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Journal of Quantitative Spectroscopy & Radiative Transfer

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

Nitrous oxide spectroscopy at 887 nm

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ARTICLE INFO

Article history:

Received 14 January 2022

Revised 15 February 2022

Accepted 21 February 2022

Available online xxx

Keywords:

Nitrous oxide

Overtone bands

Line lists

Line and band widths

Tunable diode laser

ABSTRACT

Using a tunable diode laser spectrometer 53 $^{14}\text{N}_2^{16}\text{O}$ overtone absorption lines have been detected in the range between 11,233 and 11,283 cm^{-1} (886 – 890 nm), with estimated strengths ranging around 10^{-27} – 10^{-28} $\text{cm}^2/\text{molecule}$. 9 new lines have been found. They have been measured by utilizing commercial AlGaAs/GaAs laser diodes through the wavelength modulation spectroscopy and the 2nd harmonic detection techniques. Self-broadening coefficients have been obtained for 13 of these lines for the first time. Refined molecular parameters have been achieved for this overtone band.

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1. Introduction

N_2O is a non-symmetrical linear molecule that behaves as *green house* gas due to its ability to absorb and emit e.m. radiation within the thermal infrared range. The mid infrared region is usually selected to detect it, since the fundamental ro-vibrational absorption bands [1] are located there with the highest intensities. The Fabry-Perot (F– P.) or the variant Distributed Feedback (DFB) type tunable diode lasers (DLs) are successfully utilized as coherent light sources for investigating the nitrous oxide molecular absorptions in the visible (VIS) and near-infrared range (NIR), where the combination overtone ro-vibrational bands are present, even if their line strengths are orders of magnitude lower than in the MID IR.

In particular, the N_2O absorption lines located in the 800 – 900 nm spectral range can be assigned to the sixth and seventh pseudo-quantum *polyad* numbers, as deduced from the effective Hamiltonian model introduced by Teffo et al. [2], where the vibrational-rotational eigenvalues of the excited states overlap due to “local” interactions. They have been investigated in the past by different spectroscopic methods. For instance, in 1950 G. and L. Herzberg observed many N_2O weak absorption bands in the NIR [3]. A. Campargue et al. systematically studied the N_2O spectra in this range [4] by Intracavity Laser Absorption Spectroscopy (ICLAS) and they obtained important rotational analysis results on the observed bands. Frequency modulation spectroscopy [5], conventionally called Wavelength Modulation Spectroscopy (WMS)

when the value of the frequency of the modulation is chosen much lower than the resonance line-width, is necessary to observe such very weak absorptions lines. In the present work the tunable diode laser spectroscopy is applied to the weak ro-vibrational absorption resonances of nitrous oxide around 887 nm, through WMS and the 2nd harmonic ($2f$) detection technique. In these conditions more than 50 absorption lines have been detected, including 9 new ones. The self-broadening coefficient have been measured for the first time for 13 of them at room temperature (RT).

2. Experimental details

The experimental setup is sketched in Fig. 1, following a previous work [6]. In the present case the employed sources have been two AlGaAs/GaAs double heterostructure F– P. type DLs, Roithner RLT8904-30G and RLT8710MG, with single longitudinal and transverse emission modes and power $\simeq 10$ mW cw operating in “free-running” configuration, that is without any optical feedback. With this choice, two only DLs permitted to span almost 50 cm^{-1} . For the modulation and sweeping of the source, the sinusoidal carrier wave coming from a low noise waveform generator was passively mixed to the ramp extracted from the saw-tooth signal of the oscilloscope and sent to the DL current controller. Two 30 m optical path-length custom made Herriott type multipass cells were used as sample and reference cells. The latter, containing water at room temperature vapor pressure ($\simeq 20$ torr), was used as the reference for the precise wavenumber measurements. The HITRAN water vapor absorption lines database [7] has been employed for this purpose. In case of lack of water vapor reference lines in the sampled spectrum, an iodine cell warmed up to 330 K has been used as the reference, and a I_2 precise atlas adopted [8]. The output of

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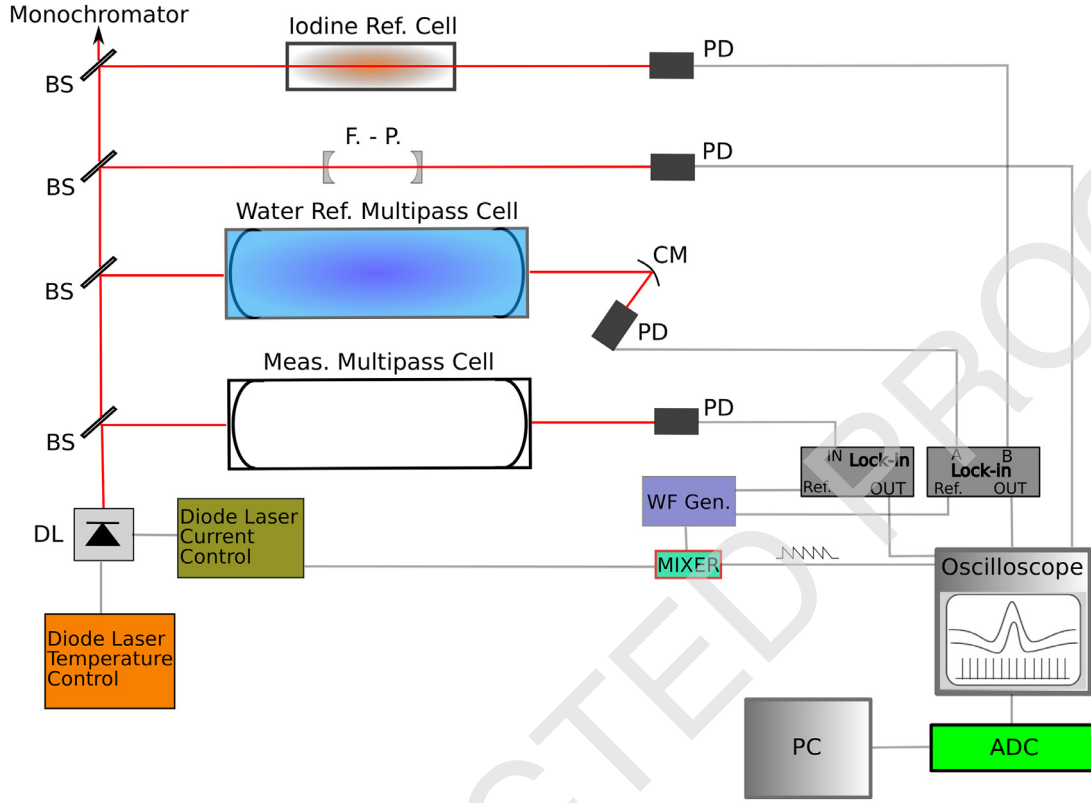


Fig. 1. Outline of the experimental apparatus. ADC: analog-to-digital converter; BS: beam splitter; CM: concave mirror; DL: diode laser; F.- P.: Fabry-Perot interferometer; PC: desk-top computer; PD: photodiode; WF Gen.: waveform generator.

56 the measurement multipass cell was focalized to the photo-diode
 57 (PD) active spot by a 5 cm f.l. concave mirror, with the aim of re-
 58 ducing the mechanical noise coming from the optical leverage of
 59 the spectroscope set. Pre-amplified silicon PDs have been used as
 60 the detectors and their signals were sent to two lock-in amplifiers
 61 tuned to the carrier frequency coming from the waveform genera-
 62 tor ($f \sim 20$ kHz). A confocal 5 cm Fabry-Perot interferometer was
 63 utilized to check the DLs modes and the linearity of their emission
 64 frequency, while a Czerny-Turner monochromator was used for the
 65 rough wavelength check (± 0.01 nm). The nitrous oxide gas has
 66 been supplied by Praxair Inc.: Grade 3.5, minimum purity 99.95%
 67 ($\text{H}_2\text{O} \leq 10$ ppm).

68 The measured transmittance $\tau(\nu)$ is assumed to follow the
 69 classical Lambert-Beer expression: $\tau(\nu) = e^{-\sigma(\nu)z}$, where $z = \rho l$
 70 is the product of the absorbing species density ρ (molecule/cm³)
 71 and the optical path l (cm) of the radiation through the sample,
 72 namely the column amount (molecule/cm²). $\sigma(\nu)$ is the absorp-
 73 tion cross section (cm²/molecule). The WMS technique, described
 74 in detail in a previous work [9], has been applied here by modu-
 75 lating the source emission frequency $\bar{\nu}$ at $\nu_m = \omega_m/2\pi$, with am-
 76 plitude a , that is $\nu = \bar{\nu} + a \cos \omega_m t$. For the detection of very weak
 77 absorbances ($\approx 10^{-6}$) the high modulation amplitude regime was
 78 necessary, with a modulation index $m \equiv a/\Gamma \gg 0.1$, where Γ is the
 79 absorption resonance line-width. The experiments were carried on
 80 at pressures ranging between 20 and 150 torr; in this regime the
 81 absorption line shape can be well described as a function of the
 82 photon energy (frequency) by the Voigt function:

$$f_2(x, m) = \frac{2}{m^2} - \frac{2^{1/2}}{m^2} \times \frac{1/2[(M^2 + 4x^2)^{1/2} + 1 - x^2][(M^2 + 4x^2)^{1/2} + M]^{1/2} + |x|[(M^2 + 4x^2)^{1/2} - M]^{1/2}}{(M^2 + 4x^2)^{1/2}}, \quad (2)$$

$$f(\nu) = \int_{-\infty}^{+\infty} \frac{\exp[-(t - \nu_0)^2/\Gamma_G^2 \ln 2]}{(t - \nu)^2 + \Gamma_L^2} dt, \quad (1)$$

83 where ν_0 is the gas resonance frequency, Γ_G and Γ_L are the Gaus-
 84 sian and the Lorentzian half widths at half the maximum (HWHM),
 85 respectively. Second order effects, like velocity changing collision
 86 or Dicke narrowing that occurs when the molecular mean free
 87 path is comparable to the wavelength of the sampling radiation,
 88 were not observed at our sensitivity and were not taken into ac-
 89 count. The utilization of the phase detection technique, obtained
 90 by tuning the lock-in amplifiers to twice the modulation frequency
 91 (~ 40 kHz), produced an almost symmetrical line-shape signal that
 92 was closer to the 2nd derivative of the absorption feature as the
 93 minor was the modulation amplitude [9]. This technique has the
 94 advantage of a flat baseline of the signal, but it cannot avoid opti-
 95 cal interferences, coming principally from the many reflecting sur-
 96 faces present in the optical path. In addition, this method cannot
 97 give reliable measurement of the intensity parameter when ap-
 98 plied to very weak resonances. For the line broadening measure-
 99 ments the general expression of the collisional half width at half
 100 the maximum (HWHM) as a function of the pressure has been ap-
 101 plied: $\Gamma_L(p) = \gamma_{\text{self}} p$, where p is the sample gas pressure and γ_{self}
 102 is the gas self-broadening coefficient.

103 When the high modulation amplitude is a mandatory choice,
 104 as for these experiments, the second derivative cannot describe
 105 the right behavior of the line-shape any more and a different ap-
 106 proach is needed. Following what explained in the Appendix of [9],
 107 the spectroscopic parameters can be still obtained with a good
 108 reliability by adopting the fit function of the modulated $2f$
 109 signal:

110 where $x = \nu/\Gamma$, $M = 1 - x^2 + m^2$ and Γ is the absorption line-
 111 width.

Table 1

Wavenumbers and wavelengths (in air at RT) of the measured N₂O absorption lines, with maximum error 0.01 cm⁻¹. The wavenumber marked with ^a are the new ones, and the one with ^b is probably due to multiple lines.

J	R(J) (cm ⁻¹)	λ (nm)	P(J) (cm ⁻¹)	λ (nm)
1	11273.54 ^a	886.794		
2	11274.28 ^a	886.736	11270.25	887.053
3	11275.02	886.678		
4	11275.71 ^a	886.624	11268.43	887.196
5	11276.37	886.572	11267.48	887.271
6	11276.99	886.523	11266.49 ^a	887.349
7	11277.59	886.476	11265.48	887.429
8	11278.16	886.431	11264.42	887.512
9	11278.70	886.389	11263.38	887.593
10	11279.22	886.348	11262.28	887.683
11	11279.71	886.309	11261.11	887.773
12	11280.13	886.276	11259.94	887.865
13	11280.54	886.244	11258.74	887.960
14	11280.94	886.213	11257.52	888.056
15	11281.29	886.184	11256.26	888.156
16	11281.63	886.158	11254.98	888.257
17	11281.93	886.135	11253.67	888.360
18	11282.19	886.114	11252.29	888.469
19	11282.41	886.097	11250.93	888.576
20	11282.60	886.082	11249.51	888.689
21	11282.80 ^a	886.067	11248.08	888.802
22	11282.97 ^a	886.053	11246.61	888.918
23	11283.05 ^a	886.047	11245.11	889.036
24	11283.13 ^a	886.041	11243.62	889.154
25	11283.20 ^b	886.035	11242.02	889.281
26			11240.43	889.406
27			11238.82	889.534
28			11237.16 ^a	889.665
29			11235.49	889.798
30			11233.77	889.934

3. Experimental results

53 detected ¹⁴N₂¹⁶O absorption lines are listed in Table 1 where the maximum wavenumber error (3σ) is 0.01 cm⁻¹; this estimation takes into account the atlas reference standard errors, which are all about ten time more precise. The peak position measurements were performed at RT, at pressures around 50 – 90 torr, and 30 m path-length. Wavelengths are reported for convenience, in air at T = 294 K, following the work of B. Edlén [10]. The newly observed lines are marked with “ a ” in the Table, while the one with “ b ” was also detected by G. Herzberg in 1950 [3]. A comparison with the spectrum coming from the work of A. Campargue on this same combination overtone 4ν₁ + 3ν₃ band [4] gives in average a difference of -0.02 cm⁻¹ with 1 SD = 0.01 cm⁻¹. Due to the derivative method adopted here for the detection, a reliable measurement of the absolute value of the line intensity was not possible. By a comparison with the water vapor absorption lines present in the spectra, whose partial pressure in the cell was always known, we could estimate the absorption line strengths to be in the range of 0.2 – 1.5 × 10⁻²⁷ cm/molecule, with the most intense of them located around 11281 cm⁻¹.

Self-broadening coefficients have been measured for the first time for some of the more intense lines of N₂O at RT. They are shown in Table 2 for the P-branch and in Table 3 for the R-branch. We did not find any other pressure broadening measurements in the literature at these wavenumbers. A comparison can only be tried with what obtained in different spectral regions. Beginning from what reported by HITRAN molecular database [7], for the ν₂ band at 17 μm the self-broadening coefficients span from 0.07 cm⁻¹/atm at high J to 0.13 cm⁻¹/atm at low J, which is similar to what observed in this work. R. Toth [11] on the ν₁ + ν₃, and 2ν₂ + ν₃ bands in the MID IR at RT gives self-broadening coefficient values similar to the ones ob-

Table 2

Measured N₂O self-broadening coefficients (HWHM) for the P-branch.

J	ν' (cm ⁻¹)	γ _{self} (cm ⁻¹ /atm)
5	11267.48	0.18 ± 0.01
6	11266.49	0.114 ± 0.009
9	11263.38	0.098 ± 0.006
10	11262.28	0.103 ± 0.004
12	11259.94	0.095 ± 0.004
20	11249.51	0.10 ± 0.01
25	11242.02	0.09 ± 0.01
26	11240.43	0.094 ± 0.005
28	11237.16	0.042 ± 0.008

Table 3

Measured N₂O self-broadening coefficients (HWHM) for the R-branch.

J	ν' (cm ⁻¹)	γ _{self} (cm ⁻¹ /atm)
3	11275.02	0.15 ± 0.01
4	11275.71	0.10 ± 0.01
9	11278.70	0.09 ± 0.01
10	11279.22	0.11 ± 0.01

served in our work: from 86 × 10⁻³ cm⁻¹/atm for high rotational quantum number J to 145 × 10⁻³ cm⁻¹/atm at low J at 297 K. The same happens in the work by N. Lacombe et al. [12] at 4 and 8 μm: from 77.44 × 10⁻³ cm⁻¹/atm at high J to 154 × 10⁻³ cm⁻¹/atm at low J at 4 μm at 295 K and a little lower at 8 μm. The Cavity Ring-Down Spectroscopy technique permitted to R. Adkins et al. [13] to obtain also the self-broadening coefficients along with the speed dependent broadening parameters in the NIR spectrum, near 1.6 μm. Their coefficients are comparable to ours: in average γ_{self} = 0.03013 MHz/Pa, that is 0.1018 cm⁻¹/atm. Finally the work of J. Loos et al. [14] measured also the self-broadening parameters for the N₂O fundamental ν₃ band at 4.5 μm by using the FTS technique. They got self-broadening coefficients ranging from 0.07076 cm⁻¹/atm at high J to 0.10075 cm⁻¹/atm at low J. These results are compatible to the ones obtained in this work.

As reported, 9 new absorption lines have been detected in the ro-vibrational band object of this work, and this permitted a refined determination of the band parameters related to the excited state. Considering the Hamiltonian of a linear molecule, the relative roto-vibrational eigenvalues as a function of the quantum number J [1], and using the ground vibrational state (0,0⁰,0) parameters from M. Vanek et al. [15] we got for the characteristic parameters of the combination overtone band (4, 0⁰, 3) ← (0, 0⁰, 0), in the normal mode notation:

$$B' = (0.40400 \pm 0.00001) \text{ cm}^{-1} \text{ and}$$

$$\nu'_0 = (11271.973 \pm 0.004) \text{ cm}^{-1}.$$

These are little smaller than the ones obtained by A. Campargue [4], where B' = 0.40411 cm⁻¹ and ν'_0 = (11271.988 ± 0.004) cm⁻¹, but ours take into account more line positions and therefore they should be more accurate.

4. Conclusion

53 nitrous oxide overtone absorption lines have been detected in the range 886 – 890 nm using a tunable diode laser spectrometer and the aid of the wavelength modulation technique with the 2nd harmonic detection. Their positions in wavenumber have been measured within 0.01 cm⁻¹ and 9 of them have been revealed for the first time. Their strengths were estimated in the range of 0.2 – 1.5 × 10⁻²⁷ cm/molecule. For some of these lines the self-broadening coefficients have been measured for the first time and the results are consistent with what previously measured using different techniques and at different wavelengths. Finally, by

185 considering the new observed lines, better rotational parameters
186 have been obtained for this combination overtone band.

187 Declaration of Competing Interest

188 The authors declare that they have no known competing finan-
189 cial interests or personal relationships that could have appeared to
190 influence the work reported in this paper.

191 CRediT authorship contribution statement

192 **A. Lucchesini:** Investigation, Data curation, Formal analysis,
193 Writing – original draft, Funding acquisition. **J. González-Rivera:**
194 Investigation, Formal analysis, Writing – review & editing.

195 Acknowledgments

196 The authors wish to thank Mr. A. Barbini for the electronic ad-
197 vising and Mr. M. Voliani for the technical assistance. They are
198 also grateful to Dr. F. Baffigi for supplying the N₂O pure gas. Dr. A.
199 Lucchesini is indebted to Dr. A. Campargue (Univ. Grenoble Alpes,
200 CNRS, LIPhy, Grenoble, France) for providing his measurements
201 data. Dr. J. Gonzalez-Rivera during this work was supported by a
202 research grant from the Project POR FSE 2014–2020 ARCO - SOPRA
203 of the Regione Toscana, Italy.

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