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First high resolution analysis of the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of $S^{18}O_2$

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ABSTRACT

The Fourier-transformed infrared spectra of the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of $S^{18}O_2$ were recorded for the first time in the region 1580–1850 cm^{-1} and theoretically analyzed. About 940 and 1210 transitions were assigned in the experimental spectra with the maximum values of quantum numbers $J^{max.}/K_a^{max.}$ equal to 60/20 and 60/21 to the bands $\nu_1+\nu_2$ and $\nu_2+\nu_3$. The weighted fit of experimentally assigned transitions was made with the Hamiltonian model which takes into account Coriolis resonance interaction between the vibrational states (110) and (011) and Fermi interaction between the states (110) and (030). To make the ro-vibrational analysis physically more suitable, the initial values of main spectroscopic parameters have been estimated from the values of corresponding parameters of the $S^{16}O_2$ species on the basis of the results of the isotopic substitution theory. Finally, the set of 26 spectroscopic parameters obtained from the fit reproduces values of 1229 initial "experimental" ro-vibrational energy levels (about 2150 transitions assigned in the experimental spectra) with the $d_{rms} = 1.8 \times 10^{-4}$ cm^{-1}.

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1. Introduction

Sulfur dioxide is an important chemical species in many fields such as chemistry, interstellar space, planetary nebulae, study of atmospheres of the Earth and Venus (where the abundance of sulfur dioxide is a million times higher than in the Earth's atmosphere), food technology, and laser techniques. It plays an important role as a pollutant in the terrestrial atmosphere. In particular, sulfur dioxide is one of the major air pollutants released in the atmosphere as a result of volcanic eruptions and of fuel combustion in human activities; it contributes to the generation of smog and constitutes a serious health hazard for the respiratory system (see, e.g., Refs. [1–9]). To solve the problems of propagation of monochromatic radiation in the atmosphere, laser sounding, information transfer, and the remote detection and monitoring of SO_2 in situ, one also should have a good knowledge of the fine structure of the SO_2 absorption spectra in different parts of the electromagnetic spectrum, in particular, in the infrared. For this reason, numerous spectroscopic studies of the sulfur dioxide molecule have been made during many years as well in the microwave, submillimeter wave and infrared regions (extensive list of references to earlier studies of sulfur dioxide spectra can be found, e.g., in Ref. [10]).

In this paper we continue our preceding study of the high resolution spectra of sulfur dioxide, Refs. [11–20], and focus on the $S^{18}O_2$ isotopologue, which spectra have been discussed before only in Refs. [21–25]. The information

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about 52 microwave transitions (34 and 18 MW transitions in the ground, (000), and the first excited, (010), vibrational states) of $S^{18}O_2$ was presented by Lovas [21]. Eleven double resonance transitions (five transitions in the ground vibrational state and six transitions in the vibrational state (100)) as well as eight MW transitions in the (100) state of S_2^{18} were recorded by Lindermayer et al. [22]. Again Lindermayer with co-authors recorded diode laser and IR-MW double resonance spectra of the ν_1 and ν_3 bands in Refs. [23,24]. The same ν_1 and ν_3 bands were re-analyzed recently in Ref. [25].

Subject of the present study is the combination bands $\nu_1+\nu_2$ and $\nu_2+\nu_3$ which are located in the region of 1580–1850 cm^{-1}. Earlier this region was discussed in Refs. [26–30], but only for the $^{32}S^{16}O_2$ and $^{34}S^{16}O_2$ isotopologues. So we present here the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of the $S^{18}O_2$ isotopologue for the first time. The conditions of the experiment are described in Section 2. In Section 3 we briefly present the Hamiltonian model used in the fit procedure with the upper energy levels obtained from experimental data. Numerical estimations of the initial values of spectroscopic parameters of the considered vibrational states are also discussed in Section 3. Section 4 describes the measured experimental spectra, the assignment of transitions, and the results of the fit of parameters of the adopted effective Hamiltonian.

2. Experimental details

As described in detail in our preceding work [25] the $S^{18}O_2$ sample gas was produced by controlled combustion of pure sulfur in naturally isotopic composition (Roth, $>99.999\%$) in $^{18}O_2$ (Sigma-Aldrich, 99 atom %). Three spectra of the spectral region between 1580 and 1850 cm^{-1} have been recorded with a Bruker IFS120HR Fourier transform infrared spectrometer by use of a stainless steel White cell of one meter base length adjusted at 24 m optical path. A globar radiation source, KBr windows, a KBr beamsplitter and a mercury–cadmium–telluride semiconductor detector have been used for the spectra. The transmission spectrum was obtained by division of the highly resolved single-channel spectrum by a background spectrum with a lower resolution of 0.1 cm^{-1} (averaged by 200 scans). The optical resolution was 0.0025 cm^{-1} for all the spectra, defined by $0.9\times 1/d_{MOPD}$ (maximum optical path difference). In combination with the weak Norton–Beer apodization this leads to an instrumental linewidth of 0.002 cm^{-1} in the 1580–1850 cm^{-1} range which is important for the present work. The Doppler broadening for $^{32}S^{18}O_2$ at 298.15 K was between 0.0024 cm^{-1} (at 1580 cm^{-1}) and 0.0028 cm^{-1} (at 1850 cm^{-1}). The pressure broadening was between 0.0012 and 0.0015 cm^{-1} at the used pressures of 360 and 450 Pa which means that it was on the edge to maximize the optical density and has to be considered. Thus the total line widths result between 0.0033 and 0.0037 cm^{-1} (root sum square approximation of convolution) which is in accordance with the experimental results. N_2O lines at a partial N_2O pressure of about 10 Pa and water lines have been used for spectral line calibration, Ref. [32]. The total recording time was 23 and 34 h (550 and 810 scans) for the spectra recorded at 450 Pa and 29 h (690 scans) for the spectrum recorded at 360 Pa. In comparison with the analogues experiment for the main species $S^{16}O_2$ which is described in Ref. [29] we could not use the 200 m long-path White cell (although available) due to the limited $S^{18}O_2$ sample quantity and therefore could not quite reach the corresponding spectral quality. During the measurement little amounts of water poured into the White cell which could be used for calibration purposes. In contrast, in the spectrometer nearly no water is detectable during recording of spectra as it is continuously pumped by a turbo molecular pump below 10^{-2} Pa.

3. Hamiltonian model and estimation of spectroscopic parameters

3.1. Effective Hamiltonian

The $^{32}S^{18}O_2$ molecule is an asymmetric top of C_{2v} symmetry with the asymmetry parameter $\kappa=(2B-A-C)/(A-C)\approx -0.948$. On this reason follows:

1. Its three vibrational modes have the following symmetry: q $q_\lambda \in A_1$ for $\lambda=1$, 2, and q $q_\lambda \in B_1$ for $\lambda=3$.
2. In the A-reduction and I^r representation (see, e.g., Refs. [31–34]) both three components of the angular momentum operator, J_x, J_y and J_z, and three values k_{zx}, k_{zy}, k_{zz} are transformed in accordance with irreducible representations B_2, B_1, and A_2, respectively.
3. As a consequence, bands of two types are allowed in absorption, Refs. [35,36]: parallel (or A_1) type bands which correspond to the vibrational transitions $(v_{A_1})\leftarrow(v_{gr.})$, and perpendicular (or B_1) type bands which correspond to the vibrational transitions $(v_{B_1})\leftarrow(v_{gr.})$. The selection rules for "allowed" transitions in the parallel bands are

   $$\Delta J=0,\pm 1,\ \Delta K_a=0,\quad \Delta K_c=\pm 1,$$

   and

   $$\Delta J=0,\pm 1,\ \Delta K_a=\pm 1,\quad \Delta K_c=\pm 1$$

   for the "allowed" transitions in the perpendicular bands. Further, weak "forbidden" transitions are also allowed both in the parallel and perpendicular bands with selection rules of the following form:

   $$\Delta J=0,\pm 1,\ \Delta K_a=even,\quad \Delta K_c=odd,$$

   and

   $$\Delta J=0,\pm 1,\ \Delta K_a=odd,\quad \Delta K_c=odd.$$

The effective Hamiltonian model, which was used for theoretical analysis of experimental data for such molecules, was discussed in the literature many times (see, e.g., Refs. [37–39]). For that reason we reproduce it here without further explanations and refer the reader to the mentioned references for details. In the present paper we followed the strategy of Refs. [25,29] and, in consequence,

Table 1
Spectroscopic parameters of the (110), (011) and (030)[d] vibrational states of $^{32}S^{18}O_2$ (in cm^{-1}).[a]

Parameter 1	$S^{16}O_2$, (000)[b] 2	$S^{18}O_2$, (000)[c] 3	$S^{16}O_2$, (110)[d] predict. 4	$S^{16}O_2$, (011)[d] predict. 5	$S^{16}O_2$, (030)[d] predict. 6
E					
A	2.02735420407	1.91415659	2.0676580790	2.0458846126	2.1505825532
B	0.344173882136	0.305895171	0.34258479604	0.34308108114	0.34437390268
C	0.293526503766	0.263167850	0.2917230612	0.2917632189	0.2919246789
$\Delta_K \times 10^4$	0.864015421	0.76864	0.97194594	0.94279520	1.17899556
$\Delta_{JK} \times 10^5$	−0.390123832	−0.33776	−0.40752705	−0.40912955	−0.44523899
$\Delta_J \times 10^6$	0.220539487	0.176670	0.2198166	0.2239141	0.2223176
$\delta_K \times 10^6$	0.846291509	0.7036	1.035275	1.043185	1.456056
$\delta_J \times 10^7$	0.567423257	0.43585	0.57096366	0.57526686	0.57863030
$H_K \times 10^7$	0.12360428	0.1061	0.156991	0.150028	0.212356
$H_{KJ} \times 10^9$	−0.64960685	−0.5309	−0.7640608	−0.7588778	−0.9723091
$H_{JK} \times 10^{11}$	0.1160311	0.0881	0.45728	0.45728	1.13939
$H_J \times 10^{12}$	0.3746170	0.270	0.371035	0.383021	0.370675
$h_K \times 10^9$	0.5679872	0.454	0.761006	0.770308	1.149858
$h_{JK} \times 10^{12}$	−0.243030	−0.184	−0.77103	−0.77103	−1.85904
$h_J \times 10^{12}$	0.18300674	0.132	0.184720	0.185116	0.183832
$L_K \times 10^{11}$	−0.2608919	−0.207	−0.382622	−0.360662	−0.581010
$L_{KKJ} \times 10^{12}$	0.1807804	0.136	0.24435	0.23255	0.35560
$L_{JK} \times 10^{13}$	−0.1097261	−0.0786	−0.1550	−0.1543	0.2447
$L_{JJK} \times 10^{16}$	−0.99508	−0.677	−0.404	−0.404	−1.045
$L_J \times 10^{17}$	−0.110360	−0.0713	−0.1060	−0.0973	−0.0795
$l_K \times 10^{12}$	−0.319192	−0.241	−0.4588	−0.4489	0.7288
$l_{KJ} \times 10^{14}$	0.254416	0.182	0.304	0.274	−0.251
$l_{JK} \times 10^{17}$			−0.24	−0.24	
$l_J \times 10^{18}$	−0.607568	−0.393	−0.64438	−0.64438	−0.74998
$P_K \times 10^{15}$	0.584163	0.438	1.0620	1.0157	1.7752
$P_{KKJ} \times 10^{16}$	−0.408713	−0.291	−0.58867	−0.58867	−0.99350
$P_{KJ} \times 10^{18}$	−0.623763	−0.422	−0.9947	−0.9947	−1.4977
$P_{JK} \times 10^{19}$	0.649369	0.417	1.222	1.222	1.981
$S_K \times 10^{19}$	−0.88587	−0.628	−2.26	−2.26	−4.01
$S_{KKJ} \times 10^{20}$	0.81536	0.548	1.156	1.156	2.192

Parameter 1	$S^{18}O_2$, (110)[d] predict. 7	$S^{18}O_2$, (011)[d] predict. 8	$S^{18}O_2$, (030)[d] predict. 9	$S^{18}O_2$, (110)[e] fit. 10	$S^{18}O_2$, (011)[e] fit. 11	$S^{18}O_2$, (030)[e] fit. 12
E	1595.2	1810.9	1487.9	1594.6731325(42)	1811.2609942(25)	1487.9
A	1.9544604650	1.9326869986	2.0373849392	1.9495952(87)	1.929189998(76)	2.0373849392
B	0.30430608504	0.30480237014	0.30609519168	0.30455399(12)	0.304968818(10)	0.30609519168
C	0.2613644072	0.2614045649	0.2615660249	0.26168238(18)	0.261648281(12)	0.2615660249
$\Delta_K \times 10^4$	0.87657052	0.84741978	1.08362014	0.96010(90)	0.4293489(76)	1.08362014
$\Delta_{JK} \times 10^5$	−0.35516322	−0.35676572	−0.39287516	−0.35516321600	−0.380242(28)	−0.39287516
$\Delta_J \times 10^6$	0.1759471	0.1800446	0.1784481	0.178061(26)	0.1789220(69)	0.1784481
$\delta_K \times 10^6$	0.892583	0.900494	1.313365	0.89258349100	0.90319(28)	1.313365
$\delta_J \times 10^7$	0.43939041	0.44369361	0.44705704	0.426990(66)	0.443743(22)	0.44705704
$H_K \times 10^7$	0.139487	0.132524	0.194852	0.13110(23)	0.1282362(96)	0.194852
$H_{KJ} \times 10^9$	−0.6453540	−0.6401710	−0.8536022	−0.6453540	−0.6401710	−0.8536022
$H_{JK} \times 10^{11}$	0.42935	0.42935	1.11146	0.42935	0.42935	1.11146
$H_J \times 10^{12}$	0.266418	0.278404	0.266058	0.266418	0.2697(18)	0.266058
$h_K \times 10^9$	0.647019	0.656321	1.03587	0.647019	0.656321	1.03587
$h_{JK} \times 10^{12}$	−0.71201	−0.71201	−1.80001	−0.71201	−0.71201	−1.80001
$h_J \times 10^{12}$	0.133714	0.134110	0.132825	0.133714	0.134110	0.132825
$L_K \times 10^{11}$	−0.328730	−0.306770	−0.527118	−0.328730	−0.306770	−0.527118
$L_{KKJ} \times 10^{12}$	0.19957	0.18777	0.31082	0.19957	0.18777	0.31082
$L_{JK} \times 10^{13}$	−0.1238	−0.1232	0.2136	−0.1238	−0.1232	0.2136
$L_{JJK} \times 10^{16}$	−0.372	−0.372	−1.013	−0.372	−0.372	−1.013
$L_J \times 10^{17}$	−0.0669	−0.0582	−0.0404	−0.0669	−0.0582	−0.0404
$l_K \times 10^{12}$	−0.3806	−0.3707	0.6506	−0.3806	−0.3707	0.6506