



High sensitivity cavity ring down spectroscopy of the $4\nu_3$ band of NO_2 near $1.59\ \mu\text{m}$



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ABSTRACT

The very weak $4\nu_3$ B-type absorption band of the nitrogen dioxide main isotopologue ($^{14}\text{N}^{16}\text{O}_2$) is investigated between 6175 and $6350\ \text{cm}^{-1}$. The absorption spectrum of this band was recorded by high sensitivity continuous wave-cavity ring down spectroscopy with noise equivalent absorption of $\alpha_{\text{min}} \approx 1 \times 10^{-10}\ \text{cm}^{-1}$. More than 1630 lines of the $4\nu_3$ band are assigned with rotational quantum numbers N and K_a up to 55 and 7, respectively, what corresponds to 1731 spin-rotation-vibration transitions. The overall measured set of the line positions is used to fit the effective Hamiltonian parameters. The effective Hamiltonian takes explicitly into account the Coriolis interactions between the spin rotational levels of the $(0,0,4)$ vibrational state and those of the nearby $(0,2,3)$ bright state at $6183.61\ \text{cm}^{-1}$ together with the electron spin-rotation interactions. The fitted set of the parameters reproduces the observed line positions with an *rms* of $2.2 \times 10^{-3}\ \text{cm}^{-1}$. A selected set of the measured line intensities are used to determine the effective dipole moment parameters including the Herman–Wallis type parameters describing the line intensities of the $4\nu_3$ band. The *rms* deviation of the fit is 5.7%.

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1. Introduction

This study completes the analysis of the very weak near infrared spectrum of nitrogen dioxide between 5855 and $6410\ \text{cm}^{-1}$ recorded in Grenoble by cavity ring down spectroscopy (CRDS). The overview of this spectrum is presented in Fig. 1 of our recent paper [1] where the analysis of the $2\nu_1 + 3\nu_2 + \nu_3$ A-type band centered at $6350\ \text{cm}^{-1}$ was reported. In Ref. [2], the $3\nu_1 + \nu_2 + \nu_3$ and $2\nu_2 + 3\nu_3$ A-type bands lying in the 6100 – $6200\ \text{cm}^{-1}$ region were assigned and modeled. The present contribution is devoted to the $4\nu_3$ B-type band centered at $6275\ \text{cm}^{-1}$. This band is the most excited B-type “bright” band ever observed in NO_2 . Usually B-type bands have considerably smaller intensities compared to A-type bands with the same variation, $\sum_i |\Delta V_i|$ of the sum of the V_i vibrational quantum numbers ($i = 1, 2, 3$). Consequently, above the $2\nu_3$ B-type band centered at $3201\ \text{cm}^{-1}$, only a few lines of five B-type “dark” bands were observed. They are all due to an intensity transfer from a nearby A-type band in local resonance interaction: (i) Two lines of the $2\nu_1 + 2\nu_2$ band were reported in Ref. [3] due to the line intensity transfer from the $2\nu_1 + \nu_3$ A-type band,

(ii) Sixty lines of the $\nu_1 + 2\nu_2 + 2\nu_3$ band were assigned in Ref. [4]. They borrow intensity from the $\nu_1 + 3\nu_3$ band, (iii) five lines of the $2\nu_1 + 2\nu_2 + 2\nu_3$ band were reported in Ref. [5] due to the line intensity transfer from the $2\nu_1 + 3\nu_3$ band. Thirty six lines of the $2\nu_1 + 3\nu_2 + 2\nu_3$ band and fifteen lines of the $5\nu_1 + 2\nu_2$ band were observed in Ref. [6] due to the line intensity transfer from the $2\nu_1 + \nu_2 + 3\nu_3$ and $5\nu_1 + \nu_3$ bands, respectively. Practically all B-type bands borrow their line intensities via Coriolis interactions from the neighboring stronger A-type bands. It leads to the importance of the Herman–Wallis terms in the expansion of the transition dipole moment squared. Indeed, while in the case of A-type band, only the principal effective dipole moment parameter is generally sufficient to reproduce the line intensities with a reasonable accuracy, it is not the case for the B-type bands. This will be demonstrated below on the example of the studied $4\nu_3$ band which has line positions mostly unperturbed while line intensities are greatly influenced by a non-resonant first-order Coriolis interaction with the considerably stronger A-type $\nu_1 + 3\nu_3$ band.

2. Experimental details and line parameters retrieval

The reader is referred to Refs. [7,8] for a detailed description of the used fiber-connected cavity ring down spectrometer. The recording of the CRDS spectra under study is presented in details

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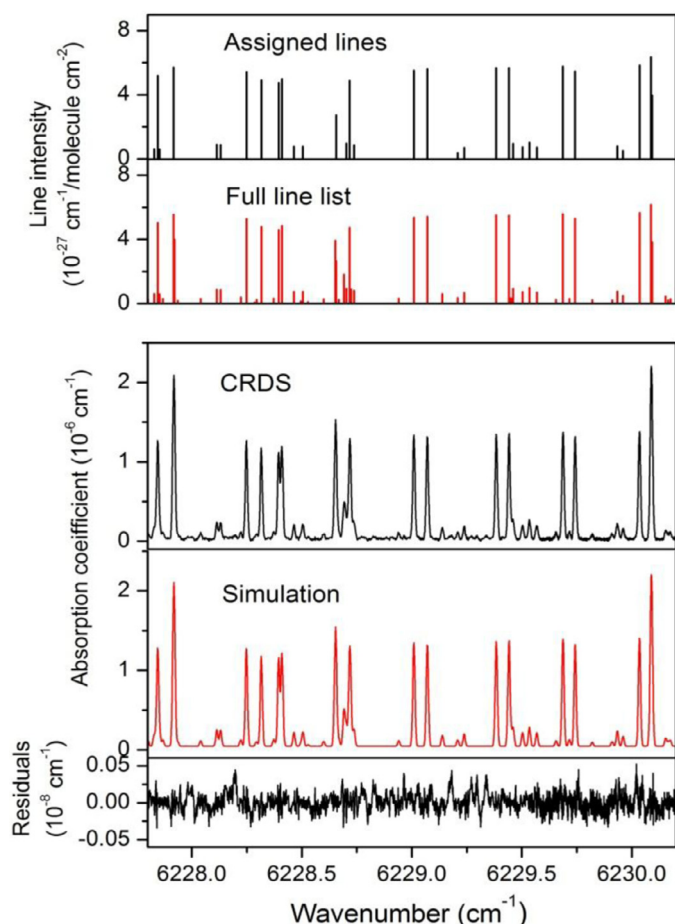


Fig. 1. Spectrum and line list of NO_2 near 6229 cm^{-1} . The three lower panels show the CRDS spectrum recorded at 1.0 Torr, the simulation performed with a multiline fitting program and the corresponding (sim.- meas.) residuals. The two upper panels show the full line list and the stick spectrum limited to the assigned lines.

in Ref. [1]. Seven Distributed Feedback (DFB) laser diodes were used as light sources to cover the $6180\text{--}6350 \text{ cm}^{-1}$ spectral region under study. The noise-equivalent absorption of the spectrum is $\alpha_{\min} \sim 1 \times 10^{-10} \text{ cm}^{-1}$. The frequency calibration was performed using a commercial Fizeau type wavemeter. We estimate an uncertainty of $1 \times 10^{-3} \text{ cm}^{-1}$ for the position of well isolated lines as checked by comparison of the measured line positions of the 30013–00001 band of $^{12}\text{C}^{16}\text{O}_2$ present as an impurity compared to those given by HITRAN2012 database [9].

The filling pressure was 1.00 Torr and the temperature was $297.3 \pm 0.3 \text{ K}$. Taking into account the $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$ dimerisation equilibrium, it corresponds to an NO_2 partial pressure of 0.987 Torr [1].

The line parameter retrieval uses the multiline fitting computer code described in Ref. [10]. 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 at 296 K ($0.095 \text{ cm}^{-1} \text{ atm}^{-1}$ [9]). Overall, the center and intensity of more than 3000 lines were retrieved in the $6180\text{--}6347 \text{ cm}^{-1}$ 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 10^{-28} and $10^{-26} \text{ cm}^{-1}/(\text{molecule cm}^{-2})$ at 296 K. The sample of spectrum displayed in Fig. 1 illustrates the achieved spectrum reproduction with the retrieved line parameters. Because of the weakness and blending of the majority of the lines the averaged accuracy of the retrieved line intensities is estimated to be about 20% or even worse for the very

weak or strongly blended lines. A selected set of 230 lines were used to derive effective dipole moment parameters (see below). The uncertainty of their intensities is estimated to be on the level of 5%.

3. Spectrum assignment and modeling

3.1. Spectrum assignment

In the lower wavenumber region ($6180\text{--}6200 \text{ cm}^{-1}$), the $4\nu_3$ band overlaps with the $3\nu_1 + \nu_2 + \nu_3$ and $2\nu_2 + 3\nu_3$ bands analyzed in Ref. [2]. In the upper wavenumber region ($6290\text{--}6347 \text{ cm}^{-1}$), it overlaps with the $2\nu_1 + 3\nu_2 + \nu_3$ band studied in Ref. [1].

For the considered $4\nu_3$ B-type band, only the $\Delta K_a = \pm 1$ transitions are observable. The assignments were performed by comparison to a predicted spectrum with line positions calculated using an effective Hamiltonian (EH) of the (0,0,4) vibrational state. This EH takes into account both vibration-rotation and electron spin-rotation (SR) interactions. For the initial values of the (0,0,4) effective Hamiltonian parameters, the predictions of the global effective Hamiltonian of $^{14}\text{N}^{16}\text{O}_2$ were adopted [11] except for the (0,0,4) initial vibrational energy (6275.98 cm^{-1}) which was taken from Ref. [12]. The ground state energy levels were calculated using the ground state parameters of Ref. [13]. In parallel the line intensity calculations were performed using the effective dipole moment parameters fitted to the selected values of the measured line intensities.

The analyzed spectrum contains a number of doublets involving upper and lower SR energy levels with the same N value, but different J rotational quantum numbers ($J = N \pm 1/2$). At the initial stage of the assignments, the dependence of the SR splitting versus N and K_a was a main criterion. Thus the preliminary assignment was performed basing on the agreement between the observed and calculated values of the splitting of the electron spin-rotation doublets as well as on the agreement between observed and calculated line intensities. Note that the measured values of the SR splittings were found in a very good agreement with their values predicted using the global effective Hamiltonian [11].

The newly assigned transitions were progressively included in the line position fitting and the refined effective Hamiltonian parameters were used to improve the prediction. In this way more than 1300 transitions of the $4\nu_3$ band were assigned. In order to validate and extend the assignments, ground state combination differences (GSCD) relations were systematically used with the help of the respective computer code [14]. Finally, 1731 spin-rotation-vibration transitions with N and K_a quantum numbers up to 55 and 7, respectively, were assigned that correspond to 616 SR energy levels of the (0,0,4) upper state. Fig. 2 shows a portion of the $R_{\Delta K_a=1}(N, K_a=0)$ series of transitions in the $6291\text{--}6294 \text{ cm}^{-1}$ spectral region. The displayed interval corresponds the band head of the $R_{\Delta K_a=1}(N, K_a=0)$ series.

3.2. Effective Hamiltonian model

The scheme of the effective Hamiltonian matrix in the basis of products of harmonic oscillator eigenfunctions (V_1, V_2, V_3) 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 total, rotational and electron spin angular momentum quantum numbers, respectively, K and σ are the quantum numbers associated with the projection on the molecular-fixed z axis of the rotational and the electron spin operators, respectively. The reader is referred to Ref. [1] for the explicit expression of the Watson-type Hamiltonian (H_{VR}) electron spin-rotation interaction operator (H_{SR}) and second order Coriolis interaction operator (H^{2C}) appearing in the effective Hamiltonian.

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