High resolution study of the rotational structure of doubly excited vibrational states of $^{32}\text{S}^{16}\text{O}^{18}\text{O}$: The first analysis of the $2\nu_1$, $\nu_1 + \nu_3$, and $2\nu_3$ bands

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1. Introduction

Sulfur dioxide is an important species in many fields of study, such as chemistry, interstellar space, planetary nebulae, study of atmospheres of the Earth and Venus, food technology, and many others (see, e.g., Refs. [1-9]). On that reason, high resolution spectra of sulfur dioxide, $^{32}\text{S}^{16}\text{O}_2$, and its isotopologues, $^{34}\text{S}^{16}\text{O}_2$ and $^{32}\text{S}^{18}\text{O}_2$, have been subject of numerous laboratory investigations for a long time (see, e.g., reviews in the recent papers, Refs. [10,11]; see also Ref. [12]). Despite the fact that it is the third most abundant isotopic impurity, 0.2%, in normal samples after $^{32}\text{S}^{16}\text{O}_2$ and $^{34}\text{S}^{16}\text{O}_2$ and, as a consequence, one can expect to observe it in the spectra of the atmospheres of the outer planetary bodies, the $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ isotopologue has rarely been investigated up to now, see Refs. [11,13-16].

The present work continues our recent study of the high resolution spectra of sulfur dioxide and its isotopologues in the infrared region, Refs. [17-26], with the $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ molecule in the spectral region of 2100 - 2700 cm$^{-1}$ where the bands $2\nu_1$, $\nu_1 + \nu_3$, and $2\nu_3$ are located. Regarding the other isotopologues of sulphur dioxide, this region was discussed earlier in Refs. [27-41]. For $^{32}\text{S}^{16}\text{O}^{18}\text{O}$, the present study is the first attempt to consider the $2\nu_1$, $\nu_1 + \nu_3$, and $2\nu_3$ bands. In Section 2 we describe the conditions of our experiment. Description of the experimental spectra and results of assignment of the transitions are given in Section 3. Section 4 presents the theoretical background of the further analysis of experimental data, including the used Hamiltonian model and numerical estimation of the initial values of the rotational and of the main resonance interaction parameters. The results of the analysis and discussion are given in Section 5.

2. Experimental details

The $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ sample was generated in two steps. In the first step the $^{32}\text{S}^{16}\text{O}_2$ sample gas was produced by controlled isochoric combustion of sulfur $^{32}\text{S}$ (Roth, purity better than 99.9995) in $^{16}\text{O}_2$ (Sigma-Aldrich, 99 atom%). The procedure is described in detail in our preceding paper, Ref. [23]. The $^{32}\text{S}^{18}\text{O}_2$ sample was treated by use of an optical White cell from stainless steel with a base length of one meter at varied optical paths (4 to 24 m) and sample gas pressures (10 to 430 Pa), see Table 1. At typical leak rates of about 10 Pa/d gaseous water from ambient penetrates into the cell so that a partial exchange of oxygen via the forming sulfuric acid takes place. In this way the portion of $^{32}\text{S}^{16}\text{O}^{18}\text{O}$ and later $^{16}\text{O}_2$ increases during a preselected reaction time and the measuring...
time (11 to 43 h) and a recording period over a few hours could be achieved in which 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.

In the spectral region between 1800 and 2800 cm$^{-1}$ four spectra have been recorded with a Bruker IFS120HR Fourier transform infrared spectrometer in combination with the described White cell. A globar radiation source (driven at 24 V, 3.8 A and about 1 Pa N$_2$ atmosphere), KBr windows, a CaF$_2$ beamsplitter and an indium antimonide (InSb) semiconductor detector have been used for recording the spectra. The whole spectrometer was pumped by a turbomolecular pump to an average pressure below 0.1 Pa. 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). Using Norton-Beer weak apodization, the nominal optical resolution was 0.0025 cm$^{-1}$ for all the spectra, defined by 0.9 $\times$ 1$/$ linewidth (maximum optical path difference) which leads to an instrumental linewidth of 0.002 cm$^{-1}$. The Doppler broadening for $^{32}$S$^{16}$O$^{16}$O at 298.15 K was between 0.0027 cm$^{-1}$ (at 1800 cm$^{-1}$) and 0.0042 cm$^{-1}$ (at 2800 cm$^{-1}$). The pressure broadening was between 0.0003 and 0.0014 cm$^{-1}$ at the used pressure range between 10 and 430 Pa. This means that it has a minor but not negligible contribution to the total line widths which result between 10 and 430 Pa. This means that it has a minor but not negligible contribution to the total line widths which result between 10 and 430 Pa. This means that it has a minor but not negligible contribution to the total line widths which result between 10 and 430 Pa.

For optimization of data recording and line calibration we used procedures described in Refs. [42,43].

3. Description of the spectra and assignment of transitions

The survey spectra I and III (for the experimental conditions, see Table 1 at the used pressure range 2/0.94 m; room temperature; number of scans is 580; Experimental conditions for the spectrum I: sample pressure is 10 Pa, absorption path length is 4 m; room temperature; number of scans is 1080. Experimental conditions for the spectrum III: sample pressure is 280 Pa, absorption path length is 24 m; room temperature; number of scans is 580.)

2), in the $A$-reduction and $f$ representation (see, e.g., Refs. [44–47]) three components of the angular momentum operator, $J_x$, $J_y$, and $J_z$, are transformed in accordance with irreducible representations $A'$, $A''$, and $A'''$, respectively. In accordance with the same irreducible representations, $A'$, $A''$, and $A'''$, the values $k_{xx}$, $k_{yy}$, $k_{zz}$, are transformed.:

3), as the consequence, any vibrational band of $^{32}$S$^{16}$O$^{32}$O is a hybrid band, Refs. [48–51], and transitions of both the $a$-, and $b$-type are allowed by the symmetry of the molecule; selection rules in this case are: $\Delta J = 0, \pm 1$ and $\Delta K_a = 0, \pm 1, \pm 2, \pm 3, \ldots$, $\Delta K_c = \pm 1, \pm 3, \ldots$ for any vibrational band of $^{32}$S$^{16}$O$^{32}$O.

Assignment of transitions was made on the basis of the Ground State Combination Differences (GSCD) method. In this case, the ground state rotational energies have been calculated with the parameters from Ref. [16] (for the convenience of the reader, parameters of the ground vibrational state from Ref. [16] are reproduced in column 2 of Table 2). As the result, about 3970, 2960 and 3450 transitions with values of quantum numbers $j_{\text{max}}$, $|K_a|_{\text{max}}$, equal to 59/20, 68/25, and 43/18 were assigned to the $2v_1$, $2v_1 + v_2$, and $2v_2$ bands, respectively (see also statistical information in Table 3). The list of assigned transitions is presented in the Supplementary Material.

4. Hamiltonian model and estimation of spectroscopic parameters

4.1. Effective Hamiltonian

The effective Hamiltonian model, which was used for theoretical analysis of experimental data, has been discussed in the preceding studies (see, e.g., Refs. [52–55]). For that reason we reproduce it here without detailed explanations. For the (200), (101) and (002) vibrational states of the $^{32}$S$^{16}$O$^{32}$O molecule it is possible to show that the Coriolis resonance interactions between them are not neglectable and therefore should be taken into account for the

<table>
<thead>
<tr>
<th>Spectr. Region/cm$^{-1}$</th>
<th>Resolution/cm$^{-1}$</th>
<th>Measuring time/h</th>
<th>No. of scans</th>
<th>Source</th>
<th>Detector</th>
<th>Beam-splitters</th>
<th>Opt. path-length/m</th>
<th>Aperture/mm</th>
<th>Temp./°C</th>
<th>Pressure/Pa</th>
<th>Calibr. gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>I 1800–2800</td>
<td>0.0025</td>
<td>43</td>
<td>1080</td>
<td>Globar InSb</td>
<td>CaF$_2$</td>
<td>4</td>
<td>1.00</td>
<td>25 ± 0.5</td>
<td>10</td>
<td>N$_2$O</td>
<td></td>
</tr>
<tr>
<td>II 1800–2800</td>
<td>0.0025</td>
<td>11</td>
<td>280</td>
<td>Globar InSb</td>
<td>CaF$_2$</td>
<td>16</td>
<td>1.00</td>
<td>25 ± 0.5</td>
<td>52</td>
<td>N$_2$O</td>
<td></td>
</tr>
<tr>
<td>III 1800–2800</td>
<td>0.0025</td>
<td>23</td>
<td>580</td>
<td>Globar InSb</td>
<td>CaF$_2$</td>
<td>24</td>
<td>1.15</td>
<td>25 ± 0.5</td>
<td>280</td>
<td>N$_2$O</td>
<td></td>
</tr>
<tr>
<td>IV 1800–2800</td>
<td>0.0025</td>
<td>21</td>
<td>520</td>
<td>Globar InSb</td>
<td>CaF$_2$</td>
<td>24</td>
<td>1.30</td>
<td>25 ± 0.5</td>
<td>430</td>
<td>N$_2$O</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Survey spectra I and III of $^{32}$S$^{16}$O$^{18}$O in the region of 2100–2700 cm$^{-1}$. Experimental conditions for the spectrum I: sample pressure is 10 Pa, absorption path length is 4 m; room temperature; number of scans is 1080. Experimental conditions for the spectrum III: sample pressure is 280 Pa, absorption path length is 24 m; room temperature; number of scans is 580.
analysis of the ro-vibrational structures of these vibrational states. On the other hand, interactions between stretching and bending excited states of the molecule are small and can be neglected. As the consequence, the effective Hamiltonian in the form

\[
\sum_{\nu, \tilde{\nu}} H_{\nu \nu}^{\text{vib.-rot}} = \sum_{\nu, \tilde{\nu}} \langle \nu | H^{\nu \nu} | \tilde{\nu} \rangle
\]

(1)
can be used in the theoretical analysis of the experimental data. In this case, the summation is taken from 1 to 3 for both \(\nu\) and \(\tilde{\nu}\) in Eq. (1), and \((1) = (200), (2) = (101), \) and \((3) = (002)\). Diagonal blocks \(H_{\nu \nu}^{\nu \nu}\) in Eq. (1) describe the unperturbed rotational structures of the corresponding vibrational states and have the following form of the reduced effective Hamiltonian in the \(A\)-reduction and \(I\) representation (see, e.g., Refs. [56–58]):

\[
H_{\nu \nu}^{\nu \nu} = E^\nu + \left[ A^\nu - \frac{1}{2} (B^\nu + C^\nu) \right] J_z^2 + \frac{1}{2} (B^\nu - C^\nu) J_y^2 - \frac{1}{2} (B^\nu + C^\nu) J_x^2
\]

\[
- 4J_x J_y \{ \delta_{\nu \tilde{\nu}} J_x J_y + 4J_x J_y \} - 4J_y J_z \{ \delta_{\nu \tilde{\nu}} J_y J_z + 4J_y J_z \} - 2J_z J_z \}
\]

\[
+ H_{J_z} J_z + H_{J_y} J_y + H_{J_x} J_x + H_{J_z} J_z + H_{J_y} J_y + H_{J_x} J_x
\]

\[
+ \left[ \delta_{\nu \tilde{\nu}} J_x J_x + 6J_x J_x \right] + \left[ \delta_{\nu \tilde{\nu}} J_y J_y + 6J_y J_y \right] + \left[ \delta_{\nu \tilde{\nu}} J_z J_z + 6J_z J_z \right]
\]

\[
+ \left[ \delta_{\nu \tilde{\nu}} J_x J_y + 6J_x J_y \right] + \left[ \delta_{\nu \tilde{\nu}} J_y J_x + 6J_y J_x \right] + \left[ \delta_{\nu \tilde{\nu}} J_z J_y + 6J_z J_y \right] + \left[ \delta_{\nu \tilde{\nu}} J_y J_z + 6J_y J_z \right]
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\]

\[
+ P_{J_x} J_x + P_{K_{xx} J_x} J_x + P_{K_{yy} J_y} J_y + \cdots
\]

(2)

where \(\hat{\mathcal{F}}_x = \hat{J}_x^2 - \hat{J}_y^2\), \(\ldots\), denotes anticommutator; \(A^\nu, B^\nu, \) and \(C^\nu\) are the effective rotational constants connected with the vibrational state \(\nu\), and the other parameters are the different order centrifugal distortion coefficients. The nondiagonal block \(H_{\nu \tilde{\nu}}^{\nu \nu}\) describes resonance interactions between vibrational states (200) and (101), (101) and (002), and have the form, Ref. [59]

\[
H_{\nu \tilde{\nu}}^{\nu \nu} = H_{\nu \nu}^{\nu \nu} + H_{\tilde{\nu} \nu}^{\nu \nu},
\]

(3)

and the two operators at the right side of Eq. (3) describe Fermi-and Coriolis-type resonance interactions:

\[
H_{\nu \nu}^{\nu \nu} = \gamma_{\nu \nu} F_{\nu 0} + \gamma_{\nu \nu} F_{\nu 2} + \gamma_{\nu \nu} F_{\nu 4} + \cdots + \gamma_{\nu \nu} (\tilde{J}_x^2 - \tilde{J}_y^2) + \cdots
\]

(4)

and

\[
H_{\nu \nu}^{\nu \nu} = \gamma_{\nu \nu} \gamma_{\nu \nu} F_{\nu 0} + \gamma_{\nu \nu} \gamma_{\nu \nu} F_{\nu 2} + \gamma_{\nu \nu} \gamma_{\nu \nu} F_{\nu 4} + \cdots + \gamma_{\nu \nu} \gamma_{\nu \nu} (\tilde{J}_x^2 - \tilde{J}_y^2) + \cdots
\]

(5)

where

\[
H_{\nu \nu}^{\nu \nu} = \frac{1}{2} \nu_c^2 + \nu_c^2 \nu_c^2 + \frac{1}{2} \nu_c^2 \nu_c^2 + \nu_c^2 \nu_c^2 + \nu_c^2 \nu_c^2 + \nu_c^2 \nu_c^2 + \frac{1}{2} \nu_c^2 \nu_c^2 + \cdots
\]

(6)

4.2. Estimation of spectroscopic parameters

The energy values obtained from experimental infrared transitions were used then in the weighted fit of parameters of the