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High sensitivity cavity ring down spectroscopy of the $3\nu_1 + 3\nu_2 + \nu_3$ band of NO_2 near 7587 cm^{-1}



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ABSTRACT

The very weak $3\nu_1 + 3\nu_2 + \nu_3$ absorption band of the main isotopologue of nitrogen dioxide, $^{14}\text{N}^{16}\text{O}_2$, is investigated for the first time near 7587 cm^{-1} . The absorption spectrum was recorded by high sensitivity Continuous Wave-Cavity Ring Down Spectroscopy with a noise equivalent absorption of $\alpha_{\min} \approx 1 \times 10^{-10} \text{ cm}^{-1}$. 414 lines of the $3\nu_1 + 3\nu_2 + \nu_3$ band were assigned with rotational quantum numbers N and K_a as high as 32 and 6, respectively, what corresponds to 518 rotation–vibration transitions. The overall set of spin–rotation energy levels was modeled in the frame of the effective Hamiltonian approach and reproduced with an RMS of $6 \times 10^{-3} \text{ cm}^{-1}$ for the (obs.–calc.) deviations. The effective Hamiltonian includes interactions with three nearby dark states – (350), (062) and (312) – in Coriolis interaction with the (331) bright state. Using a selected set of experimental line intensities and the fitted values of the vibration–rotation Hamiltonian parameters, the principal parameter in the dipole moment operator expansion is determined for the $3\nu_1 + 3\nu_2 + \nu_3$ band. With maximum line intensity on the order of $2.5 \times 10^{-27} \text{ cm}^2/\text{molecule}$ at 296 K, the $3\nu_1 + 3\nu_2 + \nu_3$ band is the weakest band of the NO_2 molecule rovibronically assigned so far.

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1. Introduction

In this paper, we continue the analysis of the spectrum of nitrogen dioxide recorded by high sensitivity Cavity Ring Down Spectroscopy (CRDS) between 7376 and 7920 cm^{-1} [1,2]. This spectral range corresponds to the most excited NO_2 vibrational bands studied so far at high resolution. Fig. 1 shows an overview of the CRDS spectrum

in 7550 – 7920 cm^{-1} region and indicates the bands previously analyzed. The well isolated (005)–(000) band located in the 7640 – 7780 cm^{-1} region has been identified and modeled in Ref. [1]. In Ref. [2], the three highly excited bands – (251)–(000), (213)–(000) and (501)–(000) – were assigned between 7780 and 7920 cm^{-1} . A system of seven interacting states including four dark states was developed to reproduce the experimental spin–rotational (SR) energy levels of the three upper states. The present contribution is devoted to the very weak (331)–(000) vibrational band centred at 7587.04 cm^{-1} [3]. The overview of Fig. 1 including the calculated stick spectrum shows that the

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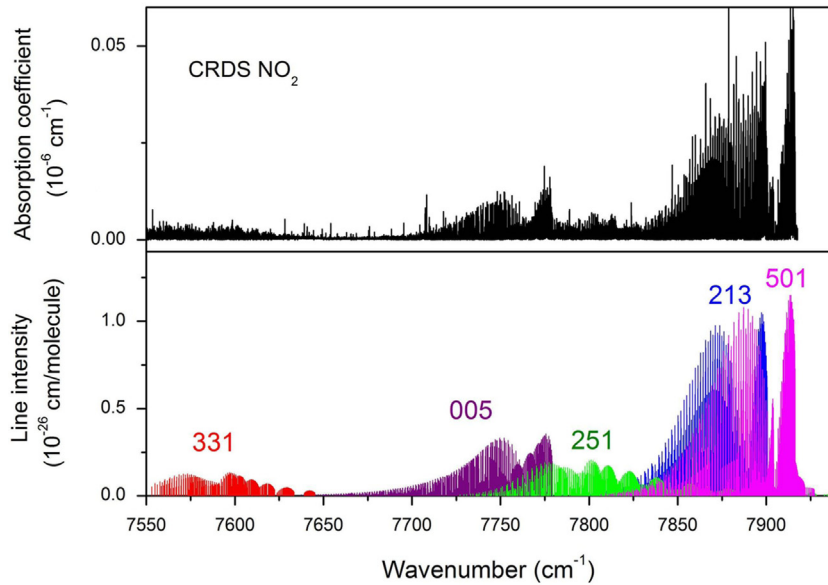


Fig. 1. Overview of the CRDS observed and calculated spectra between 7550 and 7920 cm^{-1} region. The present work is devoted to the analysis of the $3\nu_1+3\nu_2+\nu_3$ band near 7587 cm^{-1} . The other bands of the region were reported in Refs. [1,2].

presently investigated (331)-(000) band is the weakest in the region.

2. Experimental details and line parameters' retrieval

Our fiber connected DFB CW-CRDS spectrometer is described in details in Ref. [4]. The spectrum of nitrogen dioxide under analysis corresponds to a section of the CRDS recordings extending from 7376 to 7917 cm^{-1} as described in Ref. [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 ring down times of the CRDS cell was on the order of 100 μs . 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 (about 35 cm^{-1}) was achieved after about 65 min. The achieved noise equivalent absorption is typically $\alpha_{\min} \sim 1 \times 10^{-10} \text{ cm}^{-1}$. The cell temperature was $294.3 \pm 0.1 \text{ K}$. In these conditions, the gas sample consists of NO_2 monomers and N_2O_4 dimers. The monomer partial pressure was calculated in Ref. [2] and corresponds to 8.95 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 values provided by a Fizeau type wavemeter (WSU-30, Highfinesse). The calibration was further refined by stretching the whole spectrum in order to match accurate positions of HITRAN database reference lines of H_2O [5] present as an impurity in the sample. The typical absolute uncertainty on the line positions is estimated to be better than $1 \times 10^{-3} \text{ cm}^{-1}$.

A homemade computer code [6] was used to derive the line positions and intensities assuming a Voigt profile for the line shape. A typical example of the spectrum

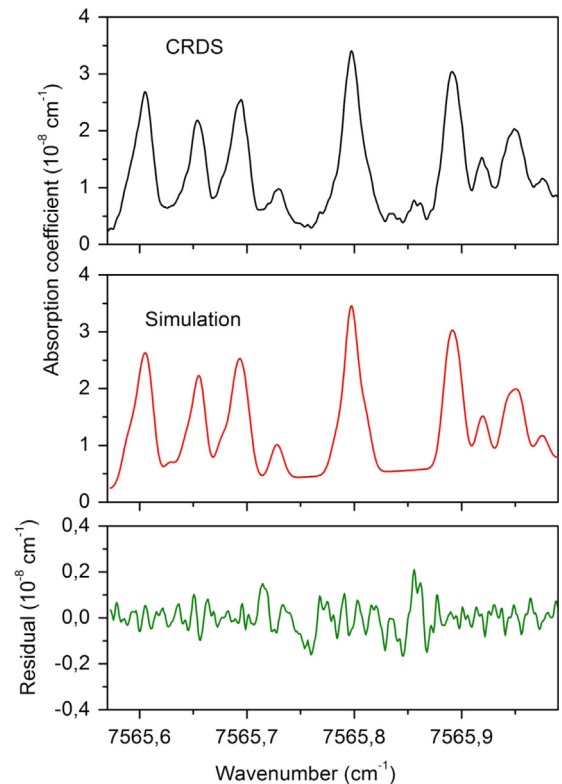


Fig. 2. Example of reproduction of the NO_2 CRDS spectrum recorded at 10.0 Torr using a multiline profile simulation.

reproduction is shown in Fig. 2. As a result of the weakness of the analyzed transitions, we estimate the average accuracy of the retrieved intensities to be about 20% and worse for the weakest or strongly blended lines. Note that

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