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On the high resolution spectroscopy and intramolecular potential function of SO_2

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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 SO_2 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, v_1 + 3 v_3 and 3 v_1 + v_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

ABSTRACT

Two weak stretching bands, $v_1 + 3v_3$ and $3v_1 + v_3$, 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 $v_1 + 3v_3$ and $3v_1 + v_3$, 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, $3v_1 + v_3$ and $v_1 + 3v_3$, respectively. The problem of determination of the intramolecular potential function of SO₂ is discussed.

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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 $3v_1 + v_3$ and $v_1 + 3v_3$. 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 $3v_1 + v_3$ and $v_1 + 3v_3$ 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 $3v_1$ band in Fig. 1 of Ref. [35]), the R-branches of the perpendicular bands, $3v_1 + v_3$ and $v_1 + 3v_3$, 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)

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Fig. 1. Survey spectrum of SO₂ in the region of the band $3v_1 + v_3$: (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 SO_2 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_{α} , 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 $v_1 + 3v_3$: (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]).

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Fig. 3. Small portion of the recorded high resolution spectrum of the SO₂ molecule in the region of the $3v_1 + v_3$ 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^r representation, [40],

$$\begin{split} H^{\nu\nu} &= E^{\nu} + \left[A^{\nu} - \frac{1}{2} (B^{\nu} + C^{\nu}) \right] J_{z}^{2} + \frac{1}{2} (B^{\nu} + C^{\nu}) J^{2} + \frac{1}{2} (B^{\nu} - C^{\nu}) J_{xy}^{2} \\ &- \Delta_{k}^{\nu} J_{z}^{4} - \Delta_{jk}^{\nu} J_{z}^{2} J^{2} - \Delta_{j}^{\nu} J^{4} - \delta_{k}^{\nu} \left[J_{z}^{2} , J_{xy}^{2} \right]_{+} - 2 \delta_{j}^{\nu} J^{2} J_{xy}^{2} + H_{k}^{\nu} J_{z}^{6} \\ &+ H_{k}^{\nu} J_{z}^{4} J^{2} + H_{jk}^{\nu} J_{z}^{2} J^{4} + H_{j}^{\nu} J^{6} + \left[h_{kJ}^{\nu} J_{z}^{4} + h_{jk}^{\nu} J_{z}^{2} J^{2} + h_{j}^{\nu} J^{4} , J_{xy}^{2} \right]_{+} \\ &+ L_{kK}^{\nu} J_{z}^{8} + L_{kKJ}^{\nu} J_{z}^{6} J^{2} + L_{jK}^{\nu} J_{z}^{4} J^{4} + L_{jjK}^{\nu} J_{z}^{2} J^{6} + L_{j}^{\nu} J^{8} \\ &+ \left[l_{kJ}^{\nu} J_{z}^{6} + l_{kJ}^{\nu} J_{z}^{4} J^{2} + l_{jK}^{\nu} J_{z}^{2} J^{4} + l_{jJ}^{\nu} J_{z}^{6} J_{xy}^{2} \right]_{+} + P_{kKJ}^{\nu} J_{z}^{10} + P_{kKJ}^{\nu} J_{z}^{8} J^{2} \\ &+ P_{kK}^{\nu} J_{z}^{2} J^{4} + P_{jK}^{\nu} J_{z}^{4} J^{6} + \ldots + S_{kJ}^{\nu} J_{z}^{12} + S_{kKJ}^{\nu} J_{z}^{10} J^{2} + \ldots \end{split}$$
(1

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 $[\ldots, \ldots]_+$ 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, $\alpha_{\lambda\mu}^{\beta}$ and $\gamma_{\lambda\mu}^{\beta}$) 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, $3v_1 + v_3$ and $v_1 + 3v_3$, 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, $E^{exp.}$ in cm⁻¹, is presented in column 2 of Tables 1 and 2 together with associated experimental uncertainties Δ in columns 3 and $\delta = (E^{exp.} - E^{calc.})$ in columns 4. The values of $E^{calc.}$ 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) 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.
- (b) 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.

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Table 1

Experimental ro-vibrational term values for the (301) vibrational state of the SO_2 molecule (in cm⁻¹).^a

J	Ka	Kc	Ε	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	4/5/.3186	3	د– د
4	1	4	4759 4223	3	-5
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	7	-0 _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	4/91.98//	2	0 12
6	5	2	4807.2177	3	12
7	Ő	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	4811.0045	12	-2 10
7	7	0	4852.1481	0	_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
0 8	8	2	4853.2149	10	-7
8	8	1	4882.4554	10	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	4/95.2132	4	4
9	4	4	4807.0410	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	4/86.3618	3	0
10	2	9	4792.8002 4801 4792	5	-1 _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		-5
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	0	-4
11	5	6	4835.4364 4854.0272	9	-13
11	7	4	4034.0272 4875 9755	6	1
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	10	4807.1737 4815 9319	4	-3 1
12	5	10	-013.3313	-7	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.

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Table 1 (continued)

J	Ka	Kc	Ε	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	2	4909.3393	0	-4 _2
12	12	1	5043.0462	5	-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	/	0 11
13	6	8	4851.1270	4	-11
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	15	14	4816 1335	6	-14
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 9	6	4923.7270	4 8	_4
14	10	5	4986.2759	0	-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	I	0
15	1	14	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	1	4935.1368	5	5
15	10	5	4995 6858	5	-1
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	4	0
16	3 4	14	4032.3932 4864 2285	4 11	-1
16	5	12	4879.3919	2	-4
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	/	5005.7237	5	0
16	11	5	5040.9478 5079 4430	0	3
16	12	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	7	10	4930 5567	2	4
17	8	9	4955.8401	7	-2

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Table 1 (continued)

J	Ka	Kc	Ε	Δ	δ
1			2	3	4
17	9	8	4984.4585	5	7
17	10	7	5016.3893	1	1
17	14	b 3	5051.6141	8	1
17	14	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	5	13	4880.2030	1	 2
18	6	13	4919.9309	8	-10
18	7	12	4941.8554	8	6
18	8	11	4967.1354	4	2
18	9 10	9	5027.6830	4	-4
18	11	8	5062.9083	5	-1
18	12	7	5101.4065	3	-1
18	13	6	5143.1546	2	3
18	14	5	5236 2988		12 _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 4887.2761	3	0
19	4	15	4898.3135	1	-1
19	5	14	4913.3472	2	2
19	6	13	4931.8678	2	0
19	/ 8	12	4953.7828 4979.0590	10	1
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	15	4	5248.2323		13
19	16	3	5299.5799		5
20	1	20	4878.2747	3	2
20	2	19	4888.7266 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	/ 8	14	4966.3405 4991.6121	/	-3 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 5167.6342	4	2
20	13	7	5212.6116	4	-1
21	0	21	4890.5986		-2
21	1	20	4900.5792	1	1
21	2	19	4907.1609 4913.6350	1	0 _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 5004 7940	5 10	
21	9	12	5033.4030	2	-1
21	10	11	5065.3321		0
21	12	9	5139.0611	3	-2
21	13	8 7	5180.8150 5225 795 <i>4</i>	5	-1
21	15	6	5273.9764	0	-4
22	1	22	4903.6196	7	5
22	2	21	4915.0940	2	0
22	3	20	4925.8515 4937 9498	9	-2
22	5	18	4953.0009	4	-3
22	6	17	4971.4667	5	-4
22	7	16	4993.3483	4	-1
22	8	15 14	5018.6060 5047 2106	4	-3
	5	17	5077.2100	5	-0

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Table 1 (continued)

J	Ka	Kc	Ε	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	0	23	4917 1221	3	-2
23	1	22	4928.4512	3	-4
23	2	21	4936.1747		-2
23	3	20	4942.6870	5	1
23	4	19	4952.7953	1	3
23	5	18	4907.3130	1 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	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 24	5	18	5022 8813	5	4
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	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 25	3	22	4974.4140 4983 9895	5 11	0
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 25	9 11	10	5092.4114 5159 5555	0	6 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	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	2	5
26	ð G	19	5108 7364	2	1
26	11	16	5175.8751	3	10
26	12	15	5214.3793		2
27	0	27	4977.0588	6	-8
27	1	26	4990.9837		1
27 27	2	25	5001.4446	7	3
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	9	19	5125.6925	5	-/
27	10	17	5157.6021	5	0
27	11	16	5192.8227	1	2
27	12	15	5231.3269		-1
27	13	14	52/3.0897	3	-2
28	2	28	5008,2729	1	-1
28	3	26	5021.4337	·	-1
28	4	25	5034.4620	3	2
28	5	24	5049.4995	4	2
28	6	23	5067.7795	4	-2
				,	

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Table 1 (continued)

J	Ka	Kc	Ε	Δ	δ
1			2	3	4
28	7	22	5089.5331	2	-2
28	8	21	5114.7160	2	1
28	9 11	20	5143.2777	2	2
28	12	17	5248.9030	7	-3
28	13	16	5290.6663	4	-7
29	0	29	5010.4765	9	6
29	2	27	5025.0405	3	-2
29	3	26	5045.7356	10	0
29	4	25	5054.4539	2	-3
29 29	5	24 23	5068.0150	6	-10
29	7	22	5107.7806	3	1
29	8	21	5132.9438	5	4
29	9	20	5161.4939		4
29	10	18	5228.6058	2	-1
29	12	17	5267.1081		2
30	1	30	5028.0512	2	1
30 30	2	29	5043.9840 5058 1128	l 12	-1
30	4	27	5071.6532	2	-1
30	5	26	5086.7659	6	-5
30	6	25	5104.9726	2	-2
30	8	24 23	5151.8036	8	7
30	9	22	5180.3397		-3
30	10	21	5212.2307		7
30 30	11	20 18	5247.4398		-2 10
31	0	31	5046.1919	6	6
31	1	30	5062.5890	4	-3
31	3	28	5085.2222	4	-2
31	5	26	5106.7299	3	-5
31	6	25	5124.5553		3
31	7	24	5146.1782	0	-2
31	8	23	5171.2958 5199.8171	8	-2
31	10	21	5231.6988	-	2
31	11	20	5266.9023		-13
31 32	13	18	5347.1667 5064.9136		0 _2
32	3	30	5097.1636	5	-8
32	4	29	5111.3264	5	1
32	5	28	5126.5825	5	2
32	7	26	5166.3284	12	0
32	8	25	5191.4213	13	16
32	9	24	5219.9248		-10
32	10	23	5325.4918		-1 -6
32	13	20	5367.2570	8	8
33	0	33	5084.2051	4	-4
33	2	32	5101.8117	3	-2
33	3	30	5127.1756	9	4
33	4	29	5135.7964	10	-9
33	6 7	27	5165.6083	1	-1 -17
33	8	25	5212.1784	3	5
33	9	24	5240.6657		2
33	10 11	23	5272.5254 5307 7177		-1 -6
33	12	21	5346.2114		3
33	13	20	5387.9754		16
34	1	34	5104.0771	8	10
34	2 3	32	5138.5711		-0 -4
34	4	31	5153.4591		1
34	5	30	5168.9412	13	8
34 34	6 7	29	5187.0203 5208 5397	4	-1 _3
34	8	27	5233.5691	10	-3

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Table 1 (continued)

J	Ka	Kc	Ε	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 5159 5190	2	2
35	2	32	5171 5258	10	-7
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	-l 10
35	10	20	5315 8728		-10 -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
30	5	32	5213.8297	3	-7
36	8	29	5278.2552	5	-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	30	5204.0483	6	8
37	4	33	5227 8591	12	-4
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
3/	9	28	5329.9440		1
38	10	27	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	-1/
38	8	31	5325 4823	o 16	-4
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	2 2	35	5207.1387	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	4	38 37	5294 3829	11	12
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 41	10	31	5435.2827	11	-6
41	1	41	5239.2427	11	-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 42	5283 7056	3	4
42	2	41	5306.6529	6	-3
	_		0	-	5

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Table 1 (continued)

1234 42 340 $527,4705$ 106 42 835 $532,274$ -2 42 835 $5427,6574$ 1 42 1033 $5487,4671$ -5 43 043 $5382,4735$ 6 43 142 $5332,2730$ 7 77 43241 $5535,5743$ -1 43 340 $5371,7467$ 18-9 43 439 $5385,0633$ 3-9 43 637 $5410,0844$ -7-7 43 736 $5432,093$ -233 44 144 $5334,5731$ -1-7 43 736 $5432,093$ 23 44 144 $5334,5731$ -1-14 44 441 $5035,673$ 194 44 41 $536,673$ 19-4 44 41 $536,673$ 19-4 44 41 $536,673$ -10-14 45 0 $5418,354$ 222 46 1 $467,0235$ 1-16 45 538,473290-11 46 1 $467,0235$ 1-14 45 146 $5387,2952$ 6-6 46 344 $5435,7781$ 22 46 344 $5435,7781$ 22 46	J	Ka	Kc	Е	Δ	δ
423405227405106425385363.5274-2428355427.6741430435308.74156431425332.7707431425332.773-1433405371.74718-9433405371.74718-9433405371.74713-10433405371.74713-7436375410.0844-7-7436375410.0844-7-7431445343.3531-1-7441435358.475790442435358.4657194444415400.20314-4445405418.3654-2-1450455360.3576-1-1450455360.5376-1-1450455360.5376-1-1450455360.5376-1-1463445407.7503-447047546.2216845047546.22168463445435.7570-1-147047544.2571222<	1			2	3	4
42538533.274 -2 428355427.56741420335487.4671 -5 430435382.7207432415335.743 -1 432415335.743 -1 433405371.746718 -9 434395385.063313 -10 435385395.7463 3 -7 437365430.2093 -72 -73 4410435514.50822 -72 437365338.4732 9 0 4414435338.4732 9 0 44145400.209214 -44 44415400.209214 -44 44415400.209214 -41 45045538.0137 -11 451445382.3965 -88 452435407.75807 -11 456395407.2556 -66 46245542.57703 -44 47445337.29526 -66 466415492.575703 -44 47485407.7781 -44 4824754464.2561 -77 4824754464.2561 -77 48247	42	3	40	5327.4705	10	6
42 8 35 $5427,5674$ -1 42 0 33 $5487,4671$ -5 43 0 43 $5308,7415$ 6 -7 43 1 42 $5322,720$ 7 7 43 3 40 $5371,7467$ 18 -9 43 3 40 $5371,7467$ 18 -9 43 5 38 $5385,0633$ 13 -10 43 6 37 $5410,0844$ -77 43 6 37 $5410,0844$ -77 43 1 44 $5384,5023$ 2 -33 44 1 $5384,5023$ 2 -33 44 1 44 $5384,3732$ 9 00 44 41 $5384,3732$ 9 01 44 44 41 $500,2002$ 14 -44 44 41 $500,2002$ 14 -41 44 41 $500,2002$ 14 -41 45 0 45 $560,576$ -8 45 2 43 $507,7580$ 7 -11 45 6 39 $547,9127$ -14 -41 45 6 39 $547,9127$ -14 -42 45 6 $398,2295$ 6 -6 6 46 3 441 $5385,2396$ 5 -8 47 0 47 $5442,2776$ 8 00 47 <t< td=""><td>42</td><td>5</td><td>38</td><td>5363.5274</td><td></td><td>-2</td></t<>	42	5	38	5363.5274		-2
4210335478/76715430435308/74156-7431425332/272077432415335/743-1433405371/746718-9434395385/63313-10436375410.0844-7437365395/74633-9436375410.0844-7437365302/27223441445338/3531-1442435358/4732900443425304/5731944443425304/57314-44443435319/27-1444435400/209214-444435400/209214-444435400/209214-4450455306/576-1451445382/2965-8456395407/7807-10456395407/235116461445435/75703-4470475442/276810482455442/2768-147443501/781-4-4474435442/2763 </td <td>42</td> <td>8</td> <td>35</td> <td>5427.5674</td> <td></td> <td>1</td>	42	8	35	5427.5674		1
430435382,2706-7431425332,7743-1433405371,746718-9434395385,063313-10435385395,74633-9436375410,0844-7-7437365430,2093-234310335514,508223441445334,3531-1442435388,473290444415400,209214-444434315380,46571944444415400,209214-445405380,5376-11451445382,23965-8452435382,33565-8453445382,33565-8453445382,33565-845441542,2776810456395467,0235114634445435,75703-4474455464,226168472455464,226122482475444,635,2287-7482475444,251287-7482475464,22616	42	10	33	5487.4671		-5
43142 3322720 7743241 53532743 143340 $5371,7467$ 18-943439 $5385,743$ 13-1043538 $5385,743$ 3-943637 $5410,0844$ -743736 $5432,093$ -23431033 $5514,5082$ 2344144 $5334,3531$ -144243 $538,4732$ 9044342 $5380,4557$ 1944441 $5400,2092$ 14-44443 $536,5736$ -1-145144 $5360,5376$ -1-145144 $5385,2396$ 5-845243 $5407,7580$ 7-1045639 $547,2756$ 81045639 $547,2952$ 6-646245 $5467,2357$ 3-446641 $5494,2976$ 8047245 $5464,2261$ 2248247 $5464,2281$ 6847245 $5464,2261$ -4447443 $501,7781$ -7-748247 $5464,2528$ 7-748247 $5464,2528$ </td <td>43</td> <td>0</td> <td>43</td> <td>5308.7415</td> <td>6</td> <td>-7</td>	43	0	43	5308.7415	6	-7
43241 3535743 143340 5317.7467 18-943439 5385.0633 13-1043538 5395.7463 3-943637 5410.0844 -7743736 5430.2093 -23431033 5514.5082 2344144 5334.3531 -1144243 5358.4732 9044441 5400.2092 14-444441 5400.2092 14-444441 5400.2092 14-444540 545.9127 -1145045 5306.5376 -1145144 5385.2396 5-845243 5407.7580 7-1045639 5467.0235 1146344 5435.7570 3-447047 5464.2261 -4-447443 501.7781 14-448148 5425.328 7748247 5464.2261 23349049 547.009 -11-149148 5492.5328 5-748247 5464.2261 23-149148 5492.53	43	1	42	5332.2720	7	7
43340 $371,7467$ 18 -9 43439 $385,0633$ 13 -10 43538 $3355,7463$ 3 -9 43637 $5410,0844$ -77 43736 $5430,2093$ -238 44144 $3334,3531$ -11 44243 $3584,8732$ 9044342 $5380,4657$ 1944441 $5380,4657$ 1944441 $5380,4657$ 194444341 $5380,3657$ 114443 $5385,2396$ 5-114504518,36542245144 $5385,2396$ 5-845243 $5407,7580$ 7-1045639 $5467,0235$ 1146146 $5387,2952$ 6-646344 $5435,7570$ 3-447047 $5464,2261$ 2246344 $5501,7781$ 14447245 $5464,2261$ 7-748247 $5464,2261$ 7-748247 $5498,0552$ 53351051 $559,06517$ -714149148 $5498,0552$ 53351051 <td>43</td> <td>2</td> <td>41</td> <td>5353.5743</td> <td></td> <td>-1</td>	43	2	41	5353.5743		-1
434395385.063313 -10 435385395.74633 -9 436375410.0844 -7 437365430.2093 -23 441445334.531 -11 442435358.47329044342580.6657194444415400.209214 -4 44435400.209214 -4 4445405418.654 -2 447385457.9127 -14 450455360.5376 -1 451445385.23965 -8 452435407.75807 -10 456395467.02551 1 461465387.29526 -6 472455412.587122463445435.75703 -4 470475444.251168472455464.261 -4 481485442.532877482475468.99265 -7 482475468.99265 -7 490475468.99265 -7 491485498.55253510515590.65179333	43	3	40	5371.7467	18	-9
435385957.4633 -9 436375410.0844 -7 437365410.0844 -23 4310335514.5082234412435334.3531 -1 442433536.473290443425380.4657194444441500.0202214 -4 4445405418.365422447385457.9127 -14 -14 45045560.5376 -1 -14 451445385.23965 -8 452435467.9127 -16 -16 456395467.0235 -11 -16 451445385.23965 -8 452435407.75807 -10 456395467.0235 -11 -16 461449.2776810 -44 470475414.62816 -8 472455467.0235 -7 -74 463445435.75703 -44 470475414.628168472455464.226124 -74 481485442.53287 -74 490475468.93265 -77 <td>43</td> <td>4</td> <td>39</td> <td>5385.0633</td> <td>13</td> <td>-10</td>	43	4	39	5385.0633	13	-10
436375410.0844 -7 437365430.2093 -23 4310335514.508223441445334.3531 -1 442435358.473290443425380.4657194444415400.209214 -4 445405418.365422447385457.9127 -14 450455360.376 -11 451445385.23965 -8 452435407.75807 -10 456395467.02351 -16 461465387.29526 -6 462455412.587122463445501.778122474435501.778124481485442.232877482475448.926157490495471.0089 -11 491485498.05525353051559.0571233	43	5	38	5395.7463	3	-9
437365430.293 -23 4310335514.50822344144534.3531 -1 44243558.473290443425380.4657194444415400.209214 -4 445405418.365422450455360.5376 -11 451445385.23965 -8 452435407.75807 -10 456395467.02356 -6 461465387.29526 -6 462455412.587122466415439.77703 -4 470475414.628168472455501.778114481485501.778114490495471.0089 -11 491485498.95253351051529.68719	43	6	37	5410.0844		-7
4310335514.508223441445334.3531-1442435358.473290443425380.4657194444415400.209214-4445405418.365422447385457.9127-14450455305.3376-1451445385.29365-8452435407.75807-10454415442.2776810456395467.023511461465387.29526-6463445435.75703-4466415494.4916-4470475414.628168474435501.77811448148542.53287490495471.0089-11491485498.05525353051559.6871233353053559.68712333	43	7	36	5430.2093		-23
441445334,3531 -1 442435384,45290443425380,4657194444415400,209214 -4 445405418,36542244738545,9127 -14 450455360,5376 -1 451445382,23965 -8 452435407,75807 -10 456395467,023511461465387,29526 -6 46344535,75703 -4 470475414,62816 8 474435501,778122481485442,532877490495471,089 -11 491485488,055253530535590,651753323	43	10	33	5514.5082	2	3
44243 $538,4732$ 9044342 $5380,4657$ 194444 $5400,2092$ 14-444540 $5418,3654$ 244738 $5457,9127$ -1445045 $5360,5376$ -145144 $5385,2396$ 5-845243 $5407,7890$ 7-1045639 $5467,0235$ 1146146 $5387,2952$ 6-64639 $5467,0235$ 1146641 $5494,4916$ -447047 $5446,2261$ 2247443 $5501,7781$ 74481 $442,2518$ 71449049 $5471,0089$ 5-749053 $559,6871$ 233353053 $559,66517$ 3333	44	1	44	5334.3531		-1
443 42 5380.4657 19 44 44 441 5400.2092 14 -4 44 5 40 5483.654 2 44 7 38 5457.9127 -14 45 0 45 5360.5376 -1 45 0 45 5385.2396 5 -8 45 1 44 5385.2396 5 -8 45 2 43 5407.7580 7 -100 45 639 5467.0235 -11 46 1 46 5387.2952 6 -6 46 3 441 5435.7570 3 -4 46 3 444 5435.7570 3 -4 47 0 47 5444.6281 6 8 47 2 45 5464.2261 7 48 1 48 5442.5328 7 49 0 49 5471.0089 5 -71 49 0 49 5471.0089 5 -71 49 0 53 5590.6517 23 53 0 53 5590.6517 53 33	44	2	43	5358.4732	9	0
44441 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 2 43 5407.7580 7 -10 45 441 5345.2396 5 -8 45 639 5467.0235 -11 46 46 1 46 5387.2952 6 -6 46 2 45 5412.5871 2 2 46 641 5494.4916 -44 47 0 47 5414.6281 6 8 47 2 45 5464.2261 -44 47 4 43 5501.7781 -14 48 1 48 542.5328 -7 49 0 49 571.0089 -11 49 1 48 5498.0552 5 -7 49 1 48 5498.0552 5 -31 53 0 53 559.06517 9	44	3	42	5380.4657	19	4
445 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 45 639 5467.0235 1 1 46 1 46 5387.2952 6 -6 46 2 45 5412.5871 2 2 46 3 44 5435.7570 3 -4 47 0 47 5414.6281 6 41 47 0 47 5414.6281 6 41 47 1 48 5407.7580 7 -4 47 0 47 5464.2261 -4 41 47 4 43 5501.7781 14 48 47 4 43 5501.7781 -11 14 48 242.5328 7 7 49 0 49 5471.089 -11 49 1 48 5498.0552 5 -7 31 49 1 48 5498.0552 5 33 53 0 53 559.6517 9 33	44	4	41	5400.2092	14	-4
44738 5457.9127 -14 45 0 45 5360.3376 -1 45 1 44 5385.2396 5 -8 45 2 43 5407.7580 7 -10 45 441 5442.2776 8 10 45 639 5467.0235 1 1 46 1 46 5387.2952 6 -6 46 2 45 5412.5871 2 2 46 6 41 5494.4916 -4 47 0 47 5414.6281 6 8 47 2 45 5501.7781 14 48 1 48 5442.5328 7 48 2 47 5468.9926 5 -7 49 0 49 5471.089 -11 49 1 48 5498.0552 5 33 51 053 5590.6517 9	44	5	40	5418.3654		2
450 45 5360.5376 -1 45 1 44 5385.2396 5 -8 45 2 43 5407.7580 7 -10 45 441 542.2776 8 10 45 639 5467.0235 11 46 1 46 5387.2952 6 -66 46 2 45 5412.5871 22 46 3 44 5435.7570 3 -4 46 641 5494.4916 -4 47 0 47 5414.6281 6 8 47 2 45 5464.2261 24 47 443 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 53 559.6871 23	44	7	38	5457.9127		-14
45144 $5385,2396$ 5 -8 45 2 43 $5407,7580$ 7 -10 45 441 $5442,2776$ 8 10 45 639 $5467,0235$ 11 46 146 $5387,2952$ 6 -6 46 245 $5412,5871$ 22 46 344 $5435,7570$ 3 -4 46 641 $5494,4916$ -4 47 047 $5414,6281$ 68 47 245 $5464,2261$ 24 47 43 $5501,7781$ 14 48 1 48 $5442,5328$ 7 48 247 $5468,9926$ 5 -7 49 049 $5471,0089$ -11 49 148 $5498,0552$ 53 51 051 $5520,6871$ 23 53 053 $5590,6517$ 9	45	0	45	5360.5376		-1
452 43 5407.7580 7 -10 45 441 5442.2776 810 45 639 5467.0235 1 46 146 5387.2952 6 -6 46 245 5412.5871 22 46 641 5494.4916 -44 47 047 5414.6281 68 47 245 5464.2261 24 47 443 5501.7781 14 48 148 5442.5328 7 48 247 5468.9926 5 -7 49 049 5471.0089 -111 49 148 5498.0552 53 51 051 5529.6871 23 53 053 559.6517 9	45	1	44	5385.2396	5	-8
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	45	2	43	5407.7580	7	-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 33 51 0 53 559.6871 23	45	4	41	5442.2776	8	10
461 46 5387.2952 6 -6 46 2 45 5412.5871 22 46 3 44 5435.7570 3 -4 46 6 41 5494.4916 -8 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 33 51 0 53 559.6871 23	45	6	39	5467.0235		1
462 45 5412.5871 22 46 3 44 5435.7570 3 -4 46 6 41 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 33 51 0 53 559.6571 23	46	1	46	5387.2952	6	-6
463 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 51 559.6871 23 53 0 53 559.6517 9	46	2	45	5412.5871	2	2
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	46	3	44	5435.7570	3	-4
	46	6	41	5494.4916		-4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	47	0	47	5414.6281	6	8
	47	2	45	5464.2261		24
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	47	4	43	5501.7781		14
482475468.99265-7490495471.0089-11491485498.055253510515529.687123530535590.65179	48	1	48	5442.5328		7
490495471.0089-11491485498.055253510515529.687123530535590.65179	48	2	47	5468.9926	5	-7
49 1 48 5498.0552 5 3 51 0 51 5529.6871 23 53 0 53 5590.6517 9	49	0	49	5471.0089		-11
51 0 51 5529.6871 23 53 0 53 5590.6517 9	49	1	48	5498.0552	5	3
53 0 53 5590.6517 9	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 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:

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

where

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

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

and

$$\begin{split} V^{(4)} &= \frac{1}{24} f_{rrrr} \left(\Delta r_1^3 + \Delta r_2^3 \right) + \frac{1}{6} f_{rrr'} \left(\Delta r_1^3 \Delta r_2 + \Delta r_2^3 \Delta r_1 \right) \\ &+ \frac{1}{4} f_{rrr'r'} \left(\Delta r_1^2 \Delta r_2^2 \right) + \frac{1}{6} f_{rrr\alpha} \left(\Delta r_1^3 + \Delta r_2^3 \right) \Delta \alpha \\ &+ f_{rrr'\alpha} (\Delta r_1 + \Delta r_2) \Delta r_1 \Delta r_2 \Delta \alpha + \frac{1}{2} f_{rr\alpha\alpha} \left(\Delta r_1^2 + \Delta r_2^2 \right) \Delta \alpha^2 \\ &+ \frac{1}{2} f_{rr'\alpha\alpha} \Delta r_1 \Delta r_2 \Delta \alpha^2 + \frac{1}{6} f_{r\alpha\alpha\alpha} (\Delta r_1 + \Delta r_2) \Delta \alpha^3 + \frac{1}{24} f_{\alpha\alpha\alpha\alpha} \Delta \alpha^4. \end{split}$$
(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 ,

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Та	ble	2

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

1 0 1 0 1010000000000000000000000000000000000	J	Ka	Kc	Ε	Δ	δ
1 0 1 316:499 - 4 1 0 316:139 7 -4 2 1 2 316:139 7 -4 2 1 2 316:139 7 -4 2 1 3173:430 3 -3 -3 3 0 2 3173:430 3 -3 3 1 2 3175:450 1 -3 3 0 318:486 -4 -4 4 1 319:5512 -6 -5 5 0 5 317:227 1 -6 5 1 2 318:426 5 -6 5 1 2 318:426 5 -6 5 1 2 318:426 5 -6 5 1 -3 316:33:1 -4 -7 5 1 -3 316:33:1 -4 -7	1			2	3	4
1 0 107/159 7 -4 2 2 1 37/3430 3 -3 3 0 3 1986113 3 -3 3 1 2 17/3430 3 -3 3 1 2 17/350 1 -4 4 1 4 517/350 5 -3 4 2 3 517/350 1 -4 4 3 2 517/350 1 -4 4 3 2 517/350 1 -4 5 0 517/3272 1 -0 5 1 4 317/350 1 -4 6 1 517/2272 1 -0 -5 5 1 4 317/3535 1 -4 6 1 517/2727 -3 -5 -6 6 1 6 517/277 -3 -5 -6 7 0 7 518/2867 -1 -7	1	0	1	5165.4790		4
2 1 2 368304	1	1	0	5167.1559	7	-4
2 1 3173480 3 3 3 1 2 1 3184.113 1 3 3 2 1 3172.223 1 -3 4 1 4 5177.3505 5 -2 4 2 3 5177.3505 5 -2 4 3 2 5179.2505 5 -2 4 4 1 497.3501 3 1 60 5 0 5 5174.227 1 60 6 7 6 6 6 7 7 6 6 7	2	1	2	5168.3104		-9
3 0 3 3168.613 1 -3 3 1 2 1 5171.7480 1 -3 4 1 2 3 5177.780 1 -9 4 1 2 3 5177.780 1 -9 4 1 2 5184.643 1 -9 4 1 317.5780 1 -0 -0 5 1 4 517.5737 -0 -0 5 2 3 5180.938 18 -4 5 3 2 5180.938 1 -0 5 3 2 5180.938 1 -0 5 3 2 5180.937 16 -3 6 5 3 0 -10 -0 6 3 1 -10 -10 -10 6 3 1 -10 -10 -10 6 3 1 -10 -10 -10 7 1 6	2	2	1	5173.3430	3	-5
3 1 2 \$170,4199 3 -2 3 0 \$152,865 5 -2 4 1 4 \$172,585 5 -2 4 2 3 \$172,585 5 -2 4 3 2 \$185,5994 3 1 -2 5 1 4 5172,528 1 -6 5 2 3 \$185,5994 3 1 -2 5 1 4 1517,528 1 -6 -6 5 2 3 \$189,1426 5 0 -7 -3 6 1 5 4 -3 -3 -4 -3 6 3 4 \$192,9149 3 -0 -0 6 4 3 \$204,629 -1 -1 -3 7 1 6 \$12,721,731 -1 -1 -3 7 1 6 \$12,721,731 -1 -1 -3 7 3	3	0	3	5168.6113	1	-3
3 2 1 91/2.229 5 3 3 4 1 61/2.258 5 -12 4 2 3 51/7.7380 1 9 4 3 2 5185.0594 3 1 5 0 5 5172.227 1 0 5 1 4 5172.227 1 0 5 2 2 5181.422 4 -4 5 3 2 5181.422 4 -4 5 3 0 5181.422 4 -3 6 2 5181.421 4 -3 3 6 2 5181.421 4 -3 3 6 2 5181.421 4 -3 3 7 0 7 16 3 3 3 7 1 6 5181.421 4 -3 7 1 6	3	1	2	5170.4199	3	-2
1 1 1972265 1 - 4 2 3972265 1 - 4 3 2 3155994 3 - 5 0 5 3155994 3 - - 5 0 5 31742272 1 - 0 5 1 4 516923 - - 5 5 3 2 3183446 5 0 0 5 3 2 3183446 - 8 - - 5 6 1 3 304639 - - 0 - - - 0 - - 0 - - 0 - - 0 - - 0 - - 0 - 0 - 0 - 0 - 0 0 0 0 0 0 0 0 0 0	3	2	1	5175.2329	15	3
1 2 3 5177.380 1 - - 4 3 2 5187.5312 - - 6 5 0 5 5172.5312 1 - 6 5 1 4 5172.5312 1 - 6 5 1 4 5172.5312 1 - 6 5 1 4 5172.532 1 - 1 5 2 2 5180.533 - - 5 6 1 6 51718.1412 4 8 6 6 2 5 5184.5427 18 8 8 0 <td>3</td> <td>3</td> <td>0</td> <td>5173 5265</td> <td>5</td> <td>4</td>	3	3	0	5173 5265	5	4
4 6 2 515 (5994) 1 1 5 0 5 31742272 1 1 5 1 4 31630136 18 4 5 2 3 31800136 18 4 5 1 4 3163033 1 1 -2 5 2 3 31800136 18 4 3 </td <td>4</td> <td>1</td> <td>3</td> <td>5172.3203</td> <td>11</td> <td>-2</td>	4	1	3	5172.3203	11	-2
4 4 1 3107,512 6 5 1 4 3176,283 11 -2 5 2 3 3100,138 18 -4 5 3 2 3161,142 5 -0 5 3 2 3161,142 4 -8 6 1 6 5151,314 4 -8 6 2 5 5146,357 16 -8 6 3 4 5152,919 3 -0 6 5 2 5131,9107 4 -7 7 6 1 2318,9107 10 -10 6 5 2 5131,9107 4 -7 7 1 6 518,91697 10 -13 7 3 4 518,71219 3 -5 7 6 1 3223,7065 8 5 7 6 1 324,7239 -10 -4 7 6 1 324,7239 3 -5 7 7 7 6 324,724,739 3 -5 7 7 6 324,723,734 10 -10<	4	3	2	5185.9994	3	1
5 0 5 114272 1 0 5 2 3 5180338 18 -2 5 3 2 5181426 5 0 5 4 1 5200641 7 -3 6 1 6191422 -4 8 6 2 5191423 -4 -8 6 3 4 5124239 -16 8 6 3 4 5124439 -11 -17 6 6 1 5237429 1 -13 7 0 7 5124783 1 -11 7 1 6 5184797 1 -13 7 1 3 52324839 10 -44 7 7 0 5232189 10 -44 7 7 0 5232184 1 -70 7 7 0 5232184 1 -71 7 7 0 5232184 1 -71 <t< td=""><td>4</td><td>4</td><td>-</td><td>5197.5512</td><td>-</td><td>-6</td></t<>	4	4	-	5197.5512	-	-6
5 1 4 516283 11 -2 5 2 3 5169138 18 -4 5 3 2 5191428 5 0 5 4 1 520413 7 -3 6 1 6 51791412 -4 -8 6 3 4 5182149 3 -0 6 5 2 52132070 -4 7 6 6 7 52132070 -4 7 -3 7 0 7 5191077 0 -3 -3 7 1 0 7 3 -4 51917219 3 -5 7 3 4 51973219 3 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -6 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5 -5	5	0	5	5174.2272	1	0
5 2 3 51809138 18 4 4 5 4 1 52003041 7 3 6 1 6 5184337 16 8 6 2 5 5184337 16 8 6 3 4 5124337 16 8 6 4 3 5204439 - -10 6 6 1 52374293 2 2 7 0 7 5184377 13 -11 7 1 6 5184377 13 -13 7 1 6 5184347 10 -14 7 1 6 5184347 10 -15 7 7 0 5242329 18 -16 -16 7 7 0 5242329 18 -16 -16 7 7 0 5242329 10 -4 -16 8 1 5242429 10 -16 -4 -16	5	1	4	5176.2883	11	-2
5 3 2 5189.1426 5 0 5 5 0 5215.333 -5 0 6 1 6 519.1412 16 -8 6 3 4 5192.1443 3 -00 6 3 4 5192.1443 3 -00 6 6 1 5227.423 -2 -3 7 0 7 5182.2683 1 -11 7 1 6 5189.1607 10 -13 7 2 5 5189.1607 10 -13 7 3 4 5129.3703 8 1 -16 7 4 3 203.8967 10 -16 -16 7 5 -4 5241.3789 10 -17 -6 7 6 1 2541.3789 10 -16 -13 -22 8 1 8 519.32737 13 -72 -6 -23 -232.324 13 -24 -24	5	2	3	5180.9138	18	4
5 4 1 2200341 7 3 6 1 6 5179,14171 16	5	3	2	5189.1426	5	0
3 3 0 2419333	5	4	1	5200.6941	7	3
0 1	5	5	0	5215.5353	Λ	-5
6 3 4 51221440 3 0 0 6 5 2 52193070 4 7 7 0 7 518237429 2 -7 7 1 6 51891707 10 -11 7 2 5 51891607 10 -13 7 3 4 51973219 3 55 7 4 3 52085675 8 55 7 6 1 5241239 -10 -4 7 7 0 5243205 8 5 7 6 1 5241239 -1 -1 8 2 7 514027 5 -1 8 1 8 5184749 2 -1 8 2 7 524329748 13 -7 8 1 524239478 13 -7 2 8 5	6	1	5	5184 6357	4	-8 8
6 4 3 504/4439 - - 0 6 6 1 5219 3070 4 7 7 0 7 5182 285 1 - 7 1 6 5184 7497 2 - 7 3 4 5197 3219 3 -5 7 3 4 5197 3219 3 -5 7 5 2 523 7065 8 -5 7 6 1 5241 828 10 -4 8 1 8 5183 1697 13 -3 8 1 8 5184 1694 -6 -6 8 2 7 5184 0279 5 -4 8 4 5 5213 8957 13 -7 8 6 3 5266 2499 -2 -2 8 6 3 5202 5521 12 15 9 <td< td=""><td>6</td><td>2</td><td>4</td><td>5192 9149</td><td>3</td><td>0</td></td<>	6	2	4	5192 9149	3	0
6 5 2 5213.3070 4	6	4	3	5204.4639	5	-10
6 6 1 537,4293 2 2 7 0 7 5182,858 1 -1 7 2 5 5189,1607 10 -13 7 3 4 5197,3219 3 3 5 7 6 1 5243,828 10 -4 7 6 1 5243,828 10 -4 7 7 0 5263,218 -3 -6 8 1 8 5188,164 -6 -6 8 2 7 5194,0279 5 -4 8 3 6 5202,354 13 -7 8 3 6 5202,354 13 -7 8 7 2 5268,249 -2 -2 8 7 2 5268,203 12 -1 8 7 2 5268,204 10 -5 9 1 5202,357 13 -7 -5 9 1 5202,9057	6	5	2	5219.3070	4	7
7 0 7 5182,2858 1 -1 7 2 5 5189,1607 10 -13 7 3 4 5193,219 3 55 7 4 3 5208,8647 10 -10 7 5 2 5222,3765 8 55 7 6 1 5241,8289 10 4 8 1 8 5188,1454 -6 6 8 2 7 51940,0279 5 -4 8 3 6 5202,3524 13 -7 8 5 4 5228,3748 13 -7 8 6 3 5246,8569 5 -1 8 7 2 5268,249 -2 2 9 0 9 5192,7374 5 -5 9 1 8 5192,7375 4 -5 9 3 6 5208,0171 10 -11 9 3 6 5208,01	6	6	1	5237.4293		2
7 1 6 184,7497 2 -3 7 2 5 181,6107 10 -13 7 3 4 1517,3219 3 5 7 5 2 5223,765 8 5 7 6 1 5241,8289 10 44 7 0 563,2218 -6 -6 8 1 8 5188,1654 -6 -6 8 2 7 5194,0279 5 -4 8 3 6 5202,3524 13 -7 8 4 5 5213,8957 13 -7 8 6 3 5246,8249 -2 15 9 0 9 5192,757 4 -5 5 9 1 8 5195,757 4 -5 5 9 3 6 520,557 19 -10 -5 9 3 6 520,557 19 -10 -5 9	7	0	7	5182.2858	1	-1
7 2 5 5189.1607 10 -13 7 3 4 5193.219 3 5 7 4 3 5208.8647 10 -10 7 5 2 5227.7065 8 5 7 6 1 5241.8289 10 -4 8 1 8 5188.1454 -6 -6 8 2 7 5194.0279 5 -4 8 3 6 5202.3524 13 -7 8 5 4 5228.7348 13 -7 8 6 3 5248.8569 -1 -1 8 7 2 5268.2499 -2 -2 9 0 9 5192.7374 5 -5 9 1 8 5196.7577 4 -5 9 2 7 5200.0171 10 -3 9 6 3 5228.549 23 -9 9 7 2 52719.	7	1	6	5184.7497	2	-3
7 3 4 5197.3219 3 5 7 6 2 5223.7065 8 5 7 6 1 5248.8289 10 4 7 7 0 5263.2218 3 3 5 8 1 8 5184.0279 5 -4 8 2 7 5194.0279 5 -4 8 3 6 5203.324 13 -7 8 5 4 5225.748 13 -7 8 6 3 5246.8569 5 -1 8 7 2 528.2499 -2 15 9 1 8 5195.757 4 -5 9 2 7 5208.0171 10 -5 9 3 6 5213.5552 12 11 9 5 4 5234.3333 15 -4 9 6 3 3252.5157 19 10 9 7 2 <	7	2	5	5189.1607	10	-13
7 4 3 5208.864/7 10 -10 7 6 1 5241.8289 10 4 7 7 0 5563.218 3 8 1 8 5188.1454 -6 8 2 7 51940279 5 -4 8 3 6 5203.3524 13 -7 8 5 4 5228.7348 13 -2 8 6 3 5268.2499 -2 15 9 0 9 5192.7374 5 -4 8 6 3 5268.2499 -2 15 9 0 9 5192.7374 10 -5 9 1 8 5195.7857 4 -5 9 2 7 5200.0171 10 -10 9 6 3 5225.25757 19 -10 9 7 2 5279.5982 12 -11 9 6 3 5225.25157 19	7	3	4	5197.3219	3	5
1 3 2 3223,003 8 3 3 7 6 1 5363,218 3 8 1 8 5184,154 -6 8 2 7 5194,0279 5 -4 8 3 6 5023,524 13 -7 8 4 5 5213,897 13 -7 8 5 4 5222,738 13 -7 8 6 3 5246,8569 5 -1 8 7 2 2628,2499 -2 15 9 0 9 519,7374 5 -5 9 1 8 5195,7857 4 -5 9 3 6 5208,0117 10 -11 9 4 5 5213,933 15 -4 9 6 3 5225,517 19 10 9 6 3 5225,517 19 10 9 6 5208,024 2 4	7	4	3	5208.8647	10	-10
1 0 1 0 1 0 1 0 1 7 7 0 56211 6 8 1 8 5188.1454 6 8 2 7 5194.0229 5 4 8 3 6 5203.3524 13 7 8 4 5 5181.8957 13 7 8 6 3 5268.3499 7 7 8 6 3 5268.349 7 7 9 0 9 5192.3734 5 7 9 0 9 5192.7374 5 5 9 0 9 5192.7374 5 5 9 1 8 5195.757 4 5 9 1 8 5195.757 4 5 9 2 7 5200.0171 10 6 6 9 6 3 5225.5157 19 10 6	7	5	2	52/1 9290	8	5
n n	7	7	0	5263 2218	10	4
8 2 7 51940279 5 -4 8 3 6 52023524 13 3 8 4 5 52133957 13 -7 8 5 4 5228.7348 13 -7 8 5 4 5228.7348 13 -7 8 7 2 5268.2499 -7 2 8 7 2 5268.2499 -7 2 9 0 9 5192.7374 5 -5 9 0 9 5192.7374 5 -5 9 2 7 5200.0171 10 -5 9 3 6 5219.5582 12 11 9 5 4 5219.5582 12 10 9 7 2 5273.9081 6 33 9 9 0 5326.4549 8 10 10 1	8	1	8	5188.1454		-6
8 3 6 520,3524 13 -7 8 5 4 5223,748 13 -7 8 6 3 5246,748 13 -2 8 6 3 5246,748 13 -2 8 7 2 528,2499 -2 -2 9 0 9 5192,7374 5 -5 9 1 8 5220,0171 10 -5 9 2 7 5200,0171 10 -5 9 3 6 5228,537 4 -5 9 3 6 5228,537 19 -10 9 6 3 5225,5157 19 10 9 7 2 5228,5600 23 39 9 9 0 5326,4549 8 10 10 1 10 5195,2544 4 -5 10 2 9 5225,8505 1 1 1 10 3 8	8	2	7	5194.0279	5	-4
8 4 5 5213897 13 7 8 5 4 52287348 13 2 8 6 3 52685499 5 -1 8 7 2 52882499 -2 -2 8 8 1 5292.3025 12 15 9 0 9 5192.7374 5 -5 9 2 7 5200.0171 10 -5 9 3 6 5219.5382 12 -11 9 4 5 5219.5382 12 -11 9 5 4 5224.3933 15 -4 9 6 3 5225.43933 15 -4 9 7 2 5273.9081 6 3 9 9 9 0 5326.4349 8 10 3 9 9 9 0 5326.4349 8 10 1 1 1 10 1 5205.052 7 -4	8	3	6	5202.3524	13	3
8 5 4 5228,7348 1.13 2 8 6 3 5226,7349 -2 8 7 2 5268,2499 -2 8 8 1 5292,9025 12 15 9 0 9 5192,7374 5 -5 9 2 7 5200,0171 10 -5 9 3 6 5208,314 9 -11 9 4 5 5219,5582 12 101 9 6 3 5223,5157 19 101 9 6 3 5225,5157 19 101 9 7 2 5232,64549 8 100 10 1 10 5199,5524 4 -5 10 2 9 5225,8506 1 -4 10 3 8 5214,3143 2 -4 10 1 5328,8024	8	4	5	5213.8957	13	-7
8 6 3 5268.2499 1 8 7 2 5268.2499 2 9 0 9 5192.7374 5 -5 9 1 8 5195.7857 4 -5 9 2 7 5200.0171 10 -5 9 3 6 5209.5822 12 11 9 4 5 5219.5582 12 11 9 6 3 5225.5157 19 10 9 7 2 5273.9081 6 3 39 9 9 0 538.5600 23 99 9 9 9 10 538.5600 23 99 30 110 10 10 10	8	5	4	5228.7348	13	-2
8 7 2 5282,9025 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 5208,0514 9 -11 9 4 5 5219,5582 12 11 9 5 4 523,3157 19 100 9 7 2 527,3157 19 100 9 7 2 529,8560 23 9 9 9 0 5326,4549 8 100 10 1 10 59,8560 23 9 9 9 0 5326,4549 8 100 10 1 10 59,8560 1 11 10 3 8 524,80821 6 -4 10 1 524,80821 6 -4 -4 10 1 532,7442	8	6	3	5246.8569	5	-1
8 8 1 329025 12 15 9 1 8 5192,7374 5 5 9 2 7 5200,0171 10 5 9 2 7 5200,0171 10 5 9 3 6 5208,0314 9 -11 9 4 5 52139582 12 11 9 6 3 52234,3933 15 -4 9 6 3 52252,5157 19 10 9 7 2 5273,9081 6 33 9 8 1 5298,5600 23 99 9 9 0 5298,500 23 99 9 9 0 5298,500 23 99 9 9 0 524,3143 2 -4 10 2 9 5214,3143 2 -4 10 7	8	7	2	5268.2499	10	-2
9 0 9 1 8 5195,7877 4 5 9 2 7 5200,0171 10 5 9 2 7 5200,0171 10 5 9 3 6 5208,0314 9 11 9 4 5 5219,582 12 1 9 6 3 5222,5157 19 10 9 7 2 5273,9081 6 3 9 9 0 5326,8549 8 10 10 1 10 5195,524 4 -5 10 2 9 5205,9052 7 -4 10 3 8 5214,3143 2 -4 10 4 7 5228,8024 12 4 10 5 6 5249,8024 12 4 10 7 4 5208,8024 12 4 <t< td=""><td>8</td><td>8</td><td>1</td><td>5292.9025</td><td>12</td><td>15</td></t<>	8	8	1	5292.9025	12	15
9 2 7 5200.0171 10 5 9 3 6 5200.0171 10 5 9 3 6 5200.0171 10 1 9 4 5 5210.5582 12 1 9 5 4 5234.3933 15 4 9 6 3 5225.157 19 10 9 7 2 5273.9081 6 33 9 8 1 5264.549 8 10 10 1 10 5199.524 4 5 10 2 9 5205.9052 7 4 10 3 8 5214.3143 2 4 10 4 7 5228.806 1 1 1 10 6 5240.6821 6 4 1 1 1 1 1 1 1 1 1 1	9	1	8	5192.7574	3	-5
9 3 6 5008.0314 9 -11 9 4 5 5219.5582 12 11 9 6 3 5252.5157 19 100 9 7 2 5273.9081 6 33 9 8 1 5298.5600 23 99 9 9 0 5326.4549 8 100 10 1 10 5199.5254 4 -54 10 2 9 5205.9052 7 -44 10 3 8 5214.3143 2 -44 10 4 7 5225.80024 12 44 10 5 6 5240.6821 6 -44 10 7 4 528.8024 12 44 10 7 4 528.80154 5 7 10 8 3 5304.8474 8 111 10	9	2	7	5200 0171	10	-5
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 33 9 8 1 5298.5600 23 9 9 9 0 5326.4549 8 100 10 1 10 5195.5254 4 -5 10 2 9 5205.5052 7 -4 10 3 8 5214.3143 2 -4 10 4 7 525.8066 1 1 1 10 5 6 5240.6821 6 -4 10 7 4 520.8024 12 7 7 10 8 3 5304.8474 8 11 1 1 -30 11 0 11 5205.5748 2 2 2 2 1 1 -22 2 2 <	9	- 3	6	5208.0314	9	-11
9 5 4 52343933 15 4 9 6 3 52525157 19 10 9 7 2 5273.9081 6 33 9 8 1 5285.600 23 99 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 11 10 5 6 5240.6821 6 4 10 7 4 5280.1954 5 7 10 8 3 5304.8474 8 11 10 9 2 5332.7442 17 233 10 10 1 5303.8617 2 -30 11 0 11 5205.5748 2 2 11 1 1	9	4	5	5219.5582	12	1
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 8 100 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 5248,024 12 4 10 7 4 528,8024 12 4 10 7 4 528,8024 12 4 10 9 2 5332,7442 17 23 11 0 11 5208,5304 4 11 12 9 5213,5147 1 -2 2 11 10 10 5208,5748 2 2 2 11 10 <	9	5	4	5234.3933	15	-4
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 11 10 5 6 5240,6821 6 -4 10 7 4 528,8024 12 4 10 7 4 528,1954 5 7 10 9 2 5332,7442 17 23 10 10 1 5304,8474 8 11 11 2 9 5213,5147 1 -2 11 10 10 5205,5748 2 22 11 1 10 5221,2914 5 -5 11 1 6 <td< td=""><td>9</td><td>6</td><td>3</td><td>5252.5157</td><td>19</td><td>10</td></td<>	9	6	3	5252.5157	19	10
9 8 1 528,5600 23 9 9 9 0 5326,549 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 5 528,8024 12 4 10 7 4 528,1054 5 7 10 8 3 5304,8474 8 11 10 9 2 5323,7442 17 233 11 0 11 5265,5348 2 22 2 11 10 10 5205,5348 2 2 2 11 1 10 5205,5348 2 2 2 <td>9</td> <td>7</td> <td>2</td> <td>5273.9081</td> <td>6</td> <td>3</td>	9	7	2	5273.9081	6	3
9 9 0 326,4349 8 10 10 1 10 5195,5254 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 4 528,1954 5 7 10 8 3 5304,8474 8 11 10 9 2 5332,7442 17 23 10 10 1 563,8617 -30 -30 11 0 11 5205,3748 2 2 2 11 10 10 5203,3704 4 1 1 11 2 9 5213,5147 1 -22	9	8	1	5298.5600	23	9
1010193,2344310295205,90527-410385214,31432-410475225,85061110565240,68216-410655258,802412410745280,19545710835304,847481110925332,74421723101015363,8617-30110115205,534822111105203,77631-211385221,29145-511475232,776318111565247,60246411745287,11153611835311,76259-311925339,6607127111015370,7800-30(continued on next page	9	9	10	5320.4549 5100.5254	8	10
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	10	1	9	5205 9052	4 7	-5
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 -30 11 0 11 5205,5348 2 2 2 11 1 10 5209,3704 4 1 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 6 111 7 4 5287,115 3 -3	10	3	8	5213.3052	2	_4 _4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	4	7	5225.8506	1	1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	5	6	5240.6821	6	-4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	6	5	5258.8024	12	4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	7	4	5280.1954	5	7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	8	3	5304.8474	8	11
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10	9	2	5332.7442	17	23
11 0 11 5205.548 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 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 -30	10	10	1	5363.8617	2	-30
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	0	10	5205.5348 5209.3704	2	2
11 3 8 521,2914 5 -5 11 4 7 5232,7763 18 1 11 5 6 5247,6024 6 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 -30 (continued on next page	11	2	9	5203.3704	4	_2
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 -30 (continued on next page	11	3	8	5221.2914	5	-5
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 -30	11	4	7	5232.7763	18	1
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 -30 (continued on next page	11	5	6	5247.6024		6
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 -30	11	6	5	5265.7186	19	-4
11 8 3 5311.7625 9 -3 11 9 2 5339.6607 12 17 11 10 1 5370.7800 -30 -30 (continued on next page	11	7	4	5287.1115	3	6
11 9 2 5339.6607 12 17 11 10 1 5370.7800 -30 -30 (continued on next page	11	8	3	5311.7625	9	-3
11 10 1 5370.7800 -30 (continued on next page	11	9	2	5339.6607	12	17
(continued on next page	11	10	I	5370.7800		-30
						(continued on next page

^a See footnote to Table 1.

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Table 2 (continued)

J	Ka	Kc	Ε	Δ	δ
1			2	3	4
11	11	0	5405.1179	2	14
12	1	12	5213.2673	4	-4
12	2	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	8	5	5319 3091	2	2
12	9	4	5347.2064	12	10
12	10	3	5378.3277	12	-28
12	12	1	5450.1907	2	0
13	0	13	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 7	5285.5540	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	6	-28
13	12	1	5458.3729	-	18
13	13	0	5499.0687		12
14	1	14	5229.3586	2	0
14 14	2	13	5237.0525	13 9	7
14	4	11	5257.3464	4	0
14	5	10	5272.1477	5	3
14	6	9	5290.2519	11	2
14 14	8	8	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 14	12	3	5407.1808	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	5255.5595	6	-5
15	4	11	5266.8204	4	10
15	5	10	5281.5942	3	1
15	6	9	5299.6918	11	7
15	8	8 7	5345.7243	o 2	-5
15	9	6	5373.6231	15	20
15	10	5	5404.7463	16	-29
15 15	11	4	5439.0889	19	0
15	13	2	5517.3210	18	-3
15	14	1	5561.1675		-24
15	15	0	5608.1404	,	-15
16 16	1	16 15	5247.7875	4	5
16	3	13	5265.3608	12	1
16	4	13	5276.8994		4
16	5	12	5291.6726	2	-7
16 16	6	11	5309.7619	3	-l _1
16	8	9	5355.7877	16	-6
16	9	8	5383.6872	7	16
16	10	7	5414.8112	18	-32
16	11	5	5449.1559 5486 6892	4 7	4
16	13	4	5527.3933	8	8
16	14	3	5571.2437		-4
16	15	2	5618.2186	3	-7
16	16	1 17	5668.2902	1	-28
17	1	16	5264.9924	1	-1
17	2	15	5269.9220		-7

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Table 2 (continued)

J	Ka	Kc	Ε	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	/	10	5341.8387	3	4
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	10	-6
17	13	4	5538.0950	10	17
17	14	2	5628.9267		-17
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	5	13	5313.7350	6	-2
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	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	5279 7032	3	-4
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	5343 7686	Z	-1
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	12	8	5520.6730	12	-13
19	13	6	5561.3838	3	1
19	14	5	5605.2452	4	6
19	15	4	5652.2313	10	8
19	16	3 20	5702.3140	19	-21
20	2	19	5301.9746	1	11
20	3	18	5311.9626		-2
20	4	17	5323.6345	1	0
20	5	16	5338.3364	1	-1
20	7	13	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	10	7
20	16	5	5714.9166	10	4 _4
21	0	21	5303.9762	2	1
21	1	20	5313.9386	5	-4
21	2	19	5320.5361		0
21 21	3	18 17	5326.8366	1	-5
21	5	16	5351.6024	2	-5
21	6	15	5369.6063	6	4
21	7	14	5390.9437	1	3
21	8	13	5415.5696	10	-5
21	9	12	5443.4596 5508 93 <i>4</i> 1	18	8
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
				,	

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Table 2 (continued)

J	Ka	Kc	Е	Δ	δ
1			2	3	4
21	16	5	5728.1506		28
22	1	22	5317.0143 5328 3901	4	-3 1
22	3	20	5338.9952	2	0
22	4	19	5350.8200	3	3
22	5	18 17	5365.4845 5383.4756	5	-2
22	7	16	5404.8005	1	-1 2
22	8	15	5429.4185	15	-11
22	9	14	5457.3062	21	15
22	10	13	5522.7781	11	-32
22	12	11	5560.3233	2	9
22	13	10	5601.0424	1	8
22	0	23	5330,5483	0	2
23	1	22	5341.8427	3	3
23	2	21	5349.6059	1	-3
23	3	20 19	5365.7377	11	-8
23	5	18	5380.0410	5	4
23	6	17	5397.9820	6	-1
23	7	16	5419.2904 5443 9027	5	2
23	9	13	5471.7829	14	18
23	10	13	5502.9037	22	-28
23	11	12	5537.2532	5	1
23	12	10	5615 5213	5	5 10
24	1	24	5344.7205	3	3
24	2	23	5357.1640	4	-3
24	3	22	5368.4896 5380 5462	2	1
24	5	20	5395.1844	0	1
24	6	19	5413.1231	12	10
24	7	18	5434.4134	4	0
24 24	8 9	17	5459.0154 5486 8908	4 13	12
24	10	15	5518.0094	20	-25
24	11	14	5552.3588	6	7
24	12	13 12	5589.9052	18	4
24	14	11	5674.5076	10	18
25	0	25	5359.4219	2	1
25	1	24	5372.0117	5	-3
25	2	23	5387.8117	4	-7
25	4	21	5397.0386	14	-9
25	5	20	5411.0481	5	-7
25 25	6 7	19	5428.9020 5450 1713	1	-3
25	8	17	5474.7607	5	10
25	9	16	5502.6297		13
25	10	15	5533.7452	21	-27
25	13	14	5646.3683	20	14
25	14	11	5690.2488	12	16
26	1	26	5374.7350	6	-3
26	2	25	5388.2825 5400.4237	2	2
26	4	23	5412.8038	2	0
26	5	22	5427.4395	2	0
26 26	6 7	21	5445.3138 5466 5622		-2
26	8	19	5491.1381		3
26	9	18	5519.0006	11	16
26 26	10	17	5550.1110	26	-37
26	12	15	5622.0057		-2 -12
26	14	13	5706.6203		21
27	0	27	5390.5990	3	4
27	1	26	5404.4491 5414 9674		-4
27	3	23	5422.2749	1	-5
27	4	23	5431.0384	10	5

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Table 2 (continued)

J	Ka	Kc	Ε	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 11	19	5601 4548	3	8
27	12	15	5639.0025	3	-4
27	13	14	5679.7335	6	8
28	1	28	5407.0583	2	1
28	3	26	5434.7745	3	-2
28	5	23	5462.2521	3	
28	6	23	5480.0569		4
28	7	22	5501.2499	8	-2
28	8	21	5525.7938	F	7
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	26	16
29	0	29	5424.0788	30	-3 -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 5498 4021	2	-2
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	11	-33
29	11	18	5674.8866	11	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 5499.6233	2	-1
30	6	25	5517.3551	3	3
30	7	24	5538.4827	13	12
30	8	23	5562.9838	10	9
30 30	9	22	5590.8019	10	13 _28
30	11	20	5656.2252	5	-1
31	0	31	5459.8645	15	9
31	1	30	5476.1562	7	7
31 31	2	29	5489.5765	5	-3 2
31	4	20	5507.2168	11	2
31	5	26	5519.6896		-2
31	6	25	5536.9969	2	-8
31 31	/	24	5558.0540	2	0
31	9	22	5610.3333	1	13
31	10	21	5641.4128	20	-22
31	11	20	5675.7438	6	2
32	1	32	5478.6218	12	-3
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	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 33	0	33	5497.9520 55154375	10	
33	2	31	5530.2601	13	-4
33	3	30	5540.9157	7	-4
33	4	29	5549.3901	2	2
33 33	5	28	5561.2032 5578 1734	2	-4 _1
	U U	21	5570.1754	2	-1

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Table 2 (continued)

J	Ka	Kc	Е	Δ	δ
1			2	3	4
33	7	26	5599.1116	_	6
33	8	25 24	5623.5265 5651 2957	3	1
33	11	24	5716.6740	5	9
34	1	34	5517.8608		-3
34 34	2	33	5535.9842 5552 1174		-11
34	4	31	5566.8485	3	-2
34	5	30	5582.0206		2
34 34	6	29	5599.6354	10	-13
34	8	28	5644.9776	9	-4
34	9	26	5672.7263		12
34	10	25	5703.7717	20	-29
35	1	34	5557.0139	23	-20
35	2	33	5573.1853		-8
35	3	32	5585.3252	14	11
35	4 5	30	5605.4254	4 7	/ _4
35	6	29	5621.9450		3
35	7	28	5642.7244	5	-9
35	8 9	27	5694.7917	12	-28 17
36	1	36	5559.4043	3	6
36	2	35	5578.6889	4	3
36	3 4	34 33	5595.9337 5611.5073	3	0 -2
36	5	32	5627.0282	25	11
36	7	30	5665.4813	8	11
36 36	8 9	29 28	5689.7907 5717 4899	2	/ 9
36	10	27	5748.5055	22	-34
37	0	37	5581.0376	10	-5
37	1	36 34	5600.8830	6	-2
37	4	33	5641.7220	20	7
37	5	32	5652.3867	8	-12
37 37	6	31	5668.3322	6	3
37	8	29	5713.1543	4	20
37	9	28	5740.8229	14	5
37	10	27	5771.8221		-28
38	2	37	5623.6967	6	7
38	3	36	5642.0763		-12
38	4	35	5658.5776	10	-2
38	6	33	5692.1826	8	4
38	7	32	5712.9294		-7
38	8	31	5737.1497	4	-2
39	0	39	5626.0351	17	5
39	1	38	5647.0502		-5
39 20	2	37	5665.7931	7	-2
39 39	3 4	36	5681.0386	6	
39	5	34	5702.1052	12	-12
39	6	33	5717.3611	6	-3
39 39	/ 8	32 31	5761 7881	12	-5 -7
39	10	29	5820.3538	.=	-23
40	1	40	5649.3989		27
40 40	2	39 38	5671.0061 5690 5392	4	6
40	4	37	5708.0364	1	1
40	5	36	5724.5771		4
40 40	6	35	5742.3032	7	13
40	8	33	5787.0627	25	12
41	0	41	5673.3293	23	-33
41	1	40	5695.5172 5715 4046	9	12
41	2 3	38	5732.2586	12	4 0
41	4	37	5744.2833	13	-18

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Table 2 (continued)

J	Ka	Kc	Ε	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 SO₂ molecule, the "experimental" dissociation energy (122 kcal/ mol \approx 42700 cm⁻¹) was obtained from Ref. [44]. The value *a* = 2.471 Å⁻¹ (see below) correctly corresponds to this value of the dissociation energy.



Fig. 4. Small portion of the recorded high resolution spectrum of the SO₂ molecule in the region of the $v_1 + 3v_3$ absorption band: (I) is the experimentally recorded spectrum; (II) is the simulated spectrum (one dipole moment parameter was used for estimation of relative intensities).

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

Parameter	(301)		(103)		
	Pred.	Fit.	Pred.	Fit.	
1	2	3	4	5	
E/v	4751.900 ^c	4751.7169(14)	5164.643 ^c	5164.8508(18))	
Α	2.0099	2.008999(315)	1.9663	1.966545(364)	
В	0.3380	0.3380517(381)	0.3390	0.339021(597)	
С	0.2853	0.2881267(268)	0.2878	0.2887454(365)	
$\Delta_{\!K} imes 10^4$	0.8875	0.8872(374)	0.8353	0.8381(599)	
$\Delta_{I\!K} imes 10^5$	-0.3663	-0.3798(254)	-0.4272	-0.4350(285)	
$\Delta_I imes 10^6$	0.220549 ^b	0.22123(920)	0.220549 ^b	0.2275(164)	
$\delta_K imes 10^6$	1.0198	1.0198	0.7532	0.7532	
$\delta_I imes 10^7$	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)	
$H_{KJ} imes 10^9$	-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 $J \le 4$ of the states (100), (001), and (010) from Refs. [20] and [29], and (b) high accuracy values of the centers of the bands, v_1 , v_3 , $2v_1$,

 $v_1 + v_3$, $2v_3$, $3v_1$, $2v_1 + v_3$, $v_1 + 2v_3$, $3v_3$, v_2 , $v_1 + v_2$, $v_2 + v_3$, $2v_1 + v_2$, $v_1 + v_2 + v_3$, $2v_2$, $2v_2 + v_3$, $v_1 + 3v_2$, and $v_1 + 3v_2 + v_3$ 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 SO_2 molecule (in cm⁻¹).^a

Parameter	(301)	(103)	(000) ^b
1	2	3	4
Е	4751,7169(14)	5164.8508(18)	
Α	2.008999(315)	1.966545(364)	2.02735433
В	0.3380517(381)	0.339021(597)	0.3441739084
С	0.2881267(268)	0.2887454(365)	0.293526529
$\Delta_{\!K} imes 10^4$	0.8872(374)	0.8381(599)	0.8640369
$\Delta_{lK} imes 10^5$	-0.3798(254)	-0.4350(285)	-0.3901187
$\Delta_I \times 10^6$	0.22123(920)	0.2275(164)	0.220549
$\delta_K \times 10^6$	1.0198 ^c	0.7532 ^c	0.846284
$\delta_I imes 10^7$	0.5711(301)	0.5883(648)	0.5674232
$\dot{H}_K \times 10^7$	0.1293(112)	0.1242(180)	0.12375
$H_{KI} imes 10^9$	-0.8076 ^c	-0.5929 ^c	-0.64936
$H_{lK} \times 10^{11}$	0.116 ^d	0.116 ^d	0.116
$H_{l} \times 10^{12}$	0.37589 ^d	0.37589 ^d	0.37589
$h_K imes 10^9$	0.5670 ^d	0.5670 ^d	0.5670
$h_{lK} \times 10^{12}$	-0.23^{d}	-0.23^{d}	-0.23
$h_{l} \times 10^{12}$	0.1829 ^d	0.1829 ^d	0.1829
$L_K imes 10^{11}$	-0.265^{d}	-0.265^{d}	-0.265
$L_{KKJ} imes 10^{12}$	$0.180^{\rm d}$	0.180^{d}	0.180
$L_{JK} \times 10^{13}$	-0.109^{d}	-0.109^{d}	-0.109
$L_{IJK} imes 10^{17}$	-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
$l_{KJ} imes 10^{14}$	0.27 ^d	0.27^{d}	0.27
$l_{JK} imes 10^{17}$	-0.2^{d}	-0.2^{d}	-0.2
$l_{J} \times 10^{18}$	-0.597^{d}	-0.597^{d}	-0.597
$P_K imes 10^{15}$	0.649^{d}	0.649^{d}	0.649
$P_{KKJ} imes 10^{16}$	-0.394^{d}	-0.394^{d}	-0.394
$P_{KJ} imes 10^{18}$	-0.703^{d}	-0.703^{d}	-0.703
$P_{JK} imes 10^{19}$	0.778 ^d	0.778 ^d	0.778
$S_{K} \times 10^{18}$	-0.12^{d}	-0.12^{d}	-0.12
$S_{KKJ} imes 10^{20}$	0.70^{d}	0.70^{d}	0.70

^a Values in parentheses are 1σ 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, v_1 , v_2 , and v_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 $B_{\beta^{\lambda}}^{\mu_{\lambda}} = B_{\beta^{T}}^{g_{\lambda}} - \alpha_{\lambda}^{\lambda}$ ($\beta = x, y, z; \lambda = 1, 2, 3$). The ground state rotational parameters, $B_{\beta^{T}}^{g_{\lambda}}$ 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_{λ} .

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, $3v_1 + v_3$ and $v_1 + 3v_3$, 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 ${}^{32}SO_2$ one. We used parameters from Table 5 for estimation of the centers of the bands of the ${}^{34}SO_2$ 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
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Potential energy parameters for the SO₂ molecule.^a

Parameter	Value
1	2
a/\dot{A}^{-1}	2.471
$f_{rr}/aJ\dot{A}^{-2}$	10.390(34)
$f_{rr}/aJ\dot{A}^{-2}$	0.067(31)
$\int_{rr}^{r_{rr}/a_{J}} \dot{A}^{-1}$ $\int_{\alpha \alpha/a_{J}}^{r_{\alpha \alpha/a_{J}}} f_{rrr}/a_{J} \dot{A}^{-3}$ $f_{rrr}/a_{J} \dot{A}^{-3}$	0.423(64) 1.6516(52) -72.66(43) -1.81(25)
$f_{rr\alpha}/a \dot{A}^{-2}$	-2.90(61)
$f_{rr\alpha}/a \dot{A}^{-2}$	-1.488(95)
$f_{rax}[\mathbf{a}] \dot{\mathbf{A}}^{-1}$	-3.248(84)
$f_{axax}[\mathbf{a}]$	-2.688(98)
$f_{rrrr}[\mathbf{a}] \dot{\mathbf{A}}^{-4}$	419.3(79)
f_{rrax} / a J Å ⁻²	7.3(18)
$f_{\alpha\alpha\alpha\alpha}$ / a J	10.1(16)
r_e/A^{o}	1.431
$\alpha_e/deg.^{b}$	119.3

^a Uncertainties in parentheses are one standard errors.

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

Table 6 Band centers of the SO₂ molecule (in cm^{-1})

2			
Band	Exp.	Ref.	Calc.
1	2	3	4
<i>v</i> ₂	517.8726	[29]	517.832
2v ₂	1035.1264	[25]	1035.009
<i>v</i> ₁	1151.7130	[25]	1151.673
<i>v</i> ₃	1362.0603	[25]	1362.088
$v_1 + v_2$	1666.3348	[22]	1666.438
$v_2 + v_3$	1875.7975	[22]	1875.755
2v ₁	2295.8083	[22]	2295.661
$2v_2 + v_3$	2388.9155	[23]	2388.667
$v_1 + v_3$	2499.8700	[27]	2499.945
$v_1 + 3v_2$	2693.6348	[30]	2693.852
2v ₃	2713.3826	[30]	2713.487
$2v_1 + v_2$	2807.1890	[22]	2807.335
$v_1 + v_2 + v_3$	3010.3178	[22]	3010.523
3v ₁	3432.2877	[35]	3431.986
$2v_1 + v_3$	3629.7619	[27]	3629.856
$v_1 + 3v_2 + v_3$	4029.3903	[26]	4029.247
3v ₃	4054.0012	[26]	4054.084
$3v_1 + v_3$	4751.7169		4751.900 ^a
$v_1 + 3v_3$	5164.8507		5164.643 ^a

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

Table 7Band centers of the ${}^{34}SO_2$ molecule (in cm ${}^{-1}$).

Band	Exp.	Ref.	Calc.
1	2	3	4
<i>v</i> ₂	513.538709	[45]	513.91
$2v_2$	1026.455469	[45]	1026.94
<i>v</i> ₁	1144.478633	[45]	1144.91
V3	1345.094641	[45]	1344.93
3v ₂	1538.720198	[46]	1539.49
$v_1 + v_2$	1654.829004	[45]	1655.88
$v_2 + v_3$	1854.610452	[45]	1854.88
$v_1 + v_3$	2475.828004	[46]	2475.98
2v ₃	2679.800919	[46]	2679.42
$v_1 + v_2 + v_3$	2982.118600	[46]	2982.81
$2v_1 + v_3$	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 ³²SO₂ 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 $f_{i,i}$ 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 42 699 cm⁻¹ (the experimental value from Ref. [44] is about 42 700 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 SO₂ spectroscopy.

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Table 8

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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
J	Ka	K _c	Ε	Δ_1	Δ_2	Ε	Δ_1	Δ_2	Ε	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 ($E^{exp.} - E^{calc.}$) × 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.

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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.
- W.H. Yang, J.A. Roberts, G.D. Tejwani, J. Chem. Phys. 58 (1973) 4916-4918.
 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. Duterage, 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. Duterage, 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. Satler, 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.