Federation, SS-871.2008.2; and from the Russian Science and Innovations Federal Agency under contract No. 02.740.11.0238.

References

- [1] E.D. Hinkley, A.R. Calawa, P.J. Kelley, S.A. Clough, J. Appl. Phys. 43 (1972) 3222–3223.
- [2] G.D. Tejwani, J. Chem. Phys. 57 (1972) 4676–4681.
- [3] W.H. Yang, J.A. Roberts, G.D. Tejwani, J. Chem. Phys. 58 (1973) 4916–4918.
- [4] M. Carlotti, G. Di Lonardo, L. Fusina, B. Carli, F. Mencaraglia, J. Mol. Spectrosc. 106 (1984) 235–244.
- [5] P.A. Helminger, F.C. De Luchia, J. Mol. Spectrosc. 111 (1985) 66–72.
- [6] A. Barbe, C. Secroun, P. Jouve, B. Dutelage, N. Mjnnanteuil, J. Bellet, G. Steenbeckeliers, J. Mol. Spectrosc. 55 (1975) 319–350.
- [7] G. Steenbeckeliers, J. Bellet, J. Appl. Phys. 46 (1975) 2620–2626.
- [8] P.J. Pilon, C. Young, J. Quant. Spectrosc. Radiat. Transfer 16 (1976) 1137–1140.
- [9] A. Barbe, C. Secroun, P. Jouve, B. Dutelage, N. Monnanteuil, J. Bellet, Mol. Phys. 34 (1977) 127–130.
- [10] A.S. Pine, P.F. Moulton, J. Mol. Spectrosc. 64 (1977) 15–30.
- [11] A.S. Pine, G. Dresselhaus, B. Palm, R.W. Davies, S.A. Clough, J. Mol. Spectrosc. 67 (1977) 386–415.
- [12] N.I. Moskalenko, V.F. Terzi, S.N. Parzhin, V.T. Pushkin, R.S. Sadydov, Izv. Acad. Sci. USSR Atmos. Oceanic Phys. 14 (1978) 901–902.
- [13] F. Herlemont, M. Lyszyk, J. Lemaire, J. Mol. Spectrosc. 77 (1979) 69–75.
- [14] J.P. Sattler, T.L. Worchesky, W.J. Lafferty, J. Mol. Spectrosc. 88 (1981) 364–371.
- [15] T. Kunitomo, H. Masuzaki, S. Ueoka, M. Osumi, J. Quant. Spectrosc. Radiat. Transfer 25 (1981) 345–349.
- [16] K. Kim, W.T. King, J. Chem. Phys. 80 (1984) 969–973.
- [17] F. Kuhnemann, Y. Heiner, B. Sumpf, K. Hermann, J. Mol. Spectrosc. 152 (1992) 1–12.
- [18] A.J. Lovas, J. Phys. Chem. Ref. Data 14 (1985) 395–488.
- [19] W.J. Lafferty, G.T. Fraser, A.S. Pine, J.-M. Flaud, C. Camy-Peyret, V. Dana, J.-Y. Mandin, A. Barbe, J.J. Plateaux, S. Bouazza, J. Mol. Spectrosc. 154 (1992) 51–60.
- [20] G. Guelachvili, O.N. Ulenikov, G.A. Ushakova, J. Mol. Spectrosc. 108 (1984) 1–5.
- [21] G. Guelachvili, O.V. Naumenko, O.N. Ulenikov, Appl. Opt. 23 (1984) 2862–2867.
- [22] G. Guelachvili, O.V. Naumenko, O.N. Ulenikov, J. Mol. Spectrosc. 125 (1987) 128–139.
- [23] G. Guelachvili, O.V. Naumenko, O.N. Ulenikov, J. Mol. Spectrosc. 131 (1988) 400–402.
- [24] L. Coudert, A.G. Maki, Wm.B. Olson, J. Mol. Spectrosc. 124 (1987) 437–442.
- [25] J.-M. Flaud, A. Perrin, L.M. Salah, W.J. Lafferty, G. Guelachvili, J. Mol. Spectrosc. 160 (1993) 272–278.
- [26] J.-M. Flaud, W.J. Lafferty, J. Mol. Spectrosc. 161 (1993) 396–402.
- [27] W.J. Lafferty, A.S. Pine, G. Hilpert, R.L. Sams, J.-M. Flaud, J. Mol. Spectrosc. 176 (1996) 280–286.
- [28] W.J. Lafferty, J.-M. Flaud, G. Guelachvili, J. Mol. Spectrosc. 188 (1998) 106–107.
- [29] H.S.P. Müller, S. Brünken, J. Mol. Spectrosc. 232 (2005) 213–222.
- [30] W.J. Lafferty, A.S. Pine, J.-M. Flaud, C. Camy-Peyret, J. Mol. Spectrosc. 157 (1993) 499–511.
- [31] B. Sumpf, O. Fleischmann, H.D. Kronfeldt, J. Mol. Spectrosc. 176 (1996) 127–132.
- [32] B. Sumpf, M. Schone, H.D. Kronfeldt, J. Mol. Spectrosc. 179 (1996) 137–141.
- [33] P.M. Chu, S.J. Wetzel, W.J. Lafferty, A. Perrin, J.-M. Flaud, Ph. Arcas, G. Guelachvili, J. Mol. Spectrosc. 189 (1998) 55–63.
- [34] S.P. Belov, M.Y. Tretyakov, I.N. Kozin, E. Klisch, G. Winnewisser, W.J. Lafferty, J.-M. Flaud, J. Mol. Spectrosc. 191 (1998) 17–27.
- [35] O.N. Ulenikov, E.S. Bekhtereva, V.-M. Horneman, S. Alanko, O.V. Gromova, J. Mol. Spectrosc. 255 (2009) 111–121.
- [36] T. Ahonen, S. Alanko, V.-M. Horneman, M. Koivusaari, R. Paso, A.-M. Tolonen, R. Anttila, J. Mol. Spectrosc. 181 (1997) 279–286.
- [37] G. Guelachvili, K.N. Rao (Eds.), Handbook of Infrared Standards II with Spectral Coverage of 1.4 μm –4 μm and 6.2 μm –7.7 μm , Academic Press, San Diego, CA, 1993.
- [38] G. Guelachvili et al., J. Mol. Spectrosc. 117 (1996) 164–179.
- [39] J.-M. Flaud, C. Camy-Peyret, J. Mol. Spectrosc. 55 (1975) 278–310.
- [40] J.K.G. Watson, J. Chem. Phys. 46 (1967) 1935–1949.
- [41] A.J.C. Varandas, S.P.J. Rodrigues, Spectrochim. Acta A 58 (2002) 629–647.
- [42] J. Zúñiga, A. Bastida, A. Requena, J. Chem. Phys. 115 (2001) 139–148.
- [43] O.N. Ulenikov, E.S. Bekhtereva, C. Leroy, O.V. Gromova, A.L. Fomchenko, J. Mol. Spectrosc. 255 (2009) 88–100.
- [44] P. Nachtigall, J. Krusak, O. Bludsky, S. Iwata, Chem. Phys. Lett. 303 (1999) 441–446.
- [45] W.J. Lafferty, J.-M. Flaud, R.L. Sams, El Hadji Abib Ngom, J. Mol. Spectrosc. 252 (2008) 72–76.
- [46] W.J. Lafferty, J.-M. Flaud, El Hadji Abib Ngom, R.L. Sams, J. Mol. Spectrosc. 253 (2009) 51–54.