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New CW-CRDS measurements and global modeling of $^{12}C^{16}O_2$ absolute line intensities in the 1.6 μm region

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ABSTRACT

Line intensities of $^{12}C^{16}O_2$ transitions have been measured by CW-Cavity Ring Down Spectroscopy in four wavenumber intervals near 1.6 μm. Intensity values of 952 transitions ranging from 1.10×10^{-28} to 4.94×10^{-25} cm/molecule were retrieved with an average accuracy of 4%. These transitions belong to a total of 30 bands corresponding to the $\Delta P = 9$ series of transitions. The achieved sensitivity (noise equivalent absorption $\alpha_{min} \sim 3 \times 10^{-10}$ cm^{-1}) allows lowering by more than two orders of magnitude the lower intensity values measured in the region. Comparison with the values included in the JPL database [R.A. Toth, L.R. Brown, C.E. Miller, V. Malathi Devi, D.C. Benner, J. Quant. Spectrosc. Radiat. Transf. 109 (2008) 906–921] shows residuals exceeding one order of magnitude for weak lines. The measured intensities together with a selection of experimental intensities available in the literature were used to extend and refine the set of effective dipole moment parameters for the $\Delta P = 9$ series of transitions of the principal isotopologue of carbon dioxide. The refined parameters allow reproducing, within the experimental uncertainties, the whole set of intensity measurements which extends over nearly six orders of magnitude (1.10×10^{-28}–6.12×10^{-23} cm/molecule). Combining the CW-CRDS line positions with the calculated line intensities, a line list has been generated for the whole 5851–7045 cm^{-1} region and is provided as Supplementary Material. The obtained effective dipole moment parameters have also been used to generate the $\Delta P = 9$ series of transitions included in the new version of the CDSD database. The comparison of the CDSD line intensities with the values provided by the HITRAN-2004 database shows discrepancies up to 80% for some of the bands while discrepancies up to three orders of magnitude are noted for the weakest bands included in the JPL database.

1. Introduction

The present contribution participates to the development of an improved version of the Carbon Dioxide Spectroscopic Databank (CDSD) [1,2]. It is devoted to the retrieval of experimental line intensities from new spectra recorded by CW-Cavity Ring Down Spectroscopy (CW-CRDS), and to the improvement of the theoretical description of the line intensities within the framework of the effective operators approach [3–8] for the principal isotopologue, $^{12}C^{16}O_2$, of carbon dioxide in the 1.6 μm region. The spectrum of carbon dioxide in this region is formed by the transitions belonging to the $\Delta P = 9$ series. According to the classification defined within the effective operators approach, the series of transitions are identified by the difference $\Delta P = P' - P''$, where $P = 2V_1 + V_2 + 3V_3$ is an integer that labels each polyad of vibrational basis states coupled by anharmonic and Coriolis resonance interactions [3]. V_i is the vibrational quantum number associated with the mode of vibration *i*.

The high sensitivity of the CW-CRDS spectrometer developed in Grenoble [9–14] makes possible to determine accurate values of line intensities down to 10^{-28} cm/molecule which is more than two orders of magnitude lower than the minimum value of the intensities previously measured in the region considered. The obtained results give the opportunity to discuss the recently elaborated JPL (Jet Propulsion Laboratory) carbon dioxide spectroscopic database [15]. This database is constructed on very precise measurements of line positions and line intensities by Fourier Transform Spectroscopy (FTS) [16–20]. However the authors of this database extrapolated their data down to a very low intensity cut-off of 4×10^{-30} cm/molecule while the minimum value of their measured line intensities was about 2×10^{-26} cm/molecule. As discussed in our recent publication devoted to the $^{13}C^{16}O_2$ isotopologue [21], this long range extrapolation leads to large residuals when compared to our observations both for line positions and line intensities. In the present study, we established a similar comparison for the principal isotopologue of carbon dioxide, $^{12}C^{16}O$.

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In the 1.6 μm region, the line intensities of the strong cold parallel bands dominating the spectrum have been measured by several authors using different experimental techniques: grating spectrometer [22], Fourier transform spectrometers [18,23–29] and diode laser absorption spectrometers [29–32]. The comparison of these measured line and band intensities has been detailed in Refs. [18,28]. The line intensities of the 3111*i*-01101 (i = 2, 3) and 01131-01101 hot bands have been measured in Ref. [28] and Ref. [26], respectively. In a recent JPL publication [18], accurate line intensity values were reported for the 00031-00001 and 3001*i*-00001 (i = 1–4) cold bands and for their respective hot bands. The line intensities of two cold perpendicular bands 1112*i*-00001 (i = 1, 2) were also obtained [18]. However, important experimental information were still missing for the determination of the effective dipole moment parameters of the $\Delta P = 9$ bands [8] which hampered a satisfactory modeling of the CO_2 absorption spectrum near 1.6 μm: no intensity measurements were available for the very weak 4110*i*-00001 (i = 1–5) and 2002*i*-01101 (i = 1–3) perpendicular bands and for the 2221*i*-00001 (i = 1–3) "forbidden" bands. These bands are showed on the lower panel of Fig. 1 together with the four spectral intervals chosen for new CW-CRDS measurements dedicated to these specific bands: 5851–5881, 5972–6035, 6373–6542 and 6622–6750 cm^{-1}. On the middle panel, the $^{12}C^{16}O_2$ overview spectrum as included in the new version of the CDSD [36] is presented for the 5800–6800 cm^{-1} region. The transitions measured by FTS in Ref. [18] are displayed in the upper

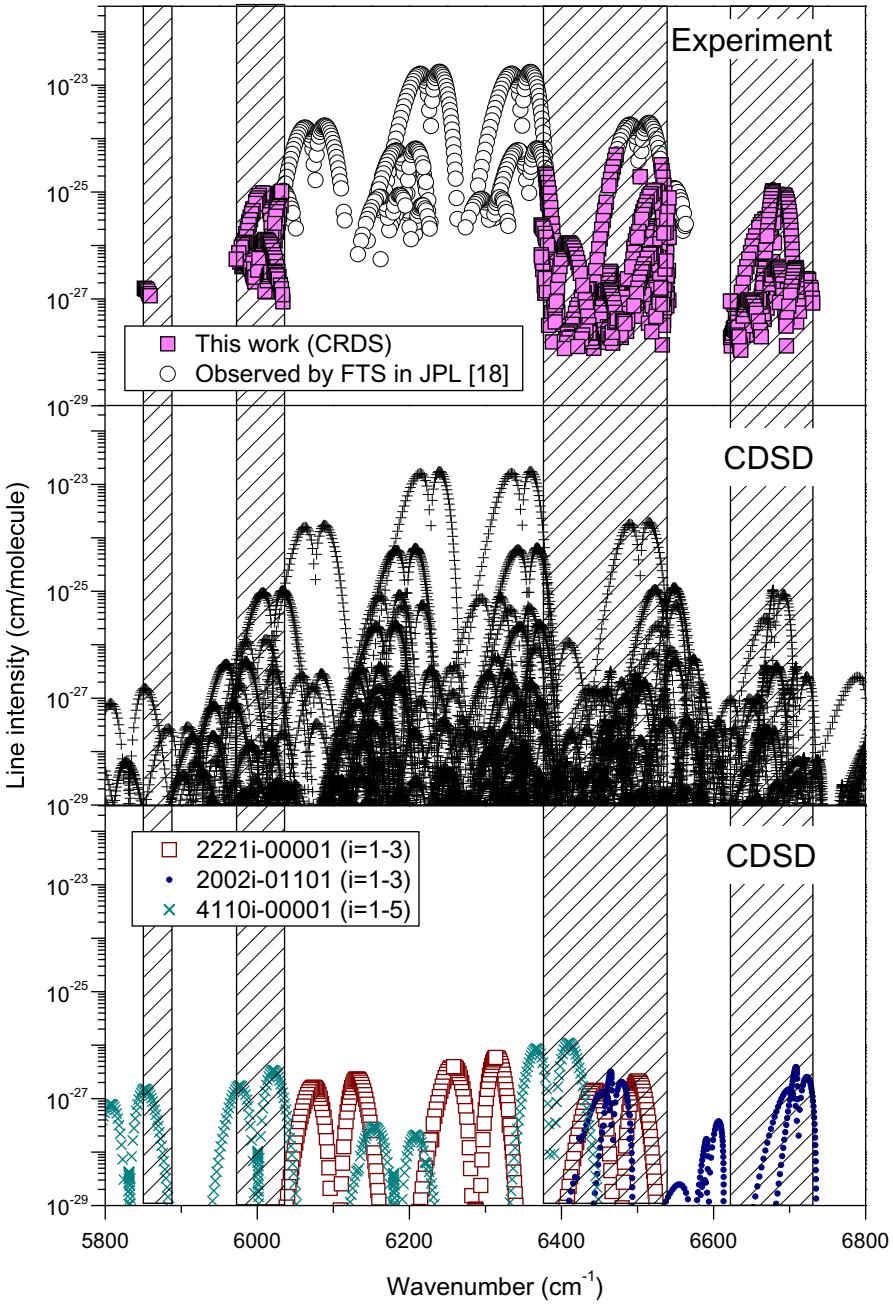

Fig. 1. Overview of the $^{12}C^{16}O_2$ measured line intensities and those provided by the most recent version of the CDSD database, in the 5800–6800 cm^{-1} spectral region. *Upper panel*: transitions whose line strengths were experimentally determined and used as input data for the dipole moment operators fit. The line strengths measured by CW-CRDS are highlighted with squares. *Middle panel*: CDSD database. *Lower panel*: the weak 4110*i*-00001 (i = 1–5), 2002*i*-01101 (i = 1–3) and 2221*i*-00001 (i = 1–3) bands as provided by the CDSD database. The CW-CRDS recordings were specifically dedicated to the line intensity measurements of these bands. The studied spectral intervals are indicated.