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High sensitivity Cavity Ring Down spectroscopy of carbon dioxide in the 1.19–1.26 μm region

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ABSTRACT

A Cavity Ring Down spectrometer using a fiber-connected External Cavity Diode Laser (ECDL) as light source has been developed to access the 1.26–1.19 μm region. We present here the first application of this newly developed CW-CRDS spectrometer to the study of the highly sensitive spectrum of natural carbon dioxide between 7909 and 8370 cm^{-1}. The spectrum is dominated by the $\nu_1+3\nu_3$ dyad at 8192.55 and 8293.95 cm^{-1} which forms the low energy border of the 1.2 μm transparency window of importance for planetary applications. The achieved sensitivity (noise equivalent absorption, α_{min}, in the 10^{-10}–10^{-11} cm^{-1} range) allowed detection of numerous new transitions with intensity values down to 10^{-30} cm/molecule, in particular hot bands reaching upper states with energy up to about 10,600 cm^{-1}.

More than 3400 transitions belonging to the six major isotopologues of 'natural' carbon dioxide were assigned using the predictions of effective Hamiltonian (EH) models. A total of 2027, 442, 548, 303, 92 and 13 transitions belonging to 37, 9, 8, 4, 2 and 1 bands were rovibrationnally assigned for $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{16}O^{13}C^{18}O$ and $^{16}O^{13}C^{17}O$, respectively. For comparison, only 14 $^{12}C^{16}O_2$ absorption bands were previously known in the region (mostly from Venus spectra). Intensity values range between 2.1×10^{-30} and 2.4×10^{-24} cm/molecule. All the identified bands correspond to the $\Delta P=11$ series of transitions, where $P=2V_1+V_2+3V_3$ is the polyad number (V_i are vibrational quantum numbers). The overall agreement of the EH predicted and measured line positions is very good (for instance, average and *rms* deviations of 0.64×10^{-3} and 3.8×10^{-3} cm^{-1} for $^{12}C^{16}O_2$, respectively).

The band-by-band analysis provided accurate spectroscopic parameters of 57 bands from a fit of the measured line positions. The global fits of the obtained intensity values of the $\Delta P=11$ series of transitions were used to refine the corresponding set of effective dipole moment (EDM) parameters of the six studied isotopologues.

The obtained results will help to improve the spectral line parameters of carbon dioxide in the most currently used spectroscopic databases. In particular, the calculated band intensities of a few weak hot bands are now in good agreement with the observations.

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1. Introduction

In recent years, we have performed systematic investigations of the near infrared absorption spectrum of carbon dioxide by high sensitivity CW-Cavity Ring Down Spectroscopy (CW-CRDS) in the 5850–7920 cm^{-1} region [1–14]. The unprecedented sensitivity of the recordings provided a considerable amount of new information. The spectra were recorded not only with natural carbon dioxide [1–7] but also with ^{13}C [8–11] and ^{18}O [12–14] enriched samples. The spectral coverage was achieved thanks to a series of about 90 Distributed Feed Back (DFB) diode lasers, each of them allowing for a 30 cm^{-1} spectral coverage, by temperature variation between − 10 and 60 °C.

In this work, we extend to higher energy the spectral region accessible with our CRDS spectrometers by using a fiber-connected External Cavity Diode Laser (ECDL) as a light source. We present here the first application of this newly developed CW-CRDS spectrometer to the study of the spectrum of natural carbon dioxide between 7909 and 8370 cm^{-1} (1.26–1.19 μm). The spectrum is dominated by the $\nu_1+3\nu_3$ dyad of $^{12}C^{16}O_2$ at 8192.55 and 8293.95 cm^{-1}. The achieved sensitivity allowed detection of numerous new transitions with intensity values down to 10^{-30} cm/molecule, including many hot bands associated with the $\nu_1+3\nu_3$ dyad and a number of bands of the first five minor isotopologues present in natural abundance in the sample: $^{13}C^{16}O_2$, $^{16}O^{12}C^{18}O$, $^{16}O^{12}C^{17}O$, $^{16}O^{13}C^{18}O$ and $^{16}O^{13}C^{17}O$.

The paper is organized as follows. After a description of the experimental details (Section 2), the rovibrational assignment performed on the basis of the predictions of the effective Hamiltonian (EH) model will be presented in Section 3. Section 4 will be devoted to the derivation of the rovibrational parameters from a band-by-band fit. In Section 5, the measured intensities will be compared to calculated values and the effective dipole moment (EDM) parameters of the $\Delta P=11$ series will be derived from a fit of the measured line intensities.

2. Experiment

The newly developed CRDS spectrometer using a fiber-connected External Cavity Diode Laser (ECDL: Toptica DL pro, 1200 nm) is very similar to the CRDS spectrometer based on DFB diode laser used in the 5850–7920 cm^{-1} region. The reader is referred to Ref. [15] for a general description. Only an outline of the data acquisition procedure and specific characteristics related to the use of the ECDL are given here.

The 1.40 m long CRDS cell is fitted with high reflectivity mirrors leading to ring down times of about 200 μs in the considered spectral interval. The CRDS cell was filled with carbon dioxide (Aldrich 99.8% stated purity). The pressure and the ring down cell temperature were monitored during the spectrum acquisition.

The typical mode-hop free tuning range of this ECDL is about 0.8 cm^{-1}. The central laser frequency was tuned by changing the grating angle together with the laser current. Consecutive and partially overlapping spectra were recorded to cover the range of interest. About 10 ring down events were averaged for each spectral data point separated by 8×10^{-4} cm^{-1}. On average, one hour was needed to record a 16 cm^{-1} wide section of the spectrum. The noise equivalent absorption, α_{min}, evaluated as the *rms* of the baseline fluctuation varies in the 10^{-10}–10^{-11} cm^{-1} range, depending on the spectral region. The sensitivity and high signal-to-noise (more than 10^4 in the displayed example) are illustrated in Fig. 1 where the 10032 − 00001 band of $^{13}C^{16}O_2$ in natural abundance is displayed.

An important advantage of the ECDL compared to DFB diode lasers used in Ref. [1–15] lies in its smaller linewidth (typically 100 kHz compared to 2 MHz) allowing for a better light injection into the CRDS cavity.

The wavenumber of the light emitted by the diode laser was measured by a commercial Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 h) that allows laser frequency to be determined at a typical 100 Hz refresh rate. The absolute calibration of the frequency axis was refined using positions of reference lines. In order to use the strong highly accurate $^{12}CO_2$ lines [16] above 8130 cm^{-1}, a

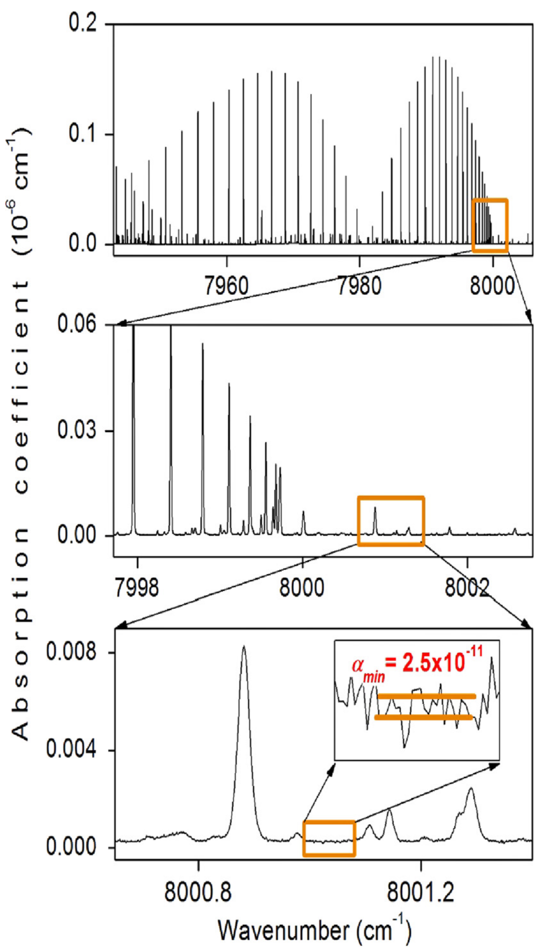

Fig. 1. CW-CRDS spectrum of carbon dioxide in natural abundance in the region of the 10032 − 00001 band of $^{13}C^{16}O_2$ at 7981.18 cm^{-1} ($P=10$ Torr). Three successive enlargements illustrate the high sensitivity and high dynamics of the recordings (noise equivalent absorption on the order of 2.5×10^{-11} cm^{-1}).