Journal of Quantitative Spectroscopy & Radiative Transfer ■ (■■■■) ■■■–■■■

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

The CO_2 absorption continuum by high pressure CRDS in the 1.74 μm window

D. Mondelain [a,b,*], A. Campargue [a,b], P. Čermák [a,b,c], R.R. Gamache [d], S. Kassi [a,b], S.A. Tashkun [e,f], H. Tran [g]

[a] Univ. Grenoble Alpes, LIPhy, F-38000 Grenoble, France
[b] CNRS, LIPhy, F-38000 Grenoble, France
[c] Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia
[d] Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts, Lowell, MA, USA
[e] Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences,1, Academician Zuev Square, 634055 Tomsk, Russia
[f] Laboratory of Climate and Environmental Physics, Ural Federal University, Mira street, 19, Yekaterinburg 620002, Russia
[g] Laboratoire de Météorologie Dynamique, IPSL, CNRS UMR 8539, Sorbonne Universités, UPMC Univ. Paris 06, 75252 Paris, France

ARTICLE INFO

Article history:
Received 24 January 2017
Received in revised form
27 February 2017
Accepted 28 February 2017

Keywords:
Carbon dioxide
CO_2
Transparency windows
Venus
Continuum

ABSTRACT

The very weak absorption continuum of CO_2 is studied by Cavity Ring Down Spectroscopy in three 20 cm^{-1} wide spectral intervals near the centre of the 1.74 μm window (5693–5795 cm^{-1}). For each spectral interval, a set of room temperature spectra is recorded at pressures between 0 and 10 bar thanks to a high pressure CRDS spectrometer. The absorption continuum is retrieved after subtraction of the contributions due to Rayleigh scattering and to local lines of CO_2 and water (present as an impurity in the sample) from the measured extinction. Due to some deficiencies of the CO_2 HITRAN2012 line list, a composite line list had to be built on the basis of the Ames calculated line list with line positions adjusted according to the Carbon Dioxide Spectroscopic Databank and self-broadening and pressure shift coefficients calculated with the Complex Robert Bonamy method. The local line contribution of the CO_2 monomer is calculated using this list and a Voigt profile truncated at $\pm$25 cm^{-1} from the line centre. Line mixing effects were taken into account through the use of the impact and Energy Corrected Sudden approximations.

The density dependence of the retrieved continuum absorption was found to be purely quadratic in the low frequency interval below 5710 cm^{-1} but a small significant linear contribution was required to reproduce the observations above this value. This linear increase is tentatively attributed to the foreign-continuum of water vapor present in CO_2 sample with a relative concentration of some tens ppm.

The retrieved binary coefficient is observed to vary smoothly with the wavenumber with a minimum value of 6×10^{-10} cm^{-1} $amagat^{-2}$. By gathering the present data with the results reported in *Kassi* et al. *J Quant Spectrosc Radiat Transf 2015;167:97*, a recommended set of binary coefficients is provided for the 5700–5950 cm^{-1} region.

1. Introduction

With a relative concentration of about 96.5%, carbon dioxide strongly dominates the absorption spectrum of Venus and only a restricted number of narrow near infrared (NIR) windows between 0.8 and 2.5 μm can be used to sound the deep atmosphere and the surface. These windows correspond to regions of low opacity between the strong absorption bands of carbon dioxide. They are of importance for the determination of the concentrations of many trace gasses like CO, H_2O, HDO, CO, OCS, SO_2, HF and HCl in different altitude ranges [1]. The 1.74 μm window, for example, provides information on H_2O and HCl mole fraction in the 15 to 30 km altitude range [1]. In these windows, the main contributions to gaseous absorption are due to a local lines (LL) contribution (pressure-broadened) and the so-called "continuum" absorption (CA) slowly varying with frequency. This latter includes absorption due to the transient dipole induced during inter-molecular collisions (or Collision-Induced Absorption, CIA) [2,3] and the far wings of allowed nearby CO_2 bands [4]. Various analyses of the Venus night side have shown that CA is a major contributor to the gas opacity in the windows. To model the spectra recorded with ground-based instruments and on board satellite platforms like the Venus Express spacecraft, spectroscopic databases like CDSD [5] and HITEMP [6] are used to calculate the local lines contribution. Note that the LL contribution in the region of the absorption bands was recently investigated experimentally and theoretically over a broad spectral range (600–9650 cm^{-1}) and up to pressures close to the liquefaction

* Corresponding author at: Université Grenoble Alpes Pôle Phitem Laboratoire LIPhy CS 40 700 38058 Grenoble Cedex 9.
E-mail address: didier.mondelain@univ-grenoble-alpes.fr (D. Mondelain).

http://dx.doi.org/10.1016/j.jqsrt.2017.02.019
0022-4073/

conditions [7,8]. Contrary to the relatively well-characterized LL opacity, the CA is mostly unknown and generally modeled with a constant value over a window with no temperature dependence [9–11]. The absence of laboratory measurements for pressure and temperature conditions relevant for Venus [12] (i.e. from 175 K and 26 μbar at 100 km altitude to 735 K and 92 bar at the surface) makes necessary to adjust the CA level to better reproduce the recorded spectra. As a result, the uncertainty on the CA in the windows leads to significant uncertainties on the retrieved mixing ratios of water vapor in Venus atmosphere. For example in the 1.18 μm window, a 40% uncertainty on the CO_2 continuum absorption adds a ± 3 ppm uncertainty on the H_2O mixing ratio which represents 6.7% of the retrieved mixing ratio [13].

Due to the difficulty of determining broad and weak absorption signal windows, only a few laboratory determinations of CA of CO_2 in the NIR have been reported so far, all at room temperature. In the 2.1 μm window, Tonkov et al. reported measurements for pressures in the 10 –50 atm range using different Fourier transform and grating spectrometers [4]. In the 1.75 and 1.18 μm windows, the continuum is weaker and its detection made necessary to develop high sensitivity laser spectrometers coupled with high pressure cells. The CA in the 1.18 μm window has been determined by Snels et al. with a high pressure Cavity Ring Down Spectrometer (CRDS) [14]. We used the same technique described in [15] to characterize the CA in the high energy edge of the 1.74 μm window (5850–5960 cm^{-1}) from CRDS spectra recorded up to 10 amagat. At 2.1 μm, the high sensitivity of the CRDS technique allowed us to determine the CO_2 CA from spectra recorded at subatmospheric pressures [16].

The aim of the present work is to extend the spectral coverage of the 1.74 μm window by high pressure CRDS in the region of lowest opacity between 5693 and 5795 cm^{-1} (see Fig. 1). The experimental set-up is briefly described in Part 2 together with the spectra calibration. The available databases of CO_2 transitions in the region were found insufficient to account for the recorded CRDS spectra and an improved CO_2 database had to be constructed in order to satisfactorily subtract the LL contribution. The construction of the LL database and the continuum retrieval with the derivation of the binary coefficients are detailed in Part 3 and Part 4, respectively. Finally, the results and their uncertainty are discussed in Part 5.

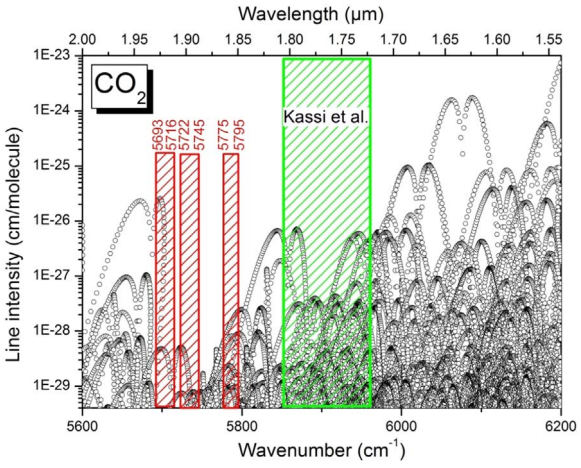

Fig. 1. Overview of the CDSD [5] line list of carbon dioxide in the 1.74 μm window. The three regions dashed in red correspond to the spectral ranges investigated in this work while the green light dashed region highlights the 5850–5960 cm^{-1} interval studied in Ref. [15]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

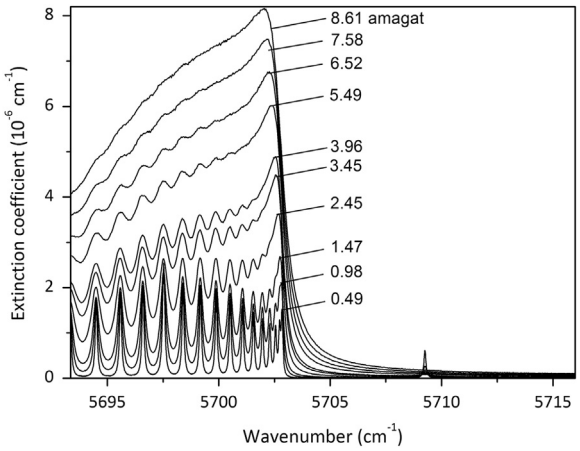

Fig. 2. Overview of the series of pure CO_2 spectra recorded at different densities in the region of R branch of the 00031–10002 band.

2. Experimental set-up and spectra calibration

2.1. High pressure CRDS

The high pressure CRDS cell was previously described in details (see Fig. 2 of Ref. [15]). Briefly, two high reflectivity mirrors are placed on both sides of a stainless steel tube (cavity length of 128 mm) with one of the mirror mounted on a piezo electric transducer (PZT). To strictly avoid perturbations of the optical alignment by pressure forces, this pre-aligned CRDS cavity is inserted into a high pressure cell consisting of a cylinder closed by two thick wedged glass windows. Several holes are drilled in the tube constituting the high finesse cavity (HFC) to allow pressure equilibrium on both sides of the mirrors when the cylinder is filled with a gas. In that way, no optical alignment perturbation is observed up to a gas pressure of 10 bar (see below). The HFC has a finesse varying from 67,000 to 146,000 depending on the wavenumber.

In this work, three fibered Distributed Feedback (DFB) laser diodes from Eblana Photonics Ltd were used as light source. These laser diodes, including a double optical isolation stage and a thermo electrical cooler, are centered at 5704, 5733 and 5785 cm^{-1} (see Fig. 1). By changing the temperature of the diode between 0 °C and 50 °C and keeping the current fixed at 120 mA, the achieved tuning range is between 18.8 and 23.6 cm^{-1} depending of the laser diode. The laser beam is sent into the HFC through a fibered acousto-optic modulator (AOM) (insertion losses of 4 dB at 1705 nm, $f_{AOM}=100.5$ MHz). To generate the ring down (RD) events the cavity length is modulated with a triangular voltage ramp applied to the PZT with amplitude sufficient to cover a little bit more than one free spectral range of the HFC. Each time a longitudinal mode falls in coincidence with the laser frequency, light is transmitted through the cavity and detected with an extended InGaAs photodiode followed by a trans-impedance amplifier (bandwidth 1 MHz). When the photodiode signal is higher than a user-defined threshold, the AOM quickly switches off the laser beam and a RD event is detected. For the evacuated cavity, the measured RD times varied from 20 μs at 5960 cm^{-1} to 10 μs at 5700 cm^{-1}. Absorption spectra were recorded with spectral steps of typically 0.04 cm^{-1} for the highest pressures and 0.007 cm^{-1} for the lowest ones. About 30 RDs were averaged per spectral points leading to a minimum detectable absorption coefficient (evaluated as the rms of the baseline fluctuation), α_{min}, between 7×10^{-10} cm^{-1} and 1.7×10^{-9} cm^{-1} depending on the RD time.

For each diode, the cell was first filled with pure carbon dioxide (Air Liquide N48, 99.998% stated purity) at a maximal pressure around 10 bar and a series of spectra was then recorded for a ten of

Please cite this article as: Mondelain D, et al. The CO_2 absorption continuum by high pressure CRDS in the 1.74 μm window. J Quant Spectrosc Radiat Transfer (2017), http://dx.doi.org/10.1016/j.jqsrt.2017.02.019