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Global modeling of $^{13}C^{16}O_2$ absolute line intensities from CW-CRDS and FTS measurements in the 1.6 and 2.0 μm regions

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Abstract

Line intensities of $^{13}C^{16}O_2$ have been measured between 5851 and 6580 cm^{-1} using CW-cavity ring down spectroscopy (CRDS) and in the 4700–5050 and 6050–6850 cm^{-1} regions using Fourier transform spectroscopy. As a result of the high sensitivity (noise equivalent absorption $\alpha_{min}\sim 3\times 10^{-10}$ cm^{-1}) and high dynamics allowed by CW-CRDS, accurate line intensities of 2039 transitions ranging between 1.1×10^{-28} and 1.3×10^{-23} cm^{-1}/(molecule cm^{-2}) were measured with an average accuracy of 4%. These transitions belong to a total of 48 bands corresponding to the $\Delta P = 9$ series of transitions. Additionally, unapodized absorption spectra of ^{13}C-enriched samples have been recorded using a high-resolution Bruker IFS125HR Fourier transform spectrometer. Spectral resolutions of 0.004 cm^{-1} (maximum optical path difference (MOPD) = 225 cm) and 0.007 cm^{-1} (MOPD = 128.6 cm), and pressure × path length products in the ranges 5.2–12 and 69–450 hPa × m have been used for the lower and higher energy spectral regions, respectively. Absolute line intensities have been measured in the 2001i−00001, 3001i−00001 (i = 1, 2, 3) and 00031−00001 bands. An excellent agreement was achieved for the line intensities of the 3001i−00001 (i = 1, 2, 3) bands measured by both FTS and CW-CRDS. The CW-CRDS and FTS experimental intensity data together with selected intensity information from the literature have been fitted simultaneously using the effective operators approach. Two sets of effective dipole moment parameters have thus been obtained, which reproduce the observed line intensities in the 2.0 and 1.6 μm regions within experimental uncertainties.

Keywords: Molecular spectroscopy; Carbon dioxide; Line intensities; Infrared; Global modeling; CW-CRDS; Cavity ring down spectroscopy; Fourier transform absorption spectroscopy

1. Introduction

The present contribution falls within the framework of the development of the Carbon Dioxide Spectroscopic Databank (CDSD) [1,2]. It aims to improve the theoretical description of the spectrum of the second most abundant isotopologue of carbon dioxide, $^{13}C^{16}O_2$, provided by the effective operators approach [3–8]. It follows

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our recent contributions dealing with the global modeling of experimental line positions and intensities in $^{13}C^{16}O_2$, available in the literature. Indeed, we were able to fit about 11,000 line positions belonging to 138 bands in the far-, mid- and near-infrared regions with a standard deviation of $0.0015\,cm^{-1}$, and about 600 line intensities in the $\Delta P = 1$ and 3 series of transitions observed in the 598–1047 and $1983–2323\,cm^{-1}$ regions, respectively [9]. 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 resulting from the approximate relations between the harmonic frequencies, $\omega_1 \approx 2\omega_2$ and $\omega_3 \approx 3\omega_2$ [3]. V_i is the vibrational quantum number associated with the mode of vibration *i*. More recently, the investigation of line intensities in $^{13}C^{16}O_2$ was extended to 13 bands in the $3090–3920\,cm^{-1}$ region ($\Delta P = 5$) [10] and to 20 bands in the $4200–8500\,cm^{-1}$ region [11]. The intensity measurements carried out in these latter two studies, together with those reported by Benner et al. [12] for the 21102-00001 band near $3290\,cm^{-1}$, by Le Barbu et al. [13] who measured the intensity of 5 lines in the 20012-00001 band near $4900\,cm^{-1}$, and very recently by Toth et al. [15] who performed extensive measurements between 2200 and $6800\,cm^{-1}$ are the only quantitative data currently available in the near-infrared spectrum of $^{13}C^{16}O_2$, above $3000\,cm^{-1}$. Let us mention that these latter measurements [15] together with many previous experimental results were used in the construction of a new spectroscopic database for carbon dioxide [14]. The line intensities available for $^{13}C^{16}O_2$ in the HITRAN database [16] above $3000\,cm^{-1}$ are calculated values, using the DND approach [17].

The present work builds upon the study by Wang et al. [11]. It involved intensity retrievals using CW-cavity ring down spectroscopy (CW-CRDS) in Grenoble and Fourier transform spectroscopy (FTS) in Brussels.

As shown in recent contributions [18–21] devoted to the investigation of the absorption spectra of carbon dioxide near 1.5 μm by CW-CRDS, the typical sensitivity achieved ($\alpha_{min} \sim 3 \times 10^{-10}\,cm^{-1}$) allows observation of very weak transitions with intensity down to $10^{-29}\,cm^{-1}/(molecule\,cm^{-2})$ at room temperature. Our CW-CRDS spectrometer uses a series of distributed feed-back (DFB) diode lasers to give access to the $5851–7045\,cm^{-1}$ spectral region. Our previous contributions were mainly focused on the detection and assignment of new bands. The present work is devoted to the intensity retrieval of weak to very weak lines from CW-CRDS spectra of $^{13}C^{16}O_2$ in the $5851–6580\,cm^{-1}$ region, to increase the experimental data set available for the refinement of the effective dipole moment parameters. Indeed, because of the high linearity and the large dynamics of the CW-CRDS spectra with respect to the line intensities, this technique is particularly suitable for absolute intensity measurements. The absolute value of the absorption coefficient is obtained straightforwardly from the measured ring down time. The same CW-CRDS spectrometer allowed performing high-sensitivity quantitative measurements for new transitions in the 1.5 μm region of the spectrum of H_2O, resulting in a significantly improved knowledge of the spectroscopy in this important atmospheric transparency window [22,23].

The study by Wang et al. [11] by FTS also involved the simultaneous treatment of all the line intensities measured in that work using the effective operators approach. Such a fitting showed that the line intensities measured for strong bands were not reproduced by the theoretical model as well as those obtained for the weaker bands, even if the observed discrepancies were within the experimental accuracy [11]. The affected bands are 20012-00001, 20011-00001, 30012-00001, 30011-00001 and 00031-00001, observed respectively near 4887, 4991, 6242, 6364 and $6780\,cm^{-1}$ and belonging to the $\Delta P = 7$ and 9 series of transitions. The intensity measurements carried out in the present contribution using high-resolution FTS is an attempt to give insight into this problem. Additionally, we also measured line intensities for the 20013-00001 and 30013-00001 bands of $^{13}C^{16}O_2$, observed near 4748 and $6120\,cm^{-1}$.

All the line intensities measured in this contribution for $^{13}C^{16}O_2$, together with those reported for the weak bands by Wang et al. [11] and the FTS measurements by Toth et al. [15], were then analyzed using the effective operators approach [6–8]. The present contribution led to a refinement of the effective dipole moment parameters for the $\Delta P = 7$ and 9 series of transitions.

2. Experimental details

2.1. CW-CRDS measurements

The fibered CW-CRDS spectrometer developed in Grenoble and the procedure adopted for an accurate calibration of the wavenumber scale are described in Refs. [18–23,24], respectively. Let us just recall that