Journal of Quantitative Spectroscopy & Radiative Transfer 211 (2018) 172–178

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Notes

High accuracy line positions of the ν_1 fundamental band of $^{14}N_2{}^{16}O$

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ARTICLE INFO

Article history:
Received 30 January 2018
Revised 6 March 2018
Accepted 6 March 2018
Available online 7 March 2018

Keywords:
Nitrous oxide
Microwave
Mid-infrared
Line position
Frequency comb
Quantum cascade laser

ABSTRACT

The ν_1 fundamental band of N_2O is examined by a novel spectrometer that relies on the frequency locking of an external-cavity quantum cascade laser around 7.8 µm to a near-infrared Tm:based frequency comb at 1.9 µm. Due to the large tunability, nearly 70 lines in the 1240–1310 cm^{-1} range of the ν_1 band of N_2O, from $P(40)$ to $R(31)$, are for the first time measured with an absolute frequency calibration and an uncertainty from 62 to 180 kHz, depending on the line. Accurate values of the spectroscopic constants of the upper state are derived from a fit of the line centers ($rms \approx 4.8 \times 10^{-6}$ cm^{-1} or 144 kHz). The ν_1 transitions presently measured in a Doppler regime validate high accuracy predictions based on sub-Doppler measurements of the ν_3 and ν_3-ν_1 transitions.

1. Introduction

Even in their most recent editions [1], a large fraction of line parameters included in spectroscopic databases relies on absorption spectra measured by Fourier Transform Spectroscopy (FTS). This approach limits traceability and accuracy of line positions to a few tens of MHz, which explains why most line frequencies, even those from the more intense bands, are usually given with a 10^{-4}–10^{-3} cm^{-1} (3–30 MHz) uncertainty. The invention of optical frequency combs at the end of the past millennium enabled the calibration of optical frequencies against primary frequency standards, whose fractional frequency uncertainty may easily attain $\sim 10^{-11}$ at 1 s. This made it possible, at least on single transitions, to retrieve line centers with uncertainties down to a few kHz [2–7].

On the other hand, optical frequency combs have been seldom applied to broad line surveys to extract spectroscopic parameters of molecular absorption bands. In the near-infrared (near-IR), extended measurements have been performed only on a few bands of C_2H_2, NH_3 and H_2O in a sub-Doppler regime [6–10] and of CO, CO_2 and H_2O in a Doppler broadening regime [11–15], quite often in conjunction with optical cavities to extend the effective absorption path length (as well as to enhance the laser intensity in saturated surveys). In the mid-infrared (mid-IR), surveys over more than 50 cm^{-1} have been provided for the ν_3 band of N_2O [16] and of CH_4 [17,18], as well as for CO_2 near 4.3 and 2.7 µm [19,20]. A technological hurdle here originates from the lack of commercial mid-IR comb synthesizers and hence from the need to resort to nonlinear optics to get referencing of a mid-IR probe laser to a near-IR comb [21–28]. A second nontrivial requirement is a widely tunable single-mode laser, most of all beyond 5 µm, where cw sources based on difference-frequency-generation or optical parametric oscillation are not available. Distributed-feedback (DFB) quantum cascade lasers are an option only for rather narrow ranges of about 10 cm^{-1} [29], whereas for ranges of $\sim$100 cm^{-1}, which are needed to cover an entire absorption band, the only solution available commercially is given by external cavity quantum cascade lasers (EC-QCLs). As these lasers usually suffer from a large amount of frequency noise [30], their use in combination with frequency combs has been firstly demonstrated in an unlocked regime, with an accuracy of 800 kHz [31], and only recently in a comb-locked regime with an accuracy of 60 kHz [32].

In this work, the spectrometer proposed in Ref. [32] is applied to the first high accuracy line position measurements of the ν_1 fundamental band of $^{14}N_2{}^{16}O$ near 1285 cm^{-1}. The measured po-

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https://doi.org/10.1016/j.jqsrt.2018.03.005

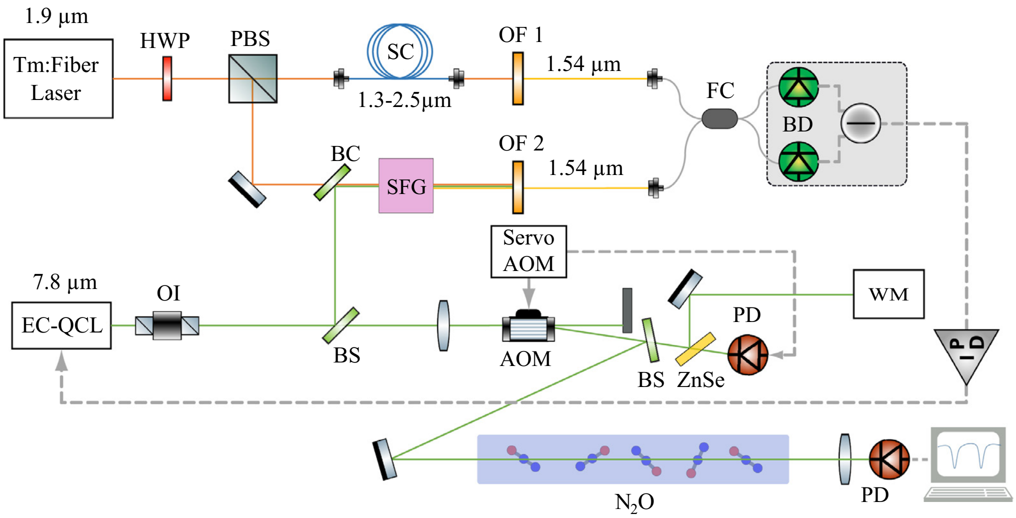

Fig. 1. Layout of the spectrometer, based on the frequency locking of a mid-IR EC-QCL to a near-IR Tm: fiber frequency comb. HWP: half wave plate, PBS: polarizing beam splitter, SC: supercontinuum, BS: beam splitter, BC: beam combiner, PD: photodetector, OF: optical filter, FC: fiber coupler, BD: balanced detector, SFG: Sum-Frequency-Generation, OI: optical isolator, AOM: acousto-optic modulator, WM: wavemeter.

sitions are used to derive spectroscopic parameters of the upper state. Specifically, nearly 70 lines equally distributed among the *P* and *R* branches have been measured with a systematic uncertainty of 60 kHz and a statistical uncertainty varying from 10 to 170 kHz depending on the line. It is worth noting that the impact of the statistical uncertainty on the spectroscopic parameters is strongly reduced by the averaging effect that takes place when all lines are considered in a global fitting procedure, this being one of the major strengths of the broadband comb-calibrated approach described herein.

2. Experimental

The spectrometer is described in detail in Ref. [32]. It is based on the frequency locking of an external cavity quantum cascade laser (EC-QCL) from Daylight Solutions, with tunability from 7.55 to 8.2 µm and optical power above 60 mW after optical isolation, to a Tm:fiber frequency comb at 1.9 µm delivering up to 1.5 W at a repetition rate of 100 MHz [33]. The layout of the spectrometer is depicted in Fig. 1. The referencing scheme relies on a sum frequency generation (SFG) process [26,34] between the comb and the EC-QCL in an 8-mm-long Zinc Germanium Phosphide (ZGP) crystal: this process generates a new comb (ν_{SFG}) near 1.54 µm whose frequency is offset from the original comb (ν_m) by the EC-QCL frequency (ν_{QCL}), i.e., $\nu_{SFG} = \nu_m + \nu_{QCL}$. Thereafter, by heterodyning the SFG comb against a spectrally broadened replica of the original near-IR comb (ν_n), a radio-frequency (RF) beat note (f_{beat}) is extracted, $f_{beat} = |\nu_{SFG} - \nu_n| = |\nu_{QCL} - (n-m)\, f_{rep}|$, which allows the EC-QCL frequency to be calibrated against an integer multiple ($n-m$) of the comb repetition frequency (f_{rep}). The stabilization of f_{beat} against an RF local oscillator (f_{LO}) is obtained by driving the EC-QCL piezo modulation port with a servo PID. By scanning the repetition rate of the frequency comb while maintaining a steady frequency lock of the EC-QCL to the comb ($f_{beat} = f_{LO}$), one can finely tune the EC-QCL over ~600 MHz. The absolute frequency calibration derives from the fact that all radiofrequencies, namely f_{rep} and f_{LO}, and hence all optical frequencies are seeded by a primary clock based on a GPS-disciplined Rb oscillator. As compared to the setup described in Ref. [32], an intensity stabilization scheme was added to compensate for laser fluctuations during the spectral scans and thus to achieve a flatter baseline. This was obtained by introducing an acousto-optic modulator in the beam path and by actively controlling its input RF power in such a way as to keep the diffracted field power stable around a 0.5 mW set-point. A photodetector placed upstream the optical cell serves as a monitor for the intensity stabilization feedback loop.

In this work, we fully exploit the wide tunability and the single-mode operation of the EC-QCL to cover 70 absorption lines of nitrous oxide (N_2O) spanning the 1240–1310 cm^{-1} range. The gas is housed in a 66 cm long optical cell kept at room temperature and at pressures of 0.01–0.04 mbar (1–4 Pa), in a regime where absorption profiles are almost exclusively determined by Doppler broadening and self-induced pressure shift of the line center is negligible. The measurements are performed by a fully automated setup that reads the EC-QCL frequency out of a wavemeter (WM), tunes it to the target absorption line, switches on the lock to the frequency comb, steps the comb repetition rate by 4 Hz (1.5 MHz in the optical domain) to scan and acquire the absorption line, switches off the lock, then again tunes the laser frequency to the next line of a preliminarily uploaded HITRAN list. Typically, a 540 MHz-wide spectrum consists of 360 evenly spaced points acquired with a dwell time of 100 ms.

An overview of the measurements of the ν_1 band of N_2O is presented in Fig. 2(a). The absorption spectra cover most part of the *P* and *R* lines up to $J = 40$ and $J = 31$, respectively. Each line results from the average of 10 spectra acquired in 6 minutes. To maintain an almost uniform signal-to-noise ratio for lines with different strengths, the acquisition has been split in separated runs at slightly different pressures, from 0.01 to 0.04 mbar (for representation purposes, the experimental absorbance values have been normalized in Fig. 2 to the same pressure condition of 0.018 mbar). Such low-pressure regime allowed us to fit the absorption lines with a Gaussian profile. As a representative case, Fig. 2(b) reports a 10-times averaged spectrum of the *P*(3) line together with the residuals obtained from a fitting that includes a linear slope for the baseline: the latter are only slightly affected by parasitic etalons and laser intensity noise. The signal-to-noise ratio is about 890.

The statistical uncertainty (Type A error calculated as the standard error of the mean) on the line centers varies, depending on the line, from 10 kHz to 170 kHz. These numbers reflect the noise level on the vertical axis of the measurement, some nonlinearity of