



High sensitivity Cavity Ring Down Spectroscopy of the $2\nu_1 + 3\nu_2 + \nu_3$ band of NO_2 near $1.57 \mu\text{m}$



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ABSTRACT

The weak $2\nu_1 + 3\nu_2 + \nu_3$ absorption band of the nitrogen dioxide main isotopologue ($^{14}\text{N}^{16}\text{O}_2$) is investigated near 6350 cm^{-1} . The absorption spectrum was recorded by high sensitivity Cavity Ring Down Spectroscopy with a noise equivalent absorption of $\alpha_{\text{min}} \approx 1 \times 10^{-10} \text{ cm}^{-1}$. In total, 1069 lines of the $2\nu_1 + 3\nu_2 + \nu_3$ band were assigned with rotational quantum numbers N and K_a up to 48 and 8, respectively, that corresponds to 1276 vibration-rotation transitions. The derived set of line positions is reproduced with an effective Hamiltonian with an *rms* of $2.35 \times 10^{-3} \text{ cm}^{-1}$ for the (obs.-calc.) deviations. The effective Hamiltonian takes explicitly into account the Coriolis interactions between the spin rotational levels of the (2,3,1) upper vibrational state and those of two nearby dark states - (2,5,0) and (2,1,2) - together with the electron spin-rotation interactions. Using the corresponding eigenfunctions the principal effective dipole moment parameter responsible for the line intensities of the $2\nu_1 + 3\nu_2 + \nu_3$ band is fitted to selected measured line intensities which are reproduced with an *rms* deviation of 6.2%.

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1. Introduction

Nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) is an important atmospheric trace species which is predominantly generated as tropospheric pollutant through the burning of fossil fuels and contributes to the pollution of the troposphere. Accurate measurements of NO_2 concentration in the atmosphere are now commonly performed in the 6.2 and $3.4 \mu\text{m}$ regions which correspond to the ν_3 and $\nu_1 + \nu_3$ bands, respectively, by means of infrared remote sensing methods [1,2]. In the stratosphere, nitrogen dioxide contributes to the natural regulation of ozone via photochemical reactions involving NO. The high temperature infrared spectrum of nitrogen dioxide is needed for a number of applications as the NO_2 detection in hot plumes emitted by industrial furnaces and engines [3] or in exoplanets [4]. A high-resolution, high-temperature Nitrogen Dioxide Spectroscopic Databank (NDS-1000) [5] has been recently released for high temperature applications. It is based on the global modeling of the line positions and intensities performed within the framework of the method of effective operators [6] and on the calculated val-

ues of line shape parameters. The databank is presently limited to five spectral regions in the $466\text{--}4776 \text{ cm}^{-1}$ spectral range. As summarized on Fig. 1 of Ref. [7], additional bands have been reported above 5000 cm^{-1} and are not yet incorporated in spectroscopic databases like the HITRAN [8] and GEISA [9] databases. As a result of the decrease of the band intensities at high wavenumbers, high sensitivity methods are needed to detect the near infrared bands. The review of the literature above 5000 cm^{-1} indicates that the previous observations are the $\nu_1 + 3\nu_3$ band at 5984.7 cm^{-1} measured by Fourier Transform Spectroscopy (FTS) [10], the $2\nu_1 + 3\nu_3$ band at 7192.2 cm^{-1} detected by Incoherent Broad Band-Cavity Enhanced Absorption Spectroscopy (IBB-CEAS) [11] and our recent CRDS studies of the $4\nu_1 + \nu_3$ and $3\nu_1 + 3\nu_2 + \nu_3$ bands at 6676.9 and 7587.0 cm^{-1} [12,13], respectively and of five bands between 7650 and 7900 cm^{-1} [14,15].

The present work aims at further improving the characterization of the near infrared spectrum of nitrogen dioxide in the \tilde{X}^2A_1 ground state focusing on the $2\nu_1 + 3\nu_2 + \nu_3$ band centered at 6351.4 cm^{-1} . The experimental spectrum under analysis is part of a new CRDS spectrum recorded in Grenoble between 5855 and 6410 cm^{-1} . As illustrated on the spectrum overview presented in Fig. 1, the $2\nu_1 + 3\nu_2 + \nu_3$ band is more than three orders of magnitude weaker than the $\nu_1 + 3\nu_3$ band. The $3\nu_1 + \nu_2 + \nu_3$ and $4\nu_3$

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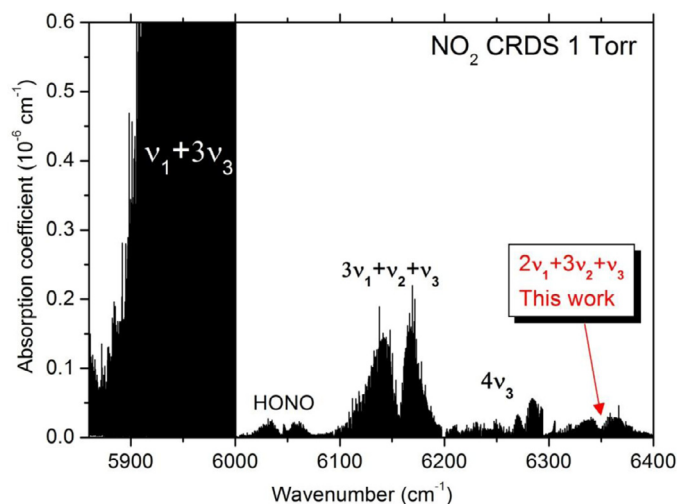


Fig. 1. Overview of the CRDS spectrum of NO_2 in the $5860\text{--}6400\text{ cm}^{-1}$ region ($P \approx 1$ Torr). The spectrum was cleaned from a few CO lines near 6316 cm^{-1} and CO_2 lines near 6227 cm^{-1} and 6347 cm^{-1} present as impurities. The $2\nu_1 + 3\nu_2 + \nu_3$ band of nitrous acid (HONO) present as an impurity is observed near 6046 cm^{-1} .

bands at 6156 and 6276 cm^{-1} , respectively, appear in the studied interval and will be reported separately.

The rest part of the article is organized as follows. Experimental aspects are presented in the next Section 2. Section 3 includes the vibration-rotation assignments and the modeling of the spectrum using an effective Hamiltonian model which accounts for explicitly spin-rotation interactions and couplings with two nearby dark states. In Section 4, some peculiarities of the $2\nu_1 + 2\nu_2 + \nu_3$ band are discussed while in Section 5, line intensities are modeled using an effective transition dipole moment operator determined from a fit of a selected set of experimental line intensities.

2. Experimental details and line parameters retrieval

The spectrum of nitrogen dioxide displayed on Fig. 1 was recorded with our fibre-connected Cavity Ring Down spectrometer described in Refs. [16,17]. A series of twenty five Distributed Feedback (DFB) laser diodes was used as light sources to cover the $5855\text{--}6410\text{ cm}^{-1}$ spectral region. Each laser diode allows for a spectral interval coverage of about 30 cm^{-1} by changing continuously the laser temperature from $-10\text{ }^\circ\text{C}$ to $60\text{ }^\circ\text{C}$. A 10% fraction of the DFB light was sent into a commercial Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 h, 100 Hz refresh rate) allowing measuring the emitted frequency. The calibration was checked and refined using reference line positions of H_2O present as an impurity using HITRAN2012 line positions [8].

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 $250\text{ }\mu\text{s}$. About 10 ring-down events were averaged for each spectral data point separated by about $2 \times 10^{-3}\text{ cm}^{-1}$ 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, 10 Torr, MKS instrument; 0.25% accuracy). The filling pressure was 1.00 Torr. Note that during the scan of the DFB laser diodes the pressure was observed to slightly decrease (up to 10%) as a result of the adsorption on the walls of the CRD cell or unknown chemical reaction. The pressure value used for the intensity calculation is the pressure value measured at the exact recording time of the considered absorption line. The cell temperature was $297.3 \pm 0.5\text{ K}$. 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 [18]. The resulting NO_2 partial pressure is $P(\text{NO}_2) = 0.987$ Torr for a 1.0 Torr total pressure.

The spectral line parameters in the $6288\text{--}6408\text{ cm}^{-1}$ spectral region were retrieved using the multiline fitting computer code described in Ref. [19] which determines the line parameters by adjustment of the synthetic spectrum to the observed one. This computer code uses for line shape the different kinds of the contour describing the pressure broadening and Doppler effect simultaneously. In the present paper, the spectral line shape was modeled with the Voigt profile in which the calculated value for the Doppler line width was used and the collision broadening coefficient was fixed to the HITRAN value of $0.095\text{ cm}^{-1}\text{atm}^{-1}$ [8]. The observed spectrum is very dense. All overlapped lines were fitted with a base line assumed to be constant over the fitted spectral interval. The adjustable parameters were then the position and intensity of each line and the base line constant. The sample of spectrum displayed in Fig. 2 illustrates the achieved spectrum reproduction with the retrieved line parameters. The intensity diagram of all retrieved lines (full peak list) is also presented in this figure (panel b). In panel (a) we selected the assigned lines (see Section 3) from the full peak list. Overall, the parameters of more than 3000 lines were retrieved in the $6288\text{--}6410\text{ cm}^{-1}$ interval. Note that in the case of unresolved spin-rotational doublets, we often fitted the absorption feature as a single line. Line intensities range between about 10^{-28} and $10^{-26}\text{ cm}^2/\text{molecule}$. Because of the weakness and blending of the majority of the lines the averaged accuracy of the retrieved line intensities was estimated to be about 20% or worse for the very weak or strongly blended lines. We estimate to $1 \times 10^{-3}\text{ cm}^{-1}$ the uncertainty on the position of well isolated lines as checked by comparison of the positions of CO lines present as an impurity which are observed near 6330 cm^{-1} .

3. Spectrum assignment and modeling

3.1. Effective Hamiltonian model

Preliminary spectrum assignment was performed using the predictions of the global effective Hamiltonian [6] but the accuracy of the predictions was not sufficient to perform the complete assignment. Thus, we perform a spectrum modeling using a local effective Hamiltonian (EH) limited to the $6288\text{--}6408\text{ cm}^{-1}$ region dominated by the $2\nu_1 + 3\nu_2 + \nu_3$ band. The EH takes into account the electron spin-rotation (SR) interaction and the second order resonance Coriolis interactions of the (2,3,1) upper vibrational state with two vibrational dark states, (2,5,0) and (2,1,2). According to Ref. [20], the vibrational energies of these states are close to each other: (2,3,1) – 6351.40 cm^{-1} , (2,5,0) – 6299.70 cm^{-1} and (2,1,2) – 6414.16 cm^{-1} . The scheme of the effective Hamiltonian matrix in the basis of products of harmonic oscillator eigenfunctions $|v_1, v_2, v_3\rangle$ and eigenfunctions of the rigid symmetric top $|NK\rangle$ and spin $|\sigma\rangle$ operators is given in Fig. 3. Here J , N and S are the quantum numbers of total, rotational and electron spin angular momentum quantum numbers, respectively, K and σ are the quantum numbers associated to the projection on the molecular-fixed z axis of the rotational and the electron spin operators, respectively.

In the scheme presented in Fig. 3 H_{VR} is the Watson-type Hamiltonian in I' representation [21]:

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