

High sensitivity CW-Cavity Ring Down Spectroscopy of N₂O near 1.28 μm

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ABSTRACT

The absorption spectrum of nitrous oxide, N₂O, in normal isotopic abundance has been recorded by CW-Cavity Ring Down Spectroscopy between 7647 and 7918 cm⁻¹. The spectra were obtained at Doppler limited resolution by using a CW-CRDS spectrometer based on a series of fibered DFB lasers. The typical noise equivalent absorption on the order of $\alpha_{\min} \approx 1 \times 10^{-10}$ cm⁻¹, allowed for the detection of lines with intensity as weak as 2×10^{-29} cm/molecule.

The positions of 2272 lines of five isotopologues (¹⁴N₂¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁴N₂¹⁸O and ¹⁴N₂¹⁷O), were measured with a typical accuracy of 1.0×10^{-3} cm⁻¹. The transitions were rovibrationally assigned on the basis of the global effective Hamiltonian models respective to each isotopologue. The band by band analysis allowed for the determination of the rovibrational parameters of a total of 30 bands, 19 of them being newly reported while new rotational transitions are measured for the others. The maximum deviation of the predictions of the effective Hamiltonian models is 0.18 cm⁻¹ for the line positions of the main isotopologue and up to 1.3 cm⁻¹ for the ¹⁴N₂¹⁸O species. Local rovibrational perturbations were evidenced for three bands of ¹⁴N₂¹⁶O and the $\nu_1 + 3\nu_3$ band of ¹⁴N₂¹⁷O. The interaction mechanisms and the perturbers were univocally assigned on the basis of the effective Hamiltonian models.

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1. Introduction

The present contribution is part of a series devoted to the study of the near infrared absorption spectrum of nitrous oxide by CW-Cavity Ring Down Spectroscopy (CW-CRDS) [1–3]. By using a set of seventy Distributed Feed-Back (DFB) laser diodes, the 5850–7920 cm⁻¹ range can be covered with a typical noise equivalent absorption on the order of $\alpha_{\min} \approx 1 \times 10^{-10}$ cm⁻¹. Compared to the previous investigations by Fourier Transform spectroscopy [4–9] associated with long multipass cells, the very high sensitivity of the CRDS technique allows for the new detection of many transitions. For instance, in Refs. [1–3], the 5905–7066 cm⁻¹ region was investigated and a total of about 10 500 transitions belonging to 132 bands of five N₂O isotopologues were reported. Fig. 1 shows the overview of the N₂O spectrum recorded by Fourier Transform Spectroscopy (FTS) at the Université Libre de Bruxelles [9] where the previously and presently studied ranges are indicated. In the present work, we focus on the 7647–7918 cm⁻¹ region dominated by the $\nu_1 + 3\nu_3$ band at 7782 cm⁻¹. As a consequence of the high density of lines detected (more than 10/cm⁻¹) resulting of the superposition of many hot bands and of the contribution of the five most abundant isotopologues, the rovibrational assignment was a

difficult task. It relied mainly on the predictions of the effective Hamiltonian models developed for each N₂O isotopologue [10–13].

2. Experiment

2.1. The CW-CRDS spectrometer

The fibered Distributed Feed-Back diode laser CW-CRDS spectrometer was described in details in Refs. [14–16]. Each DFB diode laser has a typical tuning range of 7 nm (~ 35 cm⁻¹) by temperature tuning from –15 to 60 °C. Ten diode lasers were needed to cover continuously the 7647–7918 cm⁻¹ region except for a small gap between 7897 and 7901 cm⁻¹. A single-mode fiber delivers the laser radiation to one end of a vacuum-tight ringdown cell, which is 140 cm long. The high reflectivity cavity mirrors are mounted on tilt stages, one of which includes a piezoelectric tube. The cavity losses at each laser wavelength were obtained by averaging the results of exponential fits of about 40 ringdown events, thus giving one data point in the spectrum. The typical ringdown time was 150 μs. About 60 min were needed for each DFB laser in order to complete a temperature scan.

The pressure, measured by a capacitance gauge (Baratron), as well as the ringdown cell temperature (about 293 K) were continuously recorded during the experiments. The spectra were obtained at pressures of 1.00 and 10.0 Torr for which collisional

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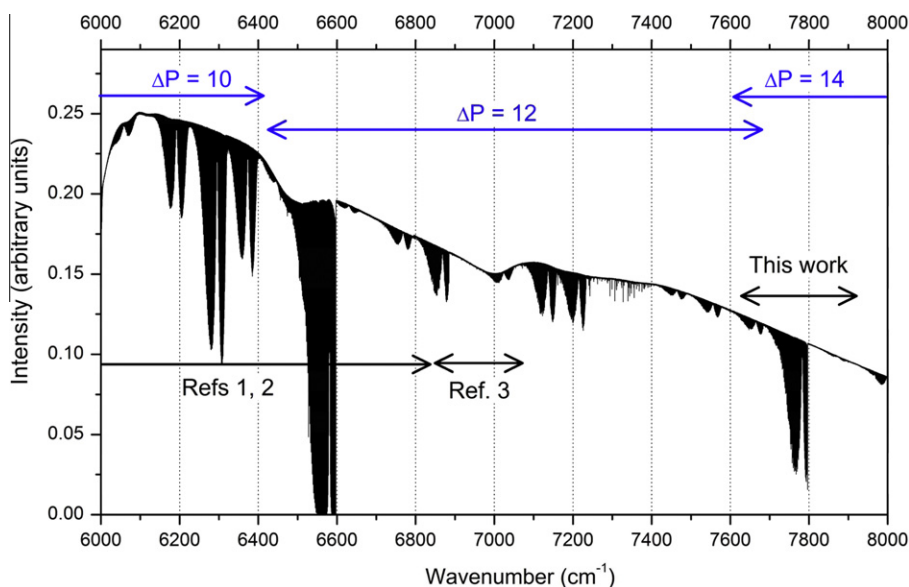


Fig. 1. Overview of the FTS spectrum of N_2O indicating the spectral ranges previously [1–3] or presently studied by CRDS. The approximate ranges of the bands corresponding to a variation of the polyad quantum number $\Delta P = 10, 12$ and 14 are indicated.

broadening is negligible and then the line profile is mostly Doppler limited.

The wavenumber calibration of the spectrum was based on the values provided by a lambdameter (Burleigh WA1640) [16]. It was then refined by using reference lines. We adopted the line positions of H_2O present as an impurity in the cell as reference lines. Their values were taken from the HITRAN database [17]. The maximum differences between line positions measured on the overlapping part of two successive spectra are less than of $2 \times 10^{-3} \text{ cm}^{-1}$. We then estimate to $1 \times 10^{-3} \text{ cm}^{-1}$ the average uncertainty on the line positions.

The achieved sensitivity is illustrated in Fig. 2. A noise equivalent absorption on the order of $\alpha_{\text{min}} \approx 1 \times 10^{-10} \text{ cm}^{-1}$ is achieved. Combined with a 4–5 orders dynamics on the line intensities which can be measured, it leads to the observation of a high

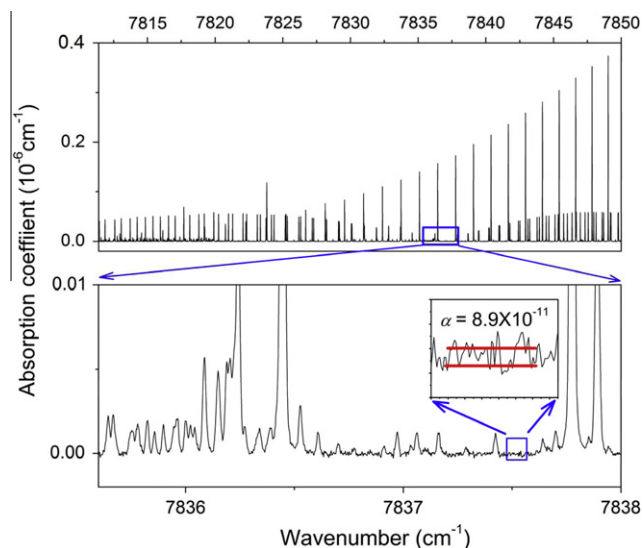


Fig. 2. CW-CRDS spectrum of natural nitrous oxide around 7837 cm^{-1} . The sample pressure was 1.0 Torr. Two successive enlargements show the typical achieved noise level: the minimum value of the absorption coefficient which can be detected is about $1 \times 10^{-10} \text{ cm}^{-1}$.

density of lines which made the analysis particularly difficult. Lines due to impurities (water, CO_2 and HF) were identified using the corresponding HITRAN line list and removed from the line list leading to a set of about 2800 lines to be assigned.

3. Rovibrational analysis

3.1. Vibrational assignment

Five isotopologues in “natural” isotopic abundance were found to contribute to the spectra: $^{14}\text{N}_2^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$ and $^{14}\text{N}_2^{17}\text{O}$. A summary of the observations is presented in Table 1 which includes the HITRAN notation of the various species. In total 2272 transitions were assigned on the basis of the predictions of the effective rovibrational Hamiltonian of Ref. [10]. The effective parameters values have been fitted to the observed line positions for each isotopic species: 446 [11], 456 [13], 546 [13], 448 [12] and 447 [12]. The used model of effective Hamiltonian is based on a polyad structure resulting from the approximate relations between the harmonic frequencies ($\omega_3 \approx 2\omega_1 \approx 4\omega_2$). As the mixing between the $(v_1 v_2^2 v_3)$ states may be strong, the energy levels are preferably labeled using the triplet $(P = 2V_1 + V_2 + 4V_3, l_2, i)$ where the index i increases with the energy. The vibrational labelings and the dominant basis states in the vibrational decomposition of the upper states of the various bands detected in this work are listed in Table 2.

The absorption in the studied region corresponds mostly to a $\Delta P = 14$ variation of the polyad quantum number (see Fig. 1). Among the 21 $^{14}\text{N}_2^{16}\text{O}$ bands which were analyzed, 17 are $\Delta P = 14$ bands. The four others are a band reaching the $(12, 0, 16)$ highly excited level of the $P = 12$ polyad with its associated hot band, and two very weak perpendicular bands ($\Delta l_2 = 1$) reaching upper states of the $P = 13$ polyad. Except two $\Delta - \Sigma$ bands ($\Delta l_2 = 2$), all the $\Delta P = 12$ and 14 bands are parallel bands ($\Delta l_2 = 0$): 11 $\Sigma - \Sigma$, 3 $\Pi - \Pi$, 2 $\Delta - \Delta$ and one $\Phi - \Phi$.

As a general rule, cold bands are dominated by transitions reaching upper vibrational states with important fractions of pure stretching states, $(v_1 v_2^2 = 0^0 v_3)$, which are considered as “bright” states. In the studied region, the $v_1 + 3v_3$ band reaching the $(P = 14, l_2 = 0, i = 3)$ state near 7782 cm^{-1} brings most of the

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