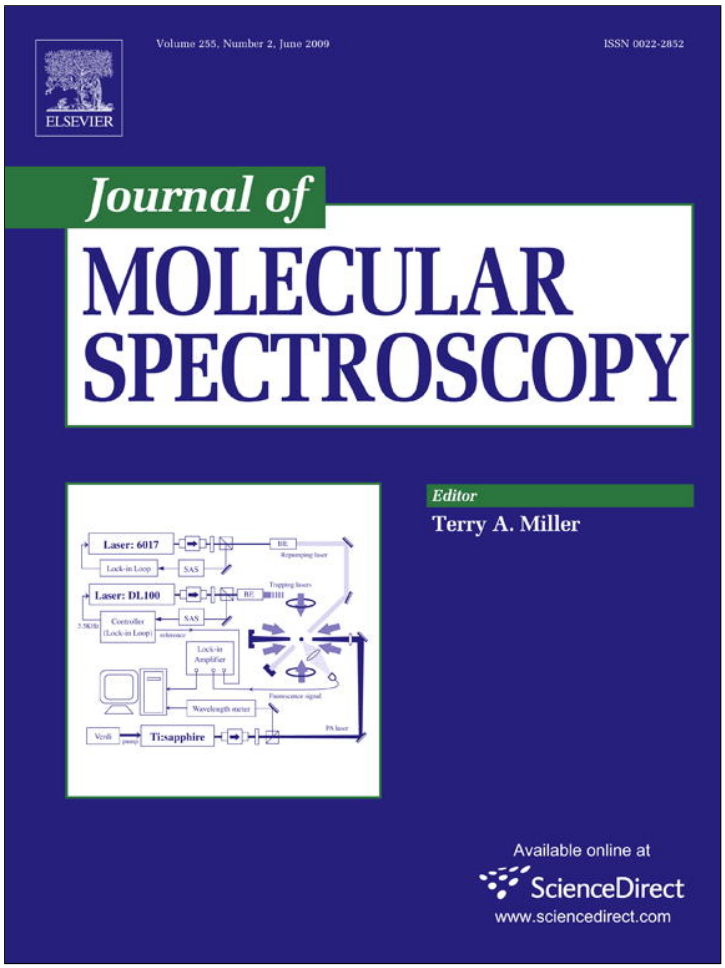

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High resolution study of the $3\nu_1$ band of SO_2

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ABSTRACT

The second overtone band $3\nu_1$ of sulfur dioxide has been studied for the first time with high resolution rotation-vibration spectroscopy. About 3000 transitions involving about 900 upper state energy levels with $J^{max.} = 66$ and $K_a^{max.} = 24$ have been assigned to the $3\nu_1$ band. In the analysis, an effective Hamiltonian taking into account accidental interactions between the vibrational states (300), (220), and (041) was used. The Watson operator in *A*-reduction and I^r representation was used in the diagonal blocks of the Hamiltonian. As the result of analysis a set of parameters reproducing the initial experimental data with the rms = 0.00028 cm^{-1} was obtained.

1. Introduction

Sulfur dioxide is an important chemical species in many fields such as chemistry, astrophysics, atmospheric optics, laser techniques, etc. (see, e.g., reviews in [1,2]). Therefore, spectroscopic studies of the sulfur dioxide molecule have been made during many years in microwave (see, e.g., review in Ref. [3]), submillimeter wave, and infrared (see, Refs. [4–33]) regions. We report in this communication the first high resolution analysis of the 3340–3520 cm^{-1} spectral region where the second stretching overtone $3\nu_1$ is located. Bands corresponding both to single and binary excitation of stretching quanta have been studied earlier in details in number of publications, see, e.g., [2], and references cited therein. At the same time, as to our knowledge of high resolution studies of bands corresponding to triple excitation of stretching quanta, only two of them have been analyzed before with high resolution: the $3\nu_3$ band has been discussed in Refs. [1,26], and $2\nu_1 + \nu_3$ band has been considered in Ref. [31].

2. Experimental details

The experimental measurements over the $3\nu_1$ region were performed in the infrared laboratory of Oulu using a Bruker IFS-120 HR Fourier spectrometer. The SO_2 sample, obtained from Sigma–Aldrich Inc. with purity of 99.9%, was used in the White type cell [34] at a pressure of 630 Pa. The absorption path length was 154 m and the cell was provided with 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 wavenumber region between 3000 and 4000 cm^{-1}. The obtained spectral resolution in the $3\nu_1$ region was 0.0075 cm^{-1} determined by aperture broadening (0.0040 cm^{-1}) and maximum optical path difference (0.0034 cm^{-1}) together with Doppler and pressure broadenings. The total registration time was more than 85 h leading to signal to noise ratio better than 1000 and even 3000 for optimal region. The spectrum was calibrated with 43 water lines [35] and the peak positions were calculated using the method of optimized center of gravity [36].

3. Analysis and results

Survey spectrum of the $3\nu_1$ band of SO_2 molecule is shown on Fig. 1. One can see all three clearly pronounced branches, *P*, *Q*, and *R*, as well as the structure of sets of transitions in the *P* and *R* branches. The upper state (300) of the $3\nu_1$ band is of A_1 symmetry and therefore the observed transitions are of *b*-type. Moreover, due to nuclear spin statistics, only transitions with even values of $K_a'' + K_c''$ of the lower quantum numbers are available. The transitions were assigned using the method of ground state combination differences (GSCD). For this purpose, the ground state rotational energies were calculated using the parameters from Ref. [33]. As the result of assignment, about 3000 transitions with upper quantum numbers $J^{max.} = 66$ and $K_a^{max.} = 24$ were found for the $3\nu_1$ band. On that basis about 900 upper state rovibrational energies were obtained. List of the obtained energies is presented in the column 2 of Table 1.

To give an impression of the relative strength of the $3\nu_1$ band in comparison with the earlier studied $2\nu_1 + \nu_3$ band, Fig. 2 presents the spectrum of SO_2 in more wide region. Fig. 3 shows, also for illustration, a small portion of the high resolution spectrum in the region of the *P*-branch of the $3\nu_1$ band.

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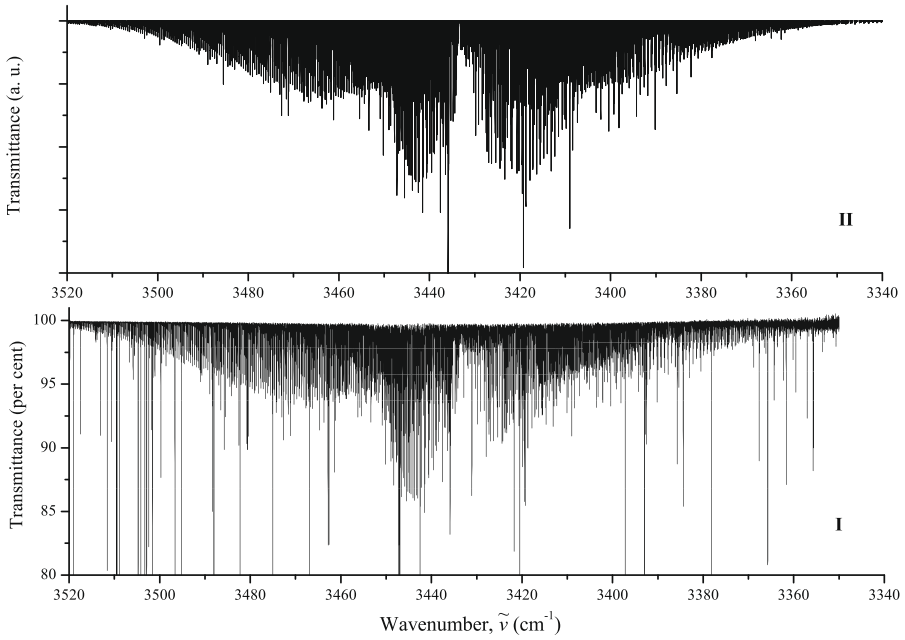

Fig. 1. Survey spectrum of SO_2 in the region of 3340–3520 cm^{-1}: I is the experimentally recorded spectrum (lines of CO_2 are seen also); II is simulated spectrum (in this case, only one dipole moment parameter was used in the simulation).

The SO_2 molecule is an asymmetric top with the value of asymmetry parameter, $\kappa = (2B - A - C)/(A - C) \approx -0.94$, close to the prolate symmetric top limit. However, the SO_2 molecule is relatively heavy, and, in spite of the small absolute value of the difference between B and C rotational constants, the centrifugal distortion parameters are considerably smaller. On that reason the A reduction and I^r representation looks suitable enough and can be applied in the analysis (see, e.g., cited references).

As has been discussed earlier (e.g., in [24,26,31,32]), weak Fermi- and/or Coriolis-type interactions should be taken into account when analyzing high resolution spectra of sulfur dioxide. On that reason we used in our analysis the Hamiltonian model which takes into account both types of these interactions:

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

where v and $\tilde{v}$ denote interacting vibrational states. In this model the diagonal block operators are the traditional Watson type operators in A reduction and I^r representation , Ref. [37]

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

where $J_\alpha (\alpha = x, y, z)$ 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 $[\cdots,\cdots]_+$ denotes anticommutator. Because of the symmetry arguments of the SO_2 molecule, the nondiagonal block operators can only be of two types. If the states v and $\tilde{v}$ in Eq. (1) are of same symmetry, the corresponding operator $H^{v\tilde{v}}$ describes the Fermi-type interaction and has the form:

$$\begin{aligned} H_F^{v\tilde{v}} = {} & F^{v\tilde{v}} + F_K^{v\tilde{v}} J_z^2 + F_J^{v\tilde{v}} J^2 + \cdots + F_{xy}^{v\tilde{v}} J_{xy}^2 + F_{xyK}^{v\tilde{v}}\left[J_{xy}^2, J_z^2\right]_+ \\ & + F_{xyJ}^{v\tilde{v}} J_{xy}^2 J^2 + \cdots. \end{aligned} \tag{3}$$

If the symmetries of the states v and $\tilde{v}$ are different (they can be of type A_1 and B_1 only), then the operator $H^{v\tilde{v}}$ describes the Coriolis-type interaction and has the following form:

$$\begin{aligned} H_{C_y}^{v\tilde{v}} = {} & (2B\zeta^y)^{v\tilde{v}} i J_y + C_{yK}^{v\tilde{v}}\left[i J_y, J_z^2\right]_+ + C_{yJ}^{v\tilde{v}} i J_y J^2 + \cdots + C_{xz}^{v\tilde{v}}[J_x, J_z]_+ \\ & + C_{xzK}^{v\tilde{v}}[[J_x, J_z]_+, J_z^2]_+ + C_{xzJ}^{v\tilde{v}}[J_x, J_z]_+ \cdots. \end{aligned} \tag{4}$$

During the analysis it became evident that local resonances between vibrational state (300) and the states (220) as well as (041) are essential in the study of the $3\nu_1$ band.As follows from estimation on the basis of parameters from Ref.[27], the separation of band centers of the bands $3\nu_1$ and $2\nu_1 + 2\nu_2$ is about 100 cm^{-1} and that of the bands $3\nu_1$ and $4\nu_2 + \nu_3$ is 19 cm^{-1} only.At the same time, we were not able to undoubtedly assign transitions to the $2\nu_1 + 2\nu_2$ and/or $4\nu_2 + \nu_3$ bands and, therefore, it was important to preliminary estimate the values of their band centers and main rotational and centrifugal parameters.In our case, the values of the band centers and effective rotational parameters were predicted using the values of harmonic frequencies, ω_λ, and anharmonic coefficients, $x_{\lambda\mu}$, from Ref.[27], and of equilibrium rotational parameters, X_β, and the vibration–rotation constants, α_λ^β and $\gamma_{\lambda\mu}^\beta$, from [26].To estimate the values of some of centrifugal distortion coefficients, Δ_K, Δ_{JK}, δ_K, H_K, and H_{KJ}, we made a linear extrapolation of the values of corresponding parameters of states (010), (020), (100), (200), (001), (002), (003), (101), (201), (110), (210), (011), and (111) (see, Refs.[21–26,31–33]).All other centrifugal distortion coefficients were constrained to the corresponding ground state values from Ref.[33].All the estimated values are collected in columns 2, 4 and 6 of Table 2, and the ground state parameters are presented in column 5 of Table 3.The estimated values were used then as an initial approximation in Hamiltonian(1)–(4).

Table 1
Experimental rovibrational term values for the (300) vibrational state of the SO_2 molecule (in cm^{-1}).[a]

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
1			2	3	4	1			2	3	4	1			2	3	4
1	1	1	3434.60712	17	−28	11	1	11	3473.67250	15	−14	15	9	7	3646.23618	9	7
2	0	2	3434.17186	16	−25	11	2	10	3480.51733	27	2	15	10	6	3678.54704	3	−9
2	1	1	3435.96397	13	−22	11	3	9	3489.29655	8	−11	15	11	5	3714.18903	7	−7
2	2	0	3441.03765		−22	11	4	8	3501.27139	4	−1	15	12	4	3753.14054	6	2
3	1	3	3437.62478	26	21	11	5	7	3516.66809	9	9	15	13	3	3795.37833	9	−11
3	2	2	3442.92220	20	−17	11	6	6	3535.47974	5	10	15	14	2	3840.87847	15	−4
3	3	1	3451.49839	37	−18	11	7	5	3557.69014	11	13	15	15	1	3889.61481	10	−17
4	0	4	3438.55645	11	3	11	8	4	3583.28355	18	9	16	0	16	3515.22593	3	15
4	1	3	3440.53532	5	−9	11	9	3	3612.24345	19	−3	16	1	15	3521.84926	4	−16
4	2	2	3445.45181	29	−8	11	10	2	3644.55243	21	26	16	2	14	3526.60669	10	−0
4	3	1	3454.01485	10	−18	11	11	1	3680.19024		21	16	3	13	3533.83037	9	−4
4	4	0	3466.01135	14	−3	12	0	12	3480.33896	8	3	16	4	12	3545.45772	28	−6
5	1	5	3443.04988	20	1	12	1	11	3484.66828	3	−6	16	5	11	3560.78321	29	13
5	2	4	3448.57576	5	−2	12	2	10	3488.97495	8	−0	16	6	10	3579.56614	12	20
5	3	3	3457.16088	28	−38	12	3	9	3496.93780	13	4	16	7	9	3601.76281	11	23
5	4	2	3469.15671		−7	12	4	8	3508.83809	8	6	16	8	8	3627.35036	19	5
5	5	1	3484.56918		69	12	5	7	3524.22609	31	20	16	9	7	3656.30960	13	5
6	0	6	3445.41057	2	−1	12	6	6	3543.03446	18	16	16	10	6	3688.62074	19	−4
6	1	5	3447.70907	10	0	12	7	5	3565.24338	38	9	16	11	5	3724.26370	30	9
6	2	4	3452.41720	7	−5	12	8	4	3590.83651	6	12	16	12	4	3763.21633	36	−5
6	3	3	3460.93934	14	2	12	9	3	3619.79678	16	8	16	13	3	3805.45620	36	15
6	4	2	3472.93204	24	3	12	10	2	3652.10605	36	−7	16	14	2	3850.95806	17	−13
6	5	1	3488.34323	15	13	12	11	1	3687.74507	2	1	16	15	1	3899.69693	13	−7
6	6	0	3507.16076	12	7	12	12	0	3726.69230	15	−2	16	16	0	3951.64512		−25
7	1	7	3450.87430	5	−3	13	1	13	3488.62013	2	−6	17	1	17	3525.55174	3	−2
7	2	6	3456.73295	15	0	13	2	12	3496.11688	20	−23	17	2	16	3534.64704	13	7
7	3	5	3465.34581	91	−9	13	3	11	3505.06693	9	−22	17	3	15	3544.18681	9	−4
7	4	4	3477.33766	30	22	13	4	10	3517.03426	19	18	17	4	14	3556.17680	20	16
7	5	3	3492.74744	39	2	13	5	9	3532.41553	18	−18	17	5	13	3571.50577	6	1
7	6	2	3511.56498	26	27	13	6	8	3551.22015	14	24	17	6	12	3590.27903	3	8
7	7	1	3533.77685	11	7	13	7	7	3573.42696	10		17	7	11	3612.47012	23	−7
8	0	8	3454.69105	22	−8	13	8	6	3599.01956	7	18	17	8	10	3638.05532	24	11
8	1	7	3457.47109	9	−11	13	9	5	3627.97992	4	12	17	9	9	3667.01350	10	15
8	2	6	3461.96906	39	−17	13	10	4	3660.29015	12	26	17	10	8	3699.32464	9	8
8	3	5	3470.39215	29	9	13	11	3	3695.92988	15		17	11	7	3734.96810	27	−3
8	4	4	3482.37373	6	9	13	12	2	3734.87841	3	−11	17	12	6	3773.92229	21	9
8	5	3	3497.78189	18	16	13	13	1	3777.11307	17	3	17	13	5	3816.16349	27	−13
8	6	2	3516.59866	27	26	14	0	14	3496.63521	5	−2	17	14	4	3861.66799	28	11
8	7	1	3538.81063	22	18	14	1	13	3502.03410	5	−14	17	15	3	3910.40905	20	−6
8	8	0	3564.40381	6	15	14	2	12	3506.46592	12	1	17	16	2	3962.35996	8	−21
9	1	9	3461.08623	5	−5	14	3	11	3514.07525	13	19	17	17	1	4017.49215		−54
9	2	8	3467.38421	31	−5	14	4	10	3525.87380	14	−1	18	0	18	3536.11006	11	22
9	3	7	3476.05666	11	5	14	5	9	3541.23827	11	6	18	1	17	3544.05887	4	−13
9	4	6	3488.04081	21	−5	14	6	8	3560.03679	15	−1	18	2	16	3549.36924	8	−1
9	5	5	3503.44642		7	14	7	7	3582.24117	20	−6	18	3	15	3556.23935		−89
9	6	4	3522.26195	20	−1	14	8	6	3607.83268	16	10	18	4	14	3567.60353	14	1
9	7	3	3544.47377	11	0	14	9	5	3636.79293	13	3	18	5	13	3582.86580	11	−3
9	8	2	3570.06736	5	13	14	10	4	3669.10355	24	2	18	6	12	3601.62497	10	7
9	9	1	3599.02655	12	24	14	11	3	3704.74477	21	23	18	8	10	3649.39100	10	−6
10	0	10	3466.34825	11	−6	14	12	2	3743.69460	11	2	18	9	9	3678.34769	7	3
10	1	9	3469.80082	13	−0	14	13	1	3785.93066	13	−11	18	10	8	3710.65858	10	0

(*continued on next page*)

Table 1 (*continued*)

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
1			2	3	4	1			2	3	4	1			2	3	4
10	2	8	3474.14552	14	−18	14	14	0	3831.42884	12	0	18	11	7	3746.30269	3	−3
10	3	7	3482.38537	19	−3	15	1	15	3505.91635	11	−36	18	12	6	3785.25790	38	−12
10	4	6	3494.34026	18	−18	15	2	14	3514.16653	4	−2	18	13	5	3827.50138	2	20
10	5	5	3509.74174	17	10	15	3	13	3523.36592	31	−0	18	14	4	3873.00741	4	−17
10	6	4	3528.55574	12	12	15	4	12	3535.33423	25	6	18	15	3	3921.75116	8	−14
10	7	3	3550.76698	13	8	15	5	11	3550.69347	10	2	18	16	2	3973.70517	21	2
10	8	2	3576.36062	5	18	15	6	10	3569.48543	12	8	18	17	1	4028.84038	16	−33
10	9	1	3605.32011	16	6	15	7	9	3591.68650	25	15	18	18	0	4087.12869		23
10	10	0	3637.62807	7	12	15	8	8	3617.27636		19	19	1	19	3547.51695	4	0
19	2	18	3557.53925	23	26	22	3	19	3609.13374	6	−12	24	19	5	4229.90643	35	27
19	3	17	3567.51966	31	3	22	4	18	3619.66068	17	13	24	20	4	4294.43080	44	5
19	4	16	3579.56549	4	22	22	5	17	3634.67235	30	−1	24	21	3	4362.01446	45	5
19	5	15	3594.85772	9	10	22	6	16	3653.34754	5	6	24	22	2	4432.62454		55
19	6	14	3613.60415		3	22	7	15	3675.48998	2	5	24	23	1	4506.22607		34
19	7	13	3635.78072	11	−4	22	8	14	3701.04830	28	−13	24	24	0	4582.78576		34
19	8	12	3661.35817	22	10	22	9	13	3729.99304	16	1	25	1	25	3627.33804	2	−4
19	9	11	3690.31274	10	11	22	10	12	3762.29894	17	−11	25	2	24	3640.49973	16	25
19	10	10	3722.62292	6	0	22	11	11	3797.94320	16	0	25	3	23	3652.43035	14	−38
19	11	9	3758.26740	17	−5	22	12	10	3836.90215	14	2	25	4	22	3665.01046	36	17
19	12	8	3797.22390	16	2	22	13	9	3879.15164	8	−4	25	5	21	3680.20285	15	−11
19	13	7	3839.46862	5	−12	22	14	8	3924.66686	6	25	25	6	20	3698.80909	9	−1
19	14	6	3884.97740	30	10	22	15	7	3973.42054		−17	25	7	19	3720.90001	16	10
19	15	5	3933.72329	13	−28	22	16	6	4025.38631		−11	25	8	18	3746.42814	10	3
19	16	4	3985.68007		−21	22	17	5	4080.53539	27	22	25	9	17	3775.35532	13	−6
19	17	3	4040.81865	12	−33	22	18	4	4138.83723		6	25	10	16	3807.65225	7	−6
19	19	1	4160.52304		−10	22	19	3	4200.26180	17	−1	25	11	15	3843.29295	3	−2
20	0	20	3559.29065	33	2	22	20	2	4264.77760	30	12	25	12	14	3882.25231	3	−9
20	1	19	3568.61000	12	4	22	21	1	4332.35207		30	25	13	13	3924.50554	40	5
20	2	18	3574.71421	20	−6	22	22	0	4402.95196		38	25	14	12	3970.02617	6	−9
20	3	17	3581.33598	18	3	23	1	23	3598.41414	8	8	25	15	11	4018.78796		−18
20	4	16	3592.32933	35	−22	23	2	22	3610.48210	16	−20	25	16	10	4070.76311	10	−9
20	5	15	3607.49305	10	12	23	3	21	3621.66040	7	0	25	17	9	4125.92241	13	−17
20	6	14	3626.21737	13	1	23	4	20	3633.98529	2	11	25	18	8	4184.23639	8	2
20	7	13	3648.38435	8	−1	23	5	19	3649.20103	20	−15	25	19	7	4245.67394		19
20	8	12	3673.95654	6	6	23	6	18	3667.86485	14	6	25	20	6	4310.20360		61
20	9	11	3702.90837	11	−3	23	7	17	3689.99263	7	0	25	21	5	4377.79190		34
20	10	10	3735.21776	8	5	23	8	16	3715.54237	37	−11	25	22	4	4448.40683		56
20	11	9	3770.86256	20	16	23	9	15	3744.48212	15	−11	25	23	3	4522.01337		3
20	12	8	3809.81984	11	2	23	10	14	3776.78581	10	−3	25	24	2	4598.57877		27
20	13	7	3852.06628	14	−5	23	11	13	3812.42933	11	9	26	0	26	3642.65190	8	15
20	14	6	3897.57720	37	16	23	12	12	3851.38848	7	−12	26	1	25	3655.99091	10	10
20	15	5	3946.32586	7	−4	23	13	11	3893.63938	2	−10	26	2	24	3665.72692		−11
20	16	4	3998.28551	61	−4	23	14	10	3939.15653	30	8	26	3	23	3672.79477	6	4
20	17	3	4053.42763	21	12	23	15	9	3987.91250	75	−67	26	4	22	3682.26612	17	−4
20	18	2	4111.72200	18	−16	23	16	8	4039.88191		−6	26	5	21	3696.73185	5	0
20	19	1	4173.13901		9	23	17	7	4095.03422	10	3	26	6	20	3715.24044	12	13
20	20	0	4237.64657		33	23	18	6	4153.33997	27	−8	26	7	19	3737.30550	8	4
21	1	21	3571.80589	9	−3	23	19	5	4214.76901		18	26	8	18	3762.82049	24	23
21	2	20	3582.82338	17	−6	23	20	4	4279.28892	38	3	26	9	17	3791.73977	28	6
21	3	19	3593.35002	3	1	23	21	3	4346.86780	46	1	26	10	16	3824.03222	10	−4
21	4	18	3605.50188	13	−1	23	22	2	4417.47301		61	26	11	15	3859.67096	27	11
21	5	17	3620.75435	22	1	23	23	1	4491.06959		59	26	12	14	3898.62989	6	4
21	6	16	3639.46456	16	−9	24	0	24	3612.55902	1	12	26	13	13	3940.88358	14	−17
21	7	15	3661.62061	11	−2	24	1	23	3624.59099	8	−6	26	14	12	3986.40630	7	5

21	8	14	3687.18663	7	11	24	2	22	3632.95162	20	−2	26	15	11	4035.17044	10	−19
21	9	13	3716.13520	20	6	24	3	21	3639.62886	16	5	26	16	10	4087.14861	15	−20
21	10	12	3748.44304	18	0	24	4	20	3649.62747	22	−13	26	17	9	4142.31178	33	−4
21	11	11	3784.08768	6	6	24	5	19	3664.41415	14	−11	26	18	8	4200.62891		−79
21	12	10	3823.04596	16	7	24	6	18	3683.02011	6	13	26	19	7	4262.07168		15
21	13	9	3865.29379	7	−18	24	7	17	3705.12930	23	10	26	20	6	4326.60585		31
21	14	8	3910.80693	33	12	24	8	16	3730.66901	30	6	26	21	5	4394.19921	42	4
21	15	7	3959.55835	34	7	24	9	15	3759.60279	12	−16	26	22	4	4464.81952		35
21	16	6	4011.52093	23	−1	24	10	14	3791.90344	13	−11	26	23	3	4538.43230		58
21	17	5	4066.66623	8	−0	24	11	13	3827.54576	72	−4	26	24	2	4615.00242		−13
21	18	4	4124.96442		−10	24	12	12	3866.50547	16	13	27	1	27	3658.57584		16
21	19	3	4186.38529		13	24	13	11	3908.75730		−11	27	2	26	3672.86143	35	9
21	20	2	4250.89750		92	24	14	10	3954.27624	9	−9	27	3	25	3685.63980		36
21	21	1	4318.46701		59	24	15	9	4003.03558	5	−7	27	4	24	3698.56770	22	−39
22	0	22	3584.77258		0	24	16	8	4055.00756	14	−1	27	5	23	3713.76325	20	−14
22	1	21	3595.46163	3	−10	24	17	7	4110.16312	28	−22	27	6	22	3732.30240	25	−5
22	2	20	3602.59382	28	17	24	18	6	4168.47323	7	8	27	7	21	3754.34606	17	16
27	8	20	3779.84573	19	1	29	20	10	4379.59469		25	32	14	18	4097.91741	38	−8
27	9	19	3808.75614	7	−3	29	21	9	4447.20462		64	32	15	17	4146.69454	12	−16
27	10	18	3841.04368	15	14	29	22	8	4517.84100		28	32	16	16	4198.69067	43	1
27	11	17	3876.67947	27	−5	29	23	7	4591.47048		−24	32	17	15	4253.87562		5
27	12	16	3915.63780	22	6	30	0	30	3709.76137		6	32	18	14	4312.21882	16	4
27	13	15	3957.89212	5	−9	30	2	28	3738.29333	29	−5	32	19	13	4373.68906		21
27	14	14	4003.41610	21	−18	30	3	27	3746.96018	12	−1	32	20	12	4438.25350		−8
27	15	13	4052.18308	12	−3	30	4	26	3755.68315	28	−11	32	24	8	4726.79171		−12
27	16	12	4104.16402		−37	30	5	25	3769.16910	11	2	33	1	33	3766.15532		18
27	17	11	4159.33080		−26	30	6	24	3787.35147	30	9	33	2	32	3783.91659	9	−10
27	18	10	4217.65338		30	30	7	23	3809.28408	19	6	33	3	31	3799.67986	2	0
27	19	9	4279.09918		−27	30	8	22	3834.72498	32	−24	33	4	30	3814.28701	4	−7
27	20	8	4343.63856		21	30	9	21	3863.60054	12	5	33	5	29	3829.80208	10	10
27	21	7	4411.23786		70	30	10	20	3895.86694	18	6	33	6	28	3848.12613	7	9
27	22	6	4481.86293		33	30	11	19	3931.49125	5	−6	33	7	27	3869.95466	23	−7
27	23	5	4555.48067		−14	30	12	18	3970.44439	21	−23	33	8	26	3895.31700	19	21
27	24	4	4632.05761		14	30	13	17	4012.69891	26	−19	33	9	25	3924.14246	22	15
28	0	28	3675.05226	9	−10	30	14	16	4058.22678	22	−1	33	10	24	3956.37796	27	8
28	1	27	3689.66420	3	4	30	15	15	4107.00010	24	−18	33	11	23	3991.98416	36	19
28	2	26	3700.85824	24	−34	30	16	14	4158.99060	9	−1	33	12	22	4030.92762	39	−3
28	3	25	3708.58950	45	−7	30	17	13	4214.16840		10	33	13	21	4073.17904	21	11
28	4	24	3717.60991	19	−29	30	18	12	4272.50306		9	33	14	20	4118.70787	15	−10
28	5	23	3731.64257	10	4	30	19	11	4333.96400		59	33	15	19	4167.48701	7	25
28	6	22	3750.01492	13	5	30	20	10	4398.51738		−18	33	16	18	4219.48556	23	20
28	7	21	3772.02235	10	−3	30	21	9	4466.13345		80	33	17	17	4274.67394	14	15
28	8	20	3797.50493	48	12	30	22	8	4536.77595		71	33	18	16	4333.02180		55
28	9	19	3826.40488	11	−8	30	23	7	4610.41126		−9	33	19	15	4394.49595		−24
28	10	18	3858.68626	10	−4	30	24	6	4687.00698		43	33	20	14	4459.06615		−17
28	11	17	3894.31909	27	0	31	1	31	3727.98519		−16	33	22	12	4597.35973		23
28	12	16	3933.27598	26	−14	31	3	29	3759.28484	23	24	33	23	11	4671.01398		−80
28	13	15	3975.53082		−8	31	4	28	3773.22495	11	−13	34	0	34	3786.10437	11	14
28	14	14	4021.05634	11	−4	31	5	27	3788.56568		40	34	1	33	3804.39495	21	−9
28	15	13	4069.82553	22	−2	31	6	26	3806.95616	10	−6	34	2	32	3819.94534	10	7
28	16	12	4121.81008		18	31	7	25	3828.86913	10	−3	34	3	31	3831.17885	38	10
28	17	11	4176.97971	10	−54	31	8	24	3854.28727	38	6	34	4	30	3840.01091	2	−3
28	18	10	4235.30656		10	31	9	23	3883.14777	5	6	34	5	29	3852.19011	18	−7
28	19	9	4296.75762		17	31	10	22	3915.40515	48	12	34	6	28	3869.75098	32	−19

(*continued on next page*)

Table 1 (*continued*)

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
1			2	3	4	1			2	3	4	1			2	3	4
28	20	8	4361.30167		33	31	11	21	3951.02422	18	4	34	7	27	3891.46014	5	−1
28	21	7	4428.90594		48	31	12	20	3989.97480	17	−6	34	8	26	3916.78540	42	7
28	22	6	4499.53669		21	31	13	19	4032.22860	10	−8	34	9	25	3945.59015	18	−8
28	23	5	4573.16085		34	31	14	18	4077.75701	6	−9	34	10	24	3977.81283	3	−11
28	24	4	4649.74296		−22	31	15	17	4126.53256	18	2	34	11	23	4013.41128	24	16
29	1	29	3692.12515	3	−4	31	16	16	4178.52581	16	7	34	12	22	4052.35054	29	21
29	2	28	3707.55688	11	5	31	17	15	4233.70688	6	−17	34	13	21	4094.59962	7	−5
29	3	27	3721.26442	18	−10	31	18	14	4292.04594	14	−5	34	14	20	4140.12892		39
29	4	26	3734.64546	20	9	31	19	13	4353.51118	7	−5	34	15	19	4188.90837		−29
29	5	25	3749.88436	33	−4	31	20	12	4418.07055	35	−9	34	16	18	4240.90994		16
29	6	24	3768.34981		−4	31	22	10	4556.34035		41	34	17	17	4296.10174	8	9
29	7	23	3790.33437		6	32	0	32	3746.77874	3	6	34	18	16	4354.45333	19	−2
29	8	22	3815.79767		−17	32	2	30	3777.99455	19	−24	34	19	15	4415.93328		10
29	9	21	3844.68647	6	15	32	3	29	3787.84530	13	−20	34	20	14	4480.50869		−6
29	10	20	3876.96074	7	4	32	4	28	3796.48975	11	6	34	21	13	4548.14715		18
29	11	19	3912.58965	9	0	32	5	27	3809.34050	26	18	34	22	12	4618.81400		−15
29	12	18	3951.54493	13	−12	32	6	26	3827.25947	27	6	34	23	11	4692.47547		−61
29	13	17	3993.79999	25	13	32	7	25	3849.09475	17	−15	35	1	35	3806.63369	16	2
29	14	16	4039.32665	24	10	32	8	24	3874.48454	51	18	35	2	34	3825.57018	18	13
29	15	15	4088.09797	27	2	32	9	23	3903.32824	6	1	35	3	33	3842.43277	7	1
29	16	14	4140.08524	16	−8	32	10	22	3935.57528	10	−2	35	4	32	3857.80920	44	−2
29	17	13	4195.25935	10	0	32	11	21	3971.18840	17	4	35	5	31	3873.58675	25	15
29	18	12	4253.58984		6	32	12	20	4010.13567	34	−17	35	6	30	3891.86275		−6
29	19	11	4315.04560		14	32	13	19	4052.38837	49	−24	35	7	29	3913.59563	23	15
35	8	28	3938.88970	5	−2	38	1	37	3892.36075	28	2	41	4	38	4002.90116	65	11
35	9	27	3967.67215	12	−11	38	2	36	3910.59460	6	8	41	5	37	4020.08900	52	47
35	10	26	3999.88028	11	−38	38	3	35	3924.91960	28	−9	41	6	36	4038.48255		−25
35	11	25	4035.47011	22	16	38	4	34	3935.02657		8	41	7	35	4059.89372	10	7
35	12	24	4074.40405	13	9	38	5	33	3946.06123	7	−3	41	8	34	4084.90376	6	−2
35	13	23	4116.65094		6	38	6	32	3962.55410	23	2	41	9	33	4113.49788	29	7
35	14	22	4162.17920	17	3	38	7	31	3983.87863		−12	41	10	32	4145.58398	23	−25
35	15	21	4210.96037	4	−4	38	8	30	4009.02669	10	8	41	11	31	4181.09525		34
35	16	20	4262.96401	5	10	38	9	29	4037.72597	21	−8	41	12	30	4219.97984	24	−12
35	17	19	4318.15935	17	23	38	10	28	4069.88175		−5	41	13	29	4262.19968	11	−15
35	18	18	4376.51520		19	38	11	27	4105.43757	28	−5	41	14	28	4307.71500	55	−6
35	19	17	4438.00028		54	38	12	26	4144.35128	42	−4	41	15	27	4356.49664	16	23
35	20	16	4502.58034		−44	38	13	25	4186.58778		19	41	16	26	4408.50960		11
35	22	14	4640.89897		39	38	14	24	4232.11190	35	22	41	17	25	4463.72241		39
36	0	36	3827.73753	3	−1	38	15	23	4280.89446		−7	42	0	42	3966.47791	9	11
36	1	35	3847.22774	14	−11	38	16	22	4332.90401	19	11	42	1	41	3989.53242		60
36	2	34	3864.14314	28	30	38	17	21	4388.10871	6	21	42	2	40	4010.30009		17
36	3	33	3876.89147	13	9	38	18	20	4446.47670		9	42	3	39	4027.74066	9	18
36	4	32	3886.20795	3	1	38	19	19	4507.97605		11	42	4	38	4040.26409		12
36	5	31	3897.75386		−15	38	20	18	4572.57304		−54	42	5	37	4050.94253	40	26
36	6	30	3914.84258	21	4	39	1	39	3894.51296		−68	42	6	36	4065.94793	3	−2
36	7	29	3936.38572	17	−1	39	2	38	3915.80652		7	42	7	35	4086.60408	33	−9
36	8	28	3961.63149	35	−2	39	3	37	3934.95469		−5	42	8	34	4111.48033		−15
36	9	27	3990.38877	8	5	39	4	36	3952.13894	23	−9	42	9	33	4140.02758	3	−2
36	10	26	4022.58130	13	5	39	5	35	3968.74774	2	2	42	10	32	4172.08650	41	14
36	11	25	4058.16050	3	−4	39	6	34	3987.04300	3	6	42	11	31	4207.57856		−44
36	12	24	4097.08848	23	−14	39	8	32	4033.67960	15	9	42	12	30	4246.45254	43	15
36	13	23	4139.33254	23	−2	39	9	31	4062.34751	25	2	42	13	29	4288.66528		−8
36	14	22	4184.85978		−13	39	10	30	4094.48183	19	−35	42	14	28	4334.17639	2	0
36	15	21	4233.64194	33	−6	39	11	29	4130.02407	17	−29	42	15	27	4382.95656		15

36	16	20	4285.64776		13	39	12	28	4168.92941	20	−11	42	16	26	4434.97013		−2
36	17	19	4340.84526		−86	39	13	27	4211.16118	11	18	42	17	25	4490.18495		3
36	18	18	4399.20601	69	−14	39	14	26	4256.68279		8	42	18	24	4548.56803		9
36	19	17	4460.69565		−12	39	15	25	4305.46557		13	42	19	23	4610.08586		−22
36	20	16	4525.28197		−36	39	16	24	4357.47663	21	32	43	1	43	3991.61908		37
36	21	15	4592.93328		69	39	17	23	4412.68370	18	−4	43	2	42	4015.26912	4	6
36	22	14	4663.61300	29	33	39	18	22	4471.05575		−1	43	3	41	4036.76405	10	5
37	1	37	3849.41996	10	−14	39	19	21	4532.56003		14	43	4	40	4056.03277	33	−20
37	2	36	3869.53410	30	0	40	0	40	3917.92518	27	14	43	5	39	4073.90771	6	5
37	3	35	3887.52852	5	11	40	1	39	3939.79497	35	−20	43	6	38	4092.48158	12	18
37	4	34	3903.76754	20	1	40	2	38	3959.31038	7	3	43	7	37	4113.79831		12
37	5	33	3919.90722	8	6	40	3	37	3975.21332	41	13	43	8	36	4138.68642		20
37	6	32	3938.16863	6	8	40	4	36	3986.40204		−14	43	9	35	4167.19387		31
37	7	31	3959.79564		−33	40	5	35	3997.12650		0	43	10	34	4199.22263		−20
37	8	30	3985.00946	45	3	40	6	34	4012.91218	6	20	43	11	33	4234.69558	5	−26
37	9	29	4013.73949	37	−35	40	7	33	4033.94794	5	3	43	12	32	4273.55626	31	−13
37	10	28	4045.91500	33	10	40	8	32	4058.97474	7	2	43	13	31	4315.76176	12	4
37	11	27	4081.48287	25	−19	40	9	31	4087.60459	28	−17	43	14	30	4361.26782	15	0
37	12	26	4120.40424	17	−15	40	10	30	4119.71662	31	36	43	15	29	4410.04621		15
37	13	25	4162.64490	29	11	40	11	29	4155.24350	19	9	43	16	28	4462.06025	13	14
37	14	24	4208.17081	12	5	40	12	28	4194.13870	36	−34	43	17	27	4517.27686		−3
37	15	23	4256.95342	26	5	40	13	27	4236.36510	19	4	43	18	26	4575.66344		16
37	16	22	4308.96102		3	40	14	26	4281.88354		−30	43	19	25	4637.18551		−42
37	17	21	4364.16266		6	40	15	25	4330.66621		13	44	0	44	4017.33547		−5
37	18	20	4422.52670	59	−1	40	16	24	4382.67816	18	−3	44	1	43	4041.57100	10	27
37	19	19	4484.02126		5	40	17	23	4437.88838		11	44	2	42	4063.57102		13
37	20	18	4548.61280		−50	40	19	21	4557.77304		8	44	3	41	4082.48993	3	19
37	21	17	4616.26956		−8	41	1	41	3941.91329	40	−17	44	4	40	4096.53823		79
37	22	16	4686.95729		97	41	2	40	3964.38516	21	−9	44	6	38	4121.69735		25
38	0	38	3871.67825		21	41	3	39	3984.70297	71	0	44	7	37	4141.86170	11	6
44	8	36	4166.54926	18	4	47	13	35	4430.45860	70	9	51	7	45	4355.13987		0
44	9	35	4194.99744	32	−8	47	14	34	4475.93434		−14	51	10	42	4439.18268		−32
44	10	34	4226.99478		81	47	15	33	4524.70009		−33	51	11	41	4474.42785		−43
44	11	33	4262.44556	36	−2	47	16	32	4576.71198		2	51	12	40	4513.13566		−22
44	12	32	4301.29192		−13	47	17	31	4631.93361		−40	51	15	37	4649.42643		5
44	14	30	4388.98941	12	7	47	18	30	4690.33203		5	52	0	52	4243.79749		−26
44	15	29	4437.76534	12	2	48	0	48	4125.96219	31	2	52	2	50	4299.55295	2	−23
44	17	27	4544.99822	15	36	48	1	47	4152.55439		44	52	3	49	4359.62570		37
44	18	26	4603.38788		43	48	2	46	4176.97693	20	−15	52	6	46	4344.47519		4
44	19	25	4664.91464		15	48	3	45	4198.67297	22	28	52	7	45	4389.34575		60
45	1	45	4043.62839	11	−13	48	4	44	4216.03832		24	52	8	44	4412.60512		75
45	2	44	4068.45679	12	10	48	5	43	4228.49194		28	52	11	41	4507.24641		−74
45	3	43	4091.13450	64	1	48	6	42	4241.45922		38	52	12	40	4545.92764		−54
45	4	42	4111.51630		−31	48	7	41	4260.25780		−29	52	14	38	4633.44438		−43
45	5	41	4130.18104		4	48	8	40	4284.40229	59	−1	52	15	37	4682.18088	9	−38
45	7	39	4170.27595		−36	48	9	39	4312.59193	35	8	53	1	53	4274.69402		−53
45	8	38	4195.03065		−21	48	10	38	4344.42984	43	−4	53	2	52	4304.22457		50
45	10	36	4255.39983	45	−9	48	11	37	4379.77664	42	4	53	3	51	4331.64075		10
45	11	35	4290.82850	35	15	48	12	36	4418.55335	45	23	53	4	50	4356.70334		27
45	12	34	4329.65912		−35	48	15	33	4554.93758		−21	53	6	48	4400.35200	6	−13
45	13	33	4371.84750		15	48	16	32	4606.94720		−42	53	7	47	4421.88517		0
45	14	32	4417.34061		−35	48	17	31	4662.17018		−1	53	8	46	4446.10354	27	−28
45	16	30	4518.12798	4	22	48	18	30	4720.57050		0	53	10	44	4505.53597		35
45	17	29	4573.34796		20	49	1	49	4154.55799	20	−14	53	11	43	4540.70029		−11

(*continued on next page*)

Table 1 (*continued*)

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
1			2	3	4	1			2	3	4	1			2	3	4
45	18	28	4631.74065		29	49	2	48	4181.73930	10	24	53	14	40	4666.83666		−44
45	19	27	4693.27076		−91	49	4	46	4229.48097		45	54	0	54	4306.16647		22
46	0	46	4070.49716		−14	49	5	45	4249.99167		−7	54	3	51	4389.82934		55
46	1	45	4095.91197	38	33	49	7	43	4290.95106		−8	54	4	50	4411.99174	35	14
46	2	44	4119.12872	23	−3	49	8	42	4315.42235	16	12	54	7	47	4457.98079		−10
46	3	43	4139.46400		31	49	9	41	4343.58394	25	18	54	8	46	4480.61948		7
46	4	42	4155.15030	18	34	49	11	39	4410.69315		−6	54	9	45	4508.18078	35	−10
46	5	41	4166.68257	25	20	49	14	36	4537.04817		−20	54	10	44	4539.66973		27
46	6	40	4180.19255	14	−15	49	16	34	4637.81194	25	−29	54	12	42	4613.41012		−35
46	7	39	4199.73866		15	50	0	50	4183.72937		−3	55	1	55	4338.21250	89	−20
46	8	38	4224.18733		6	50	1	49	4211.49653		−54	55	3	53	4397.51305	15	−17
46	10	36	4284.44100	35	−8	50	3	47	4260.12970		39	55	4	52	4423.76894		31
46	11	35	4319.84410		−24	50	4	46	4237.11897		78	55	10	46	4574.43822		0
46	12	34	4358.65850	8	−22	50	5	45	4292.83246	30	29	55	11	45	4609.51047		−67
46	13	33	4400.83723		22	50	6	44	4279.15557		47	56	0	56	4370.83388	65	9
46	14	32	4446.32279		12	50	7	43	4323.44931	12	15	56	2	54	4431.30549		−49
46	15	31	4495.09245		−8	50	8	42	4347.20400	54	8	56	3	53	4458.08710		−29
46	17	29	4602.32643		−7	50	9	41	4375.22405	45	20	56	4	52	4481.71168		54
46	18	28	4660.72156		−34	50	10	40	4406.96270		26	57	1	57	4404.02974		38
47	1	47	4097.94213	21	14	50	12	38	4480.97590	64	−11	57	2	56	4435.90365	30	−9
47	2	46	4123.94668		−35	50	14	36	4568.55011		−33	57	3	55	4465.68098		−39
47	4	44	4169.33655	38	−6	50	15	35	4617.30081		0	57	11	47	4680.86283		67
47	6	42	4208.10875		40	50	16	34	4669.30534		−39	58	1	57	4470.25863		2
47	7	41	4229.32824	9	14	50	18	32	4782.93252		9	59	2	58	4505.18783		−15
47	8	40	4253.94159		−5	51	1	51	4213.47571		−29	60	0	60	4507.06087		−63
47	9	39	4282.23356		23	51	2	50	4241.83134		−41	62	2	60	4646.13565	20	50
47	10	38	4314.11750	22	−1	51	3	49	4268.06513	6	21	64	0	64	4652.47163		29
47	12	36	4388.28982		−9	51	6	46	4333.79322		27	66	0	66	4728.61653	15	13

[a] In this table, Δ is the experimental uncertainty of the energy value, equal to one standard error in units of 10^{-5} cm^{-1}; δ is the difference $E^{exp.} - E^{calc.}$, also in units of 10^{-5} cm^{-1}. When the Δ-value is absent, corresponding energy level was determined from the only transition.

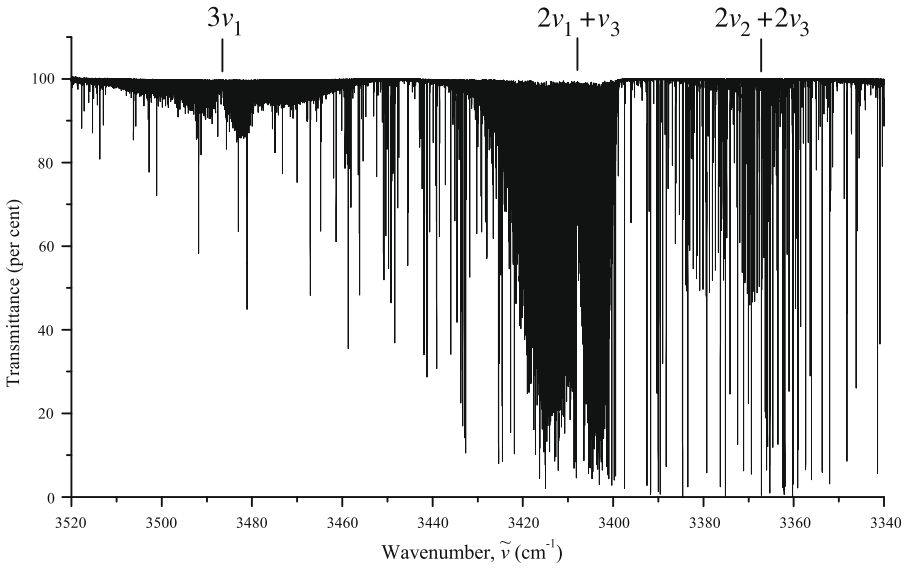

Fig. 2. Overview spectrum of SO_2 in the region of 3340–3800 cm^{-1}.

In the final fit 20 free Hamiltonian parameters (18 diagonal parameters and 2 interaction parameters) and about 900 ($J^{max.} = 66$ and $K_a^{max.} = 24$) experimental rovibrational energies were used. Results are presented in Table 3 together with 1σ statistical confidence intervals. Parameters without confidence intervals in Table 3 have been constrained to the values estimated by above discussed procedure. The rms value of the fit is 0.00028 cm^{-1} corresponding to the experimental uncertainties. To illustrate the quality of experimental data and results of the fit, the list of energy values, $E^{exp.}$, in cm^{-1}, is presented in column 2 of Table 1 together with their experimental uncertainties Δ in column 3 and $\delta = (E^{exp.} - E^{calc.})$ in column 4. The values of $E^{calc.}$ have been calculated using the parameters of Table 3. One can see good correlation between experimental and calculated values and no systematic deviations exist.

When using constrained Hamiltonian parameters in the fit, the reliability of the approximated fixed values should be discussed. Therefore in Table 2 together with the calculated band centers and extrapolated rotational and centrifugal parameters, the corresponding values, when available from the final fit in Table 3, have been collected for comparison. In case of the (300) state, all experimental and predicted values are equal within 1σ confidence interval (also v close enough). This confirms that the fixed values for states (220) and (041) can be considered reliable.

As was mentioned above, local resonance interactions are essential between the states (300), on the one hand, and the states (220) and (041), on the other hand. In this case, because (as follows from Table 3) the distance between the centers of the bands $3\nu_1$ and $4\nu_2 + \nu_1$ is 18 cm^{-1} only, interactions between sets of rovibrational states with different values of quantum number K_a

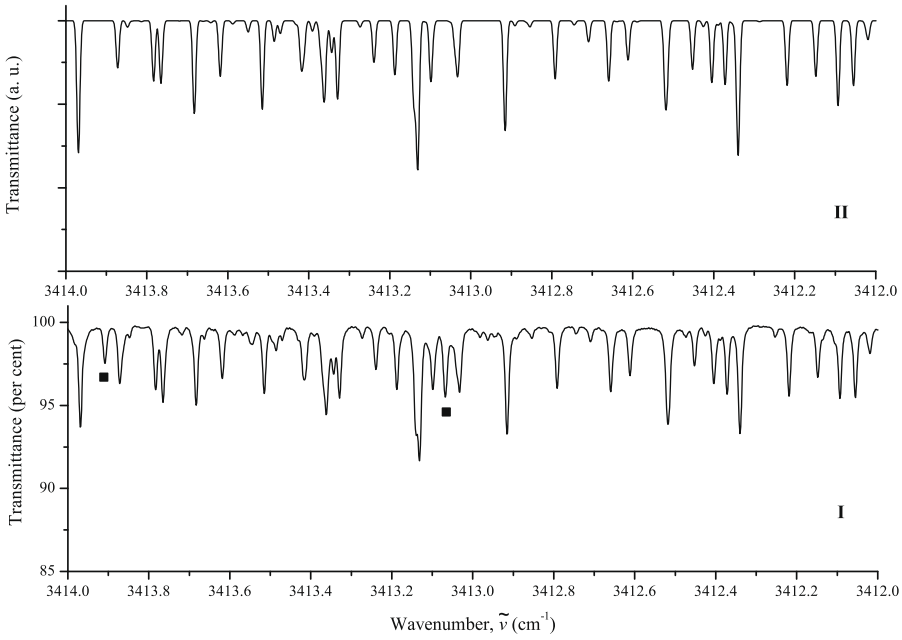

Fig. 3. Small portion of the recorded high resolution spectrum of the SO_2 molecule in the P-branch of the $3\nu_1$ absorption band: I is the experimentally recorded spectrum; II is simulated spectrum (one dipole moment parameter was used in the simulation).

Table 2
Some spectroscopic parameters of the (300), (220), and (041) states of the SO_2 molecule (in cm^{-1}).[a]

Parameter	(300)		(220)		(041)	
	Predicted	Fitted	Predicted	Fitted	Predicted	Fitted
1	2	3	4	5	6	7
ν	3432.31	3432.28768(26)	3317.91	3317.17(69)	3413.18	3414.59(70)
A	2.030	2.0304887(644)	2.110	2.1071(513)	2.167	2.167
B	0.339	0.3392004(131)	0.341	0.3409(170)	0.343	0.3259(794)
C	0.289	0.2893093(110)	0.290	0.2914(169)	0.290	0.2983(791)
$\Delta_K \times 10^4$	0.907	0.9005(864)	1.088	1.088	1.286	1.286
$\Delta_{JK} \times 10^5$	−0.347	−0.3445(678)	−0.397	−0.397	−0.478	−0.478
$\delta_K \times 10^5$	0.110	0.1116(105)	0.140	0.140	0.157	0.157
$H_K \times 10^7$	0.135	0.1348(135)	0.197	0.197	0.250	0.250
$H_{KJ} \times 10^9$	−0.909	−0.9466(149)	−1.035	−1.035	−1.033	−1.033

[a] Values presented in columns 2, 4, and 6 have been theoretically estimated (see text for details). Values in columns 3, 5, and 7 were obtained from the fit (see, for more details, Table 3). In this case, corresponding 1σ statistical confidence interval for fitted parameter is given also. Parameters presented in columns 3, 5, 7 without confidence intervals have been constrained to the predicted ones.

Table 3
Spectroscopic parameters of the (300), (220), (041), and ground vibrational states of the SO_2 molecule (in cm^{-1}).[a]

Parameter	(300)	(220)[b]	(041)[b]	(000)[c]
1	2	3	4	5
E	3432.28768(26)	3317.17(69)	3414.59(70)	
A	2.0304887(644)	2.1071(513)	2.167†	2.02735433
B	0.3392004(131)	0.3409(170)	0.3259(794)	0.3441739084
C	0.2893093(110)	0.2914(169)	0.2983(791)	0.293526529
$\Delta_K \times 10^4$	0.9005(864)	1.088†	1.286†	0.8640369
$\Delta_{JK} \times 10^5$	−0.3445(678)	−0.397†	−0.478†	−0.3901187
$\Delta_J \times 10^6$	0.2186(206)	0.220549	0.220549	0.220549
$\delta_K \times 10^5$	0.1116(105)	0.140†	0.157†	0.0846284
$\delta_J \times 10^7$	0.5627(371)	0.5674232	0.5674232	0.5674232
$H_K \times 10^7$	0.1348(135)	0.197†	0.250†	0.12375
$H_{KJ} \times 10^9$	−0.9466(149)	−1.035†	−1.033†	−0.64936
$H_{JK} \times 10^{11}$	0.116‡	0.116‡	0.116‡	0.116
$H_J \times 10^{12}$	0.37589‡	0.37589‡	0.37589‡	0.37589
$h_K \times 10^9$	0.5670‡	0.5670‡	0.5670‡	0.5670
$h_{JK} \times 10^{12}$	−0.23‡	−0.23‡	−0.23‡	−0.23
$h_J \times 10^{12}$	0.1829‡	0.1829‡	0.1829‡	0.1829
$L_K \times 10^{11}$	−0.265‡	−0.265‡	−0.265‡	−0.265
$L_{KKJ} \times 10^{12}$	0.180‡	0.180‡	0.180‡	0.180
$L_{JK} \times 10^{13}$	−0.109‡	−0.109‡	−0.109‡	−0.109
$L_{JJK} \times 10^{19}$	−0.88‡	−0.88‡	−0.88‡	−0.88
$L_J \times 10^{19}$	−0.116‡	−0.116‡	−0.116‡	−0.116
$l_K \times 10^{12}$	−0.32‡	−0.32‡	−0.32‡	−0.32
$l_{KJ} \times 10^{14}$	0.27‡	0.27‡	0.27‡	0.27
$l_{JK} \times 10^{17}$	−0.2‡	−0.2‡	−0.2‡	−0.2
$l_J \times 10^{18}$	−0.597‡	−0.597‡	−0.597‡	−0.597
$P_K \times 10^{15}$	0.649‡	0.649‡	0.649‡	0.649
$P_{KKJ} \times 10^{16}$	−0.394‡	−0.394‡	−0.394‡	−0.394
$P_{KJ} \times 10^{18}$	−0.703‡	−0.703‡	−0.703‡	−0.703
$P_{JK} \times 10^{19}$	0.778‡	0.778‡	0.778‡	0.778
$S_K \times 10^{18}$	−0.12‡	−0.12‡	−0.12‡	−0.12
$S_{KKJ} \times 10^{20}$	0.70‡	0.70‡	0.70‡	0.70
$F_{xy}^{300-220} \times 10^4$	0.57(23)			
$(2B\zeta^y)^{300-041} \times 10^4$	0.61(21)			

[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). Values marked by "‡" and "†" have been fixed to the values of corresponding parameters of the ground vibrational state and values quated in Table 2, respectively.
[b] There are no experimental transitions assigned to this state in our analysis.
[c] Recalculated from Table 3 of Ref. [33]. Number of kept digits in the values of parameters corresponds the number of digits in the initial values from Ref. [33].

should be taken into account. At the same time, if to speak about interaction between the states (300) and (220), we found for our experimental data only one essential set of strongly interacting states. They are states $[JK_a = 13K_c](300)$, on the one hand, and states $[JK_a = 15K_c](220)$, on the other hand. Fig. 4 illustrates this kind of resonance interaction. The curves I and II give the dependences of the value $\Delta_J = E^{\text{exp.}}_{[JK_a=13K_c](300)} - E^{\text{calc.}}_{[JK_a=13K_c](300)}$ as functions of the quantum number J for the situations without and with resonance operator, Eq. (3), in the Hamiltonian of the molecule. One can see that the presence of resonance operator improves the value of difference Δ. To illustrate a strength of the discussed local interaction, the top panel of Fig. 4 shows the dependence of the value $\Delta E_J = E_{[JK_a=13K_c](300)} - E_{[JK_a=15K_c](220)}$ on the value of quantum number J.

Acknowledgments

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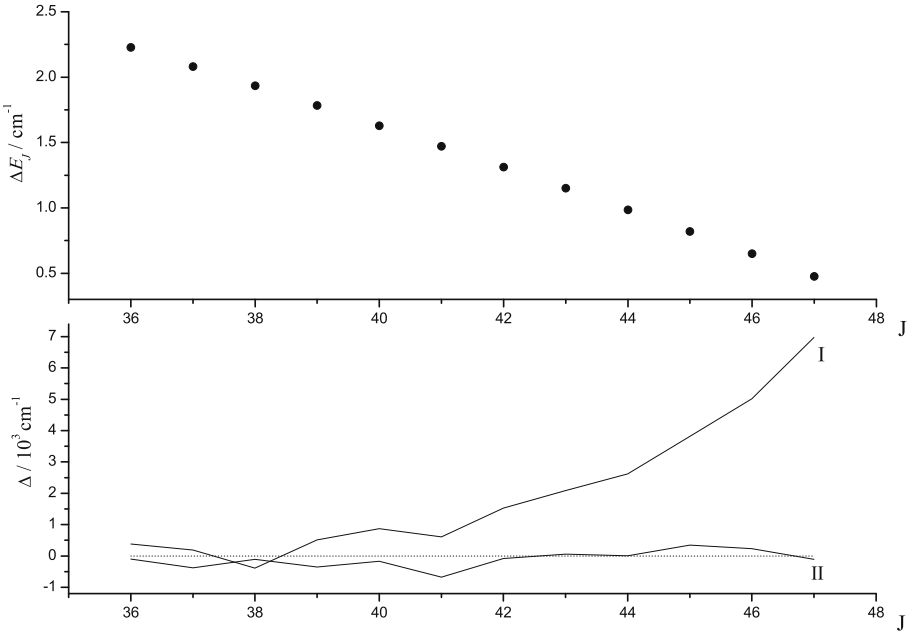

Fig. 4. Illustration of a local resonance interaction in the (300) and (220) vibrational states of SO_2. The dependences of the value $\Delta_J = E^{exp.}_{|JK_a=13K_c|(300)} - E^{calc.}_{|JK_a=13K_c|(300)}$, as functions of the quantum number J, are given by the curves I and II. The curves I and II have been constructed with the energies, $E^{calc.}$, obtained without and with resonance operator, Eq. (3), in the Hamiltonian, Eq. (1), respectively. The top panel illustrates the dependence of the difference $\Delta E_J = E_{|JK_a=13K_c|(300)} - E_{|JK_a=15K_c|(220)}$ on the value of quantum number J.

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