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High sensitivity CW-Cavity Ring Down Spectroscopy of N_2O between 6950 and 7653 cm^{-1} (1.44–1.31 μm): I. Line positions

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ABSTRACT

The absorption spectrum of nitrous oxide, N_2O, has been recorded by CW-Cavity Ring Down Spectroscopy between 6950 and 7653 cm^{-1}. The spectra were obtained at Doppler limited resolution using a CW-CRDS spectrometer based on a series of fibered DFB laser diodes. The typical noise equivalent absorption, in the order of $\alpha_{min} \approx 1 \times 10^{-10}$ cm^{-1}, allowed for the detection of lines with intensity as small as 1×10^{-29} cm/molecule.

The positions of 7203 lines of four isotopologues ($^{14}N_2{}^{16}O$, $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N_2{}^{18}O$) 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 developed for each isotopologue. The band by band analysis allowed for the determination of the rovibrational parameters of more than 95 bands, most of them being newly reported while new rotational transitions are measured for the others. The measured line positions of the main isotopologue are found to be in good agreement with the predictions of the effective Hamiltonian model but a few deviations up to 0.20 cm^{-1} are observed. Local rovibrational perturbations were evidenced for several bands. The interaction mechanisms and the perturbers were univocally assigned on the basis of the effective Hamiltonian models.

1. Introduction

The present contribution is the fifth of a series devoted to the study of the near infrared absorption spectrum of nitrous oxide by CW-Cavity Ring Down Spectroscopy (CW-CRDS). [1–4]. Compared to the previous investigations by Fourier Transform spectroscopy (FTS) [5–8] associated with long multipass cells, the very high sensitivity of the CRDS technique allowed lowering the detectivity threshold by about three orders of magnitude leading to the observation of many new bands. Using a set of about seventy Distributed Feed-Back (DFB) laser diodes, the 5905–7920 cm^{-1} range was continuously covered with a typical noise equivalent absorption of $\alpha_{min} \approx 1 \times 10^{-10}$ cm^{-1}. For instance, in the 5905–7066 cm^{-1} region, a total of about 10,500 transitions belonging to 132 bands of five N_2O isotopologues were reported [1–3]. In the present work, we fill the gap between Refs. [1–3] (5905–7066 cm^{-1}) and Ref. [4] (7647–7918 cm^{-1}) by the study of the 6950–7653 cm^{-1} interval (see Fig. 1 of Ref. [4]). More than 8000 lines involving the four most abundant isotopologues ($^{14}N_2{}^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$ and $^{14}N_2{}^{18}O$) were detected. In the following, we present the rovibrational assignment of the spectrum performed on the basis of the predictions of the effective Hamiltonian models developed for each isotopologue [9–11], and the sets of the spectroscopic parameters derived from the band by band analysis.

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2. Experiment

2.1. The CW-CRDS spectrometer

The fibered Distributed Feed-Back diode laser CW-CRDS spectrometer was described in details in Refs. [12–14]. Each DFB diode laser has a typical tuning range of 7 nm ($\sim$35 cm^{-1}) by temperature tuning from -15 to 60 °C. Twenty four diode lasers were necessary to cover continuously the 6950–7653 cm^{-1} region. 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 35 ringdown events, thus giving one data point in the spectrum. Ringdown time values ranged between 90 and 220 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 (294.6 ± 0.3 K) were continuously monitored during the recordings. The spectra were obtained at pressure of 10.0 Torr. Additional recordings were performed at 2.00 Torr in the regions corresponding to the strongest lines which were sometimes too absorptive at 10 Torr.

The wavenumber calibration of the spectra was based on the values provided by a lambdameter (Burleigh WA1650). It was then refined using line positions of H_2O present as an impurity in the cell. Their values were taken from the HITRAN database [15]. The maximum differences between line positions measured on the overlapping part of two successive spectra are less than of 2×10^{-3} cm^{-1}. We then estimate to 1×10^{-3} cm^{-1} the average uncertainty on the line positions.

The sensitivity and high signal to noise ratio of the CRDS spectra are illustrated in Fig. 1. A noise equivalent absorption on the order of $\alpha_{min} \approx 1 \times 10^{-10}$ cm^{-1} was achieved. It led to the observation of a large number of lines involving many hot bands of the main isotopologue ($^{14}N_2{}^{16}O$) and the contribution of three minor isotopologues ($^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$ and $^{14}N_2{}^{18}O$) in "natural" isotopic abundance. As an example,

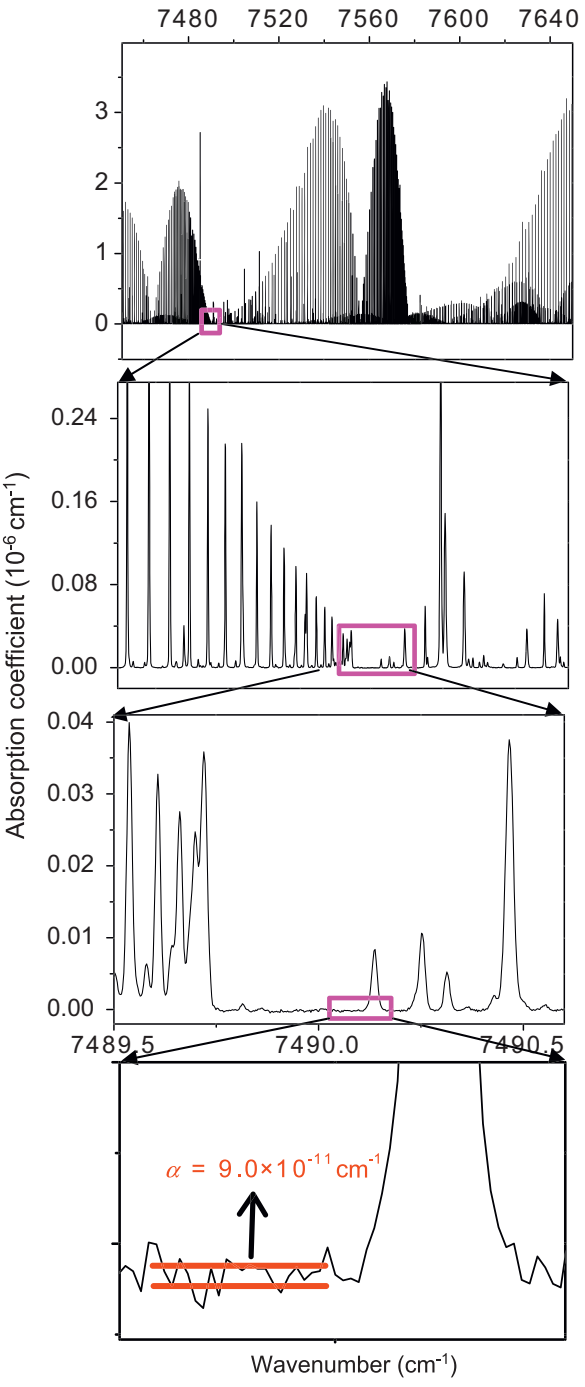

Fig. 1. CW-CRDS spectrum of N_2O near 7560 cm^{-1}. The sample pressure was 10.0 Torr. Four successive enlargements illustrate the high dynamics achieved by the CW-CRDS spectrometer allowing for the measurement of absorption coefficient differing by four orders of magnitude, from 3×10^{-6} cm^{-1} to the noise level at about 1×10^{-10} cm^{-1}.

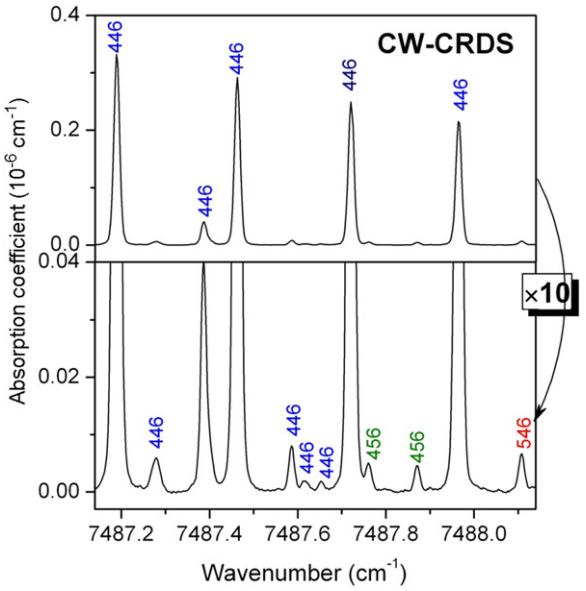

Fig. 2. Small section of the CW-CRDS spectrum of N_2O near 7488 cm^{-1} showing twelve transitions belonging to three isotopologues: $^{14}N_2{}^{16}O$ (446), $^{15}N^{14}N^{16}O$ (546) and $^{14}N^{15}N^{16}O$ (456).