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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) is based on the knowledge of the molecules that are present in 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 originates 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) 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

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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 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 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 $\nu_2=1$ state constants have been accurately re-determined about 10 years ago [32], while in the IR region the ν_1 and ν_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 ν_2 fundamental and the $2\nu_2-\nu_2$ hot band [35]. Concerning the determination of line-by-line parameters, intensity measurements have been carried out for some ν_1 and ν_3 ro-vibrational transitions [36], while a systematic study has been performed in the $940\text{--}1400\text{ cm}^{-1}$ 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 for ground state and ν_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 $9\text{ }\mu\text{m}$ 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 $9\text{ }\mu\text{m}$, 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 $92.3 (\pm 0.2)\text{ cm}$ 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 $0.3\text{--}0.5\text{ cm}^{-1}$ wide micro-window.

The measurements were carried out at a temperature of $296 \pm 2\text{ K}$ 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

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