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High sensitivity cavity ring down spectroscopy of NO₂ between 7760 and 7917 cm⁻¹



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ABSTRACT

The very weak absorption spectrum of the main isotopologue of nitrogen dioxide, ¹⁴N¹⁶O₂, is investigated for the first time between 7760 and 7917 cm⁻¹. The studied region corresponds to the highest energy range of the vibrational spectra of ¹⁴N¹⁶O₂ investigated so far at high spectral resolution. The absorption spectra were recorded by very high sensitivity Continuous Wave-Cavity Ring Down Spectroscopy with a noise equivalent absorption of $\alpha_{\min} \approx 5 \times 10^{-11}$ cm⁻¹. The spectrum results from the superposition of the rovibrational transitions of the $2\nu_1+5\nu_2+\nu_3$, $2\nu_1+\nu_2+3\nu_3$ and $5\nu_1+\nu_3$ bands at 7790.9, 7888.2 and 7904.3 cm⁻¹, respectively. The spectrum assignment and modeling were performed using the effective Hamiltonian approach, which involves altogether three bright – (2,5,1), (2,1,3) and (5,0,1) and three dark – (2,7,0), (2,3,2) and (5,2,0) states. As a result, 3020 rovibrational transitions were assigned including 51 extra lines of the $2\nu_1+3\nu_2+2\nu_3$ and $5\nu_1+2\nu_3$ bands. In this way, the overall set of 1494 spin-rotation energy levels were reproduced with an *rms* of 4.9×10^{-3} cm⁻¹ for the (obs.–calc) deviations, leading to the determination of 66 fitted parameters. The effective Hamiltonian for the {(5,2,0), (2,3,2), (2,7,0), (2,5,1), (2,1,3), (5,0,1)} interacting states takes into account both the spin–rotation interactions within each vibrational state and C-type Coriolis and anharmonic resonances between different vibrational states, according to symmetry considerations. Indeed for NO₂ the $(\nu_1, \nu_2 \pm 2, \nu_3 \mp 1) \leftrightarrow (\nu_1, \nu_2, \nu_3)$ spin rotation energy levels are usually coupled through C-type Coriolis resonances, and accordingly the (2,7,0) ↔ (2,5,1) ↔ (2,3,2) ↔ (2,1,3) and (5,2,0) ↔ (5,0,1) interactions were included in the effective Hamiltonian model. Furthermore, these two blocks of interacting states are coupled by an additional C-type Coriolis and anharmonic resonances. Using the fitted values of the Hamiltonian parameters and the values of the $2\nu_1+5\nu_2+\nu_3$, $2\nu_1+\nu_2+3\nu_3$ and $5\nu_1+\nu_3$ bands transition dipole moment operators determined from a fit of a selected set of experimental line intensities, a synthetic spectrum was generated for the entire investigated region and is provided as [Supplementary material](#).

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1. Introduction

¹⁴N¹⁶O₂ is an asymmetric rotor with \tilde{X}^2A_1 ground electronic state. The vibrational frequencies are 1320 and

1617 cm⁻¹, for the symmetric (ω_1) and antisymmetric (ω_3) NO stretching modes respectively, and 750 cm⁻¹ for the ONO bending mode (ω_2). The infrared bands exhibit a doublet structure due to the electron spin–rotation interaction.

The absorption spectrum of nitrogen dioxide has been extensively studied in the infrared because of the high interest of this species for remote sensing in the atmosphere.

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Part of the spectroscopic studies has been implemented in the HITRAN [1] and GEISA [2] databases. Fig. 1 shows an overview of the different bands listed in the HITRAN database and analyzed in the literature by Fourier Transform Spectroscopy (FTS) [3–13] and Continuous Wave–Cavity Ring Down Spectroscopy (CW-CRDS) [14,15, this work] below and above 6100 cm^{-1} , respectively.

Fig. 1 illustrates the steep decrease of the band intensities with increasing wavenumber. The ν_3 and $\nu_1+\nu_3$ bands near 6.2 and $3.4\text{ }\mu\text{m}$ are the strongest infrared bands with line intensities on the order of 1×10^{-19} and $1 \times 10^{-20}\text{ cm/molecule}$, respectively. The most excited vibrational band reported so far from FTS absorption spectra is the $\nu_1+3\nu_3$ band near 5984 cm^{-1} with maximum line intensities on the order of $2 \times 10^{-23}\text{ cm/molecule}$ [12] while the bands presently investigated by CRDS are more than three orders of magnitude weaker, i.e. seven orders of magnitude weaker than the ν_3 band. Some vibrational bands are expected to be observable with very high sensitivity absorption techniques up to 9750 cm^{-1} where they will be obscured by the much stronger first rovibronic bands of the $\tilde{A}^2B_2-\tilde{X}^2A_1$ electronic transition [15]. Nevertheless, overall only a small fraction of the vibrational states are observable by absorption from the ground vibrational state (most of them involve an odd excitation number of the ν_3 antisymmetric stretch and no bending excitation). The other upper states remain “dark” states unobserved in absorption.

In fact, the complete set of the 191 lowest vibrational levels of the \tilde{X}^2A_1 ground electronic state up to $10,161\text{ cm}^{-1}$ [17] was determined 20 years ago by Delon and Jost using Laser Induced Dispersed Fluorescence Spectroscopy (LIDFS) in a jet expansion. Interestingly, these vibrational term values could be reproduced with a typical residual error of 0.5 cm^{-1} using a 24 coefficients Dunham expansion. This regular behavior of the vibrational pattern (except for a (ν_1, ν_2, ν_3) – $(\nu_1\mp 3, \nu_2 \pm 1, \nu_3 \pm 2)$ anharmonic resonance which will be commented below) contrasts with the importance of rovibrational interactions affecting the rotational structure,

making particularly difficult the modeling of the high resolution rovibrational spectrum at room temperature. For instance, in most of the analyzed spectra [6–15], strong C-type Coriolis resonance interaction was found to couple the spin-rotational levels of the (ν_1, ν_2, ν_3) and $(\nu_1, \nu_2 \pm 2, \nu_3 \mp 1)$ vibrational states.

In the present work, we continue the systematic investigation of the high energy absorption bands of $^{14}\text{N}^{16}\text{O}_2$ spectra by CW-CRDS in the 5850 – 8000 cm^{-1} . In the two first contributions, we reported the analysis of the $4\nu_1+\nu_3$ [14] and $5\nu_3$ [15] bands near 6677 and 7766 cm^{-1} , respectively. The present work is devoted to the 7760 – 7917 cm^{-1} interval corresponding to the highest excited vibrational bands of nitrogen dioxide investigated so far by high resolution absorption spectroscopy.

The rest of the report is organized as follows. Experimental aspects are presented in the next Section 2. Section 3 includes the vibration–rotation assignments and the derivation of the upper energy levels. In Section 4, we present the modeling of the spectrum using an effective Hamiltonian model which accounts for explicitly spin–rotation interactions. Using transition dipole moment operator determined from a fit of a selected set of experimental line intensities, a synthetic spectrum is computed and compared to the experimental spectrum.

2. Experimental details

The spectrum of nitrogen dioxide analyzed in this work corresponds to the high energy range (7760 – 7917 cm^{-1}) of the recordings of Ref. [16] extending from 7376 to 7917 cm^{-1} . The pressure of the recordings was 10.0 Torr in the 7583 – 7797 cm^{-1} interval and 5.0 Torr outside this interval. The experimental setup is described in details in Ref. [18]. Briefly, our fibered CW-CRDS spectrometer uses a series of distributed feedback (DFB) laser diodes as light sources. Each DFB laser diode has a typical tuning range of about 35 cm^{-1} by temperature tuning from $-10\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$. The stainless steel CRDS cell ($l=1.4\text{ m}$, inner diameter $\phi=11.5\text{ mm}$) is fitted by a pair of super-mirrors whose reflectivity allows for ring down times on the order of $100\text{ }\mu\text{s}$. About 30 ringdown events were averaged for each spectral data point separated by about $2.5 \times 10^{-3}\text{ cm}^{-1}$ and the complete temperature scan of one DFB laser was achieved after about 65 min. In the investigated region, the achieved noise equivalent absorption is typically $\alpha_{\text{min}} \sim 1 \times 10^{-10}\text{ cm}^{-1}$. The gas pressure was continuously monitored by a capacitance gauge (Model 626, 100 Torr, MKS instrument, 0.25% accuracy). The cell temperature was $294.3 \pm 0.1\text{ K}$. In these conditions, the gas sample consists in a mixture of NO_2 monomers and N_2O_4 dimers. The monomer partial pressure is determined using the equation:

$$P(\text{NO}_2)^2 = K_P P(\text{N}_2\text{O}_4) \quad (1)$$

where K_P is the equilibrium constant whose value is 76 Torr at 294 K [19]. The resulting NO_2 partial pressures are $P(\text{NO}_2)=8.95\text{ Torr}$ and 4.71 Torr for the 10 Torr and 5 Torr total pressure, respectively.

Each 35 cm^{-1} wide spectrum corresponding to one DFB recording was calibrated on the basis of the wavenumber

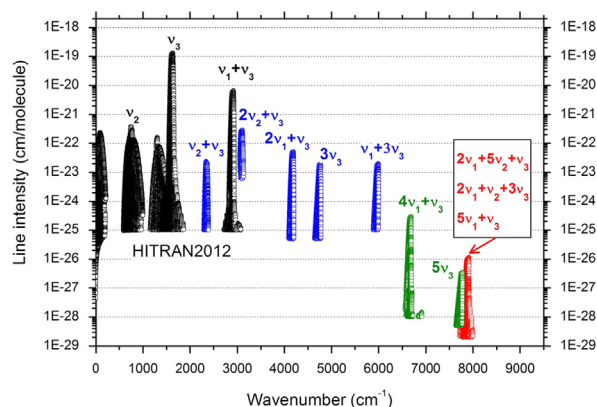


Fig. 1. Overview of the $^{14}\text{N}^{16}\text{O}_2$ line lists available in the literature. The different colors correspond to the available linelists: HITRAN database [1] in black, several FTS studies of Refs. [3–13] in blue, two recent CW-CRDS analysis [14,15] in green and this work in red. (For interpretation of references to color in this figure legend, the reader is referred to the web version of this article.)

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