

New high-resolution analysis of the $\nu_1 + 3\nu_3$ band of nitrogen dioxide in the near infrared spectral region

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In honour of Ed Cohen and Herb Pickett in recognition of their contributions to molecular spectroscopy.

Abstract

The high-resolution Fourier-transform absorption spectrum of the $^{14}\text{N}^{16}\text{O}_2$ molecule was recorded in the near infrared 5200–6005 cm^{-1} spectral range. Starting from the results of a previous study [R.E. Blank, M.D. Olman, C.D. Hause, *J. Mol. Spectrosc.* 33 (1970) 109–118] a new analysis of the $\nu_1 + 3\nu_3$ band located at 5984.705 cm^{-1} has been performed. The new assignments involve energy levels of the (103) vibrational state with rotational quantum numbers up to $K_a = 8$ and $N = 47$. The spin–rotation energy levels were satisfactorily reproduced within their experimental uncertainty using a theoretical model which takes explicitly into account the Coriolis interactions between the spin–rotational levels of the (103) vibrational state and those of (122) and of (080), the anharmonic interactions between the (122) and (080) vibrational states together with the electron spin–rotation resonances within the (103), (122) and (080) vibrational states. As a consequence, precise vibrational energies, rotational, spin–rotational, and coupling constants were obtained for the triad {(122), (080), (103)} of interacting states of $^{14}\text{N}^{16}\text{O}_2$. Using these parameters a comprehensive list of line positions and of reliable line intensities was generated for the $\nu_1 + 3\nu_3$ band of NO_2 .

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1. Introduction

Nitrogen dioxide ($^{14}\text{N}^{16}\text{O}_2$) is an important atmospheric trace species involved in the photochemistry of the stratosphere and in the pollution of the troposphere. Reliable accurate measurements of NO_2 concentration in the atmosphere are now commonly performed in the 6.2 and 3.4 μm regions which correspond to the ν_3 and $\nu_1 + \nu_3$ band,

respectively, by means of infrared remote sensing methods [1,2]. Since very accurate NO_2 line parameters are necessary for the analyses of these atmospheric spectra, numerous detailed spectroscopic studies were performed which involve $^{14}\text{N}^{16}\text{O}_2$ absorption bands from the microwave up to the 2.1 μm infrared region [3–12, and references therein]. $^{14}\text{N}^{16}\text{O}_2$ is an asymmetric rotor exhibiting in the infrared region a spectrum with a doublet structure due to the electron spin–rotation interaction, and a hyperfine structure in microwave and far infrared spectral regions. Also depending on the spectral range of interest, one has to consider vibrorotational interactions in order to calculate accurately the line positions and intensities. Two types of interactions have to be taken into account: a strong Coriolis-type interaction between the rotational levels of the vibrational states (ν_1, ν_2, ν_3) and ($\nu_1, \nu_2 \pm 2, \nu_3 \mp 1$)

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and a much weaker one between (v_1, v_2, v_3) and $(v_1 \pm 1, v_2, v_3 \mp 1)$ [13,14]. The results of these studies lead to lists of NO_2 line positions and intensities which are now implemented in spectroscopic databases such as HITRAN [15] and GEISA [16].

It is also important to understand the complex absorption behavior of the NO_2 species at higher energies. Using laser induced dispersed fluorescence technique the complete set of the 191 lowest vibrational levels of the X^2A_1 ground electronic state, up to 10000 cm^{-1} was measured [17]. However, at wavelengths lower than $2.1\text{ }\mu\text{m}$ there exist rather few detailed rotational analyses of the NO_2 infrared bands. The $v_1 + 3v_3$ band was identified at 5981.92 cm^{-1} by Arakawa and Nielsen [18] and its first rotational analysis was performed by Blank et al. [19] using medium-resolution grating spectroscopy in the $5920\text{--}6000\text{ cm}^{-1}$ spectral range. In this work transitions with K_a up to 5 and N up to 46 were identified. However, resonances were observed for transitions involving $K_a \geq 4$, and therefore series of (103) energy levels with $K_a = 4$ and 5 were excluded from the fit. In addition, the spin-splittings were not observed due to low-resolution of the recorded spectrum and the weakness of the lines.

Here we report a new high-resolution analysis of the $v_1 + 3v_3$ band of nitrogen dioxide based on the high-resolution Fourier-transform spectrum in the near infrared spectral region. The Hamiltonian matrix which explicitly accounts for the electron spin–rotation resonances, Coriolis-type resonances and anharmonic interactions was used for the energy level calculation. Therefore, significant improvements result from the present analysis as compared to the previous study.

2. Experimental data

The high-resolution absorption spectrum of NO_2 was recorded using the Bruker IFS-125HR Fourier-transform spectrometer (an upgraded version of the IFS-120HR) at LISA Créteil. The instrument was equipped with a CaF_2 beamsplitter and a Quartz–Tungsten–Halogen white light source, and evacuated down to 0.05 h Pa pressure in order to minimize residual H_2O and CO_2 absorption in the spectra. The detector was an InGaAs diode detector covering the $5500\text{--}10000\text{ cm}^{-1}$ region with maximum sensitivity around 6050 cm^{-1} .

The spectra were recorded using a mixture of NO_2 , NO and ICl at a total pressure of 9.9 h Pa in a White-type absorption cell. This cell (provided by Bruker Ltd.) has a base length of 80 cm and is mounted vertically onto the IFS-125HR in such a way that the transfer optics between the interferometer and the absorption cell is also evacuated, using wedged CsI windows between the White cell and the FTS. The total optical path inside the White cell was set to 9.60 m . Based on the partial pressures, the integrated absorption of the NO_2 lines between 5920 and 6920 cm^{-1} was estimated to

$$S_{1.7\text{ }\mu\text{m}} \approx (0.9 \pm 0.4) \times 10^{-20} \text{ cm}^{-1}/(\text{molecule cm}^{-2}) \quad (1)$$

(note that the sum of NO_2 and NO partial pressures was less than 2 h Pa).

A total of 1400 scans covering the $5300\text{--}10400\text{ cm}^{-1}$ region were recorded with a spectral resolution of 0.004 cm^{-1} (using boxcar apodization). The observed line-widths (full-width at half-maximum) are around 0.012 cm^{-1} which is close to the theoretical Doppler width of NO_2 in this spectral region.

The spectral calibration is estimated to be accurate to 0.0004 cm^{-1} (one sigma) based on calibration with H_2O lines in the $6640\text{--}6750\text{ cm}^{-1}$ region with the line positions of the HITRAN database [15].

3. Analysis

3.1. Assignment

An overview of the near infrared region, between 5920 and 6005 cm^{-1} , for nitrogen dioxide is given in Fig. 1. $^{14}\text{N}^{16}\text{O}_2$ is an asymmetric rotor exhibiting a spectrum with doublet structure due to the electron spin–rotation interaction, and according to symmetry properties, the $v_1 + 3v_3$ band is an A-type band with only $\Delta K_a = 0$ transitions.

The analysis of the $v_1 + 3v_3$ band was performed starting from the results of the study performed by Blank et al. [19]. First, a preliminary synthetic spectrum (line positions and relative line intensities) of the $v_1 + 3v_3$ band was generated, using for the calculation of the upper (103) energy levels the vibrational energy and the rotational constants for the (103) upper state achieved in Ref. [19]. In addition the ground state energy levels were calculated from the constants given in Ref. [4]. Starting from the predictions

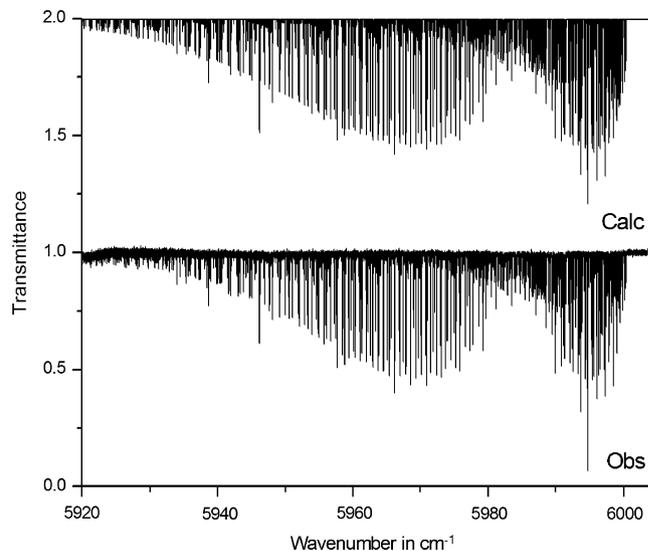


Fig. 1. Overview of the absorption spectrum of nitrogen dioxide in the $5920\text{--}6005\text{ cm}^{-1}$ spectral range. The experimental spectrum (lower trace) and the calculated spectrum (upper trace) are displaced for visual clarity. The agreement between the observed and calculated spectrum is excellent.

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