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## Cavity ring-down spectroscopy of the $6\nu_3$ bands of $^{15}\text{N}$ substituted $\text{N}_2\text{O}$

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### ABSTRACT

The  $6\nu_3$  and  $\nu_2 + 6\nu_3 - \nu_2$  bands of  $^{15}\text{N}$  substituted nitrous oxide isotopologues have been recorded by a continuous-wave cavity ring-down spectrometer (CW-CRDS) operated near  $0.8\ \mu\text{m}$ . The sensitivity limit was at the level of  $1 \times 10^{-10}/\text{cm}$ . In total, 213, 86 and 191 transitions were observed for the  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and  $^{15}\text{N}_2^{16}\text{O}$  isotopologues, respectively. The ro-vibrational spectroscopic parameters of the upper states are determined from least square fitting of the transitions. The absolute line intensities of the  $6\nu_3$  cold bands have been retrieved by a multi-line fitting procedure from the spectra with an estimated accuracy of 4% for majority of the unblended lines. The vibrational transition dipole moment squared values and the empirical Herman-Wallis coefficients are also presented.

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### 1. Introduction

Nitrous oxide is a minor constituent of the Earth atmosphere. But as a greenhouse gas it plays an important role in the atmospheric radiation balance. It also contributes to the ozone layer depletion. In addition, nitrous oxide is one of the burning products of the organic fuels in the air. As a consequence, the high resolution spectra of this molecule are widely used in various applications like monitoring its concentration in the atmosphere and in the combustion exhaust. The spectra of main isotopologue  $^{14}\text{N}_2^{16}\text{O}$  nitrous oxide has been systematically studied up to  $669\ \text{nm}$  [1]. And in the last few decades, spectroscopic studies of single  $^{15}\text{N}$  substituted nitrous oxide ( $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ ) have been carried out with microwave spectrometers (MW) [2–4], Fourier-transform infrared (FT-IR) spectrometers (FTS) [5–11], intra-cavity laser absorption spectrometer (ICLAS) [12], and cavity ring-down spectrometer (CRDS) [13–15]. All the above listed

measurements were carried out with natural nitrous oxide samples where the abundance of the single  $^{15}\text{N}$  substituted isotopologue is 0.36409% given in Hitran database. Using  $^{15}\text{N}$  enriched samples, the FT-IR spectroscopy above  $1\ \mu\text{m}$  of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and  $^{15}\text{N}_2^{16}\text{O}$  has been reported in Refs. [16–19,21].

Here we present the cavity ring-down spectroscopy of these three  $^{15}\text{N}$  substituted nitrous oxide isotopologues near the  $0.8\ \mu\text{m}$  region where the  $6\nu_3$  overtone bands are located. Since only the spectral data over  $1\ \mu\text{m}$  have been employed in the recently developed global effective Hamiltonian (EH) calculations of these molecules [20,21], the new spectral data below  $1\ \mu\text{m}$  presented here can be an interesting example to check the extrapolation and prediction capability of the EH models.

The present paper is organized as following: In Section 2, the experimental procedure and the methodology of the analysis are presented. Section 3 is devoted to the band by band analysis and the modeling of the spectral parameters. Conclusions are given in the last section. Note that throughout the paper we use the notation for the isotopologues according to HITRAN [22]:  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ : 456,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ : 546, and  $^{15}\text{N}_2^{16}\text{O}$ : 556.

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## 2. Experiment and data reduction

The CW-CRDS spectrometer has been developed using a CW tunable Ti-sapphire laser over the spectral range of 780–830 nm. The details of the cavity ring-down spectrometer are presented in Refs. [23,24]. In brief, the structure of the setup is as following: A CW tunable Ti:sapphire laser (Coherent 899-21) beam is carefully coupled into a 1.2 m long resonance cavity. The cavity mirrors (Los Gatos Inc.) have a reflectivity of 99.995% and one of the two mirrors is mounted on a piezoelectric actuator (PI Inc.). The piezoelectric actuator is driven with a triangle wave from a function generator. The Ti:Sa laser is running in a step-scan mode controlled by a personal computer (PC). On each step, typically about 100 ring-down events are recorded with a fast digitizer (ADLINK PCI-9820). The digitizer is working at a sampling rate of 1 MS/s (Mega-samples per second) with 14-bit resolution. A fitting program which follows the method proposed by Halmer et al. [25] is applied to fit the exponentially decay curve

and to give the decay time  $\tau$ . The sample absorption coefficient,  $\alpha$ , can be derived from

$$\alpha = \frac{1}{c} \left( \frac{1}{\tau} - \frac{1}{\tau_0} \right), \quad (1)$$

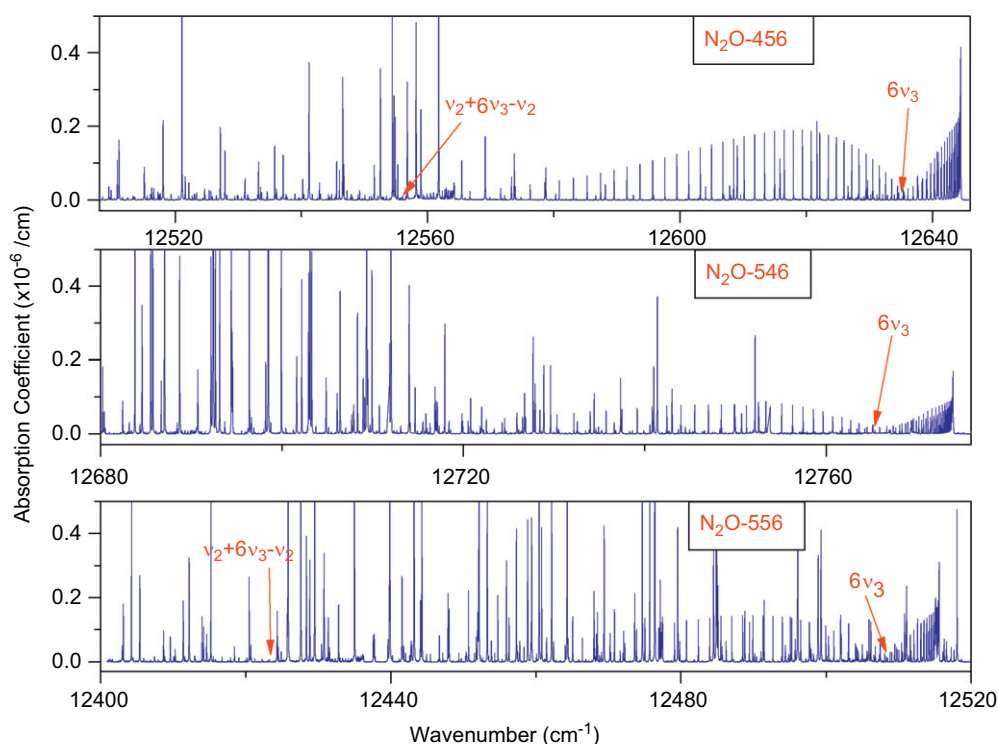
where  $c$  is the speed of light,  $\tau$  and  $\tau_0$  are the decay time of the cavity with and without sample, respectively. The minimum detectable absorption coefficient of the present spectrometer has been demonstrated to be  $7 \times 10^{-11}/\text{cm}$  [24].

Three samples with 456, 546 or 556 enriched nitrous oxide isotopes were purchased from Icon Services Inc. The stated isotopic concentrations of 456, 546 and 556 are all 99% in respective samples. Photo-ionization mass spectroscopy (PIMS) combined with IR spectroscopy gave the abundances of 97.4%, 97.6% and 97.6% (with about 0.2% uncertainty) for  $\text{N}_2\text{O}$ -456, 546 or 556 in respective samples. PIMS was performed with a time-of-flight mass spectrometer in the photochemistry end-station in National Synchrotron Radiation Laboratory (NSRL), Hefei.

**Table 1**

Experimental conditions applied in the  $^{15}\text{N}$  enriched nitrous oxide spectra measurements.

Sample	Isotope abundance (%)	Pressure (Torr)	Temperature (K)	Spectral region ( $\text{cm}^{-1}$ )
$\text{N}_2\text{O}$ -456	97.4	59.7	$297.2 \pm 1.0$	12508–12646
$\text{N}_2\text{O}$ -546	97.6	23.0	$297.8 \pm 1.0$	12600–12766
$\text{N}_2\text{O}$ -556	97.6	52.8	$297.4 \pm 1.0$	12402–12560



**Fig. 1.** Overview of the CW-CRDS spectrum of three  $^{15}\text{N}$  substituted nitrous oxide samples around the  $6\nu_3$  band region. Upper panel:  $\text{N}_2\text{O}$ -456 enriched sample, 59.7 Torr. Middle panel:  $\text{N}_2\text{O}$ -546 enriched sample, 23.0 Torr. Lower panel:  $\text{N}_2\text{O}$ -556 enriched sample, 52.8 Torr.

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