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High-accuracy $^{12}C^{16}O_2$ line intensities in the 2 μm wavelength region measured by frequency-stabilized cavity ring-down spectroscopy

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ABSTRACT

Reported here are highly accurate, experimentally measured ro-vibrational transition intensities for the R-branch of the (20012)–(00001) $^{12}C^{16}O_2$ band near $\lambda = 2\,\mu m$. Measurements were performed by a frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) instrument designed to achieve precision molecular spectroscopy in this important region of the infrared. Through careful control and traceable characterization of CO_2 sample conditions, and through high-fidelity measurements spanning several months in time, we achieve relative standard uncertainties for the reported transition intensities between 0.15 % and 0.46 %. Such high accuracy spectroscopy is shown to provide a stringent test of calculated potential energy and *ab initio* dipole moment surfaces, and therefore transition intensities calculated from first principles.

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1. Introduction

The remote sensing of atmospheric molecules relies upon first-principles, physics-based models that incorporate accurate and precise laboratory spectroscopic data. For example, current satellite-based measurements of atmospheric CO_2, such as the ongoing GOSAT (JAXA), and OCO-2 (NASA) missions and the upcoming MICROCARB (CNES) mission, as well as the worldwide terrestrial spectrometer campaign (TCCON), demand low uncertainty in the pressure, temperature and composition dependence of air-broadened O_2 and CO_2 absorption cross sections. These quantities can be calculated in terms of absolute transition frequencies and intensities, and line shape parameters that account for collisional broadening, pressure shifting, line mixing and collisional narrowing [1,2]. In the context of NASA's Earth-orbiting OCO-2 satellite mission which measures the column-integrated dry air mixing ratio of CO_2 [3], calculated cross-sections with relative uncertainties on the order of 0.3% are required [4]. In order to meet this ambitious data target and therefore maximize the scientific achievements of this and other remote-sensing missions, reference-quality, laboratory measurements of CO_2 spectroscopic parameters are required.

Here we report a detailed description of the instrumentation and methodology used to perform low-uncertainty cavity ring-down spectroscopy (CRDS) measurements of relatively strong carbon dioxide line intensities in the wave number region 4990 cm^{-1} to 5010 cm^{-1}. The resulting intensities are reproduced with high fidelity over a period of several months with relative combined standard uncertainties of 0.25%. Comprehensive comparisons with existing database parameters as well as recent *ab initio* and experimental intensities are reported and discussed.

2. Description of experiment

2.1. Survey of spectral region

The upper panel of Fig. 1 shows a simulated air-broadened absorption spectrum of carbon dioxide (with water vapor interferences) for the wave number region investigated here and for pressure, moisture, mole fraction and path length conditions representative of this study. The spectrum is dominated by 19 targeted transitions assigned to the (20012)–(00001) vibrational band of $^{12}C^{16}O_2$ lower-state rotational quantum numbers $J'' = 16, 18, \ldots 52$. The lower panel of Fig. 1 has the same calculated spectrum plotted with a logarithmic ordinate, showing that the interferences associated with other $^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and H_2O transitions are typically at most two orders of magnitude below the peak absorption of the target transitions. Although, the targeted transitions were relatively isolated, because of the high signal-to-noise ratio of the measured spectra, our analyses accounted for the wings of neighboring strong lines as well as residual contributions from some of the weak interferences.

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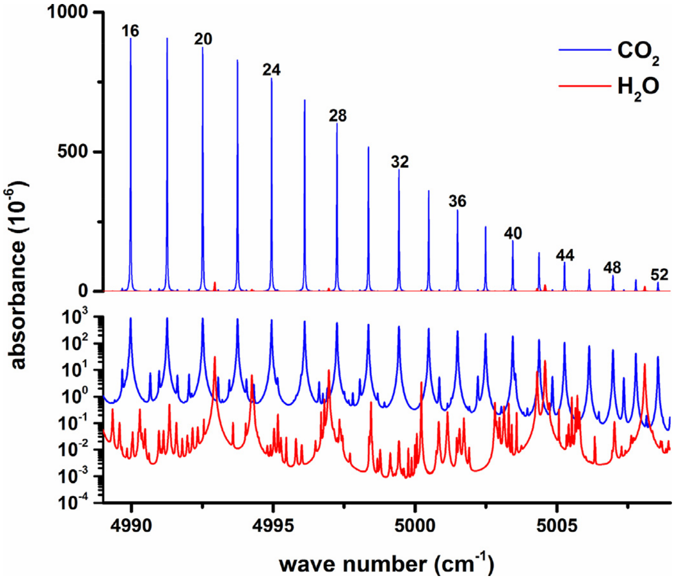

Fig. 1. Simulated absorption spectrum for the spectral region of interest revealing the dominant $^{12}C^{16}O_2$ band transitions and interferences from weaker carbon dioxide and water vapor transitions. Pressure and temperature of 133 kPa and 296 K, respectively, path length of 75 cm, and molar fractions of carbon dioxide and water vapor both equal to 10^{-4}. Air-broadening is assumed and line parameters are based on HITRAN 2012. The lower-state angular momentum quantum number J'' is indicated above every other (20012)–(00001) $^{12}C^{16}O_2$ transition.

2.2. FS-CRDS method

We acquired absorption spectra using the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) method. This is an implementation of CRDS in which the optical resonator (i.e. ring-down cavity) is length-stabilized relative to a continuous-wave (CW), frequency-stabilized reference laser and pumped by a narrow line width CW probe laser [5,6]. FS-CRDS results in high-fidelity spectra that are determined from precise measurements of optical frequency shifts and intensity decay times. The active locking scheme in FS-CRDS ensures that the cavity mode spacing provides a stable and linear frequency detuning axis, and the single-mode excitation of the resonator eliminates laser bandwidth effects that can lead to complicated multi-exponential decay signals [7]. At each frequency step, the probe laser beam is brought into resonance with a single cavity mode (designated by its mode order q) and subsequently switched off to cause single-exponential decay of the light intensity exiting the resonator. In this fashion, the spectrum detuning relative to the first mode order q_0 is equal to $(q-q_0)\nu_f = \Delta q\nu_f$ where ν_f is the cavity free spectral range (FSR). Individual intensity decay signals are converted into photocurrent with a DC-coupled photodetector, amplified and recorded using a high-speed A/D board. The time constant τ for each decay event is obtained by fitting the three-parameter function $s(t)=Ae^{-t/\tau}+s_0$ to the time-dependent photocurrent signal $s(t)$, where A and s_0 are the amplitude and time-independent offset, respectively. Multiple decays are obtained at each frequency detuning to provide an average decay time $\bar{\tau}$ and standard deviation σ_τ. Measured spectra are given by the set of values $\alpha_{tot}(\Delta q\nu_f) = (c\bar{\tau})^{-1}$ where c is the speed of light. These data quantify the total (i.e. absorption plus baseline) intensity loss-per-unit length in the sample as a function of spectrum detuning.

2.3. FS-CRDS spectrometer

The FS-CRDS spectrometer used in this study is similar to other systems that were developed at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD [8–10]. This spectrometer comprises several component sub-systems, including a high-finesse optical resonator and gas cell, a reference laser and servo controller for active resonator length stabilization, gravimetrically prepared gas mixtures of CO_2 in N_2 and associated flow delivery system, a tunable CW probe laser, a photoreceiver and digitizer, and a personal computer with high-speed data acquisition, signal analysis and control software. Each instrument sub-system is discussed in detail in this Section.

The optical instrument is assembled on a 1 m by 1.3 m breadboard seated atop a mobile cart. A standard rack mount, also on wheels, houses the fiber laser amplifier, oscilloscope, power supplies, locking and system control electronics, and a personal computer. An additional rack mount is situated next to the optical table with a gas cylinder mount and flow delivery manifold.

2.4. Optical resonator and gas cell

The optical resonator and gas cell consist of two flexure mirror mounts supported by individual steel brackets, four 2.54 cm diameter invar rods 52 cm in length connecting the brackets, and a 1.27 cm diameter tube with formed bellows to connect the two mirror mounts and house the gas sample and optical cavity [5]. As shown in Fig. 2, each flexure mirror mount has a gas inlet (outlet) port used to exchange sample gas in a flowing configuration (see Section 2.5), with the gas sweeping past both ring-down mirrors to prevent the occurrence of dead volumes. Commercial dual-wavelength-coated, high-reflectivity low-loss mirrors (2.54 cm diameter, 6 m radius of curvature) with intensity reflection coefficients of 0.99964 and 0.95 at $\lambda = 2$ μm and $\lambda = 633$ nm, respectively, are installed into each flexure mount. The distance between the ring-down cavity mirrors is nominally 75 cm and accurately determined by measurement of the cavity FSR as discussed below. The vacuum seal between the intra-cavity gas sample and the laboratory environment is made by anti-reflection-coated CaF_2 windows which are bonded to a standard knife-edge-seal flange. This design results in the low-loss, ring-down cavity mirrors experiencing zero pressure difference between their high-reflection and anti-reflection coated faces, thus mitigating potential stress-induced birefringence effects [11,12].

The FSR of the evacuated optical cavity was measured using an infrared wavelength meter (1 μm to 5 μm operating wavelength range) with a frequency resolution of 40 MHz. While a software-based dither locking scheme [13] maintained probe laser transmission, a small portion of the probe laser beam was analyzed by the wavelength meter for up to 12 s. The probe laser frequency was sequentially locked to 750 successive longitudinal modes of the optical resonator and the probe laser frequency was measured at each step. From these data, linear regression analysis yielded the empty-cavity free spectral range $\nu_f = 200.806$ MHz with a standard uncertainty of 60 kHz. This value was in good agreement with ν_f obtained by fitting a spectral model with known $^{12}C^{16}O_2$ transition frequencies [14] to a measured absorption spectrum. Also, at each pressure and temperature condition, the ν_f was corrected to account for density-dependent changes in the refractive index of the sample gas. These corrections were found to be less than 0.02% of the empty-cavity values for all conditions considered.

2.5. Active length stabilization of optical resonator

The mirror-to-mirror distance of the ring-down cavity was actively stabilized in order to provide a linear and stable relative frequency axis. To this end, a temperature-stabilized HeNe laser (100 kHz line width at 10 ms, long-term stability of 1 MHz), counter-propagating and co-linear with the probe laser, was