

Collision induced broadening of ν_1 band and ground state spectral lines of sulfur dioxide perturbed by N₂ and O₂

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Abstract

To monitor the constituents and trace pollutants of Earth atmosphere and understand its evolution, accurate spectroscopic parameters are fundamental information. SO₂ is produced by both natural and anthropogenic sources and it is one of the principal causes of acid rains as well as an important component of fine aerosol particles, once oxidized to sulfate. The present work aims at determining SO₂ broadening parameters using N₂ and O₂ as atmospherically relevant damping gases. Measurements are carried out in the infrared (IR) and mm-/sub-mm wave regions, around 8.8 μm and in the 104 GHz – 1.1 THz interval, respectively. IR ro-vibrational transitions are recorded by using a tunable diode laser spectrometer, whereas the microwave spectra are recorded by using a frequency-modulated millimeter-/submillimeter-wave spectrometer. SO₂-N₂ and SO₂-O₂ collisional cross sections are retrieved for several ν_1 band ro-vibrational transitions of ³²SO₂, for some transitions belonging to either $\nu_1 + \nu_2 - \nu_2$ of ³²SO₂ or ν_1 of ³⁴SO₂ as well as for about 20 pure rotational transitions in the vibrational ground state of the main isotopic species. From N₂- and O₂-broadening coefficients the broadening parameters of SO₂ in air are derived. The work is completed with the study of the dependence of foreign broadening coefficients on the rotational quantum numbers.

Keywords: SO₂; atmospheric monitoring; N₂-, O₂-, air-broadening parameters; infrared spectroscopy; microwave spectroscopy.

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Introduction

Nowadays, remote sensing techniques allow monitoring and accurately retrieving the concentration profiles of atmospheric constituents and trace pollutants, since these molecules have strong rotation and vibration-rotation absorptions in the microwave (MW) and infrared (IR) spectral domains, respectively [1-4]. The satellites used for sounding the terrestrial atmosphere embark spectrometers that provide a large amount of spectral information at ever increasing quality in terms of spectral coverage, resolution and signal-to-noise ratio [1]. For these reasons, spectroscopic parameters are of fundamental importance for exploiting remote sensing applications in atmospheric and climate research, environmental monitoring and gas-phase analysis. As a matter of fact, only their accurate knowledge allows an accurate retrieval of concentrations and distributions of the gas phase molecular species in the atmosphere. The relevant spectroscopic parameters include line-by-line parameters, i.e., transition frequencies and their intensities, pressure broadening coefficients and pressure induced shifts, and their temperature dependence. The existing spectroscopic data are then collected into a number of different databases, among which the most important ones are HITRAN [5], GEISA [6], JPL [7], and the Cologne database [8]. Within this framework, the aim of laboratory spectroscopy is to provide spectroscopic parameters for a wide variety of species of atmospheric, astrophysical and industrial relevance. Furthermore the study of collisional broadening and shifting coefficients, these being related to the intermolecular potential, can shed light on the driving forces ruling the scattering events in the gas phase (see e.g. Refs. 9-13 and references therein).

Sulfur dioxide (SO_2) is an important molecule for Earth atmosphere since it actively enters in the sulfur cycle and it is one of the causes of acid rains. SO_2 has a lifetime in the atmosphere of about a day, it is oxidized quickly in the atmosphere, thus leading to aerosol formation and acid deposition [14]. As sulfate, it is an important component of fine aerosol particles (PM10 and PM2.5). Furthermore, sulfate aerosol also affect Earth's radiation balance either through direct scattering of sunlight or indirectly via modification of cloud albedoes. On a global scale, the majority of natural SO_2 is produced by volcanoes [15-17] and by the oxidation of sulfur gases produced by the decomposition of plants. Therefore, natural emissions usually occur at high altitude or far from city centers, and hence the SO_2 background concentration in clear air is about 1 ppb [18]. On the other hand, a sizeable amount of SO_2 is of anthropogenic origin, being produced by combustion of fossil fuels as well as by non-ferrous smelting processes for the conversion of ores to free metals [18]. In addition, this compound is largely employed in food-preserving and wine

making industries. It is thus not surprising that SO₂ has received a great deal of attention from the scientific community and it is still the subject of a number of spectroscopic studies.

The fundamental ν_1 and ν_3 bands of ³²S¹⁶O₂ isotopologue have been thoroughly analyzed in 1980s by Guelachvili and co-workers [19,20] and subsequently reinvestigated by Flaud et al. together with the ν_2 fundamental and the $2\nu_2 - \nu_2$ hot band [21]. In 2005 Müller and Brünker have accurately re-determined the rotational parameters for the ground and $\nu_2 = 1$ states [22]. Some ro-vibrational transitions, belonging to ν_1 and ν_3 bands, have been object of study by Sumpf with the aim of determining line-by-line transition intensities [23], while accurate intensity determinations have been performed within the spectral region 940 – 1400 cm⁻¹ region by Fourier transform IR spectroscopy [24]. Since 1992 different studies have focused on the determination of SO₂ self- [23,25-32] and foreign-broadening coefficients [26,27,33-37]. A few years ago, a complete listing of sulfur dioxide self-broadening coefficients has been compiled by combining the results obtained from IR and MW spectroscopy with semiclassical calculations [38]. In addition, the homodimer of SO₂ has been investigated by Tasinato and Grimme, theoretically using dispersion-corrected density functional theory (DFT-D3) as well as experimentally by means of tunable diode laser (TDL) IR spectroscopy [39]. In that work, the dissociation energies of (SO₂)₂ and (CH₂F₂)₂ have been determined experimentally from the broadening of the ro-vibrational transitions of the corresponding monomers collisionally perturbed by a range of damping gases [39]. Recently, SO₂ has been included in an HITRAN-like database of line parameters for molecules of planetary interest perturbed by H₂, He or CO₂ [40]. Very recently, Ceselin et al. exploited IR and mm/sub-mm wave spectroscopy to retrieve new line-by-line pressure broadening parameters of SO₂ perturbed by He, H₂ and CO₂ [41].

In the present contribution, our work aiming at the determination of SO₂ broadening parameters for atmospheric and astrochemical applications is extended by considering the atmospherically relevant N₂ and O₂ buffer gases.

Experimental details

The broadening parameters of SO₂ perturbed by N₂ and O₂ as buffer gases have been determined both in the infrared (IR) and millimeter/sub-millimeter (mm-/sub-mm) wave region. IR measurements have been carried out at the Laboratory of Molecular Spectroscopy of Venice (LMS-Ve), whereas mm-/sub-mm ones have been performed in the Laboratory of mm/sub-mm wave Spectroscopy of Bologna (LMS-Bo).

For what concerns IR measurements, SO₂ high resolution spectra were recorded by using a TDL spectrometer installed at LMS-Ve and working in a three beam configuration [42], in which the radiation emitted from a lead salt laser was split into three beams. The main part of the radiation was directed through the SO₂ sample contained in either a 92.3 cm or 68.1 cm path length cell. The other two beams were sent to a Germanium etalon and to the SO₂ reference cell, respectively, both employed for calibration purposes. Each beam was collected by its own HgCdTe detector, cryogenically cooled at liquid nitrogen temperature. The acquired signals were digitized by a four channel ultrafast acquisition card with a 14 bit vertical resolution [43].

The spectra were recorded at (296 ± 1) K by using two different lasers centered at 8.1 and 8.9 μm , respectively, both cooled at liquid nitrogen temperature. Up to 1024 independent scans were averaged to generate each spectrum. Pressure broadening measurements were carried out by perturbing a fixed amount of SO₂ around 100 Pa (according to the intensities of the spectral lines) and adding increasing quantities of damping gas up to a total pressure of 45.40 hPa at most. The pressure was measured by using two different vacuum gauges with a full scale range of 10 and 100 hPa, respectively, each with a quoted manufacture accuracy of 0.15% on the full scale. Two independent series of measurements were performed in order to increase the accuracy of the retrieved pressure broadening parameters [43,44]. An elapsed time of 10 – 15 min was adopted between the filling of the sample cell and the recording of the spectra in order to promote gas homogenization inside the cell. The SO₂ gas was supplied by Sigma - Aldrich with a purity of 99.9%, whereas N₂ and O₂ damping gases were provided by SIAD with a purity greater than 99.9% and 99.5% respectively. Line frequencies that derive from high resolution Fourier Transform IR data were used for wavenumber calibration of the acquired spectra [37]. The accuracy of the calibration was estimated around $3.3 \times 10^{-4} \text{ cm}^{-1}$. Absorbance spectra were obtained from the incident and transmitted radiation intensities according to the Beer-Lambert's law, with the incident intensity retrieved by fitting no absorption regions (i.e. the baseline) to a polynomial function.

The lineshape analysis was performed by using the Visual LineShape Fitting program (VLSFP) running in multiline mode [45]. Line-by-line parameters were obtained by fitting all the absorption lines in a given micro-window to the Voigt profile (VP) and the spectra recorded at different pressures were fitted independently from each other. Concerning the two lasers adopted in the present work, the one centered at 8.1 μm presented an instrumental lineshape function that could be well reproduced as a Lorentzian function, whereas that emitting around 8.9 μm was characterized by a Gaussian instrumental function. In the first case during the fits employing the VP model, Gaussian half widths were fixed at the molecular contribution $\gamma_D^{\text{SO}_2}$ due to the thermal motion

$$\gamma_D^{\text{SO}_2} = \frac{\nu_{if}}{c} \left(\frac{2k_B N_a T \ln 2}{m} \right)^{1/2} \quad (1)$$

where ν_{if} is the frequency of the $f \leftarrow i$ ro-vibrational transition, c represents the speed of light, k_B is the Boltzman's constant, N_a is the Avogadro's constant, T is the absolute temperature and m is the mass of the radiating species. The Lorentzian instrumental half width was considered as described in the next section (see equation 3). In the case of a Gaussian instrumental function, the Doppler half width was fixed to an effective value given by the following equation

$$\gamma_D^{\text{eff}} = \left[(\gamma_D^{\text{SO}_2})^2 + (\gamma_D^{\text{TDL}})^2 \right]^{1/2} \quad (2)$$

where γ_D^{TDL} is the instrumental Doppler half width. The recording of the low-pressure (< 30 Pa) spectra of pure SO_2 and the subsequent fitting of the spectral features to a Gaussian profile provided the effective Doppler half widths with typical values around $1.15 \times 10^{-3} \text{ cm}^{-1}$. The assignments of the recorded spectral features were performed by using the HITRAN database [5].

Concerning the MW measurements, the recording of pure rotational spectra of SO_2 perturbed by either N_2 or O_2 in the mm-/sub-mm wave region was performed using a frequency-modulated computer-controlled spectrometer working in the 65 GHz – 1.6 THz frequency range, with the 104 GHz – 1.1 THz range actually considered. The detailed description of the spectrometer is provided in Refs. [46-48]. To briefly summarize, the radiation source is an interchangeable system consisting of Gunn-diode oscillators and Gunn-diode-driven frequency multipliers, phase-locked to a rubidium frequency standard. The frequency modulation is achieved by sine-wave modulating the 72 MHz local oscillator of the synchronization loop at 1.666 kHz and, by tuning the Lock-in amplifier to twice the modulation frequency, second harmonic detection is performed. The spectrometer is equipped with a liquid-He InSb detector for THz measurements and Schottky detectors for recordings below 500 GHz.

In this work, a previous investigation of the pressure broadening of rotational lines of SO_2 perturbed by N_2 and O_2 was extended. To investigate the dependence of pressure-broadening parameters on the J and K_a quantum numbers, the following $\Delta J = 0$ and $\Delta K_a = +1$ transitions were considered [36]. The first set consists of transitions with the same starting value for K_a ($K_a = 11 \leftarrow 10$) in order to investigate the J dependence: $J = 11_{11,1} \leftarrow 11_{10,2}$, $J = 12_{11,1} \leftarrow 12_{10,2}$, $J = 15_{11,5}$

$\leftarrow 15_{10,6}, J = 16_{11,5} \leftarrow 16_{10,6}, J = 26_{11,15} \leftarrow 26_{10,16}, J = 28_{11,17} \leftarrow 28_{10,18}, J = 34_{11,23} \leftarrow 34_{10,24}, J = 42_{11,31} \leftarrow 42_{10,32}, J = 51_{11,41} \leftarrow 51_{10,42}, J = 60_{11,49} \leftarrow 60_{10,50}$. In the second set, transitions with the same J value ($J = 10$) were considered in order to study the K_a dependence: $J = 10_{1,9} \leftarrow 10_{0,10}, J = 10_{2,8} \leftarrow 10_{1,9}, J = 10_{4,6} \leftarrow 10_{3,7}, J = 10_{5,5} \leftarrow 10_{4,6}, J = 10_{6,4} \leftarrow 10_{5,5}, J = 10_{7,3} \leftarrow 10_{6,4}$. In the present study, further measurements for these two sets of transitions were performed in order to confirm and improve the results of Ref. [36]. To extend the study, one $\Delta J = -1$ transition, $J = 20_{7,13} \leftarrow 21_{6,16}$, and two $\Delta J = +1$ transitions, $J = 43_{5,39} \leftarrow 42_{6,36}$ and $J = 3_{3,1} \leftarrow 2_{2,0}$, were also considered.

The rotational lines were recorded using starting pressures of SO₂ in the range 0.04 - 0.53 Pa (according to transition intensity) and then adding increasing quantities of either N₂ or O₂, from ~6.7 Pa up to ~133.3 Pa. The pressure inside the cell was measured by means of a Baratron gauge with a measurable pressure range of 0.01 - 133.3 Pa. The gas pressure was continuously monitored during the measurements and it was found stable within less than 0.01 Pa, the latter value thus providing the accuracy of its measurements. All spectra were recorded at room temperature (298 ± 1 K). For each transition, series of measurements were performed in order to have a total of 25 - 30 points.

To retrieve the collisional (also denoted Lorentzian) line width, the second harmonic profiles were fitted to a lineshape model that explicitly accounts for frequency modulation [49-51]. To correctly reproduce the lineshapes recorded at low pressure (up to a total pressure in the range 26.7 - 33.3 Pa), and in particular, to account for narrowing effects, the Speed Dependent Voigt Profile (SDVP) [52,53] was employed. The suitability of this line profile model is demonstrated by the small residuals (observed-calculated differences) observed, as shown in Figure 1, which provides an example of line profile analysis for some measurements of the $J = 43_{5,39} \leftarrow 42_{6,36}$ rotational transition broadened by oxygen.

Results and discussion

The radiating species investigated in the present work is an asymmetric near-prolate rotor belonging to the C_{2v} symmetry point group. It has three vibrational normal modes: ν_1 and ν_3 correspond to the O=S=O symmetric and asymmetric stretching, respectively, while ν_2 represents the bending motion. The ν_1 fundamental belongs to the A_1 symmetry species and it gives rise to a B -type band located at about 1151.7 cm^{-1} . The presence of two identical oxygen nuclei (zero nuclear spin) allows, for all totally symmetric states, only rotational levels with an even value of $K_a'' + K_c''$.

Concerning the work carried out for retrieving foreign-broadening coefficients of SO₂ perturbed by N₂ and O₂, as mentioned above, the line profile analysis in the IR region was performed by using the Voigt profile model. Figure 2 presents the SO₂ absorptions in the spectral micro-window between 1226.07 and 1226.78 cm⁻¹ perturbed by O₂ together with the corresponding residuals referring to total pressures between 145.1 and 3179 Pa. The good residuals shown in this figure provide the evidence that the Voigt profile well reproduces the observed features within the experimental set-up and conditions employed for the present measurements. In order to retrieve SO₂ foreign-broadening coefficients γ_X^0 (X = N₂, O₂), the collisional half widths at the temperature T , $\Gamma_L(T)$, as obtained from the lineshape analysis of the ro-vibrational transitions, were fitted against the partial pressure of N₂ or O₂ to a straight line represented by the following equation

$$\Gamma_L(T) = \Gamma_0(T) + \gamma_X^0(T) \times P_X \quad (3)$$

where $\Gamma_0(T)$ takes into account the self-broadening contribution to the line width and the Lorentzian component of the instrumental function (if needed) and P_X represents the partial pressure of damping gas. Since slightly different quantities of SO₂ were introduced into the sample cell for the two different series of measurements, to combine the results of the linear fits obtained from the two repetitions, we employed the following procedure [43,44,54,55]. For each spectral line we subtracted the value of the intercept Γ_0 from each Γ_L , thus obtaining the so-called normalized Lorentzian half width Γ_{NL} . A second fit involving all normalized half widths was then performed to retrieve the final value of the pressure broadening coefficient according to the following equation

$$\Gamma_{NL} = \gamma_X^0 \times P_X \quad (4)$$

An example of the linear fits involving normalized Lorentzian half widths obtained for the ro-vibrational transition $29_{16,14} \leftarrow 28_{15,13}$ centered at 1221.29402 cm⁻¹ and perturbed by N₂ and O₂ is shown in Figure 3. Table 1 collects the obtained SO₂-N₂ and SO₂-O₂ broadening coefficients for the ν_1 band transitions of the ³²S¹⁶O₂ isotopologue, whereas Table 2 lists the results for the $\nu_1 + \nu_2 - \nu_2$ hot band of ³²S¹⁶O₂ as well as those for the ν_1 fundamental band of ³⁴S¹⁶O₂. In fact, in addition to the transitions belonging to the ν_1 band of the main isotopic species, it was possible to assign and analyze a number of lines due to either the hot band or the ν_1 fundamental of ³⁴S¹⁶O₂. In these

tables, the SO₂-air broadening parameters (γ_{air}^0) are also reported, and they were derived from the measured N₂- and O₂- broadening coefficients by means of the following equation

$$\gamma_{\text{air}}^0 = 0.79\gamma_{\text{N}_2}^0 + 0.21\gamma_{\text{O}_2}^0 . \quad (5)$$

As it can be seen, for the ν_1 band of ³²S¹⁶O₂, the recorded transitions span the quantum number range $14 \leq J'' \leq 56$, $3 \leq K_a'' \leq 21$ and they belong to the *P*, *Q* or *R* branches. It should be noted that, for three transitions of the ν_1 band of ³²S¹⁶O₂ ($24_{8,16} \leftarrow 25_{9,17}$; $19_{13,7} \leftarrow 19_{14,6}$; $18_{13,5} \leftarrow 18_{14,4}$) and one of ³⁴S¹⁶O₂ ($25_{11,15} \leftarrow 25_{12,14}$) it has been possible to determine only N₂-broadening coefficients as from N₂ to O₂ broadening experiments, the laser emission profile shifted slightly so that it was not possible to exactly recover the same spectral region.

The dependence of the N₂- and O₂- broadening coefficients of ³²S¹⁶O₂ on the K_a'' (pseudo-) quantum number for ν_1 band transitions within each branch is illustrated in Figure 4. In this figure, the outcomes from our previous investigation [37] are also reported, showing that the present determinations confirm those findings. Concerning the *P*-branch transitions, the N₂-broadening parameters do not show any clear trend being almost uniformly scattered around 0.0958 cm⁻¹atm⁻¹. On the other hand, SO₂-O₂ collisional cross sections appear to slightly increase up to $K_a'' = 11$ and then they remain almost constant. Moving to the *Q*-branch, both N₂- and O₂-broadening coefficients keep, over the K_a'' range here considered ($13 \leq K_a'' \leq 21$), an almost constant value around 0.0946 and 0.0717 cm⁻¹atm⁻¹, respectively. As far as the *R*-branch transitions are concerned, the very small dependence on K_a'' is confirmed, even though that N₂ collisional cross sections seem to first decrease up to $K_a'' = 14, 15$ and then they tend to increase slightly as the quantum number raises further. The trend observed for O₂-broadening parameters suggests a very small increase with increasing K_a'' values. The fact that in the *R*-branch a small dependence of the broadening coefficients on K_a'' seems to emerge is probably due to the smaller uncertainties affecting these transitions. Overall, the obtained N₂- and O₂- broadening coefficients for the three branches present an average value of (0.0945 ± 0.0059) cm⁻¹atm⁻¹ and (0.0716 ± 0.0047) cm⁻¹atm⁻¹, respectively.

At this point a comment concerning the comparison with the available literature data is deserved. As already pointed out, the broadening parameters here determined are in close agreement with those found by Tasinato et al. [37], and they also well match with the N₂- and O₂-

broadening coefficients retrieved by Cazzoli et al. [36], Sumpf and collaborators [26,27] and Ball et al. [33].

Concerning the analysis in the MW region, for a given transition, for each series of measurements, the pressure-broadening coefficient γ_X^0 at 298 K, $\gamma_X^0(298)$, was derived by a linear fit of the collisional half widths, $\Gamma_L(T)$, against the perturber partial pressure P_X , as detailed in Eq. (3), with the half widths weighted according to the reciprocal of the squared uncertainties obtained from the profile analysis. To put together the data coming from the different series of measurements carried out for each transition, a procedure analogous to that described above for IR measurements and introduced in Ref. [56] was employed to obtain the normalized Lorentzian half widths, $\Gamma_{NL}(298)$. Subsequently, a second fit involving these normalized half widths was performed in order to obtain the final value of the pressure-broadening parameter $\gamma_X^0(298)$ for the transition under consideration, see Eq. (4). Figure 5, which depicts the linear fit of the normalized collisional half widths for the $J = 20_{7,13} \leftarrow 21_{6,16}$ (258.7 GHz) transition, provides a typical example, thus showing how well the collisional half widths follow a linear behavior against the pressure.

The N₂- and O₂-broadening coefficients of the rotational transitions considered are collected in Table 3 together with the corresponding quantum numbers and transition frequencies. In Table 3, the air-broadening coefficients, obtained by means of Eq. (5) are also given. Strictly speaking, the first 16 lines listed in this Table were already investigated in Ref. [36] and, as already pointed out, they have been further investigated in this work.

From the inspection of the values of Table 3, it is noted that the pressure-broadening coefficients vary slightly upon variation of either J'' or K_a'' , the largest variations being of about 10 - 15%. For example, within the set of transitions selected for investigating the J'' dependence, the maximum variation observed is $\sim 10\%$, despite the large range of J'' , from 11 to 60, considered. The very limited dependence of the pressure broadening coefficients on the J'' or K_a'' quantum numbers was already pointed out [36], even if polynomial expressions were there deduced to model the variations observed. For the sake of completeness, the K_a'' and J'' dependence of the broadening parameters is graphically illustrated in Figure S.1 of the Supplementary Information (SI). A clear trend cannot be derived in agreement with the findings reported for the ν_1 band. To the best of our knowledge, there is not available in the literature any other study reporting either J'' or K_a'' dependence of rotational transitions. However, it deserves to be mentioned the investigation of the temperature dependence carried out by Ball et al. [33], who investigated the 90 – 500 K range. If one compares the pressure-broadening coefficients determined at room temperature for the four

rotational transitions there studied, it is noted that the values are in line with those derived in the present work: $J = 18_{3,15} - 18_{2,16}$ (240.247 GHz): $\gamma_{N_2}^0 = 0.1072(54) \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{O_2}^0 = 0.0735(37) \text{ cm}^{-1} \text{ atm}^{-1}$, $J = 13_{1,13} - 12_{0,12}$ (251.199 GHz): $\gamma_{N_2}^0 = 0.0974(49) \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{O_2}^0 = 0.0814(41) \text{ cm}^{-1} \text{ atm}^{-1}$, $J = 4_{2,2} - 3_{1,3}$ (235.152 GHz): $\gamma_{N_2}^0 = 0.1202(60) \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{O_2}^0 = 0.0920(46) \text{ cm}^{-1} \text{ atm}^{-1}$, $J = 26_{4,22} - 26_{3,23}$ (280.807 GHz): $\gamma_{N_2}^0 = 0.1067(53) \text{ cm}^{-1} \text{ atm}^{-1}$, $\gamma_{O_2}^0 = 0.0776(39) \text{ cm}^{-1} \text{ atm}^{-1}$.

For the sake of completeness, even if it is not of relevance for the compilation of databases finalized at providing data for remote sensing of the Earth atmosphere, the speed dependence of the relaxation rate can be derived from line profile analyses performed using the SDVP model. As expected, the latter contribution shows a linear dependence on pressure and can be fitted with a linear expression analogous to Equations (3) and (4) to derive the so-called γ_2 parameter [12,53,57]. However, even if the expected linear behavior was confirmed in all cases, very small values, about $10^{-6} - 10^{-5} \text{ cm}^{-1} \text{ atm}^{-1}$, were obtained (see also Ref. [36]). This outcome further supports the decision to not report any results, neither graphically nor in table.

The overall trend, against K_a'' , obtained for N_2 - and O_2 -broadening coefficients of both ν_1 band- and ground state-transitions is presented in Figure 6. It is interesting to note that, actually, the range of quantum numbers accessed in the IR and MW regions is complementary: ground state transitions mostly involve K_a'' values from 0 to 6 and several transitions characterized by $K_a'' = 10$ and different values of J'' in order to access their J'' dependence. Conversely, IR measurements span the K_a'' range from 7 to 21. Some variations with the quantum number seem to take place for $K_a'' \leq 8$, and then no evident trend can be reported. This tends to suggest that more detailed information may be gained if it was possible to study the behavior of collisional cross sections within each J'' and K_a'' sub-branch, as we performed for SO_2 self-broadening parameters [38]. Under this point of view, the support coming from theoretical calculations would be very helpful in order to get deeper insights.

At this point one may wonder whether some differences between the broadening parameters obtained at LMS-Ve and LMS-Bo can be due to the different line-shape models employed or to a vibrational dependence of the collisional cross sections. The latter effect can be excluded, as previously pointed out in the study of self-broadening coefficients [38]. A possible vibrational dependence may arise when going to higher quanta of vibrational excitation. Concerning the different line-shape models employed, the broadening parameters obtained by using the SDVP which accounts for collisional narrowing effects are expected to differ by only 2 - 3% from those retrieved within the VP model, as shown in Ref. [41]. Furthermore, the use of different line-shape

functions in the IR and MW regions is well justified by the different experimental conditions employed. In fact, for IR measurements, the pressures employed are, in general, two orders of magnitude greater than those used for MW experiments. At such higher pressures narrowing effects are washed out by the collisional broadening. Rather, the differences between MW and IR collisional parameters may be ascribed to the different experimental set-up adopted in the corresponding laboratories. On the other hand, it should also be pointed out that the small differences between MW and IR broadening parameters may be only apparent, because of the limited J values covered in the MW region for $0 \leq K_a'' \leq 5$. Indeed, when more MW data are available, as in the case of $K_a'' = 10$, no evident difference is observed between the IR and MW pressure broadening coefficients.

Finally, Figure 7 depicts the SO₂-air pressure broadening coefficients as a function of the K_a'' quantum number, together with a comparison to the corresponding values in the recently updated HITRAN database [58]. The overall agreement appears quite good, yet the HITRAN values are slightly larger than those here determined: while the air broadening coefficients here derived average to $(0.0914 \pm 0.0064) \text{ cm}^{-1}\text{atm}^{-1}$, the corresponding ones listed in the HITRAN database have an average value of $(0.0986 \pm 0.0036) \text{ cm}^{-1}\text{atm}^{-1}$.

Conclusions

In the present work, a line-by-line list of SO₂ foreign-broadening coefficients has been retrieved by the analysis of several ro-vibrational transitions belonging to the ³²S¹⁶O₂ ν_1 band (in the 8.8 μm region) as well as a number of pure rotational transitions of the vibrational ground state (in the mm-/sub-mm wave range), with O₂ and N₂ as damping gases. In addition, 10 transitions of the $\nu_1 + \nu_2 - \nu_2$ ³²S¹⁶O₂ hot band and 6 lines belonging to ν_1 of ³⁴S¹⁶O₂ have also been analyzed in the IR region. IR experiments have been carried out within the atmospheric window by using the TDL spectrometer installed in the Laboratory of high resolution IR spectroscopy at University of Venice and the line-shape analysis has been performed by using the Voigt profile. For what concern pure rotational transitions, the spectra have been recorded in the 104 GHz – 1.1 THz frequency range by using the frequency-modulated spectrometer installed at the laboratory of mm-/sub-mm wave spectroscopy of University of Bologna. For the line-shape analysis, the speed-dependent Voigt profile has been employed. In addition, for both IR and MW transitions, from the measured N₂- and O₂-broadening coefficients, the air-broadening coefficients have been derived and compared to

those available in the HITRAN database. A fairly good agreement has been found, only a small overestimation with respect to the database entries has been noted.

Concerning the quantum number dependence of the collisional cross sections, the results obtained from the line-shape analysis of the spectra recorded in both the IR and MW regions point out a very small dependence on both K_a'' and J'' . In this context, theoretical calculations of collisional cross sections are strongly encouraged. We can conclude that the outcomes here presented suggest the need of further detailed studies about the pressure broadening parameters of SO₂ collisionally perturbed by different buffer gases. Under this point of view, this work represents a further extension of our project aimed at determining the broadening coefficients of SO₂ for atmospheric and astrochemical applications.

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Supplementary Information

Figure S.1 reporting the dependence of ground state N₂- and O₂- broadening coefficients of SO₂ on the rotational quantum numbers.

References

- [1] Perrin A, Ben Sari-Zizi N, Demaison J. Remote Sensing of the Atmosphere for Environmental Security. Dordrecht: Springer; 2006.
- [2] Duxbury G. Infrared vibration-rotation spectroscopy. Chichester: John Wiley & Sons; 2000.
- [3] Duxbury G, Langford N, Hay K, Tasinato N. Quantum cascade laser spectroscopy: diagnostics to non-linear optics. *J Mol Opt* 2009;56:2034-48.
- [4] McNaughton D, Robertson EG, Thompson D, Chimdi T, Bane MK, Appadoo D. Overview of high-resolution infrared measurement and analysis for atmospheric monitoring of halocarbons. *J Anal Chem* 2010;82:7958-7964.
- [5] Rothman LS, Gordon IE, Babikov Y, Barbe A, Chris Benner D, Bernath PF, et al. The HITRAN 2012 molecular spectroscopic database. *JQSRT* 2013;1304-50.
- [6] Jacquinet-Husson N, Armante R, Scott NA, Chédin A, Crépeau L, Boutammine C, et al. The 2015 edition of the GEISA spectroscopic database. *J Mol Spectrosc* 2016;327:31-72.
- [7] Pickett HM, Poynter RL, Choen EA, Delitsky ML, Perason JC, Müller HSP. Submillimeter, millimeter, and microwave spectral line catalogue. *JQSRT* 1998;60:883-90.
- [8] Endres CP, Schlemmer S, Schilke P, Stutzki J, Müller HSP. The Cologne Database for Molecular Spectroscopy, CDMS, in the Virtual Atomic and Molecular Data Centre, VAMDC. *J Mol Spectrosc* 2016;327:95-104.
- [9] Hartmann JM, Boulet C, Robert DC. Collisional effects on molecular spectra. New York: Elsevier; 2008.
- [10] Hartmann JM, Bouanich JP, Juks KW, Blanquet G, Walrand J, et al. Line-mixing effect in N₂O *Q* branches: model, laboratory and atmospheric spectra. *J Chem Phys* 1999;110:1959-68.
- [11] Tasinato N, Duxbury G, Langford N, Hay KG. An investigation of collisional processes in a Dicke narrowed transition of water vapor in the 7.8 μm spectral region by frequency down-chirped quantum cascade laser spectroscopy. *J Chem Phys* 2010;132:044316.
- [12] Tasinato N, Hay KG, Langford N, Duxbury G, Wilson D. Time dependent measurements of nitrous oxide and carbon dioxide collisional relaxation processes by a frequency down-chirped quantum cascade laser: rapid passage signals and the time dependence of collisional processes. *J Chem Phys* 2010;132:164301.
- [13] Duxbury G, Tasinato N, Hay K, Wilson D, Langford N. Collisional Effects On Quantum Cascade Laser Induced Molecular Alignment. *AIP Conf Proc* 2010;1290:194-203.

- [14] Lee C, Martin RV, van Donkelaar A, Lee H, Dickerson RR, Hains JC, Krotkov N, et al. SO₂ emission and lifetimes: Estimates from inverse modeling using in situ and global, space-based (SCIAMACHY and OMI) observations. *J Geophys Res* 2011;116:D06304.
- [15] Turnbull K, Johnson B, Marenco F, Haywood J, Minikin A, Weinzierl B, et al. A case study of observations of volcanic ash from the Eyjafjallajökull eruption: 1. In situ airborne observations. *J Geophys Res* 2012;117:D00U12.
- [16] Mankin WG, Coffey MT, Goldman A. Airborne observations of SO₂, HCl and O₃ in the stratospheric plume of the Pinatubo volcano in July 1991. *J Geophys Res Lett* 1992;19:179-82.
- [17] Goldman A, Murcray FJ, Rinsland CP, Blatherwick RD, David SJ, Murcray FH, et al. Mt. Pinatubo SO₂ column measurements from Mauna Loa. *J Geophys Res Lett* 1992;19:183-6.
- [18] Baird C. *Environmental Chemistry*. New York: W.H. Freeman and Company; 1999.
- [19] Guelachvili G, Ulenikov ON, Ushakova GA. Analysis of the ν_1 and ν_3 absorption bands of ³²S¹⁶O₂. *J Mol Spectrosc* 1984;188:1–5.
- [20] Guelachvili G, Naumenko OV, Ulenikov ON. Analysis of the SO₂ absorption Fourier spectrum in the regions 1055 to 2000 and 2200 to 2550 cm⁻¹. *J Mol Spectrosc* 1987;125:128–39.
- [21] Flaud JM, Perrin A, Salah LM, Lafferty WJ, Guelachvili GA. Reanalysis of the (010), (020), (100), and (001) rotational levels of ³²S¹⁶O₂. *J Mol Spectrosc* 1993;160:272–78.
- [22] Müller HSP, Brünker S. Accurate rotational spectroscopy of sulfur dioxide, SO₂, in its ground vibrational and first excited bending states, $\nu_2=0, 1$, up to 2 THz. *J Mol Spectrosc* 2005;232:213–22.
- [23] Sumpf B. Line intensity and self-broadening investigations in the ν_1 and ν_3 bands of SO₂. *J Mol Struct* 2001;599:39–49.
- [24] Chu PM, Wetzel SJ, Lafferty WJ, Perrin A, Flaud JM, Arcas Ph, Guelachvili G. Line intensities for the 8- μ m bands of SO₂. *J Mol Spectrosc* 1998;189:55–63.
- [25] Kühnemann F, Heiner Y, Sumpf B, Herrmann KA. Line broadening in the ν_3 band of SO₂: studied with diode laser spectroscopy. *J Mol Spectrosc* 1992;152:1–12.
- [26] Sumpf B, Fleischmann O, Kronfeldt HD. Self-, air-, and nitrogen-broadening in the ν_1 band of SO₂. *J Mol Spectrosc* 1996;176:127–32.
- [27] Sumpf B, Schöne M, Kronfeldt HD. Self- and air-broadening in the ν_3 band of SO₂. *J Mol Spectrosc* 1996;179:137–41.
- [28] Joly L, Zéninari V, Parvitte B, Weidmann, D, Courtois D, Bonetti Y, et al. Spectroscopic study of ν_1 band of SO₂ using a continuous-wave DFB QCL at 9.1 μ m. *Appl Phys B* 2003;77:703–06.

- [29] Zéninari V, Joly L, Grouiez B, Parvitte B, Barbe A. Study of SO₂ line parameters with a quantum cascade laser spectrometer around 1090 cm⁻¹: comparison with calculations of the ν_1 and $\nu_1 + \nu_2 - \nu_2$ bands of ³²SO₂ and the ν_1 band of ³⁴SO₂. JQSRT 2007;105:312–25.
- [30] Henningsen J, Barbe A, De Backer-Barilly MR. Revised molecular parameters for ³²SO₂ and ³⁴SO₂ from high resolution study of the infrared spectrum in the 7–8 μm wavelength region. JQSRT 2008;109:2491–510.
- [31] Grouiez B, Parvitte B, Joly L, Courtois D, Zéninari V. Comparison of a quantum cascade laser used in both cw and pulsed modes. Application to the study of SO₂ lines around 9 μm . Appl Phys B 2008;90:177–86.
- [32] Tasinato N, Pietropolli Charmet A, Stoppa P, Giorgianni S, Buffa G. Spectroscopic measurements of SO₂ line parameters in the 9.2 μm atmospheric region and theoretical determination of self-broadening coefficients. J Chem Phys 2010;132:044315.
- [33] Ball CD, Dutta JM, Goyette TM, Helminger P, De Lucia FC. The pressure broadening of SO₂ by N₂, O₂, He, and H₂ between 90 and 500 K. JQSRT 1996;56:109-17.
- [34] Lazarev VV, Ponomarev YuN, Sumpf B, Fleischmann O, Waschull J, Kronfeldt HD, Stroinova VN. Noble gas pressure-induced broadening and shift of H₂O and SO₂ absorption lines. J Mol Spectrosc 1995;173:177–93.
- [35] Sumpf B, Schöne M, Fleischmann O, Heiner Y, Kronfeldt HD. Quantum number and temperature dependence of foreign gas-broadening coefficients in the ν_1 and ν_3 bands of SO₂: collisions with H₂, air, He, Ne, Ar, Kr, and Xe. J Mol Spectrosc 1997;183:61–71.
- [36] Cazzoli G, Puzzarini C. N₂-, O₂-, H₂-, and He-broadening of SO₂ rotational lines in the mm-/submm-wave and THz frequency regions: the J and K_a dependence. JQSRT 2012;113:1051-7.
- [37] Tasinato N, Pietropolli Charmet A, Stoppa P, Giorgianni S, Buffa G. N₂-, O₂- and He-collision-induced broadening of sulfur dioxide ro-vibrational lines in the 9.2 μm atmospheric window. Spectrochim Acta A 2014;118:373-79.
- [38] Tasinato N, Pietropolli Charmet A, Stoppa P, Buffa G, Puzzarini C. A complete listing of sulfur dioxide self-broadening coefficients for atmospheric applications by coupling infrared and microwave spectroscopy to semiclassical calculations. JQSRT 2013;130:233-48.
- [39] Tasinato N, Grimme S. Unveiling the non-covalent interactions of molecular homodimers by dispersion-corrected DFT calculations and collision-induced broadening of ro-vibrational transitions: application to (CH₂F₂)₂ and (SO₂)₂. Phys Chem Chem Phys 2015;17:5659.

- [40] Wilzewski JS, Gordon IE, Kochanov RV, Hill C, Rothman LS. H₂, He and CO₂ line-broadening coefficients, pressure shifts and temperature-dependence exponents for the HITRAN database. Part 1: SO₂, NH₃, HF, HCl, OCS and C₂H₂. *JQSRT* 2016;168:193-206.
- [41] Ceselin G, Tasinato N, Puzzarini C, Pietropolli Charmet A, Stoppa P, Giorgianni S. CO₂-, He- and H₂-broadening coefficients of SO₂ for ν_1 band and ground state transitions for astrophysical applications. *JQSRT* 2017; accepted.
- [42] Tasinato N, Stoppa P, Pietropolli Charmet A, Giorgianni S, Buffa G, Gambi A. Toward a complete understanding of the vinyl fluoride spectrum in the atmospheric region. *ChemPhysChem* 2011;12:356–63.
- [43] Tasinato N, Turchetto A, Puzzarini C, Stoppa P, Pietropolli Charmet A, Giorgianni S. Self-, N₂-, O₂-broadening coefficients and line parameters of HFC-32 for ν_7 band and ground state transitions from infrared and microwave spectroscopy. *Mol Phys* 2014;112:2384-96.
- [44] Tasinato N, Turchetto A, Stoppa P, Pietropolli Charmet A, Giorgianni S. The energetic of (CH₂F₂)₂ investigated by TDL IR spectroscopy and DFT computations: From collision induced relaxation of ro-vibrational transitions to noncovalent interactions. *J Chem Phys* 2015;142:134310.
- [45] Tasinato N, Pietropolli Charmet A, Stoppa P, Giorgianni S. Determination of the vinyl fluoride line intensities by TDL spectroscopy: the object oriented approach of Visual Line Shape Fitting Program to line profile analysis. *Mol Phys* 2010;108:677-85.
- [46] Cazzoli G, Puzzarini C. The Lamb-dip spectrum of methylcyanide: Precise rotational transition frequencies and improved ground state rotational parameters. *J Molec Spectrosc* 2006;240:153-63.
- [47] Puzzarini C, Cazzoli G, Gauss J. The rotational spectra of HD¹⁷O and D₂¹⁷O: Experiment and quantum-chemical calculations. *J Chem Phys* 2012;137:154311.
- [48] Cazzoli G, Puzzarini C, Sub-Doppler Resolution in the THz Frequency Domain: 1 kHz Accuracy at 1 THz by Exploiting the Lamb-Dip Technique. *J Phys Chem A* 2013;117:13759–66.
- [49] Cazzoli G, Dore L. Lineshape measurements of rotational lines in the millimeter-wave region by second harmonic detection. *J Molec Spectrosc* 1990;141:49-58.
- [50] Dore L. Using Fast Fourier Transform to compute the line shape of frequency-modulated spectral profiles. *J Molec Spectrosc* 2003;221:93-8.
- [51] Puzzarini C, Dore L, Cazzoli G. A comparison of lineshape models in the analysis of modulated and natural rotational line profiles: Application to the pressure broadening of OCS and CO. *J Molec Spectrosc* 2002;216:428-36.
- [52] Rohart F, Mäder H, Nicolaisen HW. Speed dependence of rotational relaxation induced by foreign gas collisions: Studies on CH₃F by millimeter wave coherent transients. *J Chem Phys* 1994;101:6475-86.

- [53] D'Eu JF, Lemoine B, Rohart F. Infrared HCN lineshapes as a test of Galatry and Speed-Dependent Voigt profiles. *J Molec Spectrosc* 2002;212:96-110.
- [54] Cazzoli G, Dore L, Puzzarini C, Bakri B, Colmont JM, Rohart F, Wlodarczak G. Experimental determination of air-broadening parameters of pure rotational transitions of HNO₃: intercomparison of measurements by using different techniques. *J Mol Spectrosc* 2005;229:158-69.
- [55] Colmont JM, Bakri B, Rohart F, Wlodarczak G, Demaison J, Cazzoli G, et al. Intercomparison between ozone broadening parameters retrieved from millimetre-wave measurements by using different techniques. *J Mol Spectrosc* 2005;231:171–87.
- [56] Cazzoli G, Puzzarini C, Buffa G, Tarrini O. Experimental and theoretical investigation on pressure-broadening and pressure-shifting of the 22.2 GHz line of water. *JQSRT* 2007;105:438-449.
- [57] Rohart F, Wlodarczak G, Colmont J-M, Cazzoli G, Dore L, Puzzarini C. Galatry versus speed-dependent Voigt profiles for millimeter lines of O₃ in collision with N₂ and O₂. *J Mol Spectrosc* 2008;251:282–92.
- [58] <https://www.cfa.harvard.edu/HITRAN/>. Last access: 25/04/2017.

Figure Captions

Figure 1. Oxygen broadening of the 249.0 GHz line ($J = 43_{5,39} \leftarrow 42_{6,36}$) of sulfur dioxide: an example of measurements (in black) analyzed by using the SDVP model (in red). The residuals (three times the observed – calculated difference values) are also depicted (in green).

Figure 2. SO₂ ro-vibrational lines (gray circles) in the spectral region between 1226.07 and 1226.78 cm⁻¹ (experimental conditions $P_{\text{SO}_2} = 145.1$ Pa, path length = 68.1 cm, $T = 296$ K) fitted to the VP model (red line). Black traces, with the same scale as the spectrum, show the residuals of the fits and they refer to the following O₂ partial pressures (from top to bottom): 0, 430.6, 1057, 1714, 2445, 3179 Pa.

Figure 3. Foreign broadening of the $29_{16,14} \leftarrow 28_{15,13}$ ro-vibrational transition at 1221.29402 cm⁻¹ of ³²S¹⁶O₂ ν_1 band. Upper panel. Experimental collisional half widths: N₂ (blue squares) and O₂ (red circles). Dashed lines are linear fits of normalized Lorentzian half widths against the N₂ and O₂ partial pressure. Error bars are the uncertainties retrieved from the lineshape analysis. Lower panel. Residuals between experimental and fitted values.

Figure 4. Trend of N₂- (black squares) and O₂- (red circles) broadening coefficients of ³²S¹⁶O₂ ν_1 band transitions against the K_a'' pseudo-quantum number in the (a) P -, (b) Q - and (c) R - sub-branches (filled squares and circles refer to the present work; empty squares and circles are data from Ref. 37).

Figure 5. Nitrogen broadening of the 258.7 GHz line ($J = 20_{7,13} \leftarrow 21_{6,16}$) of sulfur dioxide in the vibrational ground state: linear fit of the “normalized” Lorentzian half widths against the partial pressure of N₂. Error bars are three times the uncertainties retrieved from the line profile analysis.

Figure 6. Dependence of ν_1 band and ground state N₂- (black) and O₂- (red) broadening coefficients of ³²S¹⁶O₂ on the K_a'' quantum number.

Figure 7. SO₂ - air broadening parameters as a function of K_a'' : present work (blue crosses and triangles); Ref. 40 (blue squares); HITRAN database, Ref. 61 (green circles). Ground state

broadening coefficients (blue triangles) determined at $(298 \pm 1 \text{ K})$; ν_1 broadening coefficients (blue crosses) determined at $(296 \pm 1 \text{ K})$.

Table 1. Assignment, transition frequency, N₂-, O₂-, and air- broadening coefficients of ³²S¹⁶O₂ ν₁ band transitions. ^a

J'	K'_a	K'_c	J''	K''_a	K''_c	ν_0^b	$\gamma_{N_2}^0{}^c$	$\gamma_{O_2}^0{}^c$	$\gamma_{air}^0{}^c$
34	20	14	34	21	13	1083.2225 ₀ (1 ₄)	0.081 ₅ (6 ₁)	0.075 ₀ (5 ₇)	0.080 ₁ (6 ₀)
46	10	36	47	11	37	1083.22930 ₀ (2 ₀) ^d	0.097 ₅ (1 ₁)	0.065 ₀ (5 ₅)	0.090 ₇ (2 ₀)
25	13	13	26	14	12	1083.3932 ₃ (2 ₀)	0.091 ₆ (1 ₀)	0.084 ₈ (1 ₉)	0.090 ₂ (1 ₂)
55	8	48	56	9	47	1083.4374 ₀ (2 ₆)	0.088 ₆ (7 ₄)	0.076 ₀ (1 ₉)	0.086 ₀ (6 ₂)
37	12	26	38	13	25	1083.4797 ₉ (2 ₂)	0.087 ₆ (1 ₉)	0.068 ₅ (1 ₉)	0.083 ₆ (1 ₉)
27	13	15	28	14	14	1083.4937 ₅ (1 ₂)	0.094 ₈ (6 ₈)	0.080 ₇ (9 ₄)	0.091 ₈ (7 ₃)
18	15	3	19	16	4	1083.4843 ₂ (2 ₄)	0.1012 ₇ (8 ₉)	0.093 ₉ (1 ₉)	0.099 ₇ (1 ₁)
24	15	9	25	16	10	1083.5170 ₁ (3 ₀)	0.089 ₈ (3 ₃)	0.068 ₅ (1 ₅)	0.085 ₃ (2 ₉)
16	15	1	17	16	2	1083.6045 ₃ (2 ₄)	0.098 ₇ (3 ₀)	0.072 ₁ (9 ₀)	0.093 ₁ (4 ₃)
29	12	18	30	13	17	1083.6126 ₄ (2 ₇)	0.118 ₂ (7 ₆)	0.080 ₆ (7 ₇)	0.110 ₃ (7 ₆)
28	14	14	29	15	15	1083.7636 ₉ (3 ₁)	0.105 ₇ (3 ₃)	0.073 ₉ (6 ₇)	0.099 ₀ (4 ₀)
29	20	10	29	21	9	1083.7734 ₅ (2 ₇)	0.094 ₆ (5 ₄)	0.067 ₁ (1 ₇)	0.088 ₈ (4 ₆)
28	14	14	28	15	13	1102.31102 ₀ (8 ₀)	0.087 ₁ (7 ₇)	0.065 ₄ (4 ₈)	0.082 ₅ (7 ₁)
34	7	27	35	8	28	1102.3423 ₀ (1 ₉)	0.087 ₉ (2 ₀)	0.068 ₅ (3 ₃)	0.083 ₈ (2 ₃)
20	10	10	21	11	11	1102.38693 ₅ (1 ₆)	0.096 ₉ (2 ₁)	0.082 ₅ (2 ₁)	0.093 ₉ (2 ₁)
27	14	14	27	15	13	1102.4012 ₇ (1 ₉)	0.101 ₄ (3 ₅)	0.075 ₀ (3 ₂)	0.095 ₉ (3 ₄)
25	7	19	26	8	18	1102.4451 ₆ (1 ₂)	0.092 ₄ (5 ₈)	0.067 ₀ (2 ₇)	0.087 ₁ (5 ₁)
26	14	12	26	15	11	1102.48935 ₅ (4 ₅)	0.093 ₄ (3 ₂)	0.070 ₂ (1 ₂)	0.088 ₅ (2 ₈)
14	10	4	15	11	5	1102.54508 ₀ (7 ₀)	0.083 ₉ (6 ₂)	0.073 ₇ (2 ₆)	0.081 ₈ (5 ₄)
29	8	22	30	9	21	1102.5612 ₄ (1 ₆)	0.096 ₅ (2 ₀)	0.072 ₂ (1 ₁)	0.091 ₄ (1 ₈)
25	14	12	25	15	11	1102.57416 ₀ (5 ₀)	0.092 ₇ (2 ₄)	0.0802 ₆ (9 ₈)	0.090 ₁ (2 ₁)
15	11	5	16	12	4	1102.61647 ₃ (2 ₃)	0.102 ₆ (1 ₉)	0.078 ₃ (1 ₁)	0.097 ₅ (1 ₇)
23	14	10	23	15	9	1102.73491 ₀ (5 ₀)	0.091 ₅ (4 ₇)	0.075 ₇ (1 ₅)	0.088 ₂ (4 ₀)
24	9	15	25	10	16	1102.8340 ₂ (1 ₄)	0.090 ₈ (3 ₉)	0.068 ₁ (1 ₄)	0.086 ₀ (3 ₄)
21	14	8	21	15	7	1102.8833 ₃ (3 ₂)	0.103 ₆ (5 ₁)	0.070 ₀ (1 ₄)	0.096 ₅ (4 ₃)
20	14	6	20	15	5	1102.9522 ₅ (2 ₃)	0.090 ₁ (1 ₁)	0.068 ₄ (2 ₁)	0.085 ₅ (1 ₃)
15	9	7	16	10	6	1102.9936 ₃ (3 ₆)	0.091 ₄ (4 ₂)	0.0604 ₉ (7 ₇)	0.084 ₉ (3 ₅)
19	14	6	19	15	5	1103.0182 ₀ (1 ₉)	0.104 ₈ (3 ₂)	0.0708 ₅ (3 ₇)	0.097 ₇ (2 ₆)
33	7	27	34	8	26	1103.05613 ₈ (4 ₈)	0.091 ₅ (2 ₂)	0.067 ₁ (2 ₀)	0.086 ₄ (2 ₂)
18	14	4	18	15	3	1103.08108 ₅ (8 ₅)	0.098 ₅ (2 ₀)	0.070 ₇ (3 ₆)	0.092 ₇ (2 ₃)
19	10	10	20	11	9	1103.08938 ₆ (6 ₆)	0.096 ₀ (1 ₈)	0.0806 ₆ (1 ₈)	0.092 ₈ (1 ₅)
18	9	9	19	10	10	1103.1237 ₆ (1 ₀)	0.0881 ₉ (6 ₆)	0.063 ₂ (6 ₁)	0.082 ₉ (1 ₈)
24	8	16	25	9	17	1106.143 ₃ (1 ₅)	0.095 ₃ (4 ₅)	--	--
19	13	7	19	14	6	1106.1908 ₀ (3 ₀) ^e	0.103 ₃ (3 ₂)	--	--
18	13	5	18	14	4	1106.2530 ₈ (2 ₀)	0.100 ₇ (2 ₂)	--	--
17	13	5	17	14	4	1106.31193 ₁ (6 ₁)	0.0949 ₃ (6 ₈)	0.064 ₃ (2 ₃)	0.088 ₅ (1 ₀)
19	9	11	20	10	10	1106.36812 ₄ (6 ₇)	0.109 ₁ (2 ₄)	0.077 ₃ (1 ₁)	0.102 ₄ (2 ₁)
48	12	36	48	13	35	1106.37991 ₅ (4 ₅)	0.101 ₇ (5 ₅)	0.075 ₁ (6 ₁)	0.096 ₁ (5 ₆)
23	7	17	24	8	16	1106.3885 ₆ (1 ₂)	0.086 ₈ (8 ₉)	0.072 ₅ (8 ₈)	0.083 ₈ (8 ₉)
15	13	3	15	14	2	1106.41997 ₅ (1 ₅) ^f	0.096 ₈ (1 ₉)	0.0701 ₁ (2 ₇)	0.091 ₂ (1 ₆)
14	13	1	14	14	0	1106.4691 ₆ (1 ₀)	0.090 ₆ (3 ₃)	0.075 ₄ (3 ₀)	0.087 ₄ (3 ₂)
18	8	10	19	9	11	1106.49250 ₅ (7 ₅)	0.088 ₂ (5 ₈)	0.071 ₃ (7 ₆)	0.084 ₇ (6 ₂)
33	6	28	34	7	27	1106.50768 ₃ (1 ₉) ^g	0.092 ₇ (1 ₁)	0.0670 ₉ (6 ₂)	0.087 ₃ (1 ₀)
47	12	36	47	13	35	1106.51813 ₅ (2 ₅)	0.1018 ₅ (9 ₀)	0.068 ₅ (5 ₅)	0.094 ₈ (1 ₉)

J	K'_a	K'_c	J''	K''_a	K''_c	ν_0^b	$\gamma_{N_2}^0{}^c$	$\gamma_{O_2}^0{}^c$	$\gamma_{air}^0{}^c$
14	10	4	15	11	5	1106.55602 ₅ (5 ₅)	0.101 ₉ (1 ₂)	0.072 ₈ (1 ₆)	0.095 ₈ (1 ₃)
13	9	5	14	10	4	1106.56840 ₅ (2 ₅)	0.088 ₂ (6 ₆)	0.068 ₀ (8 ₂)	0.084 ₀ (6 ₉)
41	14	28	40	13	27	1221.0639 ₇ (5 ₀)	0.090 ₄ (1 ₂)	0.068 ₁ (1 ₃)	0.085 ₇ (1 ₂)
23	17	7	22	16	6	1221.18158 ₅ (6 ₅) ^h	0.090 ₁₀ (9 ₉)	0.069 ₂₇ (6 ₈)	0.085 ₇₃ (9 ₂)
35	15	21	34	14	20	1221.2588 ₈ (1 ₂)	0.086 ₂ (1 ₃)	0.065 ₅₆ (5 ₆)	0.081 ₉ (1 ₁)
29	16	14	28	15	13	1221.2938 ₅ (1 ₇) ⁱ	0.092 ₁₆ (7 ₅)	0.067 ₅₂ (3 ₃)	0.086 ₉₉ (6 ₆)
33	16	18	32	15	17	1221.3600 ₈ (4 ₈)	0.099 ₁ (4 ₆)	0.068 ₇ (9 ₁)	0.092 ₇ (5 ₅)
26	18	8	25	17	9	1226.0960 ₂ (1 ₀)	0.089 ₃ (2 ₈)	0.071 ₁ (1 ₁)	0.085 ₅ (2 ₄)
38	16	22	37	15	23	1226.1134 ₁ (1 ₃)	0.090 ₉ (1 ₇)	0.069 ₃ (1 ₀)	0.086 ₄ (1 ₆)
32	17	15	31	16	16	1226.18016 ₃ (2 ₁)	0.098 ₇₂ (6 ₈)	0.070 ₂₈ (4 ₄)	0.092 ₇₅ (6 ₃)
30	18	12	29	17	13	1226.32107 ₀ (8 ₀)	0.101 ₀ (8 ₁)	0.081 ₂ (1 ₇)	0.096 ₈ (6 ₈)
21	19	3	20	18	2	1226.44551 ₉ (4 ₁)	0.094 ₉ (1 ₃)	0.072 ₅₃ (9 ₄)	0.090 ₂ (1 ₂)
39	16	24	38	15	23	1226.63220 ₀ (1 ₀)	0.086 ₅ (1 ₁)	0.063 ₅₂ (9 ₉)	0.081 ₇ (1 ₁)
27	18	10	26	17	9	1226.65480 ₀ (7 ₁)	0.088 ₁₇ (5 ₈)	0.068 ₄₁ (5 ₇)	0.084 ₀₂ (5 ₈)
39	13	27	38	12	26	1216.70535 ₅ (4 ₅)	0.089 ₃₅ (6 ₂)	0.067 ₀₅ (7 ₆)	0.084 ₆₇ (6 ₅)
33	17	17	32	16	16	1226.71967 ₈ (4 ₇)	0.093 ₅₀ (7 ₁)	0.073 ₆₀ (7 ₃)	0.089 ₃₂ (7 ₁)
21	16	6	20	15	5	1216.79064 ₅ (5 ₅)	0.094 ₁₉ (6 ₁)	0.075 ₆₂ (7 ₃)	0.090 ₂₉ (6 ₄)
46	12	34	45	11	35	1216.8059 ₄ (1 ₂)	0.098 ₅ (1 ₃)	0.066 ₆ (1 ₇)	0.091 ₈ (1 ₄)
19	17	3	18	16	2	1216.8277 ₇ (1 ₃)	0.090 ₉ (9 ₃)	0.080 ₂ (7 ₈)	0.088 ₇ (9 ₀)

^a Uncertainties in parentheses are one standard deviation.

^b Transition frequency in cm⁻¹.

^c Broadening coefficient in cm⁻¹ atm⁻¹.

^d Overlapped to 54_{19,35} ← 54_{20,34} ν_1 ³²S¹⁶O₂.

^e Overlapped to 15_{8,8} ← 16_{9,7} ν_1 ³⁴S¹⁶O₂; 33_{5,29} ← 34_{6,28} $\nu_1 + \nu_2 - \nu_2$ ³²S¹⁶O₂.

^f Overlapped to 24_{6,18} ← 25_{7,19} ν_1 ³⁴S¹⁶O₂.

^g Overlapped to 41_{11,31} ← 41_{12,30} $\nu_1 + \nu_2 - \nu_2$ ³²S¹⁶O₂.

^h Overlapped to 39_{15,25} ← 38_{14,24} $\nu_1 + \nu_2 - \nu_2$ ³²S¹⁶O₂; 35_{22,14} ← 35_{21,15} ν_1 ³²S¹⁶O₂.

ⁱ Overlapped to 34_{22,12} ← 34_{21,13} ν_1 ³²S¹⁶O₂.

Table 2. Assignment, transition frequency, N₂-, O₂-, and air- broadening coefficients of ³²S¹⁶O₂ ν₁ + ν₂-ν₂ hot band and ³⁴S¹⁶O₂ ν₁ band. ^a

<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J''</i>	<i>K''_a</i>	<i>K''_c</i>	<i>ν₀^b</i>	<i>γ_{N₂}^{0 c}</i>	<i>γ_{O₂}^{0 c}</i>	<i>γ_{air}^{0 c}</i>
18	15	3	19	16	4	1083.4843 ₂ (2 ₄)	0.1012 ₇ (8 ₉)	0.093 ₉ (1 ₉)	0.099 ₇ (1 ₁)
27	13	15	28	14	14	1083.4937 ₅ (1 ₂)	0.094 ₈ (6 ₈)	0.080 ₇ (9 ₄)	0.091 ₈ (7 ₃)
14	10	4	15	11	5	1102.54508 ₀ (7 ₀)	0.083 ₉ (6 ₂)	0.073 ₇ (2 ₆)	0.081 ₈ (5 ₄)
18	9	9	19	10	10	1103.1237 ₆ (1 ₀)	0.0881 ₉ (6 ₆)	0.063 ₂ (6 ₁)	0.082 ₉ (1 ₈)
23	7	17	24	8	16	1106.3885 ₆ (1 ₂) ^d	0.086 ₈ (8 ₉)	0.072 ₅ (8 ₈)	0.083 ₈ (8 ₉)
18	8	10	19	9	11	1106.49250 ₅ (7 ₅)	0.088 ₂ (5 ₈)	0.071 ₃ (7 ₆)	0.084 ₇ (6 ₂)
13	9	5	14	10	4	1106.56840 ₅ (2 ₅)	0.088 ₂ (6 ₆)	0.068 ₀ (8 ₂)	0.084 ₀ (6 ₉)
19	17	3	18	16	2	1216.8277 ₇ (1 ₃)	0.090 ₉ (9 ₃)	0.080 ₂ (7 ₈)	0.088 ₇ (9 ₀)
33	16	18	32	15	17	1221.3600 ₈ (4 ₈)	0.099 ₁ (4 ₆)	0.068 ₇ (9 ₁)	0.092 ₇ (5 ₅)
30	18	12	29	17	13	1226.32107 ₀ (8 ₀)	0.101 ₀ (8 ₁)	0.081 ₂ (1 ₇)	0.096 ₈ (6 ₈)
³⁴ S ¹⁶ O ₂									
<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J''</i>	<i>K''_a</i>	<i>K''_c</i>	<i>ν₀^b</i>	<i>γ_{N₂}^{0 c}</i>	<i>γ_{O₂}^{0 c}</i>	<i>γ_{air}^{0 c}</i>
25	13	13	26	14	12	1083.3932 ₃ (2 ₀)	0.091 ₆ (1 ₀)	0.084 ₈ (1 ₉)	0.090 ₂ (1 ₂)
16	15	1	17	16	2	1083.6045 ₃ (2 ₄)	0.098 ₇ (3 ₀)	0.072 ₁ (9 ₀)	0.093 ₁ (4 ₃)
29	12	18	30	13	17	1083.6126 ₄ (2 ₇)	0.118 ₂ (7 ₆)	0.080 ₆ (7 ₇)	0.110 ₃ (7 ₆)
25	7	19	26	8	18	1102.4451 ₆ (1 ₂)	0.092 ₄ (5 ₈)	0.067 ₀ (2 ₇)	0.087 ₁ (5 ₁)
15	9	7	16	10	6	1102.9936 ₃ (3 ₆)	0.091 ₄ (4 ₂)	0.0604 ₉ (7 ₇)	0.084 ₉ (3 ₅)
25	11	15	25	12	14	1106.2350 ₁ (7 ₁)	0.109 ₇ (3 ₆)	--	--

^a Uncertainties in parentheses are one standard deviation.

^b Transition frequency in cm⁻¹.

^c Broadening coefficient in cm⁻¹ atm⁻¹.

^d Overlapped to 42_{11,31} ← 42_{12,30} ν₁ + ν₂ - ν₂ ³²S¹⁶O₂.

Table 3. Assignments, transition frequencies, N₂- and O₂-broadening coefficients of pure rotational lines of ³²S¹⁶O₂.^a

J'	K'_a	K'_c	J''	K''_a	K''_c	ν_0^b	$\gamma_{N_2}^0{}^c$	$\gamma_{O_2}^0{}^c$	$\gamma_{air}^0{}^c$
<i>J</i> dependence									
11	11	1	11	10	2	1064050.05 ₉₍₅₀₎	0.096 ₆₍₁₃₎	0.078 ₃₍₁₅₎	0.092 ₇₍₁₃₎
12	11	1	12	10	2	1064089.71 ₈₍₅₀₎	0.0986 ₇₍₇₄₎	0.081 ₀₍₁₆₎	0.0949 ₅₍₉₃₎
15	11	5	15	10	6	1064206.09 ₆₍₅₀₎	0.1038 ₆₍₇₁₎	0.084 ₃₍₁₂₎	0.0997 ₅₍₈₁₎
16	11	5	16	10	6	1064241.22 ₉₍₅₀₎	0.1037 ₇₍₁₁₎	0.083 ₉₍₁₁₎	0.0996 ₆₍₁₁₎
26	11	15	26	10	16	1064223.09 ₅₍₅₀₎	0.1011 ₂₍₇₄₎	0.0755 ₇₍₆₁₎	0.0957 ₆₍₇₁₎
28	11	17	28	10	18	1064072.08 ₀₍₅₀₎	0.0962 ₂₍₁₃₎	0.0758 ₈₍₈₄₎	0.0919 ₁₍₁₂₎
34	11	23	34	10	24	1063097.64 ₃₍₅₀₎	0.0992 ₂₍₁₂₎	0.0729 ₆₍₅₈₎	0.0937 ₇₍₁₁₎
42	11	31	42	10	32	1059981.90 ₇₍₅₀₎	0.0979 ₁₍₁₇₎	0.0708 ₁₍₁₂₎	0.0922 ₂₍₁₆₎
51	11	41	51	10	42	1052515.11 ₉₍₅₀₎	0.0991 ₂₍₆₈₎	0.0680 ₉₍₇₁₎	0.0926 ₁₍₆₉₎
60	11	49	60	10	50	1038159.31 ₉₍₅₀₎	0.0954 ₂₍₇₁₎	0.0631 ₅₍₇₆₎	0.0886 ₄₍₇₂₎
<i>K_a</i> dependence									
10	1	9	10	0	10	104239.29 ₅₍₂₀₎	0.1151 ₄₍₃₀₎	0.0789 ₄₍₇₁₎	0.1075 ₄₍₃₉₎
10	2	8	10	1	9	129514.80 ₁₍₂₀₎	0.1143 ₁₍₇₆₎	0.0796 ₈₍₂₈₎	0.1070 ₃₍₆₆₎
10	4	6	10	3	7	356755.18 ₇₍₂₀₎	0.1106 ₈₍₂₈₎	0.0814 ₃₍₃₈₎	0.1045 ₄₍₃₀₎
10	5	5	10	4	6	459668.35 ₆₍₂₀₎	0.1089 ₃₍₃₈₎	0.0826 ₉₍₃₅₎	0.1034 ₂₍₃₇₎
10	6	4	10	5	5	561560.31 ₃₍₂₀₎	0.1071 ₁₍₇₆₎	0.0870 ₃₍₇₄₎	0.1028 ₉₍₇₆₎
10	7	3	10	6	4	662997.74 ₉₍₂₀₎	0.1041 ₂₍₇₉₎	0.0920 ₅₍₇₉₎	0.1015 ₈₍₇₉₎
$\Delta J = -1$									
20	7	13	21	6	16	258666.95 ₇₍₂₀₎	0.0951 ₇₍₈₆₎	0.0743 ₅₍₃₀₎	0.0908 ₀₍₇₄₎
$\Delta J = +1$									
43	5	39	42	6	36	248995.12 ₁₍₂₀₎	0.0967 ₄₍₂₀₎	0.0670 ₃₍₃₈₎	0.0905 ₀₍₂₄₎
3	3	1	2	2	0	313279.72 ₉₍₂₀₎	0.1121 ₅₍₂₅₎	0.0818 ₁₍₃₀₎	0.1057 ₈₍₂₆₎

^a Uncertainties in parentheses are three times the standard deviation.

^b Transition frequencies in MHz.

^c Broadening coefficient in cm⁻¹ atm⁻¹.