



## High resolution analysis of the SO<sub>2</sub> spectrum in the 2600–2900 cm<sup>-1</sup> region: 2ν<sub>3</sub>, ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> bands

O.N. Ulenikov<sup>a,\*</sup>, O.V. Gromova<sup>b</sup>, E.S. Bekhtereva<sup>a</sup>, I.B. Bolotova<sup>a</sup>, I.A. Konov<sup>a</sup>, V.-M. Horneman<sup>c</sup>, C. Leroy<sup>d</sup>

<sup>a</sup> Laboratory of Molecular Spectroscopy, Physics Department, National Research Tomsk State University, Tomsk 634050, Russia

<sup>b</sup> Department of Theoretical and Experimental Physics, Institute of Physics and Technology, National Research Tomsk Polytechnic University, Tomsk 634050, Russia

<sup>c</sup> Department of Physics, P.O. Box 3000, FIN-90014, University of Oulu, Finland

<sup>d</sup> Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR CNRS 5209, Université de Bourgogne, 21078 Dijon, France

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### ABSTRACT

Infrared spectrum of the SO<sub>2</sub> molecule was recorded with high resolution in the 2600–2900 cm<sup>-1</sup> region. Spectrum was recorded with the Fourier transform interferometer Bruker IFS-120 HR in Oulu (Finland) with the pressure of 111 Pa and the absorption path length of 163.2 m that allowed us to record 2ν<sub>3</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> weak bands. The 2ν<sub>3</sub> band discussed earlier by Lafferty et al., was re-analyzed, and considerably more information was extracted from the spectrum (more than 3800 transitions of the 2ν<sub>3</sub> band were assigned in the experimental spectrum with maximum values of quantum numbers,  $J^{max.} = 76$  and  $K_a^{max.} = 26$ ). On the basis of the procedure discussed in Ulenikov et al., about 760 transitions of the ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> hot band ( $J^{max.} = 49$  and  $K_a^{max.} = 13$ ), were assigned, and the rotational structure of the (012) vibrational state was determined for the first time with high accuracy. Very weak band, 2ν<sub>1</sub>+ν<sub>2</sub>, was analyzed also for the first time, and about 1250 transitions with  $J^{max.} = 43$  and  $K_a^{max.} = 17$  were assigned in the spectrum. Information, obtained from the experimental data, was used in the fit for the determination of spectroscopic parameters of the states (002), (012), and (210). In this case, some earlier undiscussed sets of interacting ro-vibrational states were found, and resonance interactions between the states (002)/(130) and (012)/(140) were taken into account. Obtained from the fit, 36 parameters reproduce more than 5800 initial transitions of all three bands with the accuracy close to experimental uncertainties (*rms* deviation is 0.00021 cm<sup>-1</sup>, 0.00031 cm<sup>-1</sup> and 0.00014 cm<sup>-1</sup> for the 2ν<sub>3</sub>, ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> bands, respectively).

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### 1. Introduction

Sulfur dioxide plays an important role as a pollutant in the terrestrial atmosphere. Thus to solve the problems of propagation of monochromatic radiation in the atmosphere,

laser sounding, information transfer, the remote detection and monitoring of SO<sub>2</sub> *in situ*, etc., one should have a good knowledge of the fine structure of the SO<sub>2</sub> absorption spectra in different parts of the electromagnetic spectrum, in particular, in the infrared.

The present communication is a continuation of our recent publications, Refs. [1–4], where results of studies of high resolution spectra of the SO<sub>2</sub> molecule were presented (we do not mention here complete review of publications where different problems of high resolution

\* Corresponding author.

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

analysis of the SO<sub>2</sub> spectra have been discussed; corresponding review can be found, e.g., in the above mentioned Refs., [1–4]). The object of our present study is the region of 2600–2900 cm<sup>-1</sup>, where 2ν<sub>3</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> weak bands are located. As the further analysis shows, the quality of our experiment allows us to assign in the recorded spectrum a set of transitions belonging to the ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> extremely weak “hot” band. Earlier the 2ν<sub>3</sub> band was discussed with a high resolution in Ref. [5]. However, in our case, we were able to extract from the recorded spectrum more than three times more transitions of the 2ν<sub>3</sub> band than it was made in Ref. [5]. The 2ν<sub>1</sub>+ν<sub>2</sub> and ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> bands were not previously discussed in the literature. Only few information about rotational structure of the vibrational state (210) were derived in Ref. [6] from the 2ν<sub>1</sub>+ν<sub>2</sub>-ν<sub>2</sub> hot band.

Section 2 of the present paper describes the experimental conditions of the recorded spectrum. In Section 3 we briefly discuss the Hamiltonian model used to fit the experimental line positions. The results of the analysis of the 2ν<sub>3</sub>, 2ν<sub>1</sub>+ν<sub>2</sub> and ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> bands are presented in Sections 4 and 5, respectively.

**2. Experimental details**

The analysis is based on the measurements in the wavenumber region from 2600 to 2900 cm<sup>-1</sup>. The measured range was optically limited with interference filters. The experimental work was performed in the Infrared Laboratory of Oulu with a Bruker IFS-120 HR Fourier Transform spectrometer. The SO<sub>2</sub> sample, made by Sigma-Aldrich Inc., with purity of 99.9% was studied with an absorption spectroscopic method in a multipath White cell, [7]. The sample pressure was 111 Pa and the absorption path length was 163.2 m. The cell was provided with two 6 mm thick potassium bromide windows. A Globar source, KBr beamsplitter and an indium antimonide semiconductor detector were used. The final spectral resolution limited mainly by Doppler broadening is about 0.0054 cm<sup>-1</sup> around the band center. The measurements of these weak spectra required rather long recording times. In this case the registration time was 80.5 h. The spectrum was calibrated with 326 OCS peaks [8]. The peak positions were calculated with the optimized center of gravity method discussed in Ref. [9].

**3. Hamiltonian model**

The effective Hamiltonian for the XY<sub>2</sub>-type molecule of C<sub>2v</sub>-symmetry has been discussed in the spectroscopic literature many times. For consistency, without detailed explanations, we briefly reproduce here after the main ingredients from Refs. [10,11]:

$$H^{vib.-rot.} = \sum_{\nu, \tilde{\nu}} | \nu \rangle \langle \tilde{\nu} | H^{\nu \tilde{\nu}}, \tag{1}$$

where ν and  $\tilde{\nu}$  denote possible interacting vibrational states. In this model the diagonal block operators are the traditional Watson type operators in A reduction and I'

representation [12]

$$\begin{aligned} H^{\nu \tilde{\nu}} = & E^{\nu} + [A^{\nu} - \frac{1}{2}(B^{\nu} + C^{\nu})]J_z^2 + \frac{1}{2}(B^{\nu} + C^{\nu})J^2 + \frac{1}{2}(B^{\nu} - C^{\nu})J_{xy}^2 \\ & - A_{Kz}^{\nu}J_z^4 - A_{JKz}^{\nu}J_z^2J^2 - A_j^{\nu}J^4 - \delta_K^{\nu}[J_z^2J_{xy}^2]_+ - 2\delta_j^{\nu}J_z^2J_{xy}^2 \\ & + H_{Kz}^{\nu}J_z^6 + H_{KKJz}^{\nu}J_z^4J^2 + H_{JKz}^{\nu}J_z^2J^4 + H_j^{\nu}J^6 \\ & + [h_{Kz}^{\nu}J_z^4 + h_{JKz}^{\nu}J_z^2J^2 + h_j^{\nu}J^4J_{xy}]_+ + L_{Kz}^{\nu}J_z^8 + L_{KKJz}^{\nu}J_z^6J^2 + L_{JKz}^{\nu}J_z^4J^4 \\ & + L_{JKz}^{\nu}J_z^2J^6 + L_j^{\nu}J^8 + [l_{Kz}^{\nu}J_z^6 + l_{KKJz}^{\nu}J_z^4J^2 + l_{JKz}^{\nu}J_z^2J^4 + l_j^{\nu}J^6J_{xy}]_+ \\ & + P_{Kz}^{\nu}J_z^{10} + P_{KKJz}^{\nu}J_z^8J^2 + P_{KKJz}^{\nu}J_z^6J^4 + P_{JKz}^{\nu}J_z^4J^6 + \dots \\ & + S_{Kz}^{\nu}J_z^{12} + S_{KKJz}^{\nu}J_z^{10}J^2 + \dots, \end{aligned} \tag{2}$$

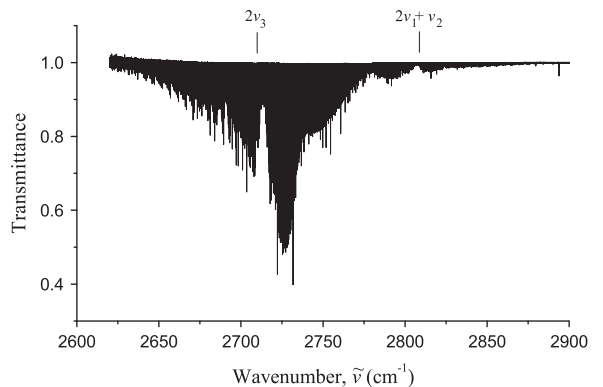
where J<sub>α</sub> (α=x,y,z) are the components of the angular momentum operator defined in the molecule-fixed coordinate system, J<sub>xy</sub><sup>2</sup> = J<sub>x</sub><sup>2</sup>-J<sub>y</sub><sup>2</sup>, and [...]<sub>+</sub> denotes an anti-commutator. Because of the symmetry arguments of the SO<sub>2</sub> molecule, the nondiagonal block operators can only be of two types: Coriolis interactions of the B<sub>1</sub>-symmetry and Fermi interactions.

In our present study we follow the paper [5], where the interaction between the (002) and (130) states was taken into account. This is the reason why only the Fermi-type interaction is considered in this communication:

$$\begin{aligned} H_F^{\nu \tilde{\nu}} = & F^{\nu \tilde{\nu}} + F_K^{\nu \tilde{\nu}}J_z^2 + F_j^{\nu \tilde{\nu}}J^2 + \dots + F_{xy}^{\nu \tilde{\nu}}J_{xy}^2 + F_{xyK}^{\nu \tilde{\nu}}[J_{xy}^2J_z^2]_+ \\ & + F_{xyj}^{\nu \tilde{\nu}}J_{xy}^2J^2 + \dots \end{aligned} \tag{3}$$

**4. The 2ν<sub>3</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> bands of SO<sub>2</sub>**

An overview of the recorded spectrum in the 2600–2900 cm<sup>-1</sup> region is shown in Fig. 1. One can see the 2ν<sub>3</sub> band centered at 2713 cm<sup>-1</sup> and the considerably weaker 2ν<sub>1</sub>+ν<sub>2</sub> band centered at 2807 cm<sup>-1</sup> (for illustration of the quality of the experimentally recorded spectrum, Fig. 2 presents small portions of the high-resolution spectrum). In both bands all branches are clearly pronounced. Thus one can expect a good fulfillment of “ground state combination differences” principle. Because, for the 2ν<sub>3</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> bands, a lower vibrational state is the ground state, and the upper vibrational states are the states of the A<sub>1</sub> symmetry, then all possible transitions for both bands will be of the b-type.



**Fig. 1.** Survey spectrum of SO<sub>2</sub> in the 2ν<sub>3</sub>, 2ν<sub>1</sub>+ν<sub>2</sub> and ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> bands region.



**Table 2**

Experimental ro-vibrational term values for the (002) vibrational state of the SO<sub>2</sub> molecule (in cm<sup>-1</sup>).<sup>a</sup>

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>
1		2	3	4	1		2		3	4	1		2		3	4	1		2		3	4	
0	0	0	2713.3821		0	11	1	11	2755.0004	3	0	15	10	6	2955.6221	1	1	19	3	17	2849.0895	2	1
1	1	1	2715.6596	0	0	11	2	10	2761.7276	1	0	15	11	5	2990.3208	1	0	19	4	16	2860.8261	1	1
2	0	2	2715.2805	1	-1	11	3	9	2770.2845	2	0	15	12	4	3028.2369	0	0	19	5	15	2875.6993	2	0
2	1	1	2717.0270	1	1	11	4	8	2781.9342	2	-1	15	13	3	3069.3608	1	0	19	6	14	2893.9361	1	0
2	2	0	2721.9599	1	0	11	5	7	2796.9134	1	0	15	14	2	3113.6656	2	1	19	7	13	2915.5148	1	0
3	1	3	2718.6984	1	-2	11	6	6	2815.2170	2	1	15	15	1	3161.1269	1	1	19	8	12	2940.4062	1	0
3	2	2	2723.8584	1	-1	11	7	5	2836.8291	1	-1	16	0	16	2796.8604	1	-1	19	9	11	2968.5875	1	0
3	3	1	2732.2020	0	0	11	8	4	2861.7350	1	0	16	1	15	2803.5129	1	0	19	10	10	3000.0383	2	0
4	0	4	2719.6966	0	0	11	9	3	2889.9192	2	0	16	2	14	2808.2141	1	0	19	11	9	3034.7420	0	0
4	1	3	2721.6328	0	0	11	10	2	2921.3649	1	0	16	3	13	2815.1821	2	1	19	12	8	3072.6656	1	1
4	2	2	2726.4075	2	0	11	11	1	2956.0574	1	-1	16	4	12	2826.4600	1	0	19	13	7	3113.7995	2	0
4	3	1	2734.7375	2	2	12	0	12	2761.7539	0	0	16	5	11	2841.3639	1	0	19	14	6	3158.1161	2	0
4	4	0	2746.4082	2	-2	12	1	11	2766.0865	0	0	16	6	10	2859.6381	0	0	19	15	5	3205.5910	2	0
5	1	5	2724.1627	2	0	12	2	10	2770.2819	3	1	16	7	9	2881.2369	2	0	19	16	4	3256.1987	3	0
5	2	4	2729.5536	1	0	12	3	9	2777.9895	3	0	16	8	8	2906.1382	1	0	19	17	3	3309.9119	1	-2
5	3	3	2737.9071	2	0	12	4	8	2789.5586	1	0	16	9	7	2934.3232	1	0	19	18	2	3366.7036	3	1
5	4	2	2749.5773	2	-1	12	5	7	2804.5287	2	1	16	10	6	2965.7735	0	0	19	19	1	3426.5437		-1
5	5	1	2764.5719	0	0	12	6	6	2822.8288	1	0	16	11	5	3000.4735	2	-1	20	0	20	2841.2103	1	-1
6	0	6	2726.5991	0	0	12	7	5	2844.4397	1	0	16	12	4	3038.3916	2	0	20	1	19	2850.5530	0	0
6	1	5	2728.8604	0	0	12	8	4	2869.3455	2	0	16	13	3	3079.5182	1	1	20	2	18	2856.6793	3	3
6	2	4	2733.4272	4	3	12	9	3	2897.5303	1	1	16	14	2	3123.8258	3	2	20	3	17	2863.0906	2	0
6	3	3	2741.7137	1	1	12	10	2	2928.9771	1	0	16	15	1	3171.2902	1	0	20	4	16	2873.7024	2	0
6	4	2	2753.3810	2	1	12	11	1	2963.6712	1	0	16	16	0	3221.8862	1	0	20	5	15	2888.4327	0	0
6	5	1	2768.3748	2	0	12	12	0	3001.5817	1	1	17	1	17	2807.2333	1	-1	20	6	14	2906.6460	1	0
6	6	0	2786.6840	1	1	13	1	13	2770.0508	1	0	17	2	16	2816.2356	1	0	20	7	13	2928.2148	1	0
7	1	7	2732.0428	0	0	13	2	12	2777.4384	1	0	17	3	15	2825.5854	1	0	20	8	12	2953.1011	0	0
7	2	6	2737.7712	3	3	13	3	11	2786.1739	2	0	17	4	14	2837.2582	1	0	20	9	11	2981.2801	1	0
7	3	5	2746.1533	1	0	13	4	10	2797.8166	1	0	17	5	13	2852.1684	1	0	20	10	10	3012.7304	1	0
7	4	4	2757.8195	1	1	13	5	9	2812.7805	1	0	17	6	12	2870.4328	1	0	20	11	9	3047.4350	0	0
7	5	3	2772.8124	1	1	13	6	8	2831.0767	3	2	17	7	11	2892.0261	1	0	20	12	8	3085.3602	1	1
7	6	2	2791.1212	3	-1	13	7	7	2852.6856	2	1	17	8	10	2916.9250	1	0	20	13	7	3126.4967	1	2
7	7	1	2812.7344	1	0	13	8	6	2877.5909	1	1	17	9	9	2945.1093	1	1	20	14	6	3170.8163	1	0
8	0	8	2735.9422	0	0	13	9	5	2905.7761	0	0	17	10	8	2976.5599	1	0	20	15	5	3218.2950	1	0
8	1	7	2738.6949	2	0	13	10	4	2937.2240	0	0	17	11	7	3011.2614	1	0	20	16	4	3268.9067	1	-1
8	2	6	2743.0552	2	0	13	11	3	2971.9196	1	-1	17	12	6	3049.1813	2	1	20	17	3	3322.6247	1	-1
8	3	5	2751.2380	3	-1	13	12	2	3009.8320	2	1	17	13	5	3090.3103	1	1	20	18	2	3379.4212	1	1
8	4	4	2762.8935	4	-1	13	13	1	3050.9512	0	0	17	14	4	3134.6208	2	0	20	19	1	3439.2667	3	0
8	5	3	2777.8846	1	0	14	0	14	2778.1523	1	-1	17	15	3	3182.0887	3	1	21	1	21	2853.7992	1	-1
8	6	2	2796.1929	1	0	14	1	13	2783.5704	5	3	17	16	2	3232.6884	1	0	21	2	20	2864.7360	2	0
8	7	1	2817.8064	1	0	14	2	12	2787.9144	1	0	17	17	1	3286.3931	4	-1	21	3	19	2875.1063	1	0
8	8	0	2842.7116	2	3	14	3	11	2795.2641	3	0	18	0	18	2817.8785	1	0	21	4	18	2886.9609	2	-1
9	1	9	2742.3263	3	-3	14	4	10	2806.7247	1	0	18	1	17	2825.8582	1	0	21	5	17	2901.7953	3	0
9	2	8	2748.5000	2	1	14	5	9	2821.6701	1	0	18	2	16	2831.1498	2	1	21	6	16	2919.9949	0	0
9	3	7	2756.9447	1	0	14	6	8	2839.9604	2	0	18	3	15	2837.7808	2	1	21	7	15	2941.5525	0	0
9	4	6	2768.6034	2	-2	14	7	7	2861.5670	1	1	18	4	14	2848.7793	1	1	21	8	14	2966.4327	1	1
9	5	5	2783.5920	3	2	14	8	6	2886.4715	3	1	18	5	13	2863.6157	1	-1	21	9	13	2994.6087	2	0
9	6	4	2801.8992	1	0	14	9	5	2914.6569	1	1	18	6	12	2881.8654	2	1	21	10	12	3026.0581	2	1

Table 2 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>
1			2	3	4	1			2	3	4	1			2	3	4	1			2	3	4
9	7	3	2823.5126	2	0	14	10	4	2946.1057	2	1	18	7	11	2903.4520	1	0	21	11	11	3060.7633	1	0
9	8	2	2848.4180	1	0	14	11	3	2980.8027	1	-1	18	8	10	2928.3476	1	1	21	12	10	3098.6900	3	1
9	9	1	2876.6008	1	0	14	12	2	3018.7171	2	1	18	9	9	2956.5306	0	0	21	13	9	3139.8289	1	1
10	0	10	2747.6749	0	0	14	13	1	3059.8386	1	1	18	10	8	2987.9814	1	0	21	14	8	3184.1517	2	0
10	1	9	2751.1141	0	0	14	14	0	3104.1406	2	1	18	11	7	3022.6842	1	0	21	15	7	3231.6340	3	0
10	2	8	2755.3310	2	1	15	1	15	2787.4651	3	-2	18	12	6	3060.6060	1	1	21	16	6	3282.2501	2	0
10	3	7	2763.3234	1	0	15	2	14	2795.6141	1	-1	18	13	5	3101.7374	2	1	21	17	5	3335.9729	2	0
10	4	6	2774.9509	1	1	15	3	13	2804.6098	1	0	18	14	4	3146.0509	1	1	21	18	4	3392.7742	1	-1
10	5	5	2789.9347	4	0	15	4	12	2816.2563	2	0	18	15	3	3193.5222	3	-1	21	19	3	3452.6250	4	-5
10	6	4	2808.2405	1	0	15	5	11	2831.1973	4	1	18	16	2	3244.1259	1	0	21	20	2	3515.4961	2	-2
10	7	3	2829.8534	2	0	15	6	10	2849.4807	1	-1	18	17	1	3297.8349	1	0	21	21	1	3581.3553		-7
10	8	2	2854.7592	0	0	15	7	9	2871.0839	1	0	18	18	0	3354.6216	3	1	22	0	22	2866.8601	2	0
10	9	1	2882.9428	2	1	15	8	8	2895.9870	1	-1	19	1	19	2829.3467	1	-1	22	1	21	2877.5584	1	0
10	10	0	2914.3873	1	0	15	9	7	2924.1724	3	0	19	2	18	2839.2827	1	-1	22	2	20	2884.7507	2	-1
22	3	19	2891.1246	1	0	24	17	7	3379.8297		6	27	4	24	2980.7288	3	0	29	15	15	3361.2102	2	1
22	4	18	2901.2565	0	0	24	18	6	3436.6470	1	0	27	5	23	2995.5247	2	2	29	16	14	3411.8629	2	1
22	5	17	2915.8232	0	0	24	19	5	3496.5162	1	1	27	6	22	3013.5497	1	0	29	17	13	3465.6276	1	0
22	6	16	2933.9845	0	0	24	20	4	3559.4060	2	0	27	7	21	3034.9915	3	0	29	18	12	3522.4759	4	1
22	7	15	2955.5282	1	0	24	21	3	3625.2860		1	27	8	20	3059.8049	2	-1	29	19	11	3582.3782	2	1
22	8	14	2980.4010	1	0	24	22	2	3694.1244		3	27	9	19	3087.9442	3	-1	29	20	10	3645.3034		-6
22	9	13	3008.5732	2	-1	24	23	1	3765.8885		4	27	10	18	3119.3758	1	0	29	21	9	3711.2222	7	-2
22	10	12	3040.0213	3	0	25	1	25	2909.7054	2	0	27	11	17	3154.0771	0	0	29	22	8	3780.1020		5
22	11	11	3074.7268	0	0	25	2	24	2922.7896	3	0	27	12	16	3192.0081	2	1	29	23	7	3851.9081		-6
22	12	10	3112.6550	2	3	25	3	23	2934.6016	1	0	27	13	15	3233.1591	1	0	30	0	30	2992.6860	1	0
22	13	9	3153.7960	2	0	25	4	22	2946.9207	2	1	27	14	14	3277.5003	0	0	30	1	29	3008.4824	1	-1
22	14	8	3198.1222	2	1	25	5	21	2961.7039	2	1	27	15	13	3325.0056	2	-1	30	2	28	3021.2535	3	2
22	15	7	3245.6082	4	0	25	6	20	2979.7967	2	0	27	16	12	3375.6498		8	30	3	27	3030.0138	1	2
22	16	6	3296.2286	1	0	25	7	19	3001.2874	2	0	27	17	11	3429.4027	2	0	30	4	26	3038.4554	1	0
22	17	5	3349.9563	1	1	25	8	18	3026.1297	0	0	27	18	10	3486.2385	2	0	30	5	25	3051.4019	1	0
22	18	4	3406.7629	4	-2	25	9	17	3054.2854	0	0	27	19	9	3546.1271	2	0	30	6	24	3069.0312	3	0
22	19	3	3466.6199	1	-1	25	10	16	3085.7254	3	-2	27	20	8	3609.0381	1	2	30	7	23	3090.3556	2	2
22	20	2	3529.4964		-6	25	11	15	3120.4300	1	0	27	21	7	3674.9401	3	-2	30	8	22	3115.1087	3	0
22	21	1	3595.3631		0	25	12	14	3158.3608	2	1	27	22	6	3743.8025	3	4	30	9	21	3143.2127	2	-2
22	22	0	3664.1870		2	25	13	13	3199.5084	3	0	27	23	5	3815.5921		7	30	10	20	3174.6247	1	0
23	1	23	2880.5866		1	0	25	14	3243.8436	2	-1	27	24	4	3890.2750	1	4	30	11	19	3209.3170	1	0
23	2	22	2892.5769		2	0	25	15	3291.3415	4	0	28	0	28	2957.7431	1	-1	30	12	18	3247.2453	1	0
23	3	21	2903.6175		1	0	25	16	3341.9754	1	0	28	1	27	2972.3103	0	0	30	13	17	3288.3997	3	1
23	4	20	2915.6613		2	1	25	17	3395.7183	1	-1	28	2	26	2983.6135	4	1	30	14	16	3332.7483	0	0
23	5	19	2930.4619		1	0	25	18	3452.5423	2	2	28	3	25	2991.3686	3	-2	30	15	15	3380.2651	3	2
23	6	18	2948.6135		1	0	25	19	3512.4175	1	0	28	4	24	3000.0477	2	-1	30	16	14	3430.9223	1	0
23	7	17	2970.1422		0	0	25	20	3575.3142		0	28	5	23	3013.5654	1	0	30	17	13	3484.6925	2	-1
23	8	16	2995.0065		2	1	25	21	3641.2014		0	28	6	22	3031.4016	2	0	30	18	12	3541.5471	3	-1
23	9	15	3023.1741		0	0	25	22	3710.0473	2	0	28	7	21	3052.8048	2	0	30	19	11	3601.4566	2	0
23	10	14	3054.6201		1	0	25	23	3781.8198		4	28	8	20	3077.6004	1	0	30	20	10	3664.3904	0	1
23	11	13	3089.3257		0	0	25	24	3856.4851		3	28	9	19	3105.7295	2	1	30	21	9	3730.3166		-4
23	12	12	3127.2548		1	0	25	25	3934.0101		1	28	10	18	3137.1555	2	1	30	22	8	3799.2051		1
23	13	11	3168.3984		0	0	26	0	2925.1249	1	-1	28	11	17	3171.8545	2	2	31	1	31	3011.0322	5	-1
23	14	10	3212.7275		0	0	26	1	2938.4368	2	-1	28	12	16	3209.7850	1	2	31	2	30	3027.5372	2	1

23	15	9	3260.2176	3	1	26	2	24	2948.2810	1	1	28	13	15	3250.9372	1	0	31	3	29	3042.1681	1	0
23	16	8	3310.8423	3	0	26	3	23	2955.3026	2	0	28	14	14	3295.2812	0	1	31	4	28	3055.9287	3	1
23	17	7	3364.5753	1	3	26	4	22	2964.3942	2	1	28	15	13	3342.7903	3	-1	31	5	27	3070.9049	2	0
23	18	6	3421.3874	2	0	26	5	21	2978.3727	2	2	28	16	12	3393.4381	1	1	31	6	26	3088.7853	1	1
23	19	5	3481.2498		-4	26	6	20	2996.3559	1	0	28	17	11	3447.1977	2	0	31	7	25	3110.0926	1	0
23	20	4	3544.1336		1	26	7	19	3017.8194	1	0	28	18	10	3504.0397	4	1	31	8	24	3134.8223	1	0
23	21	3	3610.0066	4	2	26	8	18	3042.6482	1	0	28	19	9	3563.9351	1	2	31	9	23	3162.9116	1	0
23	22	2	3678.8374	1	1	26	9	17	3070.7962	1	0	28	20	8	3626.8536	3	3	31	10	22	3194.3148	1	1
23	23	1	3750.5937		3	26	10	16	3102.2325	1	-1	28	21	7	3692.7634	1	-1	31	11	21	3229.0028	2	2
24	0	24	2894.8309	0	-1	26	11	15	3136.9355	2	-2	28	22	6	3761.6334		-5	31	12	20	3266.9290	1	1
24	1	23	2906.8544	1	0	26	12	14	3174.8668	1	1	28	23	5	3833.4326		7	31	13	19	3308.0836	2	-1
24	2	22	2915.3059	2	-1	26	13	13	3216.0162	1	0	28	24	4	3908.1251		6	31	14	18	3352.4346	1	0
24	3	21	2921.8723	2	0	26	14	12	3260.3545	2	1	29	1	29	2974.9296	1	-1	31	15	17	3399.9548	2	1
24	4	20	2931.4748	3	1	26	15	11	3307.8560	0	0	29	2	28	2990.2791	1	0	31	16	16	3450.6166	4	-1
24	5	19	2945.7984	1	1	26	16	10	3358.4947	2	0	29	3	27	3003.8991	1	0	31	17	15	3504.3927	1	0
24	6	18	2963.8858	1	0	26	17	9	3412.2431	2	1	29	4	26	3017.0710	2	1	31	18	14	3561.2540	2	3
24	7	17	2985.3952	1	0	26	18	8	3469.0726	3	0	29	5	25	3031.9255	1	0	31	19	13	3621.1703	2	0
24	8	16	3010.2492	1	0	26	19	7	3528.9544	2	-1	29	6	24	3049.8774	2	-1	31	20	12	3684.1120	2	2
24	9	15	3038.4115	1	1	26	20	6	3591.8583	2	0	29	7	23	3071.2585	1	1	31	21	11	3750.0465		-7
24	10	14	3069.8548	1	-1	26	21	5	3657.7531	2	3	29	8	22	3096.0348	1	-1	31	22	10	3818.9433		-9
24	11	13	3104.5600	1	-1	26	22	4	3726.6070		3	29	9	21	3124.1523	2	0	31	23	9	3890.7715		9
24	12	12	3142.4902	1	0	26	25	1	3950.5955		-3	29	10	20	3155.5716	2	-1	32	0	32	3029.9533	2	-1
24	13	11	3183.6360	1	2	26	26	0	4030.9564	4	-1	29	11	19	3190.2678	2	2	32	1	31	3046.9602	2	-2
24	14	10	3227.9681	1	0	27	1	27	2941.1536	1	0	29	12	18	3228.1973	2	1	32	2	30	3061.1683	3	0
24	15	9	3275.4621	2	2	27	2	26	2955.3606	4	1	29	13	17	3269.3510	4	1	32	3	29	3071.1722	1	2
24	16	8	3326.0913	4	0	27	3	25	2968.0364	2	0	29	14	16	3313.6973	2	1	32	4	28	3079.6146	1	0
32	5	27	3091.9135	1	0	34	18	16	3624.1830	1	0	37	12	26	3398.3840	3	-1	40	7	33	3316.7907	3	2
32	6	26	3109.2556	2	0	34	19	15	3684.1221	2	2	37	13	25	3439.5326	1	2	40	8	32	3341.1081	3	-1
32	7	25	3130.4765	2	1	34	20	14	3747.0876	4	-4	37	14	24	3483.8900	1	0	40	9	31	3368.9616	2	2
32	8	24	3155.1762	1	0	34	21	13	3813.0501		2	37	15	23	3531.4276	2	2	40	10	30	3400.2194	2	0
32	9	23	3183.2487	2	0	34	22	12	3881.9764		7	37	16	22	3582.1155	3	1	40	11	29	3434.8231	1	2
32	10	22	3214.6419	2	0	35	1	35	3090.2136	1	0	37	17	21	3635.9249	4	2	40	12	28	3472.6995	2	1
32	11	21	3249.3245	1	0	35	2	34	3109.0494	2	0	37	18	20	3692.8256		1	40	13	27	3513.8367	3	1
32	12	20	3287.2483	0	0	35	3	33	3125.8483	2	-1	37	19	19	3752.7876	3	3	40	14	26	3558.1919	3	-3
32	13	19	3328.4033	1	0	35	4	32	3141.1021	3	1	37	20	18	3815.7782		-9	40	15	25	3605.7346	3	0
32	14	18	3372.7560	1	0	35	5	31	3156.5735	3	-2	37	21	17	3881.7695	2	2	40	16	24	3656.4335	5	1
32	15	17	3420.2794	0	-1	35	6	30	3174.3567	2	0	37	22	16	3950.7248		-5	40	17	23	3710.2586	2	1
32	16	16	3470.9461	3	0	35	7	29	3195.4805	1	0	38	0	38	3155.6998	3	1	40	18	22	3767.1791	3	0
32	17	15	3524.7277	1	1	35	8	28	3220.0826	2	0	38	1	37	3176.2746	3	2	40	19	21	3827.1652		9
32	18	14	3581.5951	2	-1	35	9	27	3248.0930	1	1	38	2	36	3194.5038	3	-1	41	1	41	3226.4127		0
32	19	13	3641.5191	3	0	35	10	26	3279.4480	1	0	38	3	35	3209.0374	2	0	41	2	40	3248.7601	3	3
32	20	12	3704.4685	2	-3	35	11	25	3314.1095	1	1	38	4	34	3219.2463	1	0	41	3	39	3269.0094	5	0
32	21	11	3770.4128	1	1	35	12	24	3352.0218	0	0	38	5	33	3229.8479	0	0	41	4	38	3287.1497	1	0
32	22	10	3839.3188		-4	35	13	23	3393.1743	0	0	38	6	32	3245.6552	1	-1	41	5	37	3304.1466	3	-1
32	23	9	3911.1563		9	35	14	22	3437.5310	2	0	38	7	31	3266.3215	2	1	41	6	36	3322.1196	2	1
33	1	33	3049.4606	1	1	35	15	21	3485.0634	1	0	38	8	30	3290.7679	3	0	41	7	35	3342.9303	4	0
33	2	32	3067.1287	3	0	35	16	20	3535.7430		-3	38	9	29	3318.6929	2	1	41	8	34	3367.2403	1	0
33	3	31	3082.8237	1	0	35	17	19	3589.5418	2	2	38	10	28	3349.9952	1	-1	41	9	33	3395.0572	2	0
33	4	30	3097.2801	4	0	35	18	18	3646.4292	2	1	38	11	27	3384.6259	3	0	41	10	32	3426.2897	1	-1
33	5	29	3112.4575	1	1	35	19	17	3706.3758		3	38	12	26	3422.5196	1	0	41	11	31	3460.8780	2	2
33	6	28	3130.2773	1	1	35	20	16	3769.3496		-5	38	13	25	3463.6646		-3	41	12	30	3498.7440	3	0
33	7	27	3151.4984	2	0	35	21	15	3835.3216		2	38	14	24	3508.0222	1	0	41	13	29	3539.8759	2	-1
33	8	26	3176.1705	2	1	36	0	36	3111.4607	3	-1	38	15	23	3555.5616		-1	41	14	28	3584.2298	1	-1
33	9	25	3204.2243	2	-1	36	1	35	3130.8534	3	0	38	16	22	3606.2537	3	2	41	15	27	3631.7735	4	1

Table 2 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	
1		2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
33	10	24	3235.6063	2	-1	36	2	34	3147.7882	1	0	38	17	21	3660.0679	2	-3	41	16	26	3682.4752	3	-2	
33	11	23	3270.2829	2	1	36	3	33	3160.7498	3	0	38	18	20	3716.9754	5	-1	41	17	25	3736.3055	2	1	
33	12	22	3308.2036	1	0	36	4	32	3170.0632	1	0	38	19	19	3776.9454	5	3	41	18	24	3793.2327	1	3	
33	13	21	3349.3580	2	-1	36	5	31	3181.1060	2	2	38	21	17	3905.9449		-5	41	19	23	3853.2249		-5	
33	14	20	3393.7126	3	0	36	6	30	3197.5471	1	0	38	22	16	3974.9120		-1	42	0	42	3251.1443	0	0	
33	15	19	3441.2390	2	-1	36	7	29	3218.4522	1	0	39	1	39	3178.6904	0	0	42	1	41	3274.0711	3	0	
33	16	18	3491.9103	1	0	36	8	28	3243.0020	1	0	39	2	38	3199.8670	3	0	42	2	40	3294.7964	6	1	
33	17	17	3545.6974	4	-1	36	9	27	3270.9862	1	0	39	3	37	3218.9515	4	0	42	3	39	3312.3889	6	1	
33	18	16	3602.5718	3	1	36	10	26	3302.3257	2	2	39	4	36	3236.0601	4	1	42	4	38	3325.1873	0	0	
33	19	15	3662.5029	4	-1	36	11	25	3336.9777	2	-1	39	5	35	3252.4379	1	0	42	5	37	3335.6542	2	0	
33	20	14	3725.4609	2	1	36	12	24	3374.8850	1	1	39	6	34	3270.2809	1	0	42	6	36	3349.9420	3	-1	
33	21	13	3791.4143	3	3	36	13	23	3416.0355	1	-1	39	7	33	3291.1922	0	0	42	7	35	3369.8720	3	0	
33	22	12	3860.3297		0	36	14	22	3460.3930	1	0	39	8	32	3315.6136	0	0	42	8	34	3394.0280	1	0	
33	23	11	3932.1770		9	36	15	21	3507.9278	2	-1	39	9	31	3343.5066	1	0	42	9	33	3421.7949	2	-1	
34	0	34	3069.5451	2	-2	36	16	20	3558.6122	2	2	39	10	30	3374.7879	1	-1	42	10	32	3452.9995	1	0	
34	1	33	3087.7495	4	0	36	17	19	3612.4156	3	-3	39	11	29	3409.4059	1	2	42	11	31	3487.5703	4	0	
34	2	32	3103.3461	1	1	36	18	18	3669.3101	2	2	39	12	28	3447.2914	2	2	42	12	30	3525.4251	2	1	
34	3	31	3114.7741	1	0	36	19	17	3729.2644	2	3	39	13	27	3488.4329	1	-1	42	13	29	3566.5514	4	3	
34	4	30	3123.4993	1	1	36	20	16	3792.2469	4	-3	39	14	26	3532.7896	0	0	42	14	28	3610.9028	1	0	
34	5	29	3135.1363	1	-1	36	21	15	3858.2271	-7	39	15	25	3580.3305	3	-3	42	15	27	3658.4467	1	-1		
34	6	28	3152.0882	2	0	36	22	14	3927.1743		6	39	16	24	3631.0262	2	0	42	16	26	3709.1518	2	1	
34	7	27	3173.1732	1	0	37	1	37	3133.2905	2	0	39	17	23	3684.8460	2	-1	42	17	25	3762.9863	2	-2	
34	8	26	3197.8061	0	0	37	2	36	3153.2962	5	-1	39	18	22	3741.7605	1	4	42	18	24	3819.9204	2	5	
34	9	25	3225.8389	1	-1	37	3	35	3171.2281	1	-1	39	19	21	3801.7379	3	4	42	19	23	3879.9210	1	3	
34	10	24	3257.2081	2	-2	37	4	34	3187.3698	3	-1	39	21	19	3930.7568		3	43	1	43	3276.4564	1	0	
34	11	23	3291.8779	2	1	37	5	33	3203.2399	1	1	40	0	40	3202.2613	4	1	43	2	42	3299.9735	1	-1	
34	12	22	3329.7948	1	1	37	6	32	3221.0251	2	0	40	1	39	3224.0134	1	0	43	3	41	3321.3957	2	1	
34	13	21	3370.9488	4	3	37	7	31	3242.0436	1	0	40	2	38	3243.5038	4	3	43	4	40	3340.6184	3	-2	
34	14	20	3415.3043	2	1	37	8	30	3266.5625	2	1	40	3	37	3259.5919	1	0	43	5	39	3358.3426	1	1	
34	15	19	3462.8337	2	-1	37	9	29	3294.5194	1	0	40	4	36	3270.9792	2	-2	43	6	38	3376.5328	1	0	
34	16	18	3513.5093	4	-1	37	10	28	3325.8411	2	-2	40	5	35	3281.3695	2	-2	43	7	37	3397.2607	1	-1	
34	17	17	3567.3021		-1	37	11	27	3360.4835	2	2	40	6	34	3296.4421	1	0	43	8	36	3421.4465	2	-1	
43	9	35	3449.1741	0	0	46	13	33	3679.6099	2	1	50	5	45	3579.3645	3	0	54	1	53	3623.0849	4	-2	
43	10	34	3480.3486	2	0	46	14	32	3723.9463	1	6	50	6	44	3591.6672	5	-4	54	2	52	3650.9710	7	-1	
43	11	33	3514.9009	1	0	46	15	31	3771.4875	1	-1	50	7	43	3608.7212	4	-1	54	3	51	3676.4988	1	3	
43	12	32	3552.7426	2	-2	46	16	30	3822.2006	1	-3	50	8	42	3631.6403	1	-1	54	4	50	3698.8566	3	-1	
43	13	31	3593.8620	4	0	46	17	29	3876.0526	1	0	50	9	41	3658.8480	4	1	54	5	49	3716.1257	1	-2	
43	14	30	3638.2107	1	0	46	18	28	3933.0104	3	-1	50	10	40	3689.7228	4	0	54	6	48	3729.1323	2	-8	
43	15	29	3685.7549	1	-1	47	1	47	3383.5039	5	-3	50	12	38	3761.8003	2	0	54	7	47	3744.4749	6	-6	
43	16	28	3736.4626	2	0	47	2	46	3409.3593	4	2	50	13	37	3802.8430	4	-4	54	8	46	3766.1605	3	1	
43	17	27	3790.3019	1	0	47	3	45	3433.1350	3	1	50	14	36	3847.1511		-1	54	9	45	3792.8670	2	-1	
43	18	26	3847.2419	3	3	47	4	44	3454.6270	2	0	50	15	35	3894.6808		-8	54	10	44	3823.4800	4	0	
43	19	25	3907.2501	1	-1	47	5	43	3474.0941	3	0	50	16	34	3945.3973		3	54	12	42	3895.2817	7	-9	
44	0	44	3302.3484	1	1	47	6	42	3493.0275		1	50	17	33	3999.2616	2	1	54	13	41	3936.2548		2	
44	1	43	3326.4473	3	1	47	7	41	3513.7020	0	0	50	18	32	4056.2409		-2	54	14	40	3980.5190	2	1	
44	2	42	3348.3891	2	-1	47	8	40	3537.6143	1	0	51	1	51	3499.8263	0	1	54	15	39	4028.0270	4	3	
44	3	41	3367.4231	2	0	47	9	39	3565.1197	1	0	51	2	50	3528.0149	1	1	54	17	37	4132.6069	3	-3	
44	4	40	3381.7935	2	2	47	10	38	3596.1458	3	-2	51	3	49	3554.1448	5	3	55	1	55	3625.4142		1	

44	5	39	3392.6605	3	0	47	11	37	3630.6050	1	-1	51	4	48	3577.9811	3	4	55	2	54	3655.9324	4	-1
44	6	38	3406.1915	2	-1	47	12	36	3668.3818	1	1	51	5	47	3599.4946	3	3	55	3	53	3684.4101	5	0
44	7	37	3425.5823	3	1	47	13	35	3709.4640	2	-2	51	6	46	3619.6174	2	2	55	4	52	3710.6171	6	2
44	8	36	3449.5331	1	0	47	14	34	3753.7943	4	-1	51	7	45	3640.4951	2	0	55	5	51	3734.3720	3	2
44	9	35	3477.1970	2	3	47	15	33	3801.3340	2	-3	51	8	44	3664.1461	1	0	55	6	50	3756.1090	3	0
44	10	34	3508.3376	2	-1	47	16	32	3852.0489	1	2	51	9	43	3691.3705	2	2	55	7	49	3777.5647	5	0
44	11	33	3542.8693	1	0	47	17	31	3905.9043	3	1	51	10	42	3722.1978	2	1	55	8	48	3801.0569	4	0
44	12	32	3580.6970	1	-2	47	18	30	3962.8681	3	3	51	12	40	3794.2143	-1	55	9	47	47	3827.9544	1	-1
44	13	31	3621.8087	2	0	48	0	48	3411.7155	3	0	51	13	39	3835.2419	0	55	10	46	46	3858.5241	0	1
44	14	30	3666.1538	1	-1	48	1	47	3438.1532	1	0	51	14	38	3879.5406	4	3	55	12	44	3930.2477	2	2
44	15	29	3713.6978	4	-1	48	2	46	3462.4927	2	-1	51	15	37	3927.0658	4	-6	55	14	42	4015.4487	0	0
44	16	28	3764.4076	1	-1	48	3	45	3484.2372	3	3	51	16	36	3977.7811	2	2	56	0	56	3658.2580	2	2
44	17	27	3818.2515	2	1	48	4	44	3501.9263	3	2	52	0	52	3530.3547	2	-1	56	1	55	3689.3579	2	0
45	1	45	3328.8204	3	0	48	5	43	3514.5905	2	0	52	1	51	3559.1258	-2	56	2	54	54	3718.4184	2	1
45	2	44	3353.5070	1	-1	48	6	42	3527.0483	3	-5	52	2	50	3585.8344	8	1	56	3	53	3745.1649	2	0
45	3	43	3376.1055	3	3	48	7	41	3544.9773	1	-1	52	3	49	3610.1258	3	-1	56	4	52	3768.9393	4	-2
45	4	42	3396.4493	3	2	48	8	40	3568.3291	2	-2	52	4	48	3630.9994	2	1	56	5	51	3787.9638	4	11
45	5	41	3415.0002	2	0	48	9	39	3595.7191	1	1	52	5	47	3646.5697	5	0	56	6	50	3801.8565	5	-4
45	6	40	3433.5074	4	-3	48	10	38	3626.6971	2	1	52	6	46	3659.0463	4	-4	56	7	49	3816.5441	4	-9
45	7	39	3454.1850	2	0	48	12	36	3698.8840	2	0	52	7	45	3675.2089	2	-3	56	8	48	3837.4112	5	-4
45	8	38	3478.2367	4	2	48	13	35	3739.9544	3	-1	52	8	44	3697.5775	3	-3	56	9	47	3863.7709	2	-3
45	9	37	3505.8604	1	-1	48	14	34	3784.2783	3	2	52	9	43	3724.5619	2	0	56	10	46	3894.2182	4	5
45	10	36	3536.9665	0	-2	48	15	33	3831.8152	4	-3	52	10	42	3755.3161	2	-1	56	13	43	4006.7779	1	1
45	11	35	3571.4761	2	0	48	16	32	3882.5306	3	-2	52	12	40	3827.2659	3	-3	56	14	42	4051.0139	1	3
45	12	34	3609.2884	1	0	49	1	49	3440.5067	3	3	52	13	39	3868.2767	3	1	57	1	57	3691.6791	1	-9
45	13	33	3650.3913	1	0	49	2	48	3467.5289	3	2	52	14	38	3912.5645	3	-3	57	2	56	3723.3616	2	-3
45	14	32	3694.7319	1	-3	49	3	47	3492.4815	14	-4	52	15	37	3960.0853	-2	57	3	55	55	3753.0106	6	0
45	15	31	3742.2754	1	0	49	4	46	3515.1406	2	2	52	16	36	4010.7994	5	5	57	4	54	3780.4042	2	0
45	16	30	3792.9872	0	0	49	5	45	3535.5999	1	1	52	17	35	4064.6679	4	2	57	5	53	3805.3232	5	2
45	17	29	3846.8355	4	5	49	6	44	3555.0721	3	3	53	1	53	3561.4623	-2	57	6	52	52	3828.0035	4	3
45	18	28	3903.7871	1	1	49	7	43	3575.8078	2	-1	53	2	52	3590.8159	4	-9	57	7	51	3849.9126	2	2
46	0	46	3355.8722	2	-2	49	8	42	3599.5832	2	-1	53	3	51	3618.1211	1	1	57	8	50	3873.4013	3	2
46	1	45	3381.1416	2	1	49	9	41	3626.9551	1	0	53	4	50	3643.1415	4	3	57	9	49	3900.1304	4	6
46	2	44	3404.2872	4	2	49	10	40	3657.8887	2	-1	53	5	49	3665.7576	1	1	57	10	48	3930.5468	4	-3
46	3	43	3424.7019	3	2	49	12	38	3730.0234	3	-1	53	6	48	3686.6388	4	5	58	1	57	3757.9432	1	-3
46	4	42	3440.7259	1	1	49	13	37	3771.0809	2	0	53	7	47	3707.7525	2	-1	58	3	55	3816.1289	2	2
46	5	41	3452.3294	4	-2	49	15	35	3862.9317	4	3	53	8	46	3731.3044	1	1	58	4	54	3841.2628	1	4
46	6	40	3465.2216	4	0	49	16	34	3913.6472	3	3	53	9	45	3758.3691	3	1	58	5	53	3862.0268	2	-1
46	7	39	3483.9419	3	1	49	17	33	3967.5087	1	0	53	10	44	3789.0751	3	-1	58	7	51	3891.4235	4	-8
46	8	38	3507.6306	1	0	50	0	50	3469.8766	2	0	53	12	42	3860.9553	3	-2	58	8	50	3911.3603	3	-2
46	9	37	3535.1701	1	0	50	1	49	3497.4818	1	53	13	41	41	3901.9481	6	58	9	49	49	3937.2837	2	-2
46	10	36	3566.2363	3	2	50	2	48	3523.0085	4	2	53	14	40	3946.2242	1	-1	58	10	48	3967.5335	6	7
46	11	35	3600.7213	1	-1	50	3	47	3546.0415	4	0	53	16	38	4044.4504	-1	59	1	59	59	3760.2597	1	6
46	12	34	3638.5166	1	1	50	4	46	3565.3562	1	1	54	0	54	3593.1491	2	59	2	58	58	3793.1031	0	0
59	3	57	3823.9215	3	2	62	0	62	3867.4616	0	64	3	61	61	4042.8213	-2	68	4	64	64	4236.8862	4	-6
59	4	56	3852.5006	1	2	62	1	61	3902.0472	1	-5	64	4	60	4071.8017	3	-7	69	1	69	4137.8053	7	7
59	5	55	3878.8997	3	0	62	2	60	3934.6161	2	0	65	1	65	3979.8620	2	6	69	2	68	4176.4473	2	2
59	6	54	3902.2959	4	0	62	3	59	3964.9565	3	65	2	64	64	4016.1874	0	69	3	67	67	4213.0854	9	5
59	7	53	3924.7729	1	-1	62	4	58	3992.6840	7	65	3	63	63	4050.5020	-5	70	0	70	70	4178.7314	3	-1
59	8	52	3948.3304	4	1	62	5	57	4016.7344	4	-1	65	4	62	4082.6232	-1	70	1	69	69	4217.9525	2	-0
59	9	51	3974.8977	2	2	62	6	56	4035.0329	5	6	65	5	61	4112.3050	5	70	4	66	66	4322.8602	1	3
60	0	60	3795.4157	3	3	62	8	54	4067.4892	4	3	66	0	66	4018.4825	2	71	2	70	70	4260.0332	4	-6
60	1	59	3828.8400	2	-4	63	1	63	3904.3516	6	66	1	65	65	4055.3872	-4	72	0	72	72	4262.3136	5	5
60	2	58	3860.2415	4	0	63	2	62	3939.5168	-5	66	2	64	64	4090.2830	4	-8	73	1	73	4304.9693	15	15



Table 2 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	$\Delta$	$\delta$	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	$\Delta$	$\delta$	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	$\Delta$	$\delta$				
1			2	3	4	1			2	3	4	1			2	3	4				
60	5	55	3938.2874	8	63	3	61	3972.6683	2	-1	67	1	67	4057.6800	2	74	0	74	4348.1978	2	
60	8	52	3988.0413	5	63	4	60	4003.6119	5	5	67	2	66	4095.1641	2	-3	74	1	73	4389.7306	-1
61	2	60	3865.1553	2	-1	63	6	4057.9880	9	-7	67	3	65	4130.6414	3	-4	75	1	75	4392.0036	5
61	3	59	3897.1408	-2	64	0	64	3941.8181	5	5	68	1	67	4135.5173	-3	76	0	76	4436.3848	15	
61	4	58	3926.9037	2	4	64	1	3977.5636	4	-3	68	2	66	4171.5745	-8	76	1	75	4479.0705	-4	
61	5	57	3954.1933	1	3	64	2	4011.2968	4	-1	68	3	65	4205.4553	8						

<sup>a</sup> In Table 2,  $\Delta$  is the experimental uncertainty of the energy value, equal to one standard error in units of  $10^{-4}$  cm<sup>-1</sup>;  $\delta$  is the difference  $E^{\text{exp.}} - E^{\text{calc.}}$ , also in units of  $10^{-4}$  cm<sup>-1</sup>. When the  $\Delta$ -value is absent, the corresponding energy level was determined from the single transition and was not used in the fit.

the differences between predicted and “experimental” energy values from column 2 of Table 2 were determined. All the differences then were divided into groups (the first group includes differences for all energy states with  $31 \leq J \leq 40$ ; the second group includes differences for all energy states with  $41 \leq J \leq 50$ ; etc.). For each group the value of the *rms* deviation was determined, and the result is illustrated by the curve **A** in Fig. 3. The curves **B–D** in Fig. 3 illustrate the behavior of the *rms* deviation for the following test fittings: for the curve **B**, all “experimental” ro-vibrational energies with  $0 \leq J \leq 40$  were fitted, and then the *rms* deviations were determined for the groups of states with  $41 \leq J \leq 50$ ,  $51 \leq J \leq 60$ , etc. Analogously, the curves **C** and **D** correspond to the fits with  $0 \leq J \leq 50$  and  $0 \leq J \leq 60$ , respectively. As a result, one can easily make a conclusion about the predictive power of the present results from a simple visible inspection of curves in Fig. 3.

*The  $2\nu_1 + \nu_2$  absorption band.* As is seen from Fig. 1, the  $2\nu_1 + \nu_2$  band is considerably weaker in comparison with the  $2\nu_3$  band. In this case, it should be mentioned that the  $2\nu_1 + \nu_2$  band was not analyzed earlier in the literature. Only the  $2\nu_1 + \nu_2 - \nu_2$  hot band and obtained on that basis some ro-vibrational energy levels of the state, (210), were discussed in Ref. [6] (in this case, the number of assigned transitions was about 200 with  $J^{\text{max.}} = 33$  and  $K_a^{\text{max.}} = 13$ ). In our analysis, we were able to assign about 1250 transitions to the  $2\nu_1 + \nu_2$  band, with the values of quantum numbers  $J^{\text{max.}} = 43$  and  $K_a^{\text{max.}} = 17$ . The list of assigned transitions is presented electronically as Supplementary Materials of this article, and Table 5 gives the list of upper ro-vibrational levels of the state (210) obtained on that basis.

As the analysis showed, to fulfill a correct description of our “experimental” upper energy levels, it is not necessary to take into account resonance interactions in the Hamiltonian model. On that reason, the Hamiltonian of isolated vibrational state in the form of Eq. (2) was used in the fit of energies from Table 5. Results are shown in column 2 of Table 6. Values in parentheses are  $1\sigma$  statistical confidence intervals. Parameters that are given in the column 2 of Table 6 without parentheses were constrained to their initial values. In its turn, the initial values of the *A*, *B*, and *C* parameters were estimated in accordance with the formula

$$B_{\beta}^{(210)} = B_{\beta}^{(010)} - 2\alpha_{\beta}^1, \quad (6)$$

where numerical values of the  $\alpha_{\beta}^1$ -coefficients were calculated with the intramolecular potential parameters from Ref. [2] (the initial value of the band center was also calculated with the intramolecular potential parameters from Ref. [2]), and the initial values of all centrifugal distortion parameters were constrained to the values of corresponding centrifugal distortion parameters of the (010) state from Ref. [13].

For comparison with the obtained results, column 4 of Table 6 presents values of parameters obtained in Ref. [6] from analysis of the  $2\nu_1 + \nu_2 - \nu_2$  hot band.

One can see satisfactory agreement between both sets of parameters. To illustrate the accuracy of the

**Table 3**Spectroscopic parameters of the (002), and (130) vibrational states of the SO<sub>2</sub> molecule (in cm<sup>-1</sup>).

Parameter	(002) <sup>a</sup>	(130) <sup>a</sup>	(002) <sup>b</sup>	(130) <sup>b</sup>	(002) <sup>c</sup>	(130) <sup>c</sup>
1	2	3	4	5	6	7
<i>E</i>	2713.3820964 (30)	2693.72786(85)	2713.487	2693.852	2713.382639	2693.6348
<i>A</i>	1.9861939404(590)	2.15161	1.985934935	2.15161	1.986194772	2.15230
<i>B</i>	0.34183912706(823)	0.34271	0.3418419684	0.34271	0.3418394940	0.342732
<i>C</i>	0.29133785814(845)	0.290598762(646)	0.2913324449	0.29051	0.2913376139	0.290575
$\Delta_K \times 10^4$	0.83689963(228)	1.1937	0.83664393	1.1937	0.83685040	1.166
$\Delta_{JK} \times 10^5$	-0.42294977(603)	-0.4323	-0.4238669	-0.4323	-0.42264699	-0.423
$\Delta_J \times 10^6$	0.22558289(326)	0.2204	0.22562288	0.2204	0.22565387	0.222
$\delta_K \times 10^5$	0.07269326(686)	0.1525	0.0732050	0.1525	0.07294151	0.1476
$\delta_J \times 10^7$	0.58049273(911)	0.5758	0.5812692	0.5758	0.5816883	0.579
$H_K \times 10^7$	0.11760616(236)	0.2352	0.117196	0.2352	0.1166992	0.2172
$H_{KJ} \times 10^9$	-0.598864 (104)	-1.0300	-0.567638	-1.0300	-0.537558	-0.740
$H_{JK} \times 10^{11}$	1.55667(144)	0.4226	1.781	0.4226	0.13250	0.13250
$H_J \times 10^{12}$	0.443871 (494)	0.0438	0.37879	0.0438	0.424375	0.382057
$h_K \times 10^9$	1.2439	1.0519	1.2439	1.0519	0.532262	0.557913
$h_{JK} \times 10^{12}$	-0.52494	-6.4055	-0.52494	-6.4055	-0.37865	-0.37865
$h_J \times 10^{12}$	0.198218	0.2109	0.198218	0.2109	0.198255	0.1803752
$L_K \times 10^{11}$	-0.40709708(325)	-0.4751	-0.27297	-0.4751	-0.269164	-0.27665
$L_{KJ} \times 10^{12}$	0.15269	-0.1154	0.15269	-0.1154	0.193042	0.144532
$L_{JK} \times 10^{14}$	1.247		1.247		0.007728	0.007728
$L_{JJ} \times 10^{15}$	-0.36944		-0.36944		-1.2014	-1.2014
$L_J \times 10^{17}$	-0.4657		-0.4657		-0.3099	-0.3099
$P_K \times 10^{14}$	0.07708		0.07708		0.074675	0.074675
$P_{KKJ} \times 10^{16}$	-0.12873		-0.12873		-0.26122	-0.26122
$F_0$	0.0231170(720)				0.02047384	

<sup>a</sup> Obtained from the fit. Values in parentheses are 1 $\sigma$  statistical confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to values from columns 4 or 5.

<sup>b</sup> The initial values of spectroscopic parameters (see text, for details).

<sup>c</sup> Reproduced from Ref. [5].

**Table 4**Microwave transitions in the (002) state of SO<sub>2</sub> (in MHz).

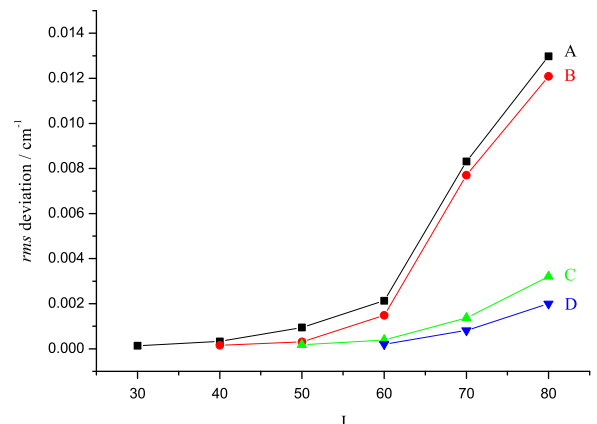
Transition	Exp. <sup>a</sup>	Our <sup>b</sup>	Ref. [5] <sup>c</sup>
1	2	3	4
1 <sub>1</sub> 1 ← 0 <sub>0</sub> 0	68276.3	68276.45	68276.49
2 <sub>1</sub> 1 ← 2 <sub>0</sub> 2	52356.93	52356.90	52356.93
4 <sub>0</sub> 4 ← 3 <sub>1</sub> 3	29922.82	29923.30	29922.82
4 <sub>2</sub> 2 ← 5 <sub>1</sub> 5	67295.4	67295.17	67294.74
6 <sub>1</sub> 5 ← 6 <sub>0</sub> 6	67790.28	67790.70	67790.28
6 <sub>2</sub> 4 ← 7 <sub>1</sub> 7	41495.15	41495.00	41494.04
8 <sub>1</sub> 7 ← 7 <sub>2</sub> 6	27700.88	27701.04	27702.28
8 <sub>2</sub> 6 ← 9 <sub>1</sub> 9	21843.68	21843.24	21841.42

<sup>a</sup> Experimental values from Ref. [16].

<sup>b</sup> Calculated with the parameters from Table 3 of the present paper.

<sup>c</sup> Reproduced from Table 3 of Ref. [5] (reproduction of the microwave experimental transitions with the parameters from Ref. [5]).

parameters from column 2 of Table 6, it should be mentioned that the *rms*-deviation between the experimental values of ro-vibrational energies from Table 5 and values calculated with the obtained parameters is 0.00014 cm<sup>-1</sup> (see also column 4 of



**Fig. 3.** Illustration of the predictive power of the model and results of the present paper: The curves A–D give the dependence of the value of the *rms* deviation of the predicted ro-vibrational energy values of the (002) vibrational state against the value of quantum number *J*. These curves A–D correspond to the cases when the parameters used for the prediction of higher ro-vibrational energies have been obtained from the fit of “experimental” energy values with  $0 \leq J \leq 30$ ,  $0 \leq J \leq 40$ ,  $0 \leq J \leq 50$ , and  $0 \leq J \leq 60$ , respectively (see text for more details).

Table 5 where the values  $\Delta$  of concrete differences are given) which is very close to the experimental uncertainty.

Table 5

Experimental ro-vibrational term values for the (210) vibrational state of the SO<sub>2</sub> molecule (in cm<sup>-1</sup>).<sup>a</sup>

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>
1			2	3	4	1			2	3	4	1			2	3	4
2	0	2	2809.0806	1	2	11	3	9	2864.7084	1	1	15	12	4	3133.5801		0
2	1	1	2810.9112	1	1	11	4	8	2876.9430	0	0	15	13	3	3176.6916		-2
2	2	0	2816.0958	3	3	11	5	7	2892.6730	1	1	15	14	2	3223.1253	1	0
3	1	3	2812.5757	1	1	11	6	6	2911.8903	2	-1	15	15	1	3272.8527		-1
3	2	2	2817.9879		-1	11	7	5	2934.5775	1	-1	16	0	16	2890.4500	0	0
3	3	1	2826.7505	1	1	11	8	4	2960.7180	1	0	16	1	15	2897.1918	1	0
4	0	4	2813.4830	0	-1	11	9	3	2990.2936		0	16	2	14	2902.0440	0	0
4	1	3	2815.5038	1	0	11	10	2	3023.2848	0	0	16	3	13	2909.4327	1	0
4	2	2	2820.5282	1	-1	11	11	1	3059.6706	1	1	16	4	12	2921.3169	1	-1
4	3	1	2829.2775	1	0	12	0	12	2855.4325	1	-1	16	5	11	2936.9752	1	0
4	4	0	2841.5339		-1	12	1	11	2859.8412	1	0	16	6	10	2956.1639	1	0
5	1	5	2818.0207	1	-1	12	2	10	2864.2412	1	0	16	7	9	2978.8378	2	-1
5	2	4	2823.6650	1	-1	12	3	9	2872.3822	2	2	16	8	8	3004.9731	1	1
5	3	3	2832.4371	2	1	12	4	8	2884.5418	1	1	16	9	7	3034.5485	3	-1
5	4	2	2844.6928	1	2	12	5	7	2900.2629	2	0	16	10	6	3067.5430	1	0
5	5	1	2860.4376	0	0	12	6	6	2919.4770	1	-1	16	11	5	3103.9348	1	1
6	0	6	2820.3654	1	-1	12	7	5	2942.1630	0	-1	16	12	4	3143.7000		2
6	1	5	2822.7108	0	0	12	8	4	2968.3033	1	1	16	13	3	3186.8135	1	1
6	2	4	2827.5233	2	0	12	9	3	2997.8791	0	0	16	15	1	3282.9795	1	1
6	3	3	2836.2310	0	0	12	10	2	3030.8713		0	16	16	0	3335.9748	2	2
6	4	2	2848.4838	1	-1	12	11	1	3067.2582	1	1	17	1	17	2900.8183	1	-1
6	5	1	2864.2282		0	12	12	0	3107.0168	0	-1	17	2	16	2910.0927	0	0
6	6	0	2883.4513	1	0	13	1	13	2863.7557	2	-2	17	3	15	2919.8320	1	1
7	1	7	2825.8737	1	-1	13	2	12	2871.4044	4	0	17	4	14	2932.0815	1	0
7	2	6	2831.8564	1	0	6	3	11	2880.5456	1	-1	17	5	13	2947.7434	1	0
7	3	5	2840.6562	0	0	13	4	10	2892.7725	4	0	17	6	12	2966.9225	1	0
7	4	4	2852.9079	1	0	13	5	9	2908.4874	1	0	17	7	11	2989.5911	0	0
7	5	3	2868.6512	1	0	13	6	8	2927.6973	1	-1	17	8	10	3015.7238	2	0
7	6	2	2887.8738	1	-2	13	7	7	2950.3816	3	0	17	9	9	3045.2983	1	0
7	7	1	2910.5628		0	13	8	6	2976.5212	1	0	17	10	8	3078.2930	1	0
8	0	8	2829.6837	0	0	13	9	5	3006.0973	2	0	17	11	7	3114.6855	0	1
8	1	7	2832.5185	2	1	13	10	4	3039.0901	1	-2	17	12	6	3154.4522	2	1
8	2	6	2837.1164	1	0	13	11	3	3075.4784	1	1	17	13	5	3197.5678		-1
8	3	5	2845.7237	3	0	13	12	2	3115.2386		-1	17	14	4	3244.0058		-3
8	4	4	2857.9653	0	-1	13	13	1	3158.3464		-1	17	15	3	3293.7391		1
8	5	3	2873.7066	1	-1	14	0	14	2871.7907	0	0	17	17	1	3402.9708		1
8	6	2	2892.9291	1	1	14	1	13	2877.2868	2	1	18	0	18	2911.4094	1	-1
8	7	1	2915.6177	1	-1	14	2	12	2881.8110	2	-1	18	1	17	2919.5011	0	1
8	8	0	2941.7576	1	-1	14	3	11	2889.5925	0	0	18	2	16	2924.9119	0	0
9	1	9	2836.1229	1	0	14	4	10	2901.6498	1	0	18	3	15	2931.9397	2	1
9	2	8	2842.5522	0	0	14	5	9	2917.3474	1	1	18	4	14	2943.5570	0	0
9	3	7	2851.4121	1	-1	14	6	8	2936.5518	3	1	18	5	13	2959.1517	1	-2
9	4	6	2863.6566	1	0	14	7	7	2959.2334	1	0	18	6	12	2978.3168	1	1
9	5	5	2879.3953	1	0	14	8	6	2985.3719	1	-1	18	7	11	3000.9788	1	0
9	6	4	2898.6166	1	0	14	9	5	3014.9483	1	1	18	8	10	3027.1081	2	1
9	7	3	2921.3052	0	0	14	10	4	3047.9418	1	0	18	9	9	3056.6812	0	0
9	8	2	2947.4454	0	0	14	11	3	3084.3312	0	0	18	10	8	3089.6758	2	0

9	9	1	2977.0198		0	14	12	2	3124.0929	4	-2	18	11	7	3126.0692	2	1
10	0	10	2841.3874	0	-1	14	13	1	3167.2027	0	-1	18	12	6	3165.8373		1
10	1	9	2844.9051	1	-1	14	14	0	3213.6341		1	18	13	5	3208.9551		1
10	2	8	2849.3460	0	0	15	1	15	2881.1139	1	-1	18	15	3	3305.1322		8
10	3	7	2857.7678	1	0	15	2	14	2889.5283	0	0	18	16	2	3358.1324		-4
10	4	6	2869.9828	2	0	15	3	13	2898.9223	1	0	18	17	1	3414.3689		-3
10	5	5	2885.7173	1	0	15	4	12	2911.1503	2	0	19	1	19	2922.8607	0	0
10	6	4	2904.9369	3	0	15	5	11	2926.8427	2	0	19	2	18	2933.0780	1	0
10	7	3	2927.6250	0	-1	15	6	10	2946.0405	1	1	19	3	17	2943.2643	1	1
10	8	2	2953.7655	1	0	15	7	9	2968.7187	1	0	19	4	16	2955.5699	1	0
10	9	1	2983.3405	0	0	15	8	8	2994.8560	1	1	19	5	15	2971.1947	0	0
10	10	0	3016.3308	1	0	15	9	7	3024.4320	1	1	19	6	14	2990.3469	1	0
11	1	11	2848.7547	0	0	15	10	6	3057.4260	1	0	19	7	13	3013.0011	1	1
11	2	10	2855.7399	1	-1	15	11	5	3093.8169	3	3	19	8	12	3039.1263	1	1
19	9	11	3068.6974	2	-1	23	12	12	3232.2549		-7	28	10	18	3238.3420		1
19	10	10	3101.6917	1	1	23	13	11	3275.3824		-3	28	11	17	3274.7265	2	-1
19	11	9	3138.0855	1	-1	24	0	24	2988.1268	0	0	28	12	16	3314.5002		5
19	12	8	3177.8553		1	24	1	23	3000.3813	1	1	28	14	14	3404.0971		5
19	13	7	3220.9748	1	-2	24	2	22	3008.8844	1	1	29	1	29	3067.9651	1	0
19	14	6	3267.4183		1	24	3	21	3015.6996	2	1	29	2	28	3083.6917	1	0
20	0	20	2934.6729	1	0	24	4	20	3025.9323		0	29	3	27	3097.6633	1	0
20	1	19	2944.1604	1	-1	24	5	19	3041.0481	1	-1	29	4	26	3111.3176	1	1
20	2	18	2950.3748	1	0	24	6	18	3060.0587	2	-2	29	5	25	3126.8856	1	0
20	3	17	2957.1453	0	0	24	7	17	3082.6457	1	0	29	6	24	3145.7541	0	0
20	4	16	2968.3886	2	0	24	8	16	3108.7339	1	1	29	7	23	3168.2155	1	-1
20	5	15	2983.8839	2	1	24	9	15	3138.2853	1	0	29	8	22	3194.2278		0
20	6	14	3003.0140	0	1	24	10	14	3171.2709	2	0	29	9	21	3223.7346	1	0
20	7	13	3025.6585	0	0	24	11	13	3207.6637	3	-2	29	10	20	3256.6952	1	0
20	8	12	3051.7783	2	-2	24	12	12	3247.4377		-5	29	11	19	3293.0764	1	0
20	9	11	3081.3472	1	-1	24	14	10	3337.0227		4	29	12	18	3332.8484		0
20	10	10	3114.3408	2	1	25	1	25	3002.9576	0	0	30	0	30	3085.6606	0	0
20	11	9	3150.7352	1	1	25	2	24	3016.3712	0	0	30	1	29	3101.8170	2	-2
20	12	8	3190.5059		0	25	3	23	3028.5375	1	1	30	2	28	3114.7132	1	1
20	13	7	3233.6275		-1	25	4	22	3041.3817	1	1	30	3	27	3123.5291	2	1
20	15	5	3329.8150		1	25	5	21	3056.9048	1	1	30	4	26	3132.4499	1	-2
21	1	21	2947.2342	1	0	25	6	20	3075.9155	2	0	30	5	25	3146.2523	2	4
21	2	20	2958.4647	0	-1	25	7	19	3098.4837	0	-2	30	6	24	3164.8372	1	2
21	3	19	2969.2049	1	0	25	8	18	3124.5604	0	0	30	7	23	3187.2465	1	-1
21	4	18	2981.6175	0	1	25	9	17	3154.1054	1	-1	30	8	22	3213.2365	1	0
21	5	17	2997.2018	1	0	25	10	16	3187.0875	1	-1	30	9	21	3242.7303	4	2
21	6	16	3016.3176	1	0	25	11	15	3223.4793		0	30	10	20	3275.6831		0
21	7	15	3038.9512	0	0	25	12	14	3263.2537		-1	31	1	31	3103.9463	1	0
21	8	14	3065.0651	1	0	26	0	26	3018.3229	2	-1	31	2	30	3120.8555	2	0
21	9	13	3094.6308	2	1	26	1	25	3031.9108	0	0	31	3	29	3135.8437		0
21	10	12	3127.6231	2	1	26	2	24	3041.8125	2	0	31	4	28	3150.0644	1	0
21	11	11	3164.0174	1	-2	26	3	23	3049.0175	0	0	31	5	27	3165.7335	2	1
21	12	10	3203.7896	3	1	26	4	22	3058.7118	1	0	31	6	26	3184.5263	1	0
21	14	8	3293.3612		-1	26	5	21	3073.5040	1	0	31	7	25	3206.9157	1	-1
21	15	7	3343.1063		3	26	6	20	3092.4170	1	1	31	8	24	3232.8822		-3
21	16	6	3396.1177		3	26	7	19	3114.9596	2	0	31	9	23	3262.3616		0
22	0	22	2960.2442	2	1	26	8	18	3141.0228	1	-1	31	10	22	3295.3057	1	1
22	1	21	2971.1285	0	0	26	9	17	3170.5603	3	1	31	11	21	3331.6776		-1
22	2	20	2978.3845	0	1	26	10	16	3203.5382	1	-1	31	12	20	3371.4456		1
22	3	19	2985.0668	1	-1	26	11	15	3239.9282	0	0	32	0	32	3122.8028	0	0

Table 5 (continued)

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>
1			2	3	4	1			2	3	4	1			2	3	4
22	4	18	2995.8366	0	0	26	12	14	3279.7025	3	0	32	1	31	3140.2081	2	-2
22	5	17	3011.1792	1	0	27	1	27	3034.3017	1	0	32	2	30	3154.5936	1	0
22	6	16	3030.2597	2	0	27	2	26	3048.8607	2	0	32	3	29	3164.6072	3	0
22	7	15	3052.8797	1	0	27	3	25	3061.8872	1	-1	32	4	28	3173.4385	2	0
22	8	14	3078.9864	2	0	27	4	24	3075.0842	1	1	32	5	27	3186.5961	0	1
22	9	13	3108.5483	1	1	27	5	23	3090.6091	2	0	32	6	26	3204.9163	1	-1
22	10	12	3141.5386	2	-1	27	6	22	3109.5521	1	0	32	7	25	3227.2280		-4
22	11	11	3177.9332	1	0	27	7	21	3132.0728		-2	32	8	24	3253.1665	1	0
22	12	10	3217.7063		0	27	8	20	3158.1214	1	0	32	9	23	3282.6291	1	0
22	13	9	3260.8311		-3	27	9	19	3187.6498	0	0	32	10	22	3315.5629	1	-1
22	14	8	3307.2814		-8	27	10	18	3220.6233		3	32	12	20	3391.6948		4
23	1	23	2973.9342	1	-1	27	11	17	3257.0104		-2	33	1	33	3142.2444	1	0
23	2	22	2986.2345	1	0	28	0	28	3050.8340	1	-1	33	2	32	3160.3460	5	3
23	3	21	2997.6360	0	0	28	1	27	3065.7205	1	0	33	3	31	3176.4084	2	0
23	4	20	3010.2230	1	0	28	2	26	3077.1069	0	1	33	4	30	3191.3046	2	1
23	5	19	3025.7701	1	0	28	3	25	3084.9784	1	0	33	5	29	3207.1487	1	1
23	6	18	3044.8389	1	-1	28	4	24	3094.2097	2	1	33	6	28	3225.8732	1	0
23	7	17	3067.4445	1	1	28	5	23	3108.5644	1	1	33	7	27	3248.1778	2	0
23	8	16	3093.5424	1	0	28	6	22	3127.3403	1	-1	33	8	26	3274.0885	2	0
23	9	15	3123.0995	1	-1	28	7	21	3149.8251	1	-1	33	9	25	3303.5329	1	0
23	10	14	3156.0881	1	1	28	8	20	3175.8561	4	-1	33	10	24	3336.4557		1
23	11	13	3192.4819		0	28	9	19	3205.3748	2	3	34	0	34	3162.2603	1	1
34	1	33	3180.8998	1	0	36	3	33	3254.0752		3	39	2	38	3292.7327		-1
34	2	32	3196.7295	1	-4	36	4	32	3263.5668	2	2	39	3	37	3312.2427		-1
34	3	31	3208.1459	1	1	36	5	31	3275.3916	1	-1	39	4	36	3329.7543	5	-2
34	4	30	3217.1572		2	36	6	30	3292.8763	1	1	39	5	35	3346.7002	1	1
34	5	29	3229.6307	1	1	36	7	29	3314.8948	7	2	39	6	34	3365.3914	2	4
34	6	28	3247.5908	2	0	36	8	28	3340.6888		1	39	7	33	3387.3810		-1
34	7	27	3269.7754	2	-3	37	1	37	3225.7877	2	1	40	0	40	3294.5200	1	-1
34	8	26	3295.6494		0	37	2	36	3246.2872	1	-1	40	1	39	3316.8101		0
34	9	25	3325.0732		-1	37	3	35	3264.6217		0	40	2	38	3336.6883	2	0
34	10	24	3357.9836		2	37	4	34	3281.1733	1	-1	40	3	37	3352.8593	0	0
35	1	35	3182.8582	3	-2	37	5	33	3297.6460	1	0	40	4	36	3364.2312	2	-3
35	2	34	3202.1574	1	0	37	6	32	3316.3046	1	-1	40	6	34	3391.3679		-3
35	3	33	3219.3394	1	0	37	7	31	3338.4060	3	1	40	7	33	3412.8771		-3
35	4	32	3235.0154	0	-1	37	9	29	3393.5167		-3	41	1	41	3318.5878	1	-2
35	5	31	3251.1236	0	0	38	0	38	3248.1197	1	1	41	2	40	3341.4921		2
35	6	30	3269.7988		1	38	1	37	3269.1987	1	-1	41	3	39	3362.1931		-1
35	7	29	3292.0065	1	1	38	2	36	3287.7687		0	41	5	37	3398.2660		-2
35	8	28	3317.8488		-2	38	3	35	3302.3302		1	41	6	36	3417.0545		-2
35	9	27	3347.2509		3	38	4	34	3312.6130		-1	42	0	42	3343.2335		-1
35	10	26	3380.1467	2	2	38	5	33	3323.9093		-4	42	2	40	3387.8882		1
36	0	36	3204.0326	1	-1	38	6	32	3340.7932	2	0	42	3	39	3405.6293		-1
36	1	35	3223.8956	2	-2	38	7	31	3362.5922		-1	42	4	39	3418.3500		2
36	2	34	3241.1191	0	-1	39	1	39	3271.0312		2	43	2	42	3392.5637		2

<sup>a</sup> In Table 5, *Δ* is the experimental uncertainty of the energy value, equal to one standard error in units of  $10^{-4}$   $\text{cm}^{-1}$ ; *δ* is the difference  $E^{\text{exp.}} - E^{\text{calc.}}$ , also in units of  $10^{-4}$   $\text{cm}^{-1}$ . When the *Δ*-value is absent, the corresponding energy level was determined from the single transition and was not used in the fit.

**Table 6**  
Spectroscopic parameters of the (210) vibrational state of the SO<sub>2</sub> molecule (in cm<sup>-1</sup>).

Parameter	Value <sup>a</sup>	Value <sup>b</sup>	Value <sup>c</sup>
1	2	3	4
<i>E</i>	2807.1880897 (257)	2807.335	2807.18895
<i>A</i>	2.069176667 (125)	2.06875033	2.069161
<i>B</i>	0.3409396413 (144)	0.34092739	0.3409372
<i>C</i>	0.2902074164 (123)	0.28823791	0.2902061
<i>A<sub>K</sub></i> × 10 <sup>4</sup>	0.9864890 (132)	0.95810872	0.98623
<i>A<sub>JK</sub></i> × 10 <sup>5</sup>	-0.3776287 (148)	-0.40713108	-0.38216
<i>A<sub>J</sub></i> × 10 <sup>5</sup>	0.21953662 (503)	0.2210206	0.21836
<i>δ<sub>K</sub></i> × 10 <sup>5</sup>	0.1213483 (442)	0.1035275	0.1200
<i>δ<sub>J</sub></i> × 10 <sup>7</sup>	0.5667696 (402)	0.57074622	0.5655
<i>H<sub>K</sub></i> × 10 <sup>7</sup>	0.1634410 (356)	0.153334	0.1570
<i>H<sub>KJ</sub></i> × 10 <sup>9</sup>	-0.95079 (107)	-0.7569297	-0.9577
<i>H<sub>JK</sub></i> × 10 <sup>11</sup>	0.45728	0.45728	
<i>H<sub>J</sub></i> × 10 <sup>12</sup>	0.374579	0.374579	0.315
<i>h<sub>K</sub></i> × 10 <sup>9</sup>	0.761006	0.761006	0.6375
<i>h<sub>JK</sub></i> × 10 <sup>12</sup>	-0.77103	-0.77103	
<i>h<sub>J</sub></i> × 10 <sup>12</sup>	0.183225	0.183225	
<i>L<sub>K</sub></i> × 10 <sup>11</sup>	-0.372154	-0.372154	
<i>L<sub>KKJ</sub></i> × 10 <sup>12</sup>	0.23830	0.23830	
<i>L<sub>JK</sub></i> × 10 <sup>13</sup>	-0.1543	-0.1543	
<i>L<sub>JK</sub></i> × 10 <sup>16</sup>	-0.404	-0.404	
<i>L<sub>J</sub></i> × 10 <sup>17</sup>	-0.1060	-0.1060	
<i>l<sub>K</sub></i> × 10 <sup>12</sup>	-0.4530	-0.4530	
<i>l<sub>KJ</sub></i> × 10 <sup>14</sup>	0.274	0.274	
<i>l<sub>JK</sub></i> × 10 <sup>17</sup>	-0.24	-0.24	
<i>l<sub>J</sub></i> × 10 <sup>18</sup>	-0.64438	-0.64438	
<i>P<sub>K</sub></i> × 10 <sup>14</sup>	0.1046	0.1046	
<i>P<sub>KKKJ</sub></i> × 10 <sup>16</sup>	-0.58867	-0.58867	
<i>P<sub>KKJ</sub></i> × 10 <sup>18</sup>	-0.9947	-0.9947	
<i>P<sub>JK</sub></i> × 10 <sup>18</sup>	0.1222	0.1222	
<i>S<sub>K</sub></i> × 10 <sup>18</sup>	-0.226	-0.226	
<i>S<sub>KKKKJ</sub></i> × 10 <sup>19</sup>	0.1156	0.1156	

<sup>a</sup> Obtained from the fit. Values in parentheses are 1σ statistical confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to values from column 3.

<sup>b</sup> The initial values of spectroscopic parameters (see text, for details).

<sup>c</sup> Reproduced from Ref. [6].

### 5. The ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> “hot” band of SO<sub>2</sub>

For the study of the ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> hot band, the same procedure, as in Refs. [3,4], was used. Firstly, the experimental spectrum was filtered by taking the lines belonging to the 2ν<sub>3</sub> and 2ν<sub>1</sub>+ν<sub>2</sub> cold bands. Weak lines remained in the experimental spectrum belong, as we believed, to the ν<sub>2</sub>+2ν<sub>3</sub>-ν<sub>2</sub> hot band. Assignments of these remaining lines were made on the basis of the following procedure:

(1) Because the relative vibrational states, (002) and (130), are strongly interacting, it was assumed that the states (012) and (140) are strongly interacting also.

(2) The potential function of the SO<sub>2</sub> molecule from Ref. [2], that allows one to predict with a good accuracy the values of band centers (vibrational energy values), was used for the estimation of the energy values of the vibrational states (012) and (140). The value of the resonance interaction parameter,  $F_0^{(012)-(140)}$ , was

estimated to 0.046234 cm<sup>-1</sup> on the basis of the general formula (see, e.g., [16])

$$F_0^{(v_1 \nu_2 \nu_3)-(v_1+1 \nu_2+3 \nu_3-2)} = f_0^{1222/33} \left(\frac{\nu_1+1}{2}\right)^{1/2} \left(\frac{\nu_2+1}{2}\right)^{1/2} \left(\frac{\nu_2+2}{2}\right)^{1/2} \times \left(\frac{\nu_2+3}{2}\right)^{1/2} \left(\frac{\nu_3}{2}\right)^{1/2} \left(\frac{\nu_3-1}{2}\right)^{1/2}, \tag{7}$$

where  $f_0^{1222/33}$  is a constant and the value  $F_0^{(002)-(130)} = 0.023117$  cm<sup>-1</sup> (see column 2 of Table 3).

(3) Initial value of any spectroscopic parameter of the state (012) was estimated in accordance with a simple formula:

$$P^{(012)} = P^{(002)} + P^{(010)} - P^{(000)}. \tag{8}$$

At the same time, for the numerical estimation of the values of the spectroscopic parameters of the (140) state,

Table 7

Experimental ro-vibrational term values for the (012) vibrational state of the SO<sub>2</sub> molecule (in cm<sup>-1</sup>).<sup>a</sup>

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	<i>E</i>	<i>Δ</i>	<i>δ</i>	
1		2		3	4	1		2		3	4	1		2		3	4	1		2		3	4	
2	0	2	3224.8692		-4	11	3	9	3280.1877	1	4	16	6	10	3370.5309	1	0	21	4	18	3397.0525	2	0	
2	1	1	3226.6552		0	11	4	8	3292.1034	3	1	16	7	9	3392.6184		0	21	5	17	3412.2271	4	-2	
2	2	0	3231.7022		1	11	5	7	3307.4241		1	16	8	8	3418.0801	2	0	21	6	16	3430.8425	2	-1	
3	1	3	3228.3225		0	11	6	6	3326.1428	1	-3	16	9	7	3446.8954	5	-4	21	7	15	3452.8893	3	0	
3	2	2	3233.5993	3		2	11	7	5	3348.2439	5	2	16	10	6	3479.0397	2	2	21	8	14	3478.3300	1	-3
3	3	1	3242.1338	3	3	11	8	4	3373.7094	4	-1	16	11	5	3514.5056	3	4	21	9	13	3507.1375	2	0	
4	0	4	3229.2818	2	-5	11	9	3	3402.5241	1	0	16	12	4	3553.2572		-6	21	10	12	3539.2812	2	2	
4	1	3	3231.2596	3	-2	11	10	2	3434.6626	3	-3	16	13	3	3595.2772		1	21	11	11	3574.7516	5	-2	
4	2	2	3236.1463		1	12	0	12	3271.3021	2	1	17	1	17	3316.7357	3	2	21	12	10	3613.5145	2	3	
4	3	1	3244.6668	5	-1	12	1	11	3275.7010	1	-1	17	2	16	3325.9027	2	0	21	13	9	3655.5458		-8	
4	4	0	3256.6055		10	12	2	10	3279.9909	3	-1	17	3	15	3335.4480	2	-1	22	0	22	3376.2724	1	0	
5	1	5	3233.7796	1		12	3	9	3287.8862	4	3	17	4	14	3347.3856		-3	22	1	21	3387.1353	3	-3	
5	2	4	3239.2901		2	12	4	8	3299.7224		5	17	6	12	3381.3179	3	4	22	2	20	3394.4236	1	2	
5	3	3	3247.8333		-10	12	5	7	3315.0335	3	0	17	7	11	3403.3998		1	22	3	19	3400.9396	1	2	
5	4	2	3259.7712	1		12	6	6	3333.7492	3	-1	17	8	10	3428.8590	2	1	22	4	18	3411.3338		1	
5	5	1	3275.1088		18	12	8	4	3381.3142		-3	17	9	9	3457.6742	4	3	22	5	17	3426.2441		-2	
6	0	6	3236.1792	1	0	12	9	3	3410.1301	3	5	17	10	8	3489.8182	2	-1	22	6	16	3444.8219	1	0	
6	1	5	3238.4873		18	12	10	2	3442.2693		-3	17	11	7	3525.2856		4	22	7	15	3466.8546	1	0	
6	2	4	3243.1602	1	-1	12	11	1	3477.7292	2	2	17	12	6	3564.0398	3	-1	22	8	14	3492.2890	1	7	
6	3	3	3251.6377		-2	12	12	0	3516.4733		-1	17	13	5	3606.0609		-9	22	9	13	3521.0920	1	0	
6	4	2	3263.5710		-7	13	1	13	3279.6053		0	18	0	18	3327.3594	0	-1	22	11	11	3588.7059	7	5	
6	5	1	3278.9070		-1	13	2	12	3287.1366		-2	18	1	17	3335.4556	4	-2	22	12	10	3627.4695	3	2	
6	6	0	3297.6317		1	13	3	11	3296.0645	3	-3	18	2	16	3340.8340	4	0	22	13	9	3669.5045		1	
7	1	7	3241.6489		-1	13	4	10	3307.9738	2	1	18	3	15	3347.6314	1	1	23	2	22	3402.1790		2	
7	2	6	3247.5006	1	-1	13	5	9	3323.2790	3	-1	18	4	14	3358.8975	3	2	23	3	21	3413.4273	3	-2	
7	3	5	3256.0740	3	-1	13	6	8	3341.9908		1	18	5	13	3374.0764	2	2	23	5	19	3440.8729	2	2	
7	4	4	3268.0071	4	2	13	8	6	3389.5533	6	-4	18	6	12	3392.7414	2	-1	23	6	18	3459.4401		1	
7	5	3	3283.3414	1	2	13	9	5	3418.3693	6	-1	18	7	11	3414.8169		-1	23	7	17	3481.4581	2	1	
7	6	2	3302.0656	1	1	13	11	3	3485.9719		3	18	8	10	3440.2733	5	2	23	8	16	3506.8832	6	1	
7	7	1	3324.1673	5	3	14	0	14	3287.6828	1	0	18	9	9	3469.0870		0	23	10	14	3567.8222	2	-4	
8	0	8	3245.5146		1	14	1	13	3293.1798	1	-1	18	10	8	3501.2309		-7	23	11	13	3603.2938	3	-2	
8	1	7	3248.3174	2	2	14	3	11	3305.1468		-3	18	11	7	3536.7002	2	3	23	12	12	3642.0598	1	6	
8	2	6	3252.7816	2	0	14	4	10	3316.8743		-6	18	12	6	3575.4570		4	23	13	11	3684.0963	5	-4	
8	3	5	3261.1555		6	14	5	9	3332.1619	2	0	18	13	5	3617.4813		1	24	0	24	3404.2017		-1	
8	4	4	3273.0773	3	1	14	6	8	3350.8682	2	3	19	1	19	3338.8168		-2	24	1	23	3416.4156	1	-2	
8	5	3	3288.4096	2	1	14	7	7	3372.9634	3	3	19	2	18	3348.9305	4	-3	24	2	22	3424.9742		-3	
8	6	2	3307.1336	3	2	14	8	6	3398.4278	4	1	19	3	17	3358.9358	2	0	24	3	21	3431.6710	1	-1	
8	7	1	3329.2351	1	0	14	9	5	3427.2437		0	19	4	16	3370.9365		1	24	4	20	3441.5280		1	
8	8	0	3354.7003		3	14	10	4	3459.3859	0	19	5	15	15	3386.1508	7	1	24	5	19	3456.1969	2	1	
9	1	9	3251.9190	1	0	14	11	3	3494.8486	2	2	19	6	14	3404.8033	1	-1	24	6	18	3474.7013	4	4	
9	2	8	3258.2216	2	3	14	12	2	3533.5967	3	-1	19	7	13	3426.8709	2	0	24	7	17	3496.6996	3	0	
9	3	7	3266.8572	2	-1	14	13	1	3575.6111	1	1	19	8	12	3452.3223		-6	24	8	16	3522.1149	2	2	
9	4	6	3278.7829	3	1	15	1	15	3296.9955		0	19	9	11	3481.1353		1	24	9	15	3550.9084	3	-1	
9	5	5	3294.1127	2	1	15	2	14	3305.2980		-1	19	10	10	3513.2796	4	-3	24	10	14	3583.0469		3	
9	6	4	3312.8353	2	-1	15	3	13	3314.4873	-1	-1	19	11	9	3548.7496	1	5	24	11	13	3618.5173	4	-1	
9	7	3	3334.9373		3	15	4	12	3326.3998	4	2	20	0	20	3350.6594	1	0	24	12	12	3657.2840	2	0	
9	8	2	3360.4025		1	15	5	11	3341.6833		13	20	1	19	3360.1418	1	-2	24	13	11	3699.3243		5	
9	9	1	3389.2152	2	-2	15	6	10	3360.3813	5	1	20	2	18	3366.3568	1	-1	25	1	25	3419.0552	3	3	
10	0	10	3257.2368	1	0	15	7	9	3382.4727	4	-3	20	3	17	3372.9235	3	2	25	2	24	3432.3640	1	0	
10	1	9	3260.7331	5	2	15	8	8	3407.9360		-4	20	4	16	3383.8017	1	4	25	3	23	3444.3915	2	0	

10	2	8	3265.0491	1	0	15	9	7	3436.7524	2	0	20	5	15	3398.8744	1	0	25	4	22	3456.9708	2	0
10	3	7	3273.2310	3	-1	15	10	6	3468.8954	2	0	20	6	14	3417.5039	4	2	25	5	21	3472.0919	3	2
10	4	6	3285.1252	5	0	15	11	5	3504.3599	3	3	20	7	13	3439.5613	2	-2	25	6	20	3490.6002	1	1
10	5	5	3300.4505	-	-1	15	12	4	3543.1105	5	4	20	8	12	3465.0086	2	1	25	7	19	3512.5802	3	2
10	6	4	3319.1723	3	3	15	13	3	3585.1268	-	0	20	9	11	3493.8190	1	4	25	8	18	3537.9835	1	-1
10	7	3	3341.2731	3	-1	16	0	16	3306.3689	1	2	20	11	9	3561.4341	3	10	25	9	17	3566.7710	-	0
10	8	2	3366.7391	4	2	16	1	15	3313.1171	1	0	20	12	8	3600.1937	-	1	25	10	16	3598.9060	1	-1
10	9	1	3395.5524	3	-3	16	2	14	3317.9058	2	-1	20	13	7	3642.2233	-	3	25	11	15	3634.3765	1	4
10	10	0	3427.6907	4	4	16	3	13	3325.0497	0	1	21	1	21	3363.2336	1	25	12	14	3673.1438	-	3	
11	1	11	3264.5755	4	-1	16	4	12	3336.5951	3	-1	21	2	20	3374.3622	1	-1	25	13	13	3715.1854	-	-3
11	2	10	3271.4387	2	1	16	5	11	3351.8412	4	2	21	3	19	3384.9352	6	1	26	0	26	3434.4494	-	-2
26	1	25	3447.9769	2	-3	29	2	28	3499.7889	2	1	33	1	33	3558.5885	5	0	37	1	37	3642.2813	-	1
26	2	24	3457.9461	1	1	29	3	27	3513.6440	4	-2	33	2	32	3576.5586	-	0	37	2	36	3662.6304	4	1
26	4	22	3474.4216	3	6	29	4	26	3527.0762	0	33	3	31	3592.5169	2	1	37	3	35	3680.8596	1	1	
26	5	21	3488.7464	-	1	29	5	25	3542.2627	-5	33	4	30	3607.5384	-	2	37	4	34	3697.2789	-	4	
26	6	20	3507.1470	-	1	29	6	24	3560.6293	0	33	5	29	3622.7404	9	-3	37	5	33	3713.4662	-	-2	
26	7	19	3529.0998	3	-2	29	7	23	3582.5000	-	2	33	6	28	3640.9710	2	2	37	6	32	3731.6541	4	-3
26	8	18	3554.4902	2	2	29	8	22	3607.8378	3	1	33	7	27	3662.6810	2	-1	37	7	31	3753.1607	1	1
26	9	17	3583.2698	3	-1	29	9	21	3636.5871	3	-4	33	8	26	3687.9154	-	3	38	0	38	3664.6533	1	0
26	11	15	3650.8705	4	4	29	11	19	3704.1642	-	1	33	9	25	3716.6018	5	-1	38	1	37	3685.5801	-	-4
26	12	14	3689.6376	6	-4	30	0	30	3501.9046	3	-2	34	0	34	3578.6400	-	4	38	2	36	3704.0973	2	1
27	1	27	3450.4541	-	-1	30	1	29	3517.9653	4	2	34	1	33	3597.1536	-	0	38	4	34	3729.1392	-	2
27	2	26	3464.9044	1	0	30	2	28	3530.9104	1	0	34	2	32	3612.9822	1	-1	38	5	33	3740.0191	2	2
27	3	25	3477.8045	5	-2	30	3	27	3539.7800	4	-4	34	3	31	3624.5354	-	-2	38	6	32	3756.2572	3	3
27	4	24	3490.7570	2	1	30	4	26	3548.4265	2	-2	34	4	30	3633.4222	-	1	39	1	39	3687.6061	3	2
27	5	23	3505.8882	-	1	30	5	25	3561.7184	1	0	34	5	29	3645.3847	7	4	39	2	38	3709.1468	-	1
27	6	22	3524.3280	5	-1	30	6	24	3579.7685	3	2	34	6	28	3662.7628	-	0	39	3	37	3728.5473	-	0
27	7	21	3546.2597	3	3	30	7	23	3601.5825	-	-2	34	7	27	3684.3396	7	-2	39	4	36	3745.9432	-	6
27	8	20	3571.6342	1	0	30	8	22	3626.8983	-	5	34	8	26	3709.5349	4	-2	40	0	40	3711.1374	-	0
27	9	19	3600.4054	1	0	30	9	21	3655.6346	4	3	35	1	35	3599.2752	-	1	40	2	38	3753.0665	1	1
27	10	18	3632.5322	1	0	30	11	19	3723.1996	4	-3	35	2	34	3618.4334	-	0	40	3	37	3769.3571	1	-1
27	11	17	3668.0007	-	14	31	1	31	3520.2212	-	-9	35	3	33	3635.5121	-	0	40	4	36	3780.8654	-	0
27	13	15	3748.8133	1	-2	31	2	30	3537.0094	-	5	35	4	32	3651.0357	1	41	3	39	3778.5655	-	-7	
28	0	28	3467.0174	2	2	31	3	29	3551.8886	2	3	35	5	31	3666.8282	1	-5	41	4	38	3797.0050	1	-1
28	1	27	3481.8244	1	-1	31	4	28	3565.9105	-	1	35	6	30	3685.0190	3	2	42	0	42	3759.9389	-	2
28	2	26	3493.2751	-	-2	31	5	27	3581.2156	2	-1	35	7	29	3706.6312	4	1	42	1	41	3783.2611	-	2
28	3	25	3501.1434	-	2	31	8	24	3646.5973	-	2	35	8	28	3731.7953	3	-2	42	2	40	3804.3229	3	-3
28	4	24	3510.0468	1	-1	31	9	23	3675.3189	2	1	36	0	36	3620.4877	4	3	42	3	39	3822.1514	-	4
28	5	23	3523.9118	2	-1	32	1	31	3556.4065	3	3	36	1	35	3640.2107	-	-2	43	2	42	3809.1319	2	-1
28	6	22	3542.1667	-	1	32	2	30	3570.8172	-	-2	36	2	34	3657.4062	-	1	43	3	41	3830.9106	-	8
28	7	21	3564.0594	2	-2	32	3	29	3580.9345	-	-1	36	3	33	3670.5124	-	-1	44	0	44	3811.0567	-	2
28	8	20	3589.4167	2	0	32	4	28	3589.5603	4	4	36	4	32	3679.9692	-	10	44	2	42	3857.8749	-	2
28	9	19	3618.1778	2	0	32	5	27	3602.1973	7	1	36	5	31	3691.3143	-14	45	2	44	3862.5979	-	-3	
28	10	18	3650.2988	4	-4	32	6	26	3619.9624	-	-1	36	6	30	3708.1871	1	5	46	0	46	3864.4894	-	-4
28	11	17	3685.7638	4	-1	32	7	25	3641.6741	3	-2	36	7	29	3729.5857	5	1	47	2	46	3918.3789	-	2
28	12	16	3724.5317	3	-4	32	8	24	3666.9361	2	0	36	8	28	3754.6989	-	6	49	2	48	3976.4723	1	-1
29	1	29	3484.1770	1	0	32	9	23	3695.6413	-	0	-	-	-	-	-	-	-	-	-	-	-	-

<sup>a</sup> See footnote to Table 2.



we used the following relation:

$$P^{(140)} = P^{(040)} + P^{(100)} - P^{(000)}, \quad (9)$$

where

$$P^{(0v0)} = P^{(000)} + \alpha v + \beta v^2 \quad (10)$$

and, as the consequence,

$$P^{(040)} = 3P^{(000)} + 6P^{(020)} - 8P^{(010)}. \quad (11)$$

As in the previous section,  $P^{(v_1 v_2 v_3)}$  is any of the rotational,  $A, B, C$ , or centrifugal distortion,  $\Delta_K, \Delta_{JK}, \Delta_J$ , etc., parameter of the  $(v_1 v_2 v_3)$  vibrational state; parameters of the vibrational states,  $(000)/(010)$  and  $(020)/(100)$ , were taken from Refs. [13] and [14], respectively. Initial values of the  $(002)$  state were taken from column 2 of Table 3.

(4) Estimation of ro-vibrational energy values and line positions of the  $\nu_2 + 2\nu_3 - \nu_2$  band was made on the basis of above predicted spectroscopic parameters. In this case, it is necessary to take into account that such an estimation will determine the values of the rotational energy spacings within a given vibrational state much better than the values of the band centers. This is due to the fact, mentioned in Ref. [2], that the rotational energy spacings for the states with the value of the quantum number  $J \leq 4$  are reproduced by the potential parameters from [2] with an accuracy about 300 times better than the values of the

band centers. Thus, we have expected that the accuracy of the spacings between line positions within the  $\nu_2 + 2\nu_3 - \nu_2$  hot band, is generally better than  $0.04\text{--}0.05 \text{ cm}^{-1}$  for the transitions with  $J^{upper} \leq 6\text{--}8$ .

(5) As in Refs. [3,4,17,18], we then varied the vibrational energy,  $E$ , and the rotational parameters,  $A, B$ , and  $C$ , of the state  $(012)$  with steps of  $0.005, 0.0005, 0.0005$ , and  $0.0005 \text{ cm}^{-1}$ , respectively. For each value of the vibrational energy and for each  $A, B$  and  $C$  parameters we obtained the number  $N$  of experimental transition wavenumbers that coincided with the calculated ones to  $0.005 \text{ cm}^{-1}$  or better. We believed then that the set of the  $E, A, B$  and  $C$  values, which correspond to the maximum value of  $N$ , is the optimal one, and corresponding transition wavenumbers were used as the initial data in the inverse spectroscopic problem (fit of spectroscopic parameters).

(6) Improved fit values of the rotational and centrifugal distortion parameters were used in the search for additional transitions of the  $\nu_2 + 2\nu_3 - \nu_2$  band, and a second fit was performed. At the final step of the analysis, the 386 experimental energy levels ( $J^{max} = 49$  and  $K_a^{max} = 13$ ) obtained from about 760 assigned transitions of the  $\nu_2 + 2\nu_3 - \nu_2$  band were fitted with eight parameters (seven parameters of the  $(012)$  vibrational state and the vibrational energy of the  $(140)$  state which is interacted

**Table 8**

Spectroscopic parameters of the  $(012)$ , and  $(140)$  vibrational states of the  $\text{SO}_2$  molecule (in  $\text{cm}^{-1}$ ).

Parameter	(012) <sup>a</sup>	(140) <sup>a</sup>	(012) <sup>b</sup>	(140) <sup>b</sup>
1	2	3	4	5
$E$	3222.9725043 (47)	3206.6520(11)	3222.94	3206.46
$A$	2.024244956 (149)	2.196	2.025170939	2.196
$B$	0.3419057161 (131)	0.3428	0.3419194550	0.3428
$C$	0.2907799020 (142)	0.290	0.2908038232	0.290
$\Delta_K \times 10^4$	0.92709739(828)	1.323	0.93071578	1.323
$\Delta_{JK} \times 10^5$	-0.4409517 (144)	-0.4541	-0.4408793	-0.4541
$\Delta_J \times 10^6$	0.22603974 (486)	0.2201	0.22609453	0.2201
$\delta_K \times 10^5$	0.0921	0.175	0.0921	0.175
$\delta_J \times 10^7$	0.5846	0.5796	0.5846	0.5796
$H_K \times 10^7$	0.1468	0.2829	0.1468	0.2829
$H_{KJ} \times 10^9$	-0.6752	-1.129	-0.6752	-1.129
$H_{JK} \times 10^{11}$	2.122	0.03066	2.122	0.03066
$H_J \times 10^{12}$	0.3775	-0.2925	0.3775	-0.2925
$h_K \times 10^9$	1.438	1.162	1.438	1.162
$h_{JK} \times 10^{11}$	-0.1064	-1.136	-0.1064	-1.136
$h_J \times 10^{12}$	0.1985	0.2426	0.1985	0.2426
$L_K \times 10^{11}$	-0.3797	-0.4563	-0.3797	-0.4563
$L_{KJ} \times 10^{12}$	0.2110	-0.4729	0.2110	-0.4729
$L_{JK} \times 10^{14}$	0.7973	0.7973		
$L_{JK} \times 10^{15}$	-0.4010	-0.4010		
$L_J \times 10^{17}$	-0.4554	-0.4554		
$P_K \times 10^{14}$	0.1167	0.1167		
$P_{KJK} \times 10^{16}$	-0.3237	-0.3237		
$F_0$	0.046234		0.046234	

<sup>a</sup> Obtained from the fit. Values in parentheses are  $1\sigma$  statistical confidence intervals (in last digits). Parameters presented without confidence intervals were constrained to values from columns 4 or 5.

<sup>b</sup> The initial values of spectroscopic parameters (see text, for details).

with the (012) state). The achieved *rms*-deviation of the fit was  $0.00031 \text{ cm}^{-1}$  that can be considered as a satisfactory result if one will remember that the  $\nu_2 + 2\nu_3 - \nu_2$  band is very weak, and, as the consequence, experimental accuracy in its line positions is not too high.

Results of the final fit are shown in columns 2 and 3 of Table 8, together with their  $1\sigma$  statistical confidence intervals. The values of the parameters that are given in columns 2 and 3 without confidence intervals were constrained to corresponding predicted values from columns 4 and 5, respectively. From comparison of predicted and fitted parameters (see columns 2 and 4, and 3 and 5, respectively), one can see more than satisfactory correlations between both sets of data. As an illustration of the correctness of the obtained parameters, column 4 of Table 7 presents the differences,  $E^{\text{exp.}} - E^{\text{calc.}}$ , between ro-vibrational energy terms obtained from the analysis of experimental data, and ones calculated with the parameters obtained from the final fit. One can see more than satisfactory correspondence between experimental and calculated values.

## 6. Conclusion

We have presented the first high resolution analysis of the  $\nu_2 + 2\nu_3 - \nu_2$  very weak hot band, which allowed us to obtain 386 ro-vibrational energies of the (012) vibrational state. Our analysis was based on a variational procedure that gave us the possibility to assign about 760 transitions belonging to the  $\nu_2 + 2\nu_3 - \nu_2$  band. Re-analysis of the  $2\nu_3$  band was made, and the number of assigned transitions was increased more than three times in comparison with the previous results of Ref. [5]. The  $2\nu_1 + \nu_2$  weak band was analyzed also for the first time. The spectroscopic parameters for all three discussed excited vibrational states were determined and reproduced the corresponding line positions with a *rms*-deviation of  $0.00021 \text{ cm}^{-1}$ ,  $0.00031 \text{ cm}^{-1}$ , and  $0.00014 \text{ cm}^{-1}$  for the  $2\nu_3$ ,  $\nu_2 + 2\nu_3 - \nu_2$  and  $2\nu_1 + \nu_2$  bands, respectively. The variational procedure used in the present study demonstrates a high efficiency and, we believe, can also be applied to the study of weak bands of other polyatomic molecules.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi: [10.1016/j.jqsrt.2012.01.006](https://doi.org/10.1016/j.jqsrt.2012.01.006).

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