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A complete listing of sulfur dioxide self-broadening coefficients for atmospheric applications by coupling infrared and microwave spectroscopy to semiclassical calculations



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ABSTRACT

Sulfur dioxide (SO₂) is a molecule of proved atmospheric relevance, the main sources being anthropogenic, which is one of the main causes of acid rains. Besides, it is also of interest in astrophysics, as it is present in the atmosphere of Venus and in star forming regions. For these reasons SO₂ is one of the target molecules in all of the most important spectroscopic databases which collect the spectroscopic line-by-line parameters for atmospheric remote sensing, astrophysics soundings, and climate changing investigations. Although over the years the spectroscopic properties of this molecule have been widely studied, and line-by-line listings of line positions and intensities have been compiled, at present an analogous systematic and complete database of broadening coefficients is still lacking. The aim of this work is to fill in this vacancy, starting from self-broadening coefficients, by coupling experimental measurements to theoretical calculations. The laboratory experiments are carried out for 12 pure rotational transitions of the vibrational ground state (and 2 of vibrational excited states) and for 25 ro-vibrational lines of the ν_1 band, lying in the 9 μm atmospheric window. Theoretical calculations of broadening coefficients are performed employing a semiclassical formalism based on the ATC (Anderson–Tsao–Curnutte) approximation. From the interplay between theory and experiment the vibrational and quantum number dependence of the collisional cross-sections is first assessed and studied and then a complete database of self-broadening coefficients for 1635 transitions in a wide quantum number range ($0 \leq K''_a \leq 16$, $2 \leq J'' \leq 68$) is compiled, presented and made available.

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1. Introduction

Although gas phase molecular spectroscopy dates back to the beginning of 1800s, when it was used to explore the composition of the sun, it remains an active field which,

during last years, has become of essential importance in many disciplines such as atmospheric chemistry and astrophysics. Indeed, the study of the Earth's and planetary atmospheres, and of the interstellar medium by means of spectroscopic techniques has rapidly grown up and, nowadays, remote sensing techniques are widely used to probe the atmospheres and retrieve the concentration profiles of many species. Among the various spectroscopic methods, microwave (MW) and infrared (IR) spectroscopies play a

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significant and complementary role for the remote sensing of either the terrestrial and planetary atmospheres as well as for probing the interstellar medium [1–8].

On this basis, spectroscopic line parameters (transition frequencies, broadening and shift coefficients with their temperature dependence, and integrated absorption coefficients) obtained from laboratory experiments, are of fundamental importance for remote sensing applications used in atmospheric and climate research, environmental monitoring, and astronomy: their accurate knowledge is a prerequisite for a reliable retrieval of the distribution profiles of the molecular species of interest. Besides, the analysis of spectral line shapes, and in particular of broadening and shifting coefficients gives a deep insight about collisional processes, their dynamics and the energetic driving them [9–21].

Sulfur dioxide is a molecule of proved importance in atmospheric chemistry, industry and astrophysics. It plays a fundamental role for the Earth's atmosphere as it actively enters in the sulfur cycle. Biomass burning and volcanic eruptions are the main natural sources of SO₂: although sporadic, they can cause huge local fluctuations in the SO₂ atmospheric concentration. For example the eruption of Mt. Pinatubo volcano in 1991 was able to increase the vertical column amount of SO₂ from undetectable levels to $5.1(\pm 0.5) \times 10^{-16}$ molecules cm⁻² [22,23]. Nevertheless, the main sources of atmospheric SO₂ arise from anthropogenic activities as this compound is widely employed by industry, in particular in winemaking and food preserving. Once in the atmosphere, sulfur dioxide is one of the main sources of acid rains. Moreover, the radiative effects of the compounds originating from the atmospheric oxidation of SO₂ (e.g. sulfate aerosols) affect stratospheric chemistry and contribute to global climate changes.

In addition to this atmospheric importance, sulfur dioxide has an astrophysical relevance since it has been detected in the interstellar medium, particularly in star forming regions [24,25], and it has been identified in the atmosphere of Venus [26] as well as on the surface of Io [27].

For these reasons, sulfur dioxide has been widely studied using spectroscopic methods and it is still the subject of considerable interest (Refs. [28–32] and references therein).

Although rotational and ro-vibrational line positions are already well studied and determined [33–35], and a complete set of line strengths has been obtained for the ν_1 band transitions located at about 1151 cm⁻¹ [36], at present a complete and systematic listing of broadening coefficients is still lacking. To the best of our knowledge, the most extensive studies have been carried out by Sumpf and co-workers who obtained pressure broadening coefficients of sulfur dioxide perturbed by either itself or different collisional partners [37–42], and gave an estimate of their quantum number dependence. More recently, self-broadening coefficients have been obtained for a large number of transitions in the 9 μ m spectral region from tunable diode laser measurements [29].

In this view, here we present the results of a joint experimental and theoretical study on self-broadening coefficients, carried out in order to explore the vibrational

and quantum number dependence of collisional cross-sections of self-perturbed SO₂. To accomplish this objective, self-broadening coefficients for new ro-vibrational transitions of the ν_1 band have been determined at the Laboratory of Molecular Spectroscopy of Venice (LMS-Ve) while those in the ground state have been measured at the Laboratory of Millimeter/Submillimeter-wave Spectroscopy of Bologna (LMS-Bo). As concern the investigation of pure rotational transitions, the selection of lines was made in order to have the quantum numbers involved as much similar as possible to the ro-vibrational ones (according to accessibility of the rotational spectrum) as well as to gain information on the dependence of the pressure broadening coefficients on the quantum numbers J and K_a . One transition was selected to be investigated not only in the vibrational ground state but also in the $\nu_1=1$ and $\nu_2=1$ states. For this transition and a second one, the determination of the self-broadening coefficient was also carried out for the ³⁴SO₂ isotopic species.

From the IR and MW sets of data, and on comparison with the theoretical collisional cross-sections calculated by a semiclassical approach, the vibrational dependence of self-broadening coefficients has been assessed. The experimental–theoretical intercomparison has also been pursued to check the precision of the experimental determinations and to give more insight about the quantum number dependence of collisional broadening. Then, by using the set of experimental self-broadening coefficients for the ν_1 and ground state transitions, in conjunction with the theoretical collisional decay rates, a complete line list of self-broadening coefficients has been generated.

The work is structured as follows: in Section 2 the experimental set-up and data inversion procedure of both LMS-Ve and LMS-Bo are described, while in Section 3 the theoretical calculation of collisional cross-sections is outlined. The obtained results, covering the variation with quantum numbers, the experimental–theoretical comparison and the vibrational dependence of broadening coefficients are presented in Section 4. Conclusions and remarks are addressed in Section 5.

2. Experimental details and data inversion

As pointed out in Section 1, in order to retrieve information about the vibrational and the quantum number dependence of collisional decay rates, sulfur dioxide self-broadening coefficients have been determined in the IR region at University of Venice and in the MW region at University of Bologna. The corresponding experimental and data inversion procedures are described in Sections 2.1 and 2.2, respectively.

2.1. Infrared experiments at the Laboratory of Molecular Spectroscopy of Venice

Line-by-line parameters (i.e. resonant frequencies, self-broadening coefficients and integrated absorption coefficients) were retrieved for 25 SO₂ ro-vibrational transitions belonging to either the Q or P branches of the ν_1 band. The experimental set-up employed for these measurements has been described previously [29,43] and

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