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Intracavity Laser Absorption Spectroscopy of $^{13}C^{16}O_2$ near 734 nm

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ABSTRACT

We report the first intensity measurements for the very weak 20052-00001 band of the $2\nu_1 + 5\nu_3$ triad of $^{13}C^{16}O_2$ near 734 nm by high sensitivity Intracavity Laser Absorption Spectroscopy. A noise equivalent absorption $\alpha_{min} \sim 2 \times 10^{-10}$ cm^{-1} was achieved with an absorption pathlength equivalent to 50.3 km. The derived intensity values (on the order of 10^{-28} cm/molecule) are found in good agreement with recent *ab initio* calculations. The dominant term of the effective dipole moment of the $2\nu_1 + 5\nu_3$ triad was obtained from a fit of the measured line intensity values and used to generate the line list of the $2\nu_1 + 5\nu_3$ triad of $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$.

1. Introduction

The $2\nu_1 + 5\nu_3$ triad is the most excited band system observed so far by absorption spectroscopy, both for $^{13}C^{16}O_2$ and for the main isotopologue, $^{12}C^{16}O_2$. It corresponds to the [(20^05), (12^05), (04^05)] triplet of upper states highly mixed by strong anharmonic interactions. The HITRAN notation of the resulting eigenstates is 20051, 20052 and 20053, in decreasing order of the energy.

As a result of their weakness, previous observations of components of the $2\nu_1 + 5\nu_3$ triad are scarce.

In 1953, Herzberg and Herzberg observed the faint *R* branch head of the 20052-00001 band of the main isotopologue, $^{12}C^{16}O_2$, on their photographic plates [1] using long exposure times and a pressure × pathlength product of 1/3 atm × 5500 m. Fifteen years ago, we reported the positions of about twenty lines of each of the 20051-00001 and 20052-00001 bands of $^{12}C^{16}O_2$, near 14065.7 and 13957.2 cm^{-1}, respectively, by Intracavity Laser Absorption Spectroscopy (ICLAS) [2]. Finally, Yang and Noda detected the three components of the triad by photoacoustic spectroscopy (PAS) but the quality of the spectra did not allow for rotational analysis or quantitative intensity measurements [3].

As concerns the $^{13}C^{16}O_2$ isotopologue, the only previous detection was achieved by PAS and about thirty line positions were reported for the 20051-00001 and 20052-00001 bands near 13725.6 and 13623.9 cm^{-1}, respectively [4].

The 20051 and 20052 spectroscopic constants of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ were derived from a fit of the line positions in Ref. [2] and in Ref. [4], respectively.

In absence of intensity measurements, the bands of the $2\nu_1 + 5\nu_3$ triad are absent from the most currently used spectroscopic databases of carbon dioxide which were generated using the effective operator approach. In the present work, we report the first intensity measurements for the 20052-00001 band of $^{13}C^{16}O_2$ which were used to determine the dominant parameter of the effective dipole moment of the $2\nu_1 + 5\nu_3$ triad. As a result, it will be possible to include in the spectroscopic databases not only the 20052-00001 band but the three bands of the $2\nu_1 + 5\nu_3$ triad of both $^{13}C^{16}O_2$ and $^{12}C^{16}O_2$.

2. Experiment

Intracavity Laser Absorption Spectroscopy is a highly sensitive technique for quantitative absorption spectroscopy [5]. It takes advantage of the high sensitivity of a laser spectrum to intracavity losses due to an absorber placed in an intracavity absorption cell. Our ICLAS spectrometer has been described previously in Refs. [5–9]. We use a standing wave Ti:Sapphire cavity pumped by an Ar$^+$ laser, with a 65 cm cell inserted in the long arm of the cavity. A first acousto-optic modulator chops the pumping beam at a high repetition rate (a few kHz). After a given delay from the rising edge of the pump pulse, called the generation time, t_g, the second acousto-optic modulator deflects the laser beam during a short time interval Δt ($\ll t_g$) to the entrance slit of a high resolution grating

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spectrograph. The laser beam is dispersed and a portion of the absorption spectrum is observed superimposed on the broad mostly Gaussian envelope of the laser spectrum. Each 12 cm^{-1} wide portion of the spectrum is recorded with a 3754 silicon diode array placed in the focal plane of the grating spectrograph [5,6]. Each spectrum corresponds to the averaging of about 10^5 laser generations within about 10 s. An 8 μm thick pellicle acting as a low finesse etalon is inserted in the laser cavity in order to tune the central wavelength of the laser.

The intracavity absorption cell with two glass windows at Brewster angle was filled with highly ^{13}C enriched carbon dioxide (Aldrich, >99% $^{13}CO_2$) at pressure values ranging between 150 and 220 Torr. The chosen pressure value leads to a line broadening on the same order than the Doppler line broadening (1.25×10^{-2} - cm^{-1} HWHM).

The occupation ratio of the cavity of the Ti:Sapphire by the absorption cell is 42%, the remaining part being occupied by the atmosphere. The ICLAS spectra show then the spectrum of the species present in the cell superimposed to the atmospheric spectrum. The $2\nu_1 + 5\nu_3$ triad of both $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ falls in a spectral region where water absorption is relatively strong (the strongest water lines have intensities in the 10^{-24}–10^{-23} cm/molecule range). This adds to the difficulty of the detection of the CO_2 bands as the strongest CO_2 lines to be detected have intensities on the order 5×10^{-28} cm/molecule and may be obscured by lines of atmospheric water present in the laser cavity. Among the bands of the $2\nu_1 + 5\nu_3$ triad of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$, the 20052-00001 band of $^{13}C^{16}O_2$ centered at 13623.9 cm^{-1} has the advantage to be located in a spectral interval where water absorption is less intense and was then chosen for intensity measurements. It was nevertheless necessary to drastically reduce the water concentration present in the laser cavity by placing the Ti:Sapphire laser in a box where a continuous flow of dry nitrogen was injected. After a few minutes, the water absorption was decreased by about a factor 30. The residual absorption was further removed by using the procedure described in Fig. 1. It consists in recording with a vacuumed cell the ICLAS background spectrum showing the water lines, filling the cell with carbon dioxide and recording the corresponding ICLAS spectrum consisting in the superposition of the water background and CO_2 absorption. By division of this last spectrum by the background spectrum, most of the water absorption is eliminated. The division has also the advantage of increasing the signal to noise ratio by suppressing parasitic fringes frequently appearing on the spectrum baseline.

The recordings were performed in the *P* and *R* branches of the 20052-00001 band of $^{13}C^{16}O_2$ with a generation time of 400 μs. The wavenumber axis of each 12 cm^{-1} wide spectrum was calibrated using the positions of the lines of the 20052-00001 band measured in Ref. [4] by photoacoustic spectroscopy.

In ICLAS, the generation time determines the equivalent absorption path length:

$$L_{eq} = ct_g l/L \tag{1}$$

where *c* is the speed of light, and *l* and *L* the length of the absorption cell (65 cm) and of the laser cavity length (155 cm) respectively. Consequently, for t_g = 400 μs, the recorded ICLAS spectra are similar to spectra recorded in direct absorption with a pathlength of 50.3 km. The ICLAS spectrum has a Gaussian envelope with a width decreasing as $1/\sqrt{t_g}$ [5–7]. The spectra displayed in Fig. 1 shows that in our experimental conditions, the FWHM of the spectrum is limited to 5–10 cm^{-1}.

The line intensities were determined using an interactive least squares multi-line fitting program assuming a Voigt profile (http://sourceforge.net/projects/fityk/ version v 1.1.1). As the spectrograph apparatus function contributes partly to the measured line profile, the Gaussian width was not fixed to the corresponding Doppler value but fitted. Line position, integrated line absorbance, Gaussian and Lorentzian widths of each line and the corresponding baseline (assumed to be a linear function of the wavenumber) were derived from the multiline fitting procedure. Fig. 2 shows an example of spectrum reproduction in the *P* branch region. The noise level estimated from the *rms* value of the difference of the measured and simulated absorbances is 1.0×10^{-3} which corresponds to an absorption coefficient of 2×10^{-10} cm^{-1}. This noise

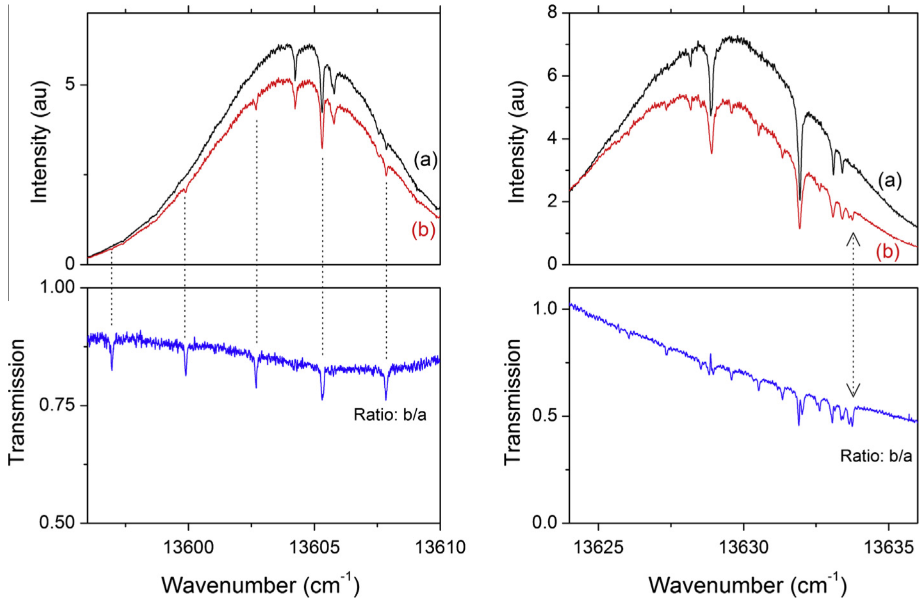

Fig. 1. Illustration of the procedure adopted to remove the atmospheric water contribution to the ICLAS spectrum in the region of the *P* and *R* branches of the 20052-00001 band of $^{13}C^{16}O_2$ (left and right hand, respectively). The considered spectral region shows relatively strong lines of water which are efficiently removed by recording successively two spectra corresponding to the same spectral window and to the same generation time (presently t_g = 400 μs, l_{eq} = 50.3 km). The background spectrum (a) recorded with evacuated ICLAS cell shows the ICLAS spectrum of the residual water present in part of the cavity of the Ti:Sapphire laser. When carbon dioxide is injected in the ICLAS cell, the ICLAS spectrum (b) shows the CO_2 lines superimposed to the background spectrum. The ratio of the second spectrum by the first one (lower panel) provides the $^{13}C^{16}O_2$ spectrum free of water absorption.