CO₂-, He- and H₂-broadening coefficients of SO₂ for ν_1 band and ground state transitions for astrophysical applications

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Abstract

The discovery of the Universe and of the interstellar medium (ISM) passes through the knowledge of the molecules that populate those places. Most of our understanding about the composition of the ISM and planetary atmospheres has been made possible almost entirely thanks to spectroscopic observations. Sulfur dioxide, SO₂, is one of the about 200 molecules that have been detected in the ISM or circumstellar shells. In addition to its astrophysical relevance, SO₂ has a proved role in the Earth's atmosphere. It origins from biomass burning and volcanic eruptions and directly enters in the sulfur cycle. In this work high-resolution tunable diode laser (TDL) infrared (IR) spectroscopy and mm-/sub-mm wave spectroscopy are exploited to retrieve the broadening parameters of sulfur dioxide perturbed by H₂, He and CO₂. IR measurements are carried out for ν_1 band transitions around 9 μm by using He and CO₂ as damping gases. As far as the vibrational ground state is concerned, about 20 rotational transitions are analyzed by means of the speed dependent Voigt profile to retrieve H₂- and He-broadening coefficients. From the experimental results some conclusions about the quantum number dependence of the H₂-, CO₂- and He-collisional cross sections are drawn. Both IR and MW experiments highlight a very weak dependence of He broadening parameters on the K_a and J rotational quantum numbers. In a similar way, also SO₂ - H₂ broadening coefficients show a negligible dependence on the rotational quantum numbers. Conversely, when CO₂ is employed as perturbing species, the observed collisional cross sections tend to decrease with increasing K_a values and to increase against J, at least over the range of quantum numbers considered. The present results provide the first systematic determination of line-by-line SO₂ - CO₂ broadening coefficients and they are of relevance to increase the potential use of spectroscopic databases for astronomical applications.

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1. Introduction

Astrochemistry deals with the study of the chemical composition and reactivity of chemical species in the Universe and their interaction with the electromagnetic radiation [1]. Starting from the origins of the Universe and the early formation of hydrogen, helium and a little of lithium, it aims at understanding the evolution toward molecular complexity. Under this point of view, the synthesis, chemical abundance, and processing of gas-phase species within molecular clouds are of particular interest as solar systems stem from the evolution of these clouds. Since the first molecules identified in the interstellar medium (ISM) in the early 1940s [2-4], almost 200 molecules have been detected in the ISM or circumstellar shells, including neutrals, radicals, and ions as well as many prebiotic species [5]. Most of our knowledge about the composition of the ISM and planetary atmospheres has been made possible almost entirely thanks to spectroscopic observations [6-14]: as a matter of fact, light tells the molecular story thus providing fundamental information on the formation and evolution of stars and galaxies. For this reason, in the last years, many efforts have been spent for the development of ground- and space-based observatories (e.g. ALMA, SOFIA, Spitzer, Herschel, Voyager, Cassini-Huygens, ISO, CIRS) which operate from infrared (IR) to millimeter/sub-millimeter (mm/sub-mm) wavelengths and are providing a wealth of spectroscopic information at ever increasing quality in terms of accuracy, spectral coverage, resolution and signal-to-noise ratio [15].

To fully exploit these unique observational data, spectroscopic information needs to be determined for a wide range of astrochemical molecules. This represents a huge and time-consuming work, that can be accomplished by combining experimental measurements, theoretical modeling and computational simulations. In this context, the aim of laboratory spectroscopy is to provide accurate spectroscopic parameters for a wide variety of species, which are then collected into a number of continuously updated spectroscopic databases (e.g. HITRAN [16], JPL [17], GEISA [18], Cologne [5]) of relevance for different applications, including: (i) modeling the chemistry of Earth's atmosphere and astronomical objects; (ii) predicting the fate of our atmosphere in relation to global climate changes; (iii) understanding cosmic evolution and reactivity. The foremost spectroscopic parameters include transition frequencies and intensities, pressure broadening- and shifting-coefficients and, eventually, their temperature dependence.

Due to environmental concerns related to global climate changes, many research efforts have been made to retrieve the spectroscopic line-by-line parameters for species of relevance to Earth's atmosphere, i.e. pressure broadening and shifting parameters have been mostly determined by using N_2 and O_2 as collisional partners that represent buffer gases of atmospheric relevance.

Yet, additional parameters that take into account the physical-chemical conditions of extraterrestrial atmospheres and astronomical environments, are required to infer the mixing ratios in these places. In particular, H_2 and He line parameters need to be determined because these gases represent the main constituents of the gas giant atmospheres, whereas CO_2 is of relevance for the atmospheres of some rocky planets [19].

Among astrochemical molecules, sulfur dioxide (SO_2) has been detected in star-forming regions [20-25], in the atmosphere of Venus [26], on the surface of Io [27] as well as on Mars [28]. Besides to its astrophysical relevance, this molecule has an undisputable importance for the chemistry of our atmosphere. Indeed, it actively enters in the sulfur cycle and it is emitted in the atmosphere by either natural processes [29,30] and anthropogenic activities [31]. Because of its importance, over the years sulfur dioxide has been, and it is still, the subject of numerous spectroscopic investigations. Concerning the microwave (MW) region, ground and $v_2 = 1$ state constants have been accurately re-determined about 10 years ago [32], while in the IR region the v_1 and v_3 bands of $^{32}SO_2$ have been investigated by Guelachvili and co-workers [33,34]; some years later these bands have been studied in further detail by Flaud et al. who also analyzed the high resolution spectra of the v_2 fundamental and $2v_2 - v_2$ hot band [35]. Concerning the determination of line-by-line parameters, intensity measurements have been carried out for some v_1 and v_3 ro-vibrational transitions [36], while a systematic study has been performed in the 940 - 1400 cm^{-1} region by Fourier transform IR spectroscopy [37]. Plenty of work has also been devoted to the determination of pressure broadening coefficients, either on SO_2 self-broadened [36,38-45] or perturbed by different collisional partners [39,40,46-50]. Recently, the quantum number dependence of SO_2 self-broadening coefficients has been investigated in detail by combining IR and MW spectroscopy to semiclassical calculations, thus allowing the compilation of a line-by-line database of SO_2 self-broadening coefficients for ground state and v_1 band transitions [51]. Furthermore, the dissociation energy of the $(SO_2)_2$ dimer has been experimentally derived from the foreign-broadening coefficients of the monomer compound, collisionally perturbed by different damping gasses, and theoretically by means of quantum chemical calculations [52]. Very recently, SO_2 has been included in an Hitran-like database of line parameters for molecules of planetary interest perturbed by H_2, He or CO_2 [19]. In the latter work, it has been pointed out that the amount of data for SO_2 - CO_2 collisions is minimal (actually, it consists of only one transition measured long time ago) and hence new measurements are strongly required.

The present work aims at providing new IR and MW experimental measurements of sulfur dioxide perturbed by a range of collisional partners of astrophysical relevance. In particular, in the IR region, ro-vibrational transitions perturbed by He and CO_2 have been measured in the 9 μm

region by tunable diode laser (TDL) spectroscopy at the Laboratory of Molecular Spectroscopy of University Ca' Foscari Venezia (LMS-Ve). Concerning the MW region, He- and H_2- foreign broadening parameters have been determined for about 20 pure rotational transitions of the ground vibrational state at the laboratory of mm/sub-mm-wave spectroscopy of University of Bologna (LMS-Bo). The work is structured as follows: in Section 2 the experimental set-up and methods of analysis of LMS-Ve and LMS-Bo are presented; in Section 3 the obtained results in the IR and MW regions are reported and compared, and the quantum number dependence of the broadening coefficients is discussed. Finally, conclusions and further remarks are addressed in Section 4.

2. Experimental details and data inversion procedure

He broadening coefficients were determined for both ground state and ν_1 band transitions, whereas the effects of collisions with CO_2 and H_2 were measured in the IR and MW regions, respectively. As anticipated in the Introduction, experiments in the IR spectral range were carried out at LMS-Ve, whereas MW ones were performed at LMS-Bo. The experimental set-up and data treatment at both laboratories are presented in the following subsections.

2.1 IR tunable diode laser spectroscopy at LMS-Ve

SO_2 high resolution IR spectra were recorded around 9 μm, within the atmospheric window, by using the tunable diode laser spectrometer installed at LMS-Ve in a three beam configuration [50,53]. The radiation emitted by a commercial lead-salt laser was split into three different beams: the main part passed through a 92.3 (± 0.2) cm path-length cell containing the SO_2 sample, whereas the two other beams were sent through a second cell filled with low-pressure SO_2 gas and a Ge-etalon, both used for frequency calibration. These beams were gathered by three different mercury-cadmium-telluride IR detectors cryogenically cooled at liquid N_2 temperature. The acquired signals were then digitized by a four-channel digital oscilloscope in the case of He-broadening experiments, whereas a four channel ultrafast digitizer card [54] was employed for SO_2 - CO_2 broadening measurements. Up to 1024 independent scans were averaged to yield the resulting spectra, each consisting of a 0.3 - 0.5 cm^{-1} wide micro-window.

The measurements were carried out at a temperature of 296 ± 2 K by perturbing the radiating species by He or CO_2 following a well established procedure [50,54]. During the

experiments the SO_2 partial pressure was kept fixed at about 100 Pa depending on the intensity of the spectral features and increasing amounts of damping gas were added up to a total pressure of 44.80 hPa at most. Two independent series of measurements were performed, in order to increase the accuracy of the retrieved pressure broadening parameters [54,55]. For promoting gas homogenization, an elapsed time of 10 - 15 min was adopted between the filling of the cell and the recording of the spectra. The pressure in the cell was measured by using two Alcatel capacitance vacuum gauges with a full scale range of 10 hPa and 100 hPa, respectively, and a quoted accuracy of 0.15% on the full scale. All the measurements were performed on a SO_2 gas sample supplied by Sigma-Aldrich with a purity of 99.9%, whereas He and CO_2 damping gases were provided by SIAD with a purity greater than 99.9%.

The acquired spectra were first wavenumber calibrated by employing suitable SO_2 line frequencies from high resolution Fourier Transform IR data and then the transmittance 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 accuracy of the calibration was estimated around 3.0×10^{-4} cm^{-1}. Line-by-line parameters were retrieved by fitting all the lines in a given spectral micro-window to the Voigt profile (VP) in absorbance units by using the multi-line feature of VLSFP [56]. Spectra recorded at different pressures were fitted independently from each other. Since the instrumental line shape function of the laser employed in this work can be reproduced as a Gaussian function, during the fits with the VP, the Doppler half-width was fixed to an effective value given by the following equation

$$\gamma_D^{e\,f\!f} = \left[\left(\gamma_D^{S\,O_2}\right)^2 + \left(\gamma_D^{T\,D\!L}\right)^2\right]^{1/2} \tag{1}$$

where $\gamma_D^{SO_2}$ and γ_D^{TDL} are the molecular and instrumental Doppler half-widths, respectively. To determine the effective Doppler half-width, low-pressure (< 50 Pa) spectra of pure SO_2 were recorded and the corresponding spectral features were fitted to the Gaussian profile. The instrumental half-width was, on average, 7.4×10^{-4} cm^{-1}. The assignment of the spectral lines was based on the Hitran 2012 database [16].

2.2 mm-/sub-mm spectroscopy at LMS-Bo

Measurements were carried out using a frequency-modulated computer-controlled spectrometer working in the 65 GHz - 1.6 THz frequency range. As a complete account of the spectrometer can be found in Refs. [57-59], we only briefly summarize the relevant features. In the present study, the measurements were carried out in the 104 GHz – 1.1 THz interval, with the radiation source being an interchangeable system consisting of Gunn-diode oscillators and Gunn-diode-driven frequency multipliers, which were phase-locked to a rubidium frequency standard. The frequency modulation was achieved by sine-wave modulating the 72 MHz local oscillator of the synchronization loop at 1.666 kHz. In the present study, the detectors employed were a liquid-He InSb hot-electron bolometer (for THz measurements) or a Schottky detector (at frequencies below 500 GHz). Second harmonic detections were performed as the Lock-in amplifier was tuned to twice the modulation frequency.

The pressure broadening of rotational lines of SO_2 with H_2 and He as perturbing gases was already investigated in Ref. [49]. To address 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, with the same starting value for K_a ($K_a = 11 \leftarrow 10$), were considered for investigating the J dependence: $J = 11_{11,1} \leftarrow 11_{10,2}$, $J = 12_{11,1} \leftarrow 12_{10,2}$, $J = 15_{11,5} \leftarrow 15_{10,6}$, $J = 16_{11,5} \leftarrow 16_{10,6}$, $J = 26_{11,15} \leftarrow 26_{10,16}$, $J = 28_{11,17} \leftarrow 28_{10,18}$, $J = 34_{11,23} \leftarrow 34_{10,24}$, $J = 42_{11,31} \leftarrow 42_{10,32}$, $J = 51_{11,41} \leftarrow 51_{10,42}$, $J = 60_{11,49} \leftarrow 60_{10,50}$. Transitions with the same J value ($J = 10$) were considered for 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 this work, further measurements for these transitions have been performed in order to confirm the results of Ref. [49]. In addition, 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 considered.

According to the line intensity, pressures of SO_2 in the range 0.04 - 0.53 Pa were used; then, increasing quantities of either H_2 or He were added starting from ~6.7 Pa up to ~133.3 Pa, with the sample pressure measured by a Baratron gauge with a measurable pressure range of 0.01 - 133.3 Pa. During the recording of a spectrum the pressure of the gas was found stable within less than 0.01 Pa. All the spectra were recorded at room temperature (298 ± 1 K). For each transition investigated in Ref. [49], an additional series of measurements was carried out, while for the newly studied transitions, 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 [60-62]. The line profile analysis was performed by employing the Speed Dependent Voigt Profile (SDVP) using the

formulation of Refs. [61,63-65], which is able to well reproduce the experimental lineshapes as well as the narrowing effects observed at low pressure values (see also Ref. [49]). A graphical example of the line profile analysis is provided by Figure 1 which depicts the line profile analysis for a series of measurements for the $J = 20_{7,13} \leftarrow 21_{6,16}$ rotational transition: the small residuals allow us to point out that the experimental line shapes are well reproduced by the chosen model.

3. Results and discussion

The SO_2 molecule is an asymmetric near prolate rotor, having C_{2v} point group symmetry, and three normal modes of vibration. The ν_1 fundamental, corresponding to the SO_2 symmetric stretching, 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 even values of $K_a + K_c$.

For retrieving SO_2 - CO_2 ($\gamma_{CO_2}^0$) and SO_2 - He (γ_{He}^0) pressure broadening coefficients, the line profile analysis in the IR spectral region was performed by adopting the Voigt model which appears a well suited choice to reproduce the observed line shapes within the experimental set-up and conditions here employed, as illustrated by the good residuals of Figure 2. The upper panel of this figure presents the spectral region between 1102.86 and 1103.60 cm^{-1} perturbed by CO_2 and the residuals corresponding to six different CO_2 partial pressures. The lower panel, instead, shows the SO_2 spectrum from 1083.20 to 1083.80 cm^{-1} when He is employed as damping gas with partial pressures in the range 669.3 - 2370 Pa. As it can be seen, for both collisional partners the synthetic spectrum closely reproduces the experimental line shapes, the only small deviations being observed for the line around 1103.3 cm^{-1} perturbed by 357.5 Pa of CO_2. Anyway, as it can be appreciated on the same figure, this small difference promptly disappears as the CO_2 pressure is raised further. In this context, it should be noted that the use of more refined line shape functions (e.g. including narrowing effects) does not provide any significant improvement over the Voigt profile (at least in the experimental conditions employed during the measurements), as already pointed out in previous investigations [50-52,54,55]. Furthermore, as highlighted by Wilzewski et al. [19], at present the VP is properly suited for the spectral resolution of most instruments probing planetary atmospheres.

During the fits, resonant frequencies, collisional (i.e. Lorentzian) half-widths and line intensities have been refined, whereas the Gaussian contribution to the line width has been constrained to γ_D^{eff}, Eq. (1), that takes into account both the molecular broadening due to thermal

motion and the laser line shape function. In order to retrieve SO_2 foreign-broadening coefficients, γ_X^0 (X = He, CO_2), for each line, the collisional half-widths at temperature T, $\Gamma_L(T)$, obtained from the line shape analysis were fitted against the buffer gas partial pressure to a straight line represented by the following equation

$$\Gamma_L(T) = \Gamma_0 + \gamma_X^0(T) \times P_X \tag{2}$$

where P_X represents the partial pressure of the damping gas and the intercept Γ_0 takes into account the self-broadening contribution to the line width. The linear fits have been carried out by weighting the collisional half-widths on the basis of the corresponding errors derived from the line profile analysis.

In the previous Section it has been pointed out that two independent series of measurements have been carried out for each spectral micro-window. The results of the linear fits obtained for these two repetitions have been combined adopting the following procedure: [54,55,66,67] for each spectral line, the value of the intercept Γ_0 has been subtracted from each collisional half-width Γ_L obtaining, in this way, the so-called normalized Lorentzian half-width, Γ_{NL}. In a successive step, the obtained normalized half widths have been employed in a second linear fit according to

$$\Gamma_{NL} = \gamma_X^0 \times P_X \tag{3}$$

thus retrieving the ultimate value of the foreign-broadening coefficient. This procedure is exemplified in Figure 3 and the SO_2 foreign-broadening coefficients obtained for CO_2 and He buffer gases are listed in Tables 1 and 2, respectively.

The quantum number dependence of the foreign-broadening coefficients is depicted in Figure 4, where for the sake of completeness the He-broadening coefficients obtained in a previous work are also included [50]. Concerning the K_a dependence, the observed trends suggest that for CO_2 the collisional cross sections tend to decrease with increasing K_a values. Conversely, He-broadening coefficients do not display any evident dependence, but rather they are slightly scattered around a mean value of $0.063_6 \pm 0.007_3$ cm^{-1}atm^{-1}. It is worth noticing that this value and the observed trend confirm our previous findings [50], as clearly evident from Figure 4 in which the SO_2-He broadening coefficients obtained in our previous investigation are also included. Concerning the comparison with prior studies, the reader is referred to Ref. [50], where a detailed comparison is performed for SO_2 perturbed by He as well as by N_2, O_2 and air. Taking into account

the quantum numbers of the transitions investigated, it has been possible to access the J dependence of the broadening parameters for transitions belonging to the $K_a^{"} = 15$ sub-branch. Again, SO_2 - He broadening coefficients do not show any significant dependence over the range of quantum numbers investigated, whereas in the case of CO_2 the tendency of collisional cross sections to increase with increasing J'' values can be reported. The only exception to this trend is given by the transition $25_{14,12} \leftarrow 25_{15,11}$ located at about 1102.574 cm^{-1} whose CO_2 broadening coefficient appears slightly low. Anyway, at the higher pressures this transition significantly overlaps with the neighboring ones, thus making it difficult a precise location of the base line that, therefore, can influence the value of the obtained pressure broadening parameter. Indeed, it has been estimated that for an error in the base line which is 1% of the absorption coefficient value at line center, the error in the retrieved collisional half-width is on the order of 12% [68].

Finally, it should be noted that some transitions belonging to the $\nu_1 + \nu_2 - \nu_2$ hot band of $^{32}SO_2$ and to the ν_1 fundamental of $^{34}SO_2$ have also been considered and analyzed. The results obtained for these transitions are included in Tables 1 and 2 for CO_2- and He-broadening coefficients, respectively.

Concerning the analysis in the MW region, for a given transition, for each series of measurements, the pressure-broadening coefficient $\gamma_X^0(298)$ at 298 K has been obtained by a linear fit of the collisional half-widths, $\Gamma_L(298)$, retrieved by the lineshape analysis against the perturber partial pressure P_X, as reported in Equation 2, with $T = 298$ K and the half-widths being weighted according to the reciprocal of the squared uncertainties obtained from the profile analysis. Since in each set of measurements slightly different quantities of SO_2 were used, in order to put all data together, we have employed the following procedure [69]. For each series, we have subtracted the value of the intercept Γ_0 obtained in the fit mentioned above from each $\Gamma_L(298)$. In this way, we have subtracted the contribution due to the self-broadening and all other broadening effects (like wall broadening) from the collisional half-widths. We refer to the $\Gamma_L(298)$ obtained in such a way as normalized Lorentzain half-widths $\Gamma_{NL}(298)$. Subsequently, a second fit involving the normalized half-widths has been performed in order to obtain the final value of the pressure-broadening parameter $\gamma_X^0(298)$ for the transition under consideration, see Equation (3). An example is provided by Figure 5, which depicts the linear fit of normalized collisional half widths for the $J = 3_{3,1} \leftarrow 2_{2,0}$ (313.3 GHz) transition.

The pressure broadening coefficients of the rotational transitions considered are collected in Table 3, where the experimental uncertainties reported are three times the standard deviation of the fit. Figure 6 shows the values of the pressure-broadening coefficients as a function of J and K_a.

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Inspection of this figure and of the values of Table 3 also reveals that the pressure-broadening coefficients vary a little upon variation of either J or K_a, the largest variations being about 10 - 15%. This was also already observed in the literature (see Ref. [49] and references therein). To the best of our knowledge, there are 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. [46], who investigated the 90-500 K range for four rotational transitions: $J = 18_{3,15} - 18_{2,16}$ (240.247 GHz; $\gamma_{H_2} = 0.1387(68)$ cm^{-1} atm^{-1}, $\gamma_{He} = 0.0659(33)$ cm^{-1} atm^{-1}), $13_{1,13} - 12_{0,12}$ (251.199 GHz; $\gamma_{H_2} = 0.1366(68)$ cm^{-1} atm^{-1}, $\gamma_{He} = 0.0621(30)$ cm^{-1} atm^{-1}), $4_{2,2} - 3_{1,3}$ (235.152 GHz; $\gamma_{H_2} = 0.1483(74)$ cm^{-1} atm^{-1}, $\gamma_{He} = 0.0761(38)$ cm^{-1} atm^{-1}), $26_{4,22} - 26_{3,23}$ (280.807 GHz; $\gamma_{H2} = 0.1415(71)$ cm^{-1} atm^{-1}, $\gamma_{He} = 0.0705(36)$ cm^{-1} atm^{-1}). We note that the pressure-broadening coefficients determined at room temperature (reported within parentheses here above) are perfectly in line with those evaluated in the present work.

From the line profile analyses performed employing the SDVP model, the speed-dependence contributions to the line widths can be derived. As expected [63-65], these show a linear dependence on pressure and can be fitted with a linear expression analogous to Eq. (3) in order to derive the so-called γ_2 parameter [63-65], which describes the speed dependence of the relaxation rate. While the expected linear behavior was confirmed in all cases, no results are here reported, neither graphically nor in table, because this parameter results to be very small, about 10^{-6}-10^{-5} cm^{-1} atm^{-1}. To give an example, for the $J = 60_{11,49} - 60_{10,50}$ transition broadened by hydrogen, γ_2 was found to be $5.30(46)\times10^{-5}$ cm^{-1} atm^{-1}, while for the $J = 3_{3,1} - 2_{2,0}$ transition using He as foreign gas a value of $6.21(98)\times10^{-6}$ cm^{-1} atm^{-1} for γ_2 was obtained. We furthermore point out that the knowledge of this parameter is not relevant for the compilation of databases finalized at providing data for remote sensing of planetary atmospheres.

Comparing the He-broadening coefficients obtained for ν_1 band transitions with those of the ground state, it can be concluded that both series of measurements point to a very week dependence of SO_2 - He collisional cross sections on the rotational quantum numbers. Indeed, for the ν_1 band, the retrieved SO_2 - He pressure broadening coefficients appear uniformly scattered around 0.064 ± 0.007 cm^{-1}atm^{-1}, while for the ground state they are nearly constants, at least over the range of quantum numbers here investigated, the average value of He-broadening coefficients for MW transitions being 0.071 ± 0.002 cm^{-1}atm^{-1}. The latter value lies on the upper side of the confidence interval obtained from the analysis in the IR spectral region. The slight differences observed between IR and MW measurements for the He-broadening parameters can be largely explained by considering the different experimental set-up of the two laboratories as well as the fact that in the

spectral region around 9 μm, there are significant overlaps among different ro-vibrational transitions, whereas the lines are almost isolated in the ground state. Concerning the possible vibrational dependence of collisional cross sections, it may become observable when going to higher vibrational energies, i.e. when the molecule gains three or more quanta of vibrational excitation, but in the present case it is expected to be negligible, also based on the outcomes of our previous study [51].   On this basis we can conclude that SO_2 - He broadening coefficients derived for ν_1 band transitions are consistent with those of the ground vibrational state. Furthermore, in order to exclude that the differences in the He-broadening parameters are related to the different line profile models used in the analysis of IR and MW measurements, for two MW transitions, this analysis has been performed also employing the VP model: $J = 43_{5,39} - 42_{6,36}$ and $J = 3_{3,1} - 2_{2,0}$. As expected (see, for example, Refs. [62,65]), the pressure-broadening coefficients determined agree well with those previously derived using the SDVP model. For the $J = 43_{5,39} - 42_{6,36}$ transition, we obtained $\gamma_{He}(VP) = 0.0694(24)$ cm^{-1} atm^{-1} to be compared with $\gamma_{He}(SDVP) = 0.0702(15)$ cm^{-1} atm^{-1}, and for the $J = 3_{3,1} - 2_{2,0}$ transition, $\gamma_{He}(VP) = 0.0677(10)$ cm^{-1} atm^{-1} should be compared with $\gamma_{He}(SDVP) = 0.0676(7)$ cm^{-1} atm^{-1}. For the same two transitions, the analysis using the VP model has been carried out also for H_2 as foreign gas. Analogously, and as expected, a similar agreement between the results obtained with the two different line profile models is noted ($J = 43_{5,39} - 42_{6,36}$: $\gamma_{H_2}(VP) = 0.1449(21)$ cm^{-1} atm^{-1} vs. $\gamma_{H_2}(SDVP) = 0.1426(10)$ cm^{-1} atm^{-1}; $J = 3_{3,1} - 2_{2,0}$: $\gamma_{H_2}(VP) = 0.1410(24)$ cm^{-1} atm^{-1} vs. $\gamma_{H_2}(SDVP) = 0.1408(8)$ cm^{-1} atm^{-1}). The obtained data also shows that H_2-broadening coefficients are about twice those obtained by using He as buffer gas. This behavior can be understood by considering that collisional broadening is ruled by intermolecular interactions in the gas-phase, the electrostatic dipole - dipole or quadrupole - dipole interactions being the foremost ones when neutral species are involved. He is an atomic noble gas and hardly polarizable, and hence its broadening efficiency is smaller than that of H_2, whose scattering events with SO_2 are driven by dipole-quadrupole interactions.

Finally, it should be noticed that this is the first line-by-line analysis that led to determine the SO_2 - CO_2 broadening coefficients for several ro-vibrational transitions and provide the first hints on their quantum number dependence. By considering the transitions investigated, SO_2 - CO_2 broadening parameters range from 0.087 to 0.147 cm^{-1}atm^{-1} and they average to 0.12 ± 0.02 cm^{-1}atm^{-1}. This value may be compared with those obtained for N_2 and O_2 perturbing gases, 0.096 cm^{-1}atm^{-1} and 0.071 cm^{-1}atm^{-1}, respectively: CO_2 appears more efficient than atmospheric buffer gases in broadening the SO_2 transitions. This behavior of CO_2 has already been reported also for other active species (e.g. see Refs. [70-72]). Furthermore, the present results can be compared with the

line-by-line listing of SO_2 - CO_2 pressure broadening coefficients compiled by Wilzewski et al [19], in which they take values in the range 0.16 - 0.23 $cm^{-1}atm^{-1}$ and have an average of 0.181 $\pm$ 0.005 $cm^{-1}atm^{-1}$. These SO_2 - CO_2 collisional parameters are somewhat larger than those determined in the present work, nevertheless this difference can be explained by considering that in Ref. [19] the broadening parameters of SO_2 perturbed by CO_2 have been derived by scaling the corresponding SO_2 - H_2 broadening coefficients according to a factor based on only one line measured in 1963 [73].

Conclusions

Foreign broadening coefficients of sulfur dioxide perturbed by H_2, He and CO_2 have been retrieved for both ground state and ν_1 band transitions by means of mm/sub-mm wave and high resolution TDL spectroscopy, respectively. IR experiments have been carried out in the spectral region around 9 μm and the analysis, performed by using the Voigt profile, has led to the determination of He- and CO_2-broadening parameters for several transitions belonging to the ν_1 band of $^{32}SO_2$ as well as some ro-vibrational transitions of $\nu_1 + \nu_2 - \nu_2$ of $^{32}SO_2$ and ν_1 of $^{34}SO_2$. MW measurements have been carried out within the 104 GHz - 1.1 THz spectral range and 19 pure rotational transitions perturbed by H_2 and He buffer gases have been analyzed on the basis of the speed-dependent Voigt profile model.

Concerning the obtained results, both IR and MW experiments have highlighted a very weak dependence of He collisional cross sections on the K_a and J rotational quantum numbers, with an average He broadening parameter of 0.064 ± 0.007 and 0.071 ± 0.002 cm^{-1}atm^{-1} for IR and MW transitions, respectively. In a similar way, also SO_2 - H_2 broadening coefficients show a negligible dependence on the rotational quantum numbers, keeping an almost constant value of 0.145 ± 0.004 cm^{-1}atm^{-1}. Conversely, when CO_2 is employed as perturbing species, the observed collisional cross sections tend to decrease with increasing K_a values. The quantum numbers of the transitions investigated also allowed us to access the J dependence for the $K_a^{"} = 15$ subbranch, in which the broadening parameters increase by enlarging the J value. The obtained SO_2 - CO_2 pressure broadening coefficients take values between 0.087 and 0.147 cm^{-1}atm^{-1} and they present an average value of 0.12 ± 0.02 cm^{-1}atm^{-1}.

All in all, by combining IR and MW experiments we have measured foreign broadening coefficients of SO_2, a molecule of proved astrophysical relevance due to its presence in the interstellar medium and in the atmospheres of Earth, Venus and Mars. The present results are important for increasing the potential use of spectroscopic databases for astronomical applications, indeed they not only represent the first determination of CO_2 broadening parameters, but they also provide new data for collisions with He and H_2, which are buffer gases important for the atmospheres of gas giants.

Acknowledgments

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Figure captions

Figure 1. H_2 broadening of the 258.7 GHz line of sulfur dioxide: a series of measurements analyzed by using the speed dependent Voigt profile. Partial pressure values (from the inner to the outer curve): 13.39, 19.51, 25.84, 32.84, 39.45 Pa.

Figure 2. (a) SO_2 spectrum between 1102.86 and 1103.60 cm^{-1} perturbed by different amounts of CO_2. Experimental spectrum (gray circles): P_{SO_2} = 106.1 Pa, path length = 92.3 cm, T = 296 K. Fit of the spectral lines to the Voigt profile (red line). Residuals, with the same scale as the spectrum, have been displaced for clarity and they refer to the following CO_2 partial pressures (Pa) from top to bottom: 357.5, 813.7, 1314, 2114, 3004, 4024.
(b) SO_2 spectrum between 1083.20 and 1083.80 cm^{-1} perturbed by different amounts of He. Experimental spectrum (gray circles): P_{SO_2} = 95.9 Pa, path length = 92.3 cm, T = 296 K. Fit of the spectral lines to the Voigt profile (red line). Residuals, with the same scale as the spectrum, have been displaced for clarity and they refer to the following He partial pressures (Pa) from top to bottom: 669.3, 1140, 1700, 2370.

Figure 3. CO_2 (blue) and He (black) broadening of the $15_{11,5} \leftarrow 16_{12,4}$ ro-vibrational transition at 1102.61656 cm^{-1} of SO_2: experimental collisional half widths (squares) and linear fit (dashed line) of normalized Lorentzian half-widths against the buffer gas partial pressure. Error bars are the uncertainties retrieved from the line profile analysis.

Figure 4. Dependence of CO_2- and He- broadening coefficients of SO_2 ν_1 band transitions on (a) the $K_a^"$ pseudo-quantum number and (b) the $J"$ quantum number for the $K_a^"$ = 15 sub-branch.

Figure 5. He broadening of the 313.3 GHz line of sulfur dioxide in the vibrational ground state: linear fit of the normalized Lorentzian half-widths against the partial pressure of He for the $J = 3_{3,1} \leftarrow 2_{2,0}$ transition. Error bars are three times the uncertainties retrieved from the line profile analysis.

Figure 6. Dependence of H_2- and He- broadening coefficients of SO_2 ground state transitions on (a) the $K_a^"$ pseudo-quantum number and (b) the $J"$ quantum number for the $K_a^"$ = 10 subbranch.

Table 1. Assignments, transition frequencies, intensities and CO_2-broadening coefficients for ro-vibrational transitions of v_1, $v_1 + v_2 - v_2$ bands of $^{32}SO_2$ and v_1 band of $^{34}SO_2$.[a]

v_1 $^{32}SO_2$

J'	K_a'	K_c'	J''	K_a''	K_c''	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	$\gamma_{CO_2}^0$ (cm^{-1} atm^{-1})
15	15	1	16	16	0	$1089.8725_4(1_4)$	$7.8_6(7_2)$	$0.115_2(3_3)$
27	18	10	27	19	9	$1089.9881_1(4_7)$	$0.73_7(7_6)$	$0.107_8(3_7)$
37	10	28	38	11	27	$1090.0297_9(3_5)$	$3.4_0(7_0)$	$0.116_7(3_6)$
27	11	17	28	12	16	$1090.0592_5(3_3)$	$0.83_9(7_1)$	$0.106_8(4_6)$
26	18	8	26	19	7	$1090.0793_6(4_3)$	$0.84_8(7_9)$	$0.103_6(5_4)$
46	8	38	47	9	37	$1090.1412_2(2_1)$	$0.91_2(6_5)$	$0.117_9(2_4)$
28	12	16	29	13	17	$1090.1593_4(1_5)$	$4.7_8(4_5)$	$0.125_9(3_0)$
25	18	8	25	19	7	$1090.1674_6(2_2)$	$0.61_4(6_2)$	$0.114_3(2_4)$
19	14	6	20	15	5	$1090.22661_9(7_9)$	$6.0_4(4_4)$	$0.111_8(1_8)$
27	14	14	27	15	13	$1102.403_2(1_7)$	$2.55_0(3_0)$	$0.147_1(3_2)$
26	14	12	26	15	11	$1102.4898_6(3_4)$	$2.6_2(1_2)$	$0.134_8(3_4)$
29	8	22	30	9	21	$1102.56137_5(9_5)$	$6.6_3(1_9)$	$0.133_8(1_4)$
25	14	12	25	15	11	$1102.5743_8(1_4)$	$2.5_2(3_3)$	$0.104_4(2_6)$
15	11	5	16	12	4	$1102.6165_6(1_5)$	$12.1_7(3_9)$	$0.128_4(1_4)$
24	14	10	24	15	9	$1102.65617_5(3_5)$	$2.84_2(5_2)$	$0.116_0(2_8)$
51	13	39	51	14	38	$1102.6632_1(3_1)$	$0.43_4(9_6)$	$0.102_4(3_7)$
23	14	10	23	15	9	$1102.73510_5(2_6)$	$2.59_5(2_5)$	$0.12085_5(9_4)$
24	9	15	25	10	16	$1102.83383_3(8_3)$	$8.6_3(4_7)$	$0.130_2(4_0)$
21	14	8	21	15	7	$1102.8829_8(1_4)$	$2.4_4(1_3)$	$0.117_6(3_3)$
20	14	6	20	15	5	$1102.95215_0(2_1)$	$2.33_4(3_4)$	$0.116_0(1_6)$
49	13	37	49	14	36	$1102.9612_9(1_9)$	$0.63_9(5_2)$	$0.087_0(2_2)$
19	14	6	19	15	5	$1103.01811_1(3_0)$	$2.24_(1_3)$	$0.112_7(3_4)$
33	7	27	34	8	26	$1103.05607_2(7_0)$	$4.7_3(1_9)$	$0.127_4(2_7)$
18	14	4	18	15	3	$1103.08116_1(6_0)$	$1.9_0(1_4)$	$0.112_0(2_5)$
19	10	10	20	11	9	$1103.08937_8(7_2)$	$10.9_7(5_6)$	$0.132_9(1_4)$
17	14	4	17	15	3	$1103.1408_0(1_5)$	$1.4_7(1_2)$	$0.100_2(2_3)$
16	14	2	16	15	1	$1103.19674_(2_9)$	$1.0_1(1_2)$	$0.091_6(3_8)$
38	6	32	39	7	33	$1103.2430_0(1_7)$	$2.7_1(2_4)$	$0.140_5(3_7)$
47	13	35	47	14	34	$1103.25017_(3_4)$	$1.4_9(1_3)$	$0.107_2(1_9)$
28	8	20	29	9	21	$1103.28239_(1_2)$	$7.3_7(3_6)$	$0.140_1(2_0)$
14	11	3	15	12	4	$1103.30453_(1_0)$	$12.9_2(3_3)$	$0.1412_0(8_4)$
46	13	33	46	14	32	$1103.3920_8(2_7)$	$1.00_6(4_2)$	$0.138_4(2_4)$
45	13	33	45	14	32	$1103.5306_2(4_2)$	$1.0_3(1_3)$	$0.112_8(1_3)$
23	9	15	24	10	14	$1103.5460_5(2_2)$	$9.4_7(2_8)$	$0.145_9(2_1)$
17	13	5	17	14	4	$1106.3114_7(3_8)$	$2.88_5(5_5)$	$0.122_8(2_1)$
19	9	11	20	10	10	$1106.36808_7(5_1)$	$14.7_7(3_8)$	$0.137_9(1_3)$
31	2	30	32	3	29	$1106.3772_7(9_0)$	$0.56_8(9_3)$	$0.148_0(9_2)$
15	13	3	15	14	2	$1106.41998_5(2_5)$	$1.8_7(1_1)$	$0.105_9(1_7)$
14	13	1	14	14	0	$1106.46902_5(6_5)$	$0.75_4(2_7)$	$0.094_1(2_2)$
33	6	28	34	7	27	$1106.50761_2(5_8)$	$5.71_0(1_0)$	$0.132_1(2_4)$
47	12	36	47	13	35	$1106.51809_1(3_9)$	$0.97_1(6_2)$	$0.119_6(6_0)$
14	10	4	15	11	5	$1106.55599_8(2_4)$	$14.7_4(1_3)$	$0.124_4(2_7)$

Table 1 (continued 2/2)

$v_1 + v_2 - v_2 \; ^{32}SO_2$

J'	K_a'	K_c'	J''	K_a''	K_c''	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	$\gamma_{CO_2}^0$ (cm^{-1} atm^{-1})
19	9	11	20	10	10	1102.4298(47)	0.861(11)	0.1233(78)
14	10	4	15	11	5	1102.545315(55)	1.011(23)	0.1219(54)
23	8	16	24	9	15	1102.982967(67)	0.725(69)	0.1131(52)
13	10	4	14	11	3	1103.22870(14)	1.01(12)	0.1208(52)
23	7	17	24	8	16	1106.388355(85)	1.008(72)	0.116(12)
18	8	10	19	9	11	1106.492415(55)	1.07(12)	0.1146(28)
13	9	5	14	10	4	1106.568255(23)	0.965(65)	0.0932(20)

$v_1 \; ^{34}SO_2$

J'	K_a'	K_c'	J''	K_a''	K_c''	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	$\gamma_{CO_2}^0$ (cm^{-1} atm^{-1})
11	10	2	12	11	1	1102.540400 (40)	0.583(13)	0.0702(22)
20	8	12	21	9	13	1102.729440(50)	0.5215(65)	0.1098(43)
27	12	16	27	13	15	1102.93245(15)	0.254(28)	0.1337(68)
15	9	7	16	10	6	1102.99359(15)	0.562(62)	0.1096(52)
19	8	12	20	9	11	1103.42640(29)	0.568(44)	0.1395(63)
10	9	1	11	10	2	1106.384770(30)	1.365(25)	0.10114(40)
15	13	3	15	14	2	1106.42001(25)	1.76(19)	0.1059(17)

[a] Figures in parentheses are one standard deviation.

Table 2. Assignments, transition frequencies, intensities and He-broadening coefficients for ro-vibrational transitions of v_1, $v_1 + v_2 - v_2$ bands of $^{32}SO_2$ and v_1 band of $^{34}SO_2$.[a]

						v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	γ^0_{He} (cm^{-1} atm^{-1})

v_1 $^{32}SO_2$

J'	K'_a	K'_c	J''	K''_a	K''_c	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	γ^0_{He} (cm^{-1} atm^{-1})
20	16	4	21	17	5	1083.2563$_7$(1$_5$)	6.5$_4$ (1$_7$)	0.0760$_4$ (8$_5$)
33	20	14	33	21	13	1083.3397$_6$(2$_1$)	0.29$_6$ (2$_6$)	0.0604$_4$ (2$_2$)
55	8	48	56	9	47	1083.4375$_0$(3$_1$)	0.22$_0$ (4$_6$)	0.0567$_7$ (1$_0$)
37	12	26	38	13	25	1083.4800$_3$(2$_2$)	1.7$_6$ (1$_8$)	0.0520$_0$ (1$_7$)
24	15	9	25	16	10	1083.5169$_6$(1$_6$)	3.5$_7$ (1$_2$)	0.0636$_0$ (8$_5$)
31	20	12	31	21	11	1083.5636$_0$(4$_3$)	0.25$_0$ (1$_9$)	0.0518$_8$ (3$_1$)
50	9	41	51	10	42	1083.6280$_7$(3$_2$)	0.54$_9$ (1$_2$)	0.0696$_6$ (3$_8$)
30	20	10	30	21	9	1083.6702$_5$(2$_2$)	0.32$_9$ (1$_5$)	0.0670$_0$ (3$_4$)
41	11	31	42	12	30	1083.7144$_2$(2$_3$)	1.37$_9$ (2$_5$)	0.0642$_2$ (1$_4$)
28	14	14	29	15	15	1083.7632$_6$(1$_5$)	3.32$_0$ (3$_1$)	0.0704$_9$ (5$_5$)
29	20	10	29	21	9	1083.7732$_0$(1$_4$)	0.28$_8$ (5$_7$)	0.0514$_4$ (1$_6$)
28	14	14	28	15	13	1102.3111$_2$(1$_2$)	2.5$_4$ (2$_8$)	0.0720$_0$ (4$_9$)
34	7	27	35	8	28	1102.3424$_5$(1$_7$)	4.7$_8$ (1$_4$)	0.0693$_3$ (1$_8$)
53	13	41	53	14	40	1102.355$_1$ (1$_9$)	0.3$_6$ (1$_2$)	0.0769$_9$ (2$_1$)
20	10	10	21	11	11	1102.38692$_3$(6$_1$)	11.1$_0$ (4$_8$)	0.0713$_4$ (8$_8$)
27	14	14	27	15	13	1102.403$_2$(1$_7$)	2.55$_0$(3$_0$)	0.0567$_1$ (9$_6$)
26	14	12	26	15	11	1102.4898$_6$(3$_4$)	2.6$_2$(1$_2$)	0.0638$_8$ (1$_9$)
29	8	22	30	9	21	1102.56137$_5$(9$_5$)	6.6$_3$(1$_9$)	0.0733$_3$ (1$_0$)
25	14	12	25	15	11	1102.5743$_8$(1$_4$)	2.5$_2$(3$_3$)	0.0671$_1$ (1$_9$)
15	11	5	16	12	4	1102.6165$_6$(1$_5$)	12.1$_7$(3$_9$)	0.0701$_7$ (7$_0$)
24	14	10	24	15	9	1102.65617$_5$(3$_5$)	2.84$_2$(5$_2$)	0.0718$_8$ (1$_6$)
51	13	39	51	14	38	1102.6632$_1$(3$_1$)	0.43$_4$(9$_6$)	0.0501$_1$ (9$_2$)
23	14	10	23	15	9	1102.73510$_5$(2$_6$)	2.59$_5$(2$_5$)	0.0625$_5$ (1$_6$)
22	14	8	22	15	7	1102.8092$_6$ (8$_7$)	4.8$_3$ (3$_1$)	0.0555$_7$ (4$_6$)
24	9	15	25	10	16	1102.83383$_3$(8$_3$)	8.6$_3$(4$_7$)	0.0774$_4$ (1$_1$)
21	14	8	21	15	7	1102.8829$_8$(1$_4$)	2.4$_4$(1$_3$)	0.0750$_0$ (5$_6$)
20	14	6	20	15	5	1102.95215$_0$(2$_1$)	2.33$_4$(3$_4$)	0.0675$_5$ (1$_4$)
49	13	37	49	14	36	1102.9612$_9$(1$_9$)	0.63$_9$(5$_2$)	0.0542$_2$ (4$_5$)
19	14	6	19	15	5	1103.01811$_1$(3$_0$)	2.2$_4$(1$_3$)	0.0606$_6$ (9$_0$)
33	7	27	34	8	26	1103.05607$_2$ (7$_0$)	4.7$_3$(1$_9$)	0.0591$_1$ (1$_6$)
18	14	4	18	15	3	1103.08116$_1$(6$_0$)	1.9$_0$(1$_4$)	0.0513$_3$ (2$_2$)
19	10	10	20	11	9	1103.08937$_8$(7$_2$)	10.9$_7$(5$_6$)	0.0707$_9$ (6$_4$)
17	14	4	17	15	3	1103.1408$_0$(1$_5$)	1.4$_7$(1$_2$)	0.0554$_8$ (1$_6$)
48	13	35	48	14	34	1103.1076$_4$ (1$_4$)	0.59$_0$ (3$_0$)	0.0554$_1$ (1$_6$)
19	13	7	19	14	6	1106.1904$_7$ (2$_5$)	4.7$_2$ (5$_5$)	0.0657$_7$ (8$_0$)
18	13	5	18	14	4	1106.25273$_9$ (8$_7$)	2.8$_3$ (2$_1$)	0.0695$_5$ (2$_7$)
17	13	5	17	14	4	1106.3114$_7$(3$_8$)	2.88$_5$(5$_5$)	0.0661$_1$ (2$_6$)
19	9	11	20	10	10	1106.36808$_7$(5$_1$)	14.7$_7$(3$_8$)	0.0689$_9$ (1$_3$)
31	2	30	32	3	29	1106.3772$_7$ (9$_0$)	0.56$_8$ (9$_3$)	0.0561$_1$ (9$_9$)
48	12	36	48	13	35	1106.3796$_1$ (2$_6$)	1.0$_1$ (1$_2$)	0.05$_6$ (1$_3$)
15	13	3	15	14	2	1106.41998$_5$(2$_5$)	1.8$_7$(1$_1$)	0.0720$_0$ (5$_9$)
14	13	1	14	14	0	1106.46902$_5$(6$_5$)	0.75$_4$(2$_7$)	0.0546$_6$ (3$_3$)
33	6	28	34	7	27	1106.50761$_2$(5$_8$)	5.71$_0$(1$_0$)	0.0692$_2$ (1$_1$)
47	12	36	47	13	35	1106.51809$_1$(3$_9$)	0.97$_1$(6$_2$)	0.0632$_2$ (7$_4$)
14	10	4	15	11	5	1106.55599$_8$(2$_4$)	14.7$_4$(1$_3$)	0.0662$_2$ (8$_9$)

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Table 2 (continued 2/2)

$v_1 + v_2 - v_2$ $^{32}SO_2$

J'	K_a'	K_c'	J''	K_a''	K_c''	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	γ_{He}^0 (cm^{-1} atm^{-1})
18	15	3	19	16	4	$1083.4847_3\ (2_6)$	$0.52_5\ (9_0)$	$0.062_5\ (4_0)$
14	10	4	15	11	5	$1102.54531_5(5_5)$	$1.01_1(2_3)$	$0.066_6(4_1)$
23	8	16	24	9	15	$1102.98296_7(6_7)$	$0.72_5(6_9)$	$0.060_0(2_2)$
38	6	32	37	5	33	$1103.0008_6\ (1_8)$	$0.17_8\ (1_9)$	$0.052_8\ (2_6)$
18	9	9	19	10	10	$1103.1239_4\ (1_7)$	$0.86_6\ (6_6)$	$0.049_7\ (1_6)$
28	6	22	29	7	23	$1106.3253_2\ (2_8)$	$0.64_9\ (3_6)$	$0.064_0\ (4_3)$
18	8	10	19	9	11	$1106.49241_5(5_5)$	$1.0_7(1_2)$	$0.060_6(5_7)$
13	9	5	14	10	4	$1106.56825_5(2_3)$	$0.96_5(6_5)$	$0.055_1(8_0)$

v_1 $^{34}SO_2$

J'	K_a'	K_c'	J''	K_a''	K_c''	v_0 (cm^{-1})	S^0 (10^{-22} cm molecule^{-1})	γ_{He}^0 (cm^{-1} atm^{-1})
25	13	13	26	14	12	$1083.3940_2\ (5_6)$	$0.27_1\ (2_3)$	$0.071_4\ (6_0)$
16	15	1	17	16	2	$1083.6043_5\ (3_6)$	$0.23_8\ (2_5)$	$0.048_2\ (1_2)$
29	12	18	30	13	7	$1083.6124_8\ (4_5)$	$0.166_0(9_4)$	$0.064_7\ (3_1)$
16	9	7	17	10	8	$1102.3072_4\ (2_1)$	$1.0_2\ (1_3)$	$0.071_5\ (5_5)$
11	10	2	12	11	1	$1102.5404_0\ (4_0)$	$0.58_3(1_3)$	$0.053_9(5_3)$
20	8	12	21	9	13	$1102.72944_0(5_0)$	$0.521_5(6_5)$	$0.062_7(3_1)$
15	9	7	16	10	6	$1102.9935_9(1_5)$	$0.56_2(6_2)$	$0.064_8(2_5)$
24	7	17	25	8	18	$1103.1511_7\ (4_9)$	$0.47_3\ (4_0)$	$0.053_3\ (7_8)$
10	9	1	11	10	2	$1106.38477_0(3_0)$	$1.36_5(2_5)$	$0.060_8\ (5_7)$
22	11	11	22	12	10	$1106.4553_0\ (38)$	$0.26_9\ (3_9)$	$0.059_3\ (8_5)$
21	11	11	21	12	10	$1106.5234_6\ (6_2)$	$0.33_7\ (1_3)$	$0.07_4\ (1_6)$

[a] Figures in parentheses are one standard deviation.

Table 3. Experimental He- and H_2-broadening parameters of pure rotational lines of SO_2.[a]

J'	K'_a	K'_c	J''	K''_a	K''_c	v_0 (MHz)	$\gamma^0_{H_2}$ (cm^{-1} atm^{-1})	γ^0_{He} (cm^{-1} atm^{-1})
J dependence								
11	11	1	11	10	2	1064050.059(50)	0.1368 (10)	0.0702 (11)
12	11	1	12	10	2	1064089.718(50)	0.14397 (94)	0.0723 (10)
15	11	5	15	10	6	1064206.096(50)	0.14696 (89)	0.07339 (84)
16	11	5	16	10	6	1064241.229(50)	0.14939 (53)	0.0740 (10)
26	11	15	26	10	16	1064223.095(50)	0.15023 (76)	0.0735 (11)
28	11	17	28	10	18	1064072.080(50)	0.14582 (61)	0.0745 (10)
34	11	23	34	10	24	1063097.643(50)	0.14726 (91)	0.07235 (30)
42	11	31	42	10	32	1059981.907(50)	0.14501 (74)	0.07131 (94)
51	11	41	51	10	42	1052515.119(50)	0.14019 (79)	0.06977 (53)
60	11	49	60	10	50	1038159.319(50)	0.1455 (10)	0.06655 (91)
K_a dependence								
10	1	9	10	0	10	104239.295(20)	0.1424 (18)	0.06966 (30)
10	2	8	10	1	9	129514.801(20)	0.14141 (94)	0.0687 (11)
10	4	6	10	3	7	356755.187(20)	0.1472 (17)	0.0695 (10)
10	5	5	10	4	6	459668.356(20)	0.1463 (10)	0.0705 (11)
10	6	4	10	5	5	561560.313(20)	0.1500 (18)	0.0701 (10)
10	7	3	10	6	4	662997.749(20)	0.1506 (10)	0.07240 (91)
$\Delta J = -1$								
20	7	13	21	6	16	258666.957(20)	0.1438 (13)	0.07309 (91)
$\Delta J = +1$								
43	5	39	42	6	36	248995.121(20)	0.1426 (10)	0.0702 (15)
3	3	1	2	2	0	313279.729(20)	0.14077 (81)	0.06759 (74)

[a] Uncertainties in parentheses are three times the standard deviation.