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High sensitivity Cavity Ring Down Spectroscopy of N₂O near 1.22 μm: (I) Rovibrational assignments and band-by-band analysis

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ABSTRACT

The absorption spectrum of nitrous oxide (N₂O) in natural isotopic abundance has been recorded near 1.22 μm by Cavity Ring Down Spectroscopy using an External Cavity Diode Laser (ECDL) as light source. The room temperature recordings were performed at a pressure of 10.0 Torr in the 7915–8334 cm⁻¹ spectral range (1.26–1.19 μm). The typical noise equivalent absorption of the spectra, on the order of $\alpha_{min} \sim 2 \times 10^{-11}$ cm⁻¹, allowed for the detection of lines with intensities on the order of 5×10^{-29} cm/molecule.

More than 3300 transitions belonging to 64 bands of five nitrous oxide isotopologues (¹⁴N₂¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N₂¹⁸O and ¹⁴N₂¹⁷O) have been rovibrationally assigned on the basis of the predictions of the effective Hamiltonian models developed for each isotopologue. For comparison, only 13 bands were previously measured by Fourier Transform spectroscopy in the studied region. All identified bands belong to the $\Delta P=13$ and 14 series of transitions, where $P=2V_1+V_2+4V_3$ is the polyad number (V_i are vibrational quantum numbers). The line positions and intensities are provided for all assigned lines. The maximum deviations between the measured position values and those predicted by the effective Hamiltonian models are about 0.2 cm⁻¹ for the main isotopologue but reach values larger than 1 cm⁻¹ for the less abundant minor isotopologues.

The band-by-band analysis led to the determination of the rovibrational parameters of a total of 62 bands. The typical *rms* value of the ($\nu_{obs}-\nu_{fit}$) differences is 0.7×10^{-3} cm⁻¹. Among the 62 bands, 49 are newly measured, for 13 others the rotational analysis is significantly improved and extended. A few resonance perturbations due to intra- and inter-polyad couplings are identified and discussed.

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1. Introduction

In recent years, we have performed systematic investigations of the near infrared absorption spectrum of nitrous oxide by high sensitivity CW-Cavity Ring Down Spectroscopy (CW-CRDS) in the 5850–7920 cm⁻¹ region

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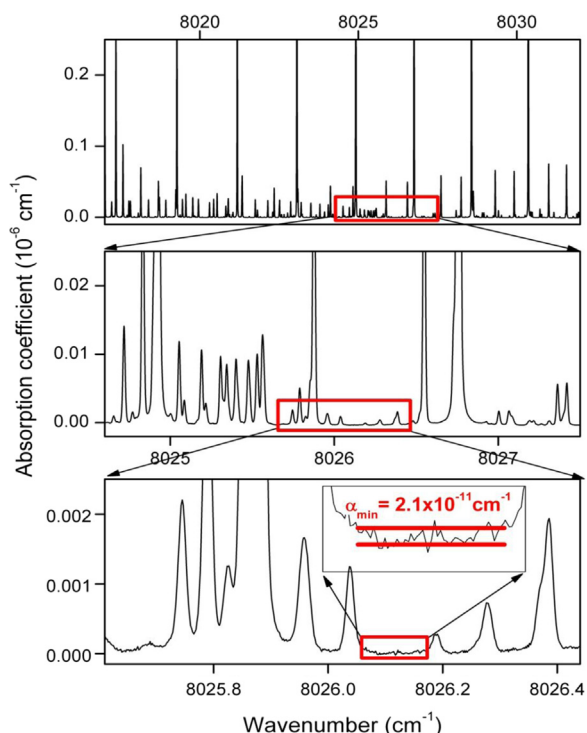


Fig. 1. CRDS spectrum of nitrous oxide in natural isotopic abundance ($P=10$ Torr). Three successive enlargements illustrate the high sensitivity and high dynamics of the recordings (noise equivalent absorption on the order of $\alpha_{\min} \sim 2.1 \times 10^{-11} \text{ cm}^{-1}$). The R branch of the 32021–10001 band of $^{14}\text{N}_2^{16}\text{O}$ at 8010.09 cm^{-1} is observed superimposed on the P branch of 30021–00001 band of $^{14}\text{N}_2^{16}\text{O}$ at 8083.95 cm^{-1} .

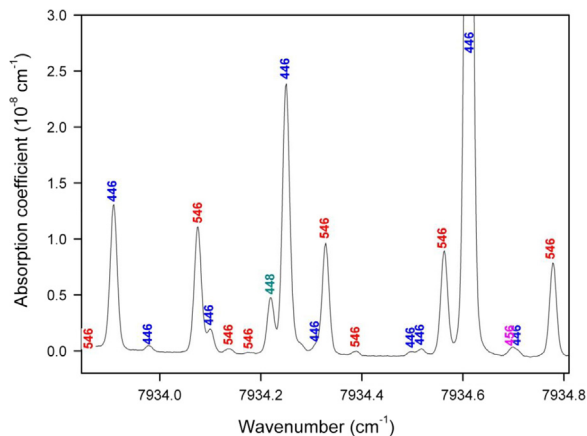


Fig. 2. CRDS spectrum of nitrous oxide in natural isotopic abundance recorded at 10 Torr near 7934.4 cm^{-1} . The displayed spectrum shows lines due to four isotopologues which are marked as: 446 ($^{14}\text{N}_2^{16}\text{O}$), 456 ($^{14}\text{N}^{15}\text{N}^{16}\text{O}$), 546 ($^{15}\text{N}^{14}\text{N}^{16}\text{O}$) and 448 ($^{14}\text{N}_2^{18}\text{O}$).

[1–6]. The unprecedented sensitivity of the recordings provided a considerable amount of new information. The spectral coverage was achieved thanks to a series of about ninety Distributed Feed Back (DFB) diode lasers, each of them allowing for a 30 cm^{-1} spectral coverage. In this work, we extend to higher frequency the spectral region

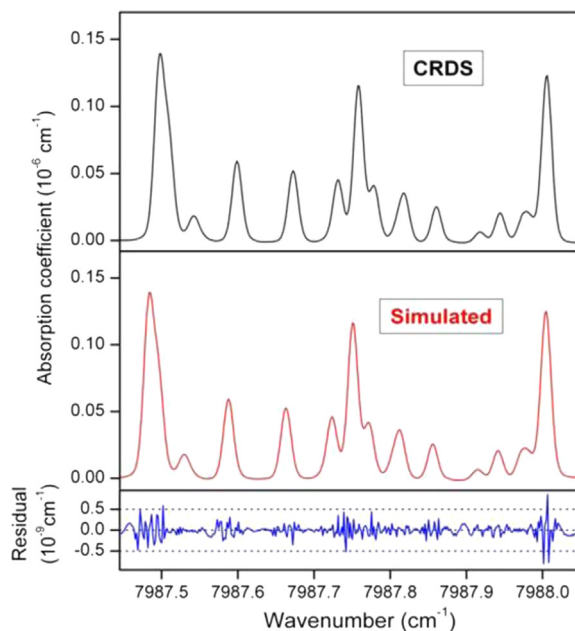


Fig. 3. Comparison of the CRDS spectrum of nitrous oxide in natural isotopic abundance recorded at 10 Torr with a simulation using a Voigt profile for each line. The residuals are displayed on the lower panel.

accessible with our CRDS spectrometers by using a fiber-connected External Cavity Diode Laser (ECDL) as light source. This set up gives access to the $7915\text{--}8334 \text{ cm}^{-1}$ spectral range for which only a few previous observations of N_2O bands were reported [7–9].

The present report is devoted to the rovibrational assignments and band-by-band analysis. In a future contribution, the constructed experimental line list and literature data will be used for refining and improving the parameters of the global effective operators for the various nitrous oxide isotopologues.

The paper is organized as follows. After a description of the experimental details (Section 2), the rovibrational assignment performed on the basis of the predictions of the effective Hamiltonian (EH) model [10–12] is presented in Section 3 together with the band by band fit. The comparison with the effective Hamiltonian predictions and the analysis of a number of intra- and inter-polyad resonance interactions are presented in Section 4.

2. Experiment

The CRDS spectrometer using a fiber-connected External Cavity Diode Laser (ECDL: Toptica DL pro, 1200 nm) is very similar to the CRDS spectrometer based on DFB diode laser used in the $5850\text{--}7920 \text{ cm}^{-1}$ region. The reader is referred to Refs. [13–15] for a general description.

The 1.40 m long CRDS cell is fitted by high reflectivity mirrors leading to ring down times of about $200 \mu\text{s}$ in the considered spectral interval. The CRDS cell was filled with nitrous oxide in natural isotopic abundance (Alphagaz 99.99% stated purity). The spectra were recorded at a

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