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Study of the high resolution spectrum of $^{32}S^{16}O^{18}O$: The ν_1 and ν_3 bands

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ABSTRACT

The high resolution infrared spectrum of the $^{32}S^{16}O^{18}O$ molecule was recorded for the first time with a Bruker IFS 120 HR Fourier transform interferometer in the region of 930–1580 cm^{-1} where the bands ν_1 and ν_3 are located. More than 3000 and about 2400 transitions were assigned in the experimental spectrum with the maximum values of quantum numbers $J^{max.}/K_a^{max.}$ equal to 58/23 and 68/23 to the bands ν_1 and ν_3, respectively. The further weighted fit of experimentally assigned transitions was made with the Hamiltonian model which takes into account Coriolis resonance interaction between the vibrational states (100) and (001). The 81 microwave transitions of the states (100) and (001) known from the literature also were taken into account. As the result, a set of 26 fitted parameters was obtained which reproduces the experiment-based 2690 ro-vibrational energy values of the two bands with the $d_{rms} = 1.8 \times 10^{-4}$ cm^{-1}. Microwave transitions are also reproduced with the accuracy close to experimental uncertainty.

1. Introduction

Sulfur dioxide is an important species in many fields such as chemistry, astrophysics, planetology, study of atmospheres of the Earth and Venus and many others (see, e.g., Refs. [1–6]). On that reason the SO_2 molecule was a subject of numerous high resolution spectroscopic studies both in the microwave (MW) and infrared (IR) spectral regions (for the laboratory high resolution studies of sulfur dioxide during last thirty years, see Refs. [7–38]). As to the $^{32}S^{16}O^{18}O$ isotopologue (natural abundance is about 0.2% species of sulfur dioxide), its high resolution spectra were discussed earlier only in Refs. [39–42]. The 106 microwave transitions belonging to the ground vibrational state and 46 transitions belonging to the state (010) were recorded and discussed in Ref. [39]. A set of MW transitions both in the ground, and in the (010), (100), (020) and (001) vibrational states was recorded in Ref. [40] (in this case, 51 transitions were assigned for the (100) state, and 30 transitions were assigned for the (001) state). Twelve double resonance transitions (6 ground state transitions and 6 transitions belonging to the (100) state) were recorded in Ref. [41]. Being used in the fit together with MW transitions from Ref. [40], they gave the possibility to obtain for the first time a set of 10 rotational and centrifugal distortion parameters of the (100) vibrational state. Again, 342 pure rotational transitions of $^{32}S^{16}O^{18}O$ were recorded in the millimeter, submillimeter, and terahertz spectral regions in Ref. [42], and accurate ground state rotational and centrifugal distortion parameters were determined. However, infrared spectra of $^{32}S^{16}O^{18}O$ were not discussed in the spectroscopic literature earlier.

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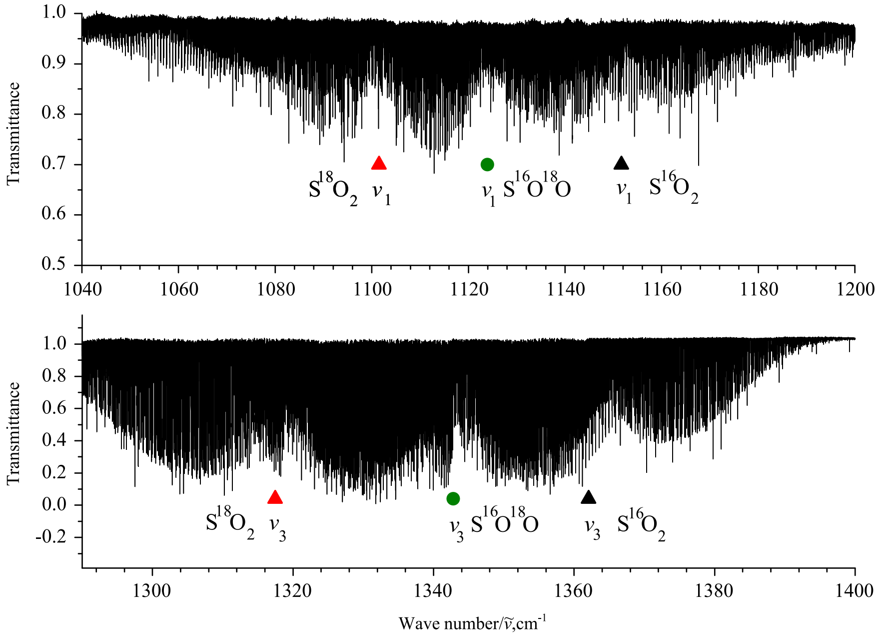

Fig. 1. Survey spectrum of $^{32}S^{16}O^{18}O$ in the region of the ν_1 (upper trace) and ν_3 (lower trace) bands. Corresponding ν_1 and ν_3 bands of $^{32}S^{16}O_2$ and $^{32}S^{18}O_2$ are also seen. Experimental conditions: sample pressure is 170 Pa, absorption path length is 0.23 m; room temperature; number of scans is 530.

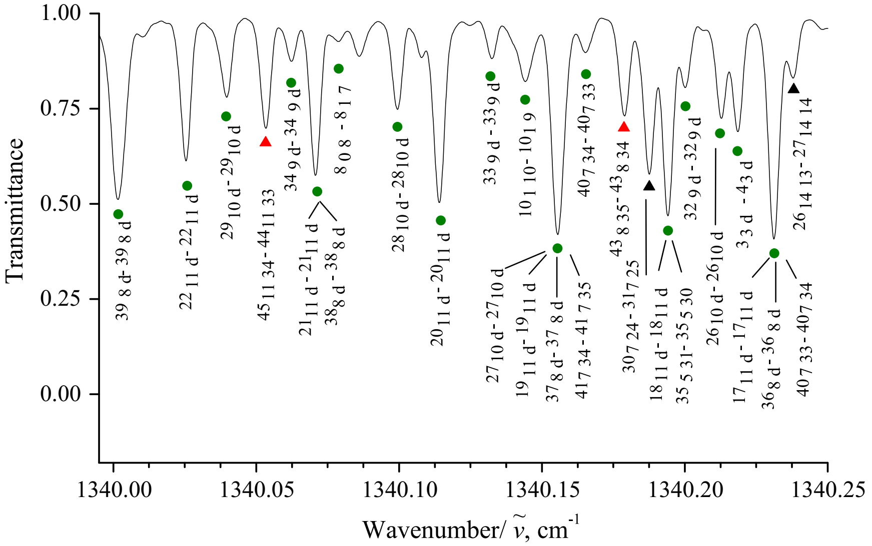

Fig. 2. Detail of the high resolution experimental spectrum of $^{32}S^{16}O^{18}O$ in the Q-branch region of the ν_3 band. Assigned lines of $^{32}S^{16}O^{18}O$ are marked by circles. Lines, which are marked by triangles, belong to the SO_2 species. Index "d" in notations of transitions denotes "doublet", i.e., the energy values of the ro-vibrational states $[JK_aK_c{=}J{-}K_a]$ and $[JK_aK_c{=}J{-}K_a{+}1]$ coincide with each other within 0.0001 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this paper we present the first high resolution FTIR spectra of the $^{32}S^{16}O^{18}O$ species in the region of the ν_1 and ν_3, which have been recorded with a high resolution Fourier Transform spectrometer Bruker IFS-120 HR at the Technische Universität Braunschweig (Germany). Section 2 presents the corresponding experimental details. Theoretical background of our study is briefly 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

In the first step, $^{32}S^{18}O_2$ sample was generated by controlled isochoric combustion of sulfur (Roth, purity better than 99.999 %) in $S^{18}O_2$ (Sigma-Aldrich, 99 atom%) in naturally isotopic composition. The procedure is described in detail in our preceding paper [38].

The $^{32}S^{18}O_2$ sample was treated by use of two optical stainless steel cells in combination with a Bruker IFS120 HR Fourier transform infrared spectrometer. The first cell

Table 1

Spectroscopic parameters of the (100) and (001) vibrational states of the $^{32}S^{16}O^{18}O$ molecule (in cm^{-1})

Parameter 1	(000)[a] 2	(100)[b] 3	(001)[b] 4	(100)[c] 5	(001)[c] 6	(100)[d] 7
E		1123.930266(91)	1342.812057(94)	1124.008	1342.856	1123.93114
A	1.97140279376	1.97285823(97)	1.95147660(86)	1.97286307	1.95148564	1.9728646
B	0.32437916881	0.32283364(20)	0.32330228(21)	0.322835744	0.32330422	0.3228359
C	0.27791093317	0.27672382(19)	0.27676014(21)	0.276591065	0.27689515	0.27659137
$\Delta_K \times 10^4$	0.814875996	0.82670(21)	0.80220(13)	0.8259297	0.8120361	0.82806
$\Delta_{JK} \times 10^5$	−0.361443882	−0.34657(88)	−0.37942(83)	−0.3441918	−0.400203	−0.35074
$\Delta_J \times 10^6$	0.1969054	0.18398(96)	0.21161(89)	0.199927	0.18658	0.1967
$\delta_K \times 10^6$	0.7714684	0.7886(61)	0.7741(76)	0.8254944	0.717576	0.83834
$\delta_J \times 10^7$	0.49628003	0.5562(73)	0.4416(71)	0.499502	0.489609	0.49457
$H_K \times 10^7$	0.1092023	0.11221(94)	0.10686(19)	0.13283	0.19363	0.131
$H_{KJ} \times 10^9$	−0.5606275	−0.5606275	−0.5549(94)	−0.71759	−1.1108	−0.708
$H_{JK} \times 10^{12}$	0.242	0.242	0.242			
$H_J \times 10^{12}$	0.30118	0.30118	0.30118	0.27272		
$h_K \times 10^9$	0.442889	0.442889	0.442889	0.439554		
$h_{JK} \times 10^{13}$	−0.3813	−0.3813	−0.3813			
$h_J \times 10^{12}$	0.149629	0.149629	0.149629	0.1457	0.21	
$L_K \times 10^{12}$	−0.54591	−1.00(12)	−0.54591			
$L_{KKJ} \times 10^{13}$	0.58154	0.58154	0.58154			
$L_{JK} \times 10^{14}$	−0.1410	−0.1410	−0.1410			
$L_{JJK} \times 10^{17}$	−0.6878	−0.6878	−0.6878			
$L_J \times 10^{18}$	−0.325	−0.325	−0.325			
$P_K \times 10^{15}$	0.62209	0.62209	0.62209			
$P_{KKKJ} \times 10^{16}$	−0.50742	−0.50742	−0.50742			
$P_{KKKJJ} \times 10^{17}$	0.1331	0.1331	0.1331			

[a] Vibrational ground state parameters of $^{32}S^{16}O^{18}O$ which are reproduced from Ref. [42].

[b] Parameters of the states (100) and (001) obtained from the fit in the present study. Values in parentheses are 1σ confidence intervals (in last digits). Parameters presented without confidence intervals have been constrained to values of corresponding parameters from column 2.

[c] Reproduced from Ref. [40].

[d] Reproduced from Ref. [35].

(White type) was used with an optical path of 4 m and a sample gas pressure of 10 Pa (spectrum I), the second cell (single path) with 0.23 m optical path and a pressure of 170 Pa (spectrum II). At typical leak rates of such cells of about 10 Pa/d gaseous water from ambient penetrates into the cells so that a partial exchange of oxygen via the forming sulfurous acid takes place. In this way the portion of $^{32}S^{16}O^{18}O$ and later $^{32}S^{16}$ O_2 increases during the measuring time of up to about 30 h. During the second halve of the recording period the portion of the here favored $^{32}S^{16}O^{18}O$ isotopologue appeared to be rather constant between 30 and 40% of the total sulfur dioxide so that it could be recorded over a few hours. The recorded spectral range was 930–1580 cm^{-1}. A global IR radiation source, a KBr beamsplitter, a mercury–cadmium–telluride (MCT) semiconductor detector and KBr windows have been used. We ran the spectrometer with maximum optical resolution at 0.0021 cm^{-1}, defined by $1/d_{MOPD}$ (maximum optical path difference, here 486 cm). In combination with the weak Norton–Beer apodization this leads to an instrumental resolution of 0.0017 cm^{-1}. As the Doppler broadening for $^{32}S^{16}O^{18}O$ at 298.15 K was between 0.0016 cm^{-1} (at 1050 cm^{-1}) and 0.0021 cm^{-1} (at 1400 cm^{-1}) and the pressure broadening was about 0.0006 cm^{-1} (at 170 Pa), the total line width results between 0.0024 and 0.0028 cm^{-1} (root sum square approximation of convolution). The calibration of the spectral lines was performed with water lines and N_2O lines at a partial N_2O pressure of about 10 Pa. The total recording time was 19 h for 370 scans (4 m path) and 27 h for 530 scans (0.23 m path).

3. Theoretical background and the Hamiltonian model

The $^{32}S^{16}O^{18}O$ molecule is an asymmetric top with the value of the asymmetry parameter $\kappa = (2B - A - C)/(A - C) \simeq -0.945$ and with the symmetry isomorphic to the C_s point symmetry group. As the consequence,

1. All three vibrational coordinates, q_1, q_2, and q_3, are symmetric, and all the vibrational states of the $^{32}S^{16}O^{18}O$ molecule are of the A' symmetry.