Journal of Quantitative Spectroscopy & Radiative Transfer 111 (2010) 345–356

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Line parameters of $^{15}N_2\,^{16}O$ from Fourier transform measurements in the 5800–7600 cm^{-1} region and global fitting of line positions from 1000 to 7600 cm^{-1}

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ARTICLE INFO

Article history:
Received 10 December 2008
Received in revised form
11 October 2009
Accepted 12 October 2009

Keywords:
Nitrous oxide
$^{15}N_2\,^{16}O$
Infrared
Fourier transform spectroscopy
Line positions
Line intensities
Global modeling

ABSTRACT

Using FT spectra (unapodized resolution ~0.0056 cm^{-1}) of the nitrous oxide isotopologue $^{15}N_2\,^{16}O$, the line positions and intensities have been measured for 511 lines of 8 cold bands and one hot band lying between 5800 and 7600 cm^{-1}. A multispectrum fitting procedure has been used to retrieve line parameters from 5 experimental spectra recorded at different pressures. An absolute wavenumber calibration has been performed using acetylene line positions around 6500 cm^{-1} and water line positions in the 7100–7300 cm^{-1} region. The average absolute accuracy of the line parameters obtained in this work has been estimated to be $\pm$0.0005 cm^{-1} for the line positions, 2–5% for the line intensities depending on the transitions. For each studied band, the vibrational transition dipole moment squared value and the empirical Herman–Wallis coefficients have been determined. Moreover, the line positions measured in this work and those collected from the literature allowed the global fitting of the effective Hamiltonian parameters for this isotopologue.

1. Introduction

Nitrous oxide is a minor constituent of the earth atmosphere, but it plays an essential role in the physical and chemical processes. The isotopologue $^{15}N_2\,^{16}O$ of nitrous oxide has a very small natural abundance (0.0013%), but the line parameters of this isotopologue can be useful for having a better accuracy of atmospheric spectra simulation and also for developing theoretical models describing the influence of the isotopic substitution on the spectral line parameters.

To our knowledge only two works [1,2] are available in the literature for the line positions measurements of this isotopic species. No works have been found in the literature concerning the line intensity measurements. This explains why spectroscopic databases HITRAN [3] or GEISA [4] do not contain any line parameters of $^{15}N_2\,^{16}O$.

In the present work, 511 lines of 9 bands, namely the $3\nu_3$, $\nu_2+3\nu_3-\nu_2$, $\nu_1+3\nu_3$, $2\nu_1+2\nu_3$, $3\nu_1+\nu_3$, $4\nu_1+\nu_3$I, $4\nu_1+\nu_3$II, $5\nu_1$I and $5\nu_1$III bands, have been studied between 5800 and 7600 cm^{-1} for the $^{15}N^{15}N^{16}O$ isotopologue. The line positions, intensities, self-broadening and self-shifting coefficients have been measured using a multispectrum fitting procedure [5] applied to five experimental spectra recorded at different pressures of $^{15}N_2\,^{16}O$. In this paper we publish only the line positions and line intensities. For each studied band, the vibrational transition dipole moment squared and empirical Herman–Wallis coefficients have been obtained.

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doi:10.1016/j.jqsrt.2009.10.010

Using the measured line positions of this work and those from the literature, a global fitting of the effective Hamiltonian parameters has been performed.

The experimental procedure and the methodology of the analysis are presented in Sections 2 and 3 respectively. Section 4 is devoted to the analysis and the modeling of the spectral line parameters. In Section 5 the results of the global fitting of the effective Hamiltonian parameters are presented.

2. Experimental procedure

To record the spectra, the rapid scan Bruker IFS 120 HR interferometer of the LADIR (Laboratoire de Dynamique, Interactions et Réactivité, Paris) has been used. The unapodized spectral resolution used for each spectrum was equal to $5.6\times10^{-3}\,\mathrm{cm}^{-1}$ ($1/2\Delta_{\max}$) that corresponds to a maximal optical path difference $\Delta_{\max}$ of 90 cm. The interferometer was equipped with a CaF_2 beam splitter, an InGaAs detector, a tungsten source, and no optical filter in order to cover the whole 5500–9000 cm^{-1} spectral region. Five spectra have been recorded at room temperature with various gas pressures; experimental conditions are summarized in Table 1. The whole optical path was under vacuum and a multipass White type cell of one meter base length was used for a total absorption path of 2015 ± 1 cm. The cell was equipped with KCl windows. The commercial gas sample has been furnished by Campro Scientific Gmbh, the given isotopic assay is: 99.9% of ^{15}N, 0.1% of ^{14}N and 98.3% of ^{16}O, 0.1% of ^{17}O and 1.6% of ^{18}O. The stated purity of the sample of N_2O is 99.1%. Using these specifications, the partial pressure of the various isotopologues can be calculated for each spectrum (the partial pressures of the more abundant isotopologues are given as percentage of the total pressure in Table 1). The temperature of the gas in the cell was monitored with the help of four platinum probes at different places in the cell. The accuracy of the averaged temperature is estimated to be ±1 K (this accuracy takes into account small temperature gradients inside the cell). The pressure of the gas was measured with a capacitive MKS Baratron manometer with an accuracy equal to ±1%. For each spectrum, a total of 300 scans have been recorded and individually transformed using the Fourier transform procedure included in the Bruker software OPUS package [6], selecting a Mertz phase error correction [7,8]. The final spectrum is then the result of the co-addition of the 300 spectra.

3. Line parameter measurements

In this study, the line assignment has been performed on the basis of the predictions performed using global effective Hamiltonian for $^{15}N_2\,^{16}O$ isotopologue obtained in Ref. [9].

The wavenumber calibration has been performed using $^{12}C_2H_2$ transitions around 6500 cm^{-1} and $H_2\,^{16}O$ transitions between 7100 and 7350 cm^{-1} (these two gases are present in the sample as impurities). The reference values of the line positions have been taken from the HITRAN 2004 database [3]. Using the values of the line intensities of Ref. [3], the partial pressures of $^{12}C_2H_2$ and $H_2\,^{16}O$ have been determined in each spectrum (see Table 1). For the wavenumber calibration, the quantity $\varepsilon=(\nu_{\mathrm{HITRAN}}-\nu_{\mathrm{this\ work}})/\nu_{\mathrm{HITRAN}}$ has been calculated individually in each spectrum for 35 isolated lines of H_2O and 10 isolated lines of $^{12}C_2H_2$. The uncertainties of these reference lines vary from 0.0001 to 0.001 cm^{-1}. The plot of ε for each line versus pressure demonstrates its linear dependence on pressure (see Fig. 1). Taking into account that the same experimental setup was used to record all spectra, this

Table 1
Experimental conditions and characteristics of the recorded spectra.

Unapodized apparatus function					
Maximum optical path difference					90 cm
Resolution					~0.0056 cm^{-1}
Effective iris radius					0.59–0.72 mm
Collimator focal length					418 mm
Absorbing sample					
Percentages of the total pressure for the various molecules:					
$^{15}N^{15}N^{16}$	97.2%	$^{15}N^{15}N^{18}$	1.6%	others N_2O isotopologues	~0.1%
$^{15}N^{15}N^{17}$	~0.1%	$^{15}N^{14}N^{16}$	~0.1%	impurities (N_2, O_2, H_2O, C_2H_2… etc.)	0.9%
Experimental conditions					
SNR					~100
Absorption path					2015 cm
	Total pressure (× 10^{-2} atm)[a]	Temperature (K)	Partial pressure C_2H_2 (× 10^{-6} atm)	Partial pressure H_2O (× 10^{-5} atm)	ε_j[b] (× 10^{-6})
1	0.828	298.0	2.8	1.6	1.17(1)
2	1.35	298.2	4.1	1.8	1.19(2)
3	2.30	298.4	6.4	2.1	1.27(3)
4	3.21	298.1	8.3	2.4	1.28(4)
5	4.31	298.6	6.3	2.6	1.31(6)

[a] 1 atm=1013 mbar=1013 hPa.

[b] Wavenumber calibration factor for spectrum *j* (see text in Section 3).