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Intercomparison between ozone-broadening parameters retrieved from millimetre-wave measurements by using different techniques

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Abstract

For atmospheric purposes, the N_2- and O_2-, or Air-broadenings of selected transitions of ozone have been investigated in the 195–300 K temperature range. More precisely, the following 13 transitions in the 280–345 GHz frequency range have been studied: the $2_{2,0} \leftarrow 2_{1,1}$ (279.5 GHz), $24_{2,22} \leftarrow 24_{1,23}$ (286.2 GHz), $3_{2,2} \leftarrow 3_{1,3}$ (286.3 GHz), $5_{2,4} \leftarrow 5_{1,5}$ (293.2 GHz), $13_{4,10} \leftarrow 14_{3,11}$ (300.7 GHz), $14_{0,14} \leftarrow 13_{1,13}$ (301.8 GHz), $7_{2,6} \leftarrow 7_{1,7}$ (303.2 GHz), $26_{2,24} \leftarrow 26_{1,25}$ (315.9 GHz), $5_{3,3} \leftarrow 6_{2,4}$ (317.2 GHz), $20_{1,19} \leftarrow 20_{0,20}$ (320.0 GHz), $26_{6,20} \leftarrow 27_{5,23}$ (343.2 GHz), $26_{2,24} \leftarrow 25_{3,23}$ (343.2 GHz), and $4_{3,1} \leftarrow 5_{2,4}$ (343.5 GHz) lines. Systematic errors are known to be the principal error source and recent intercomparisons of line-broadening coefficients showed differences up to 20%, thus a large effort in minimizing systematic error sources has been taken and cross check measurements with different techniques have been carried out. The conclusion of the intercomparison performed indicates an excellent agreement of the results and that an uncertainty less than 3%, which also takes into account the systematic errors, can be claimed for the line-broadening parameters.

1. Introduction

There is a growing need for a better understanding of the processes that control the environment and for the development of reliable technologies for the prediction of environmental changes. In particular, the fate of ozone molecule, i.e., its layer depletion, has been and still is widely investigated since O_3 is a very important constituent of earth atmosphere and plays a fundamental role in the habitability of the planet. As a consequence, the ozone concentration has been continuously monitored in the last decades.

Concentration profiles of O_3 can be obtained from spectroscopic remote sensing measurements, but they require accurate parameters for the spectral region in question. The data required are unperturbed line positions, transition intensities, pressure-broadening half-widths and their temperature dependence, and pressure-induced line shifts. To this purpose, databases of spectroscopic parameters have been set up since 1960s, and these databases are regularly updated and improved.

Even if ozone was widely studied in the past (see for instance [1]), either a lot of data are missing or available data do not have the required accuracy, i.e., 1–5% [1], to be implemented in spectroscopic databases for atmospheric spectra analysis.

It is clearly out of question to exhaustively cover vast spectral ranges and the environmental conditions in the

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laboratory. However, accurate spectroscopic parameters for some "well chosen" lines determined experimentally would be sufficient for remote sensing measurements. On this topic, the microwave limb sounding instrument MASTER is now under development at the European Space Agency (ESA). In view of future space missions, most of the ozone lines investigated in this work are target lines in the B, C, and D bands of MASTER; they are: the $13_{4,10} \leftarrow 14_{3,11}$ (300.7 GHz), $14_{0,14} \leftarrow 13_{1,13}$ (301.8 GHz), $7_{2,6} \leftarrow 7_{1,7}$ (303.2 GHz), $5_{3,3} \leftarrow 6_{2,4}$ (317.2 GHz), $20_{1,19} \leftarrow 20_{0,20}$ (320.0 GHz), $26_{2,24} \leftarrow 25_{3,23}$ (343.2 GHz), and $4_{3,1} \leftarrow 5_{2,4}$ (343.5 GHz) lines. In addition, the following transitions were also studied: $2_{2,0} \leftarrow 2_{1,1}$ (279.5 GHz), $24_{2,22} \leftarrow 24_{1,23}$ (286.2 GHz), $3_{2,2} \leftarrow 3_{1,3}$ (286.3 GHz), $5_{2,4} \leftarrow 5_{1,5}$ (293.2 GHz), $26_{2,24} \leftarrow 26_{1,25}$ (315.9 GHz), and $26_{6,20} \leftarrow 27_{5,23}$ (343.2 GHz). For the major part of these selected transitions, the N_2- and O_2-broadening have been studied, whereas for the others the Air-broadening effect has been directly observed.

Furthermore, although a large number of experimental measurements of ozone pressure-broadening were carried out (see [1] and references therein), only few of them were made over an extended temperature range. To this purpose, we have performed the investigations of some transitions (the 301.8, 303.2, 317.2, and 320.0 GHz lines) in the 195–300 K temperature range. In addition, the pressure shift effect, which is expected to be small but poorly studied in the past, has been investigated for the 301.8, 317.2, and 320.0 GHz lines. An additional question that should be treated is the presence of systematic errors affecting pressure-broadening measurements. This is well represented by the considerable scatter among measurements reported in the literature; actually, recent intercomparisons of line-broadening parameters showed differences up to 20% [1]. Consequently, the standard deviation of the parameters, as deduced from the fits, is not a reliable indicator of their accuracy. To this purpose, the measurements of the present work have been carried out in two laboratories by using different techniques. In particular, in order to check the consistency and to estimate the accuracy of measured data, the 301.8 GHz line (and the 317.2 GHz and 320.0 GHz lines but only at one temperature) has been measured in both laboratories. The retrieved linewidths have been analysed independently and then an intercomparison of the results has been carried out.

This article essentially consists of four parts. In Section 2, the experimental details concerning the two laboratories set up are given. In Sections 3 and 4, the line profile analyses performed and the retrieved parameters obtained in the two laboratories are presented, respectively. Finally, Section 5 is devoted to the intercomparison of the results of the two laboratories.

2. Experimental details

2.1. Experimental set-up of the Laboratory of Millimeter-wave Spectroscopy of Bologna

2.1.1. Spectrometer

A detailed description of the millimeter-wave spectrometer and the experimental set-up (for pressure-broadening measurements) used at the Laboratory of Millimeter-wave Spectroscopy of Bologna (LMSB) can be found in [2,3]. Briefly, a frequency modulation spectrometer whose radiation source is a Gunn-driven frequency multiplier has been employed in the measurements. The source is phase-locked to a rubidium frequency standard. The frequency modulation is performed by sine-wave modulating (1.666 kHz) the 90 MHz reference signal of the source-synchronizer; this is achieved by using an HP 8642A synthesized signal generator. The Lock-in amplifier is tuned at twice the modulation frequency so that the second derivative of the natural lineshape is recorded. The cell is a Pyrex tube either 148 or 55 cm long and 5 cm in diameter. In both cases, the cell is thermally insulated. The measurements have been performed at 195, 240, and 296 K. For measurements at 240 and 296 K, the temperature has been kept fix by a cryostat; while in the case of measurements at 195 K, the temperature has been maintained by employing an ethyl alcohol–dry ice bath. In both cases, the temperature accuracy is ±1 K. An homogeneous temperature inside the cell is provided by ad hoc windows: they allow the gas occupies only that part of the cell in which the temperature is kept fix. The sample pressure has been measured by a baratron gauge (MKS type 220 B) with a measurable pressure range of 10^{-4}–1 Torr ($\sim 1.33 \times 10^{-2}$–133 Pa), and with 0.1 mTorr resolution. For the measurements performed at 195 and 240 K, the correction due to the thermal transpiration effect has been experimentally investigated and evaluated by employing the equations reported in [4]. This correction, that comes from the fact that the baratron is placed at ~296 K even when the measurements are performed at lower temperatures, has been found to be negligible (0.2%) for both temperatures.

The spectrometer is equipped with a liquid-helium cooled InSb detector.

2.1.2. Modulation technique

The source frequency modulation technique has been employed throughout; a detailed description can be found in [2,3]. In order to be sure that the requirement needed by the frequency modulation technique (i.e., absorption $\leqslant 6\%$ [2]) is fulfilled, for each transition preliminary natural line profile measurements have been carried out using the amplitude modulation technique, as described in [5].