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The 4-0 band of carbon monoxide by high sensitivity Cavity Ring Down spectroscopy near 8200 cm^{-1}

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ABSTRACT

The room temperature spectrum of carbon monoxide in natural isotopic abundance is recorded by Cavity Ring Down Spectroscopy between 8094 and 8317 cm^{-1}. The investigated range covers the low frequency region of the third overtone band centered at 8414 cm^{-1}. The achieved sensitivity of the recordings corresponds to a noise equivalent absorption, $\alpha_{min} \sim 5 \times 10^{-12}$ cm^{-1}. 94 transitions are measured with intensity ranging between 3×10^{-27} and 1×10^{-30} cm/molecule. They include the first observation of *(i)* high *J* lines of the P branch of the 4-0 band of $^{12}C^{16}O$, *(ii)* the 4-0 band of $^{13}C^{16}O$ and $^{12}C^{18}O$ present in natural abundance in the sample (35 and 38 transitions, respectively), *(iii)* a few lines of the 4-0 band of $^{12}C^{17}O$ and of the 5-1 hot band of $^{12}C^{16}O$. The spectroscopic parameters of the $v=4$ upper level of $^{13}C^{16}O$ and $^{12}C^{18}O$ are obtained from a fit of the measured line positions.

The line positions reported with an accuracy of 5×10^{-4} cm^{-1} and the derived line intensities are used for comparison to various theoretical line lists of carbon monoxide available in the literature. The agreement between the obtained experimental data and the most recent theoretical line lists available in the literature is discussed.

1. Introduction

As species of high interest for astrophysics and environmental science, carbon monoxide has been the subject of a considerable number of spectroscopic studies (see for instance the recent critical review included in Ref. [1]). The absorption spectrum of carbon monoxide consists in a series of $0 \rightarrow v$ overtone bands separated by about 2100 cm^{-1} with intensity decreasing by about two orders of magnitude for each additional vibrational excitation. The highest overtone bands detected so far ($0 \rightarrow 5$ [2] and $0 \rightarrow 6$ [3] near 10,400 and 12,400 cm^{-1}, respectively) were detected by Cavity Ring Down Spectroscopy (CRDS). The previous reports of the 4-0 band are scarce. In their pioneer work, Herzberg and Rao used pressure × path length products of 500 to 1000 m × atm to detect 4-0 transitions up to $J=20$ on their photographic plates [4]. Later Chackerian and Valero reported the first intensity measurements with a path length of 2.1 km and a pressure of 49.3 Torr [5]. More recently, Ogilvie et al. used Fourier Transform Spectroscopy with an absorbing pass of 107 m and a CO pressure of about 1 atm to detect absorption lines up to P(20) and R(25) [6]. The very high sensitivity provided by the CRDS technique allows extending significantly the observations while using sample pressure values limited to a few Torr. The present contribution

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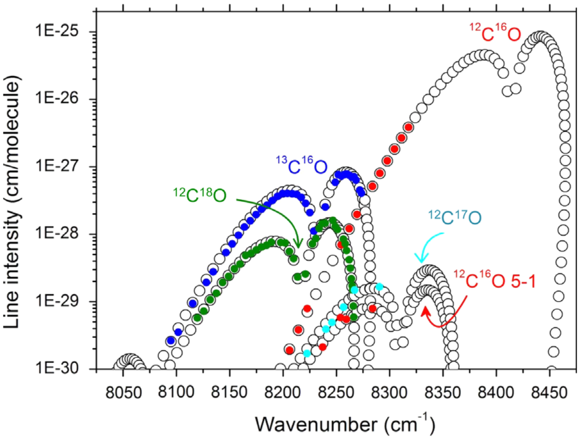

Fig. 1. Calculated [3] spectrum of carbon monoxide in natural isotopic abundance, in the region of the 4-0 band. The displayed spectrum includes the 4-0 band of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ and the 5-1 hot band of $^{12}C^{16}O$. The transitions measured in this work are highlighted with full circles.

presents the first CRDS measurements of the third overtone band of CO. The External Cavity Diode Laser (ECDL) at disposal gives access to the 7910–8320 cm^{-1} spectral range significantly shifted below the centre of the 4-0 band of $^{12}C^{16}O$ at 8414 cm^{-1}. Compared to previous FTS studies, the gain in sensitivity – on the order of three orders of magnitude – allows detecting not only high *J* lines in the P branch of the 4-0 band of $^{12}C^{16}O$ but also the 4-0 band of $^{13}C^{16}O$, $^{12}C^{18}O$ and $^{12}C^{17}O$ which are significantly shifted compared to the $^{12}C^{16}O$ band and fall in the accessible frequency range. Note that the "natural" concentration of these minor isotopologues in the sample is expected to be about 1.1%, 0.2% and 0.04%, respectively.

We present in Fig. 1 an overview of the absorption spectrum of natural carbon monoxide as predicted by Li et al. [3] for lines with intensity above an cut off of 1×10^{-30} cm/molecule at 296 K. The present CRDS observations have been highlighted on this plot.

2. Experiment

The recordings were performed with a CRDS spectrometer which uses a fiber-connected External Cavity Diode Laser (ECDL: Toptica DL pro, 1200 nm) giving access to the 7910–8320 cm^{-1} spectral range. This spectrometer is very similar to the CRDS spectrometer based on DFB diode laser that we routinely use to access the 5850–7920 cm^{-1} region [7–12]. The reader is referred to Refs. [7,8] 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 by high reflectivity mirrors leading to ring down times of about 200 μs in the considered spectral interval. An important advantage of the ECDL compared to DFB diode lasers used in Refs. [7–12] lies in its smaller linewidth (typically 100 kHz compared to 2 MHz) allowing for a better light injection into the CRDS cavity. The typical mode-hop free tuning range of the used 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 is about $\alpha_{min} \sim 5 \times 10^{-12}$ cm^{-1}. The sensitivity and high signal to noise of the recordings are illustrated in Fig. 2.

The CRDS cell was filled with carbon monoxide (Air Liquide 99.997% stated purity). The pressure and the ring down cell temperature were monitored during the spectrum acquisition. The present recordings consist in continuous coverage of the 8084–8274 and 8031–8212 cm^{-1} spectral ranges with pressure values of 5.0 and 10.0 Torr, respectively.

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. In order to obtain the absolute calibration of the frequency axis, positions of reference lines are needed. In a first step, we used the positions of the numerous lines of water present as an impurity in the gas sample and adopted as reference positions the values given in the HITRAN database [13]. The average uncertainty on the HITRAN line positions used for calibration is about 1×10^{-3} cm^{-1}. After calibration by statistical matching, typical *rms* values of the deviations between our line centers and the corresponding HITRAN positions are 5×10^{-4} cm^{-1} for several hundred water lines.

In fact, the positions of the observed CO absorption lines can be calculated with an accuracy on the order of

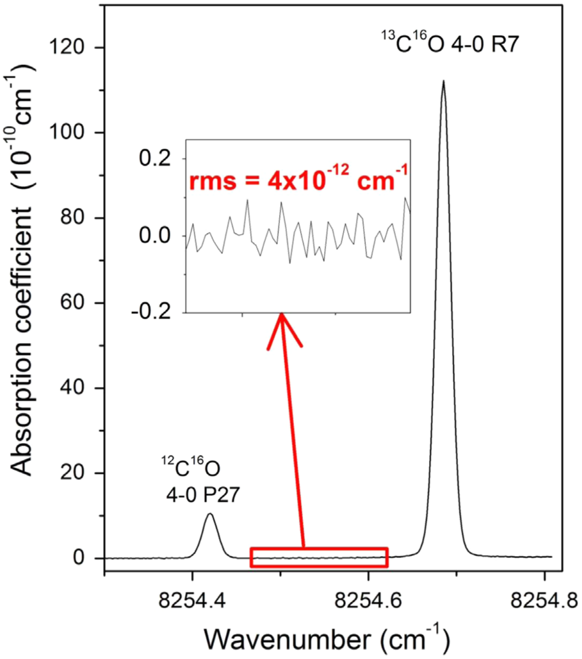

Fig. 2. CRDS spectrum of carbon monoxide in natural isotopic abundance recorded at 5 Torr near 8254.5 cm^{-1}. The P(27) 4-0 of $^{12}C^{16}O$ and the R(7) 4-0 of $^{13}C^{16}O$ present in natural abundance are observed. The insert illustrates the noise level on the order of $\alpha_{min} \sim 4 \times 10^{-12}$ cm^{-1} level.