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# Measurements of the $3\nu_3$ band of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ using continuous-wave cavity ring-down spectroscopy

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**ABSTRACT** The absorption spectra of the  $3\nu_3$  band of nitrous oxide isotopologues,  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ , have been measured using diode laser cavity ring-down spectroscopy in 6400–6463 and 6465–6532  $\text{cm}^{-1}$ , respectively. Spectroscopic parameters and the rotational line intensities of the bands have been determined. We have applied this spectroscopic technique to the measurements of the absolute isotope ratio of those isotopologues using the absolute line intensities.

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## 1 Introduction

Nitrous oxide ( $\text{N}_2\text{O}$ ) is an important atmospheric minor constituent, which has significantly contributed to global warming in the troposphere and is a main source of  $\text{NO}_x$  in the stratosphere. Measurement of isotope ratios is a powerful tool for understanding the production, release and transportation processes of environmentally relevant constituents [1, 2]. Isotopologues of  $\text{N}_2\text{O}$  include  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$  (446),  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (456),  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (546),  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$  (448), and  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$  (447) with natural abundance ratios of about 0.9903, 0.0036, 0.0036, 0.0020, and 0.0004, respectively. Infrared absorption spectroscopy using diode lasers is especially required for the direct measurement of isotopologues that have the same mass, such as 456 and 546. There are few spectroscopic measurements of the relative isotope ratios using the “reference” method. Uehara et al. [3, 4] performed isotope ratio measurements of  $\text{N}_2\text{O}$  for 456, 546, 448, and 446 at 2  $\mu\text{m}$  by using a wavelength modulated diode laser and a multipass cell with precisions of 0.2–0.6%. Gagliardi et al. [5] reported a precision of 9% based on audio-frequency and radio-frequency modulation spectroscopy at 8.06  $\mu\text{m}$ . Waechter and Sigrist [6] performed the 546/456 ratio measurements using wavelength modulation and balanced path length detection at 4.3–4.7  $\mu\text{m}$  with a precision of 3%.

Cavity ring-down spectroscopy is one of the most sensitivity spectroscopic absorption techniques [7–13]. Since high resolution diode lasers for telecommunication use at 1.5  $\mu\text{m}$  have become widely used, the application of continuous-wave cavity-ring spectroscopy (cw-CRDS) using a diode laser to detection of the minor isotopologues of  $\text{N}_2\text{O}$  in the  $3\nu_3$  band at 1.5  $\mu\text{m}$  is a challenge. Recently, Wang et al. [14] reported the spectroscopic parameters for the  $3\nu_3$  band of 456 based on Fourier transform spectroscopic measurements. No reports exist on the detection of the  $3\nu_3$  band of 546. In the present study, we performed the absolute isotope ratio measurement of 546/456 using cw-CRDS at 1.5  $\mu\text{m}$  by determining the absolute line intensities.

## 2 Experimental

The experimental setup used in the present study is similar to that described in previous studies [15, 16]. An external cavity diode laser (Ando Electronics, AQ4321D, 1520–1620 nm, 6 mW, line width: 0.2 MHz) was used as the near-infrared light source. The output laser beam, deflected by an acousto-optical modulator (ISOMET, 1205-C2, 80 MHz), was directed into the optical cavity. The optical cavity consisted of two high reflectivity mirrors (II-VI Optics, reflectance > 0.999, with 1 m radius of curvature and 7.8 mm diameter) with a separation of 60 cm. One of the two mirrors was incorporated in a tube-type Piezo actuator (Piezomechanik, HPSt 150/20) for cavity length modulation, with a rate of about 300 Hz. The transmitted light from the cavity was directed to an InGaAs photodiode detector (Hamamatsu Photonics, G5851-11) attached to a preamplifier (NF, SA220F5). When the transmitted beam reached a threshold level, the deflected beam was switched off by the acousto-optical modulator crystal and the light stored within the cavity started to ring-down.

In the presence of an absorbing species, the light intensity within the cavity is given by the expression

$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma Nct), \quad (1)$$

where  $I_0$  and  $I(t)$  are the light intensities at times 0 and  $t$ ,  $\tau$  is the cavity ring-down time in the presence of an absorbing sample,  $\tau_0$  is the cavity ring-down time without the absorber present (typically 3  $\mu\text{s}$ ), and  $c$  is the velocity of light.  $N$  and  $\sigma$  are the concentration and absorption cross section of the absorbing species, respectively.

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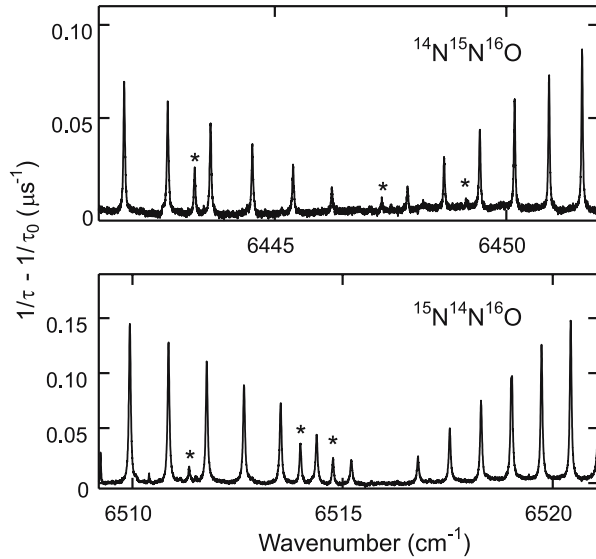
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The exponential decay data were digitized with an A/D converter (National Instruments, NI5122 100 MHz, 14 bit) and processed using LabVIEW software. Our program averaged the profile of several ring-down waveforms and individual ring-down decay curves were fitted to a single-exponential function. For each spectral data point, 36 ring-down events were averaged. Pressure and temperature of the sample gases in the cavity were monitored by pressure gauges (MKS, Baratron 622) and thermocouples at the monitor ports, respectively. All experiments were performed at  $296 \pm 2$  K. Commercially available isotopologue gases (456 and 546, ICON, > 99%) and  $N_2O$  in a conventional gas cylinder (Japan Air Gases, > 99.9%) were used without further purification.  $N_2O$  in the gas cylinder was reportedly synthesized from  $NH_4NO_3$ .

### 3 Results and discussion

#### 3.1 Determinations of spectroscopic parameters and line intensities

The absorption spectra of the  $3\nu_3$  band of pure 456 and 546 were measured at 6400–6463 and 6465–6532  $cm^{-1}$ , respectively. Figure 1 shows the spectra around the band centers, which were measured at the partial pressures of 0.30 Torr 456 or 0.36 Torr 546 under total pressure of 160 Torr  $N_2$  buffer. The asterisks in Fig. 1 indicate the water vapor absorption lines. The line positions of each rovibrational transi-



**FIGURE 1** Cavity ring-down spectra of the  $3\nu_3$  band of  $^{14}N^{15}N^{16}O$  (upper panel) and  $^{15}N^{14}N^{16}O$  (lower panel) near the band centers. The asterisks indicate the lines due to water vapor

tion were determined by fitting the measured spectral profiles with the Voigt function. The Gaussian component in the Voigt function was constrained to the Doppler width at 296 K. The wavelengths of the band centers were calibrated using  $CO_2$  and  $H_2O$  as internal standard gases [17]. Four (one  $H_2O$  and three  $CO_2$ ) and six (two  $H_2O$  and four  $CO_2$ ) reference lines were used for 456 and 546, respectively. The obtained band centers were listed in Table 1. Our results for 456 are in good agreement with those obtained with Fourier transform spectroscopy by Wang et al. [14].

The rotational analysis of the band was performed using the standard expression for rotational energy levels in a given vibrational state.

$$F_v(J) = G_v + B_v J(J+1) + D_v J^2(J+1)^2, \quad (2)$$

where  $G_v$  is the vibrational term value,  $B_v$  the rotational constant,  $D_v$  the centrifugal distortion constant, and  $J$  the angular momentum quantum number. An equation for the wavenumber's difference is described as follows with the index  $m$ ,

$$\begin{aligned} F_v(m) - F_v(m-1) &= (B_v + B_{gs}) + (B_v - B_{gs})(2m-1) \\ &\quad - 4(D_v - D_{gs})m^3 - D_{gs}(12m^2 - 12m + 4), \end{aligned} \quad (3)$$

$$m = -J'' \quad \text{for P-branch } (J'' - 1 \leftarrow J''),$$

$$m = J'' + 1 \quad \text{for R-branch } (J'' + 1 \leftarrow J''),$$

where  $B_{gs}$  and  $D_{gs}$  are the rotational and centrifugal distortion constants for the ground vibrational state, as shown by Toth et al. [18]. From the fit to the data with (3) for  $(0\ 0^0\ 3)$  vibrational states it was determined that  $B_v = 0.408995(49)$  and  $D_v = 1.67(32) \times 10^{-7}$  for 456, and  $B_v = 0.394850(35)$  and  $D_v = 1.52(18) \times 10^{-7}$  for 546, respectively, in units of  $cm^{-1}$ . The uncertainties in parentheses are one standard deviation of the least square fit of (3) to the data in units of the last digits quoted. Obtained spectroscopic parameters are summarized in Table 1. Our results for 456 are in good agreement with the values  $B_v = 0.4089692(36)$  and  $D_v = 1.730(31) \times 10^{-7}$  reported by Wang et al. [14]. No clear evidence of local perturbation was observed in our experiments.

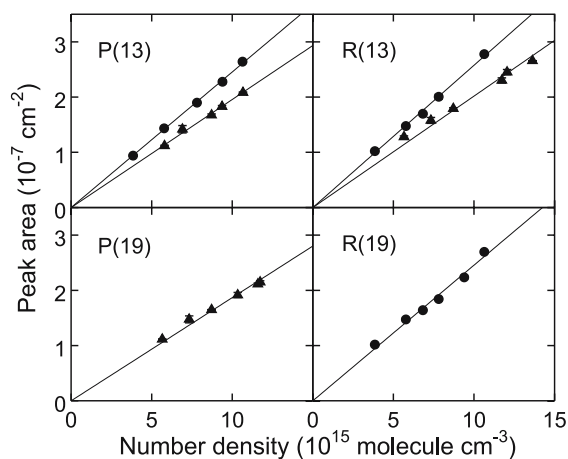
Line intensities,  $S$  ( $cm\ molecule^{-1}$ ) for the 64 individual lines of 456, and 59 lines of 546 were determined. First, the absolute line intensities of P(13), R(13), and R(19) for 456 and P(13), P(19), and R(13) for 546 were determined. The spectra of these transitions were measured at the partial pressure of  $N_2O$  isotopologues, 0.11–0.41 Torr, in total pressure of 100 Torr with  $N_2$  buffer. No absorption of water vapor or 446 was observed when the cell was filled only

	$G_v$	$B_v$	$D_v \times 10^7$	$J_{max}P/R^b$	$n/N^b$	Ref.
$^{14}N^{15}N^{16}O$	6446.8987(21)	0.408995(49)	1.67(32)	38/38	74/76	this work
$^{14}N^{15}N^{16}O$	6446.89423(78)	0.4089692(36)	1.730(31)	37/30	62/69	[14]
$^{15}N^{14}N^{16}O$	6515.9814(24)	0.394850(35)	1.52(18)	42/36	72/78	this work

<sup>a</sup> Numbers in parentheses are one standard deviation for fitting in units of the last digits quoted.

<sup>b</sup>  $J_{max}P/R$ , the maximum values of the rotational quantum numbers for the P- and R-branches included in the fitting procedure;  $n$ , number of the line positions included in the fitting;  $N$ , number of the line positions observed in the present study.

**TABLE 1** Spectroscopic parameters (in  $cm^{-1}$ ) of the  $3\nu_3$  band of 456 and 546 from the absorption spectra analysis in the 6400–6463 and 6465–6532  $cm^{-1}$  regions and literature data<sup>a</sup>



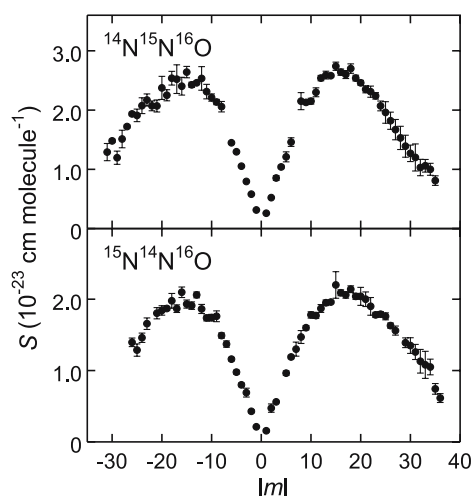
**FIGURE 2** Line intensities versus number density of the isotopologues of P(13), P(19), R(13), and R(19) of the  $3\nu_3$  band for  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (circles) and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (triangles). The solid lines are obtained by linear least square fit analysis to the data

with the 456 or 546 gases. These results indicated that water vapor and 446 impurities in the 456 and 546 gases are less than  $< 0.1$  and  $< 0.03\%$ , respectively. Figure 2 shows the partial pressure dependence of the peak areas. Least squares fit analysis of the data yielded the absolute line intensities of  $2.455(17) \times 10^{-23}$ ,  $2.576(26) \times 10^{-23}$ , and  $2.456(41) \times 10^{-23}$  cm molecule $^{-1}$  for P(13), R(13), and R(19) of 456, and  $2.057(40) \times 10^{-23}$ ,  $1.868(29) \times 10^{-23}$ , and  $1.956(21) \times 10^{-23}$  cm molecule $^{-1}$  for P(13), P(19), and R(13) of 546, respectively, at  $296 \pm 2$  K. The numbers in parentheses include one standard deviation uncertainty for the fits and the uncertainties for the pressure measurements, which were  $< 0.4\%$ . The possible contributions due to the uncertainties in temperature measurements ( $\pm 2$  K) were also taken into account. Secondly, the relative line intensities of other transitions were determined by comparing peak areas to those of P(13), R(13), R(19) for 456 and P(13), P(19), R(13) for 546. Line intensities for P(7) and R(7) of 456, and for R(3), R(27), and P(22) of 546 were not determined due to interference by water absorption lines or mode hopping of the diode laser. Figure 3 shows the obtained line intensities as functions of  $m$ .

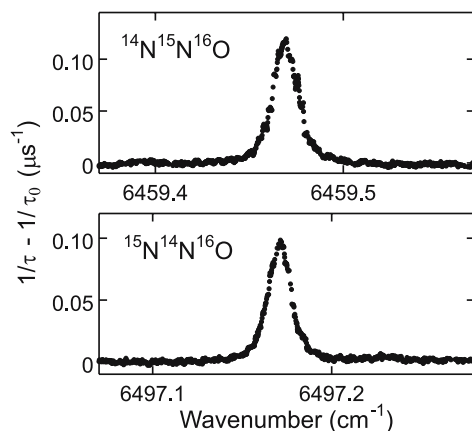
### 3.2 Isotope ratio measurements

For the isotopic ratio measurements, relatively strong lines of 456 and 546 with the same rotational quantum number were selected to avoid the population change by temperature fluctuation. In addition, interference by the major isotopologue (446), water vapor, and other possible contaminants were also eliminated. Finally, the selected lines were the R(19) transition at  $6459.49$  cm $^{-1}$  for 456 and the P(19) transition at  $6497.17$  cm $^{-1}$  for 546. Possible change in the isotope ratio of 456/546 by temperature change of 1 K at 296 K was calculated to be  $< 1 \times 10^{-4}$ .

Typical spectra of R(19) for 456 and P(19) for 546 measured at 32 Torr of cylinder  $\text{N}_2\text{O}$  gas without buffer gas are shown in Fig. 4. One set of measurements of 456 and 546 takes 20 min including the switching of the laser wavelength (typically 15 s). From the four alternative sets of spectral measurements, the 546/456 ratio was determined to



**FIGURE 3** Line intensity versus rotational level  $m$  for the  $3\nu_3$  band of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (upper panel) and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (lower panel) at  $296 \pm 2$  K. See (3) for  $m$



**FIGURE 4** CRDS spectra of R(19) of the  $3\nu_3$  band for  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (upper panel) and P(19) for  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (lower panel). The spectra were measured using cylinder  $\text{N}_2\text{O}$  at 32 Torr without buffer gas

be  $1.0041(51)$ . The uncertainty shown in parentheses is one standard deviation for the alternative measurements, which corresponds to the precision (5.1%) of the isotope ratio measurements. By taking the uncertainties of the line intensities into account, the accuracy of the measurements is estimated to be 2.3%.

The previously reported 546/456 ratios of commercially available  $\text{N}_2\text{O}$  gas in a cylinder using isotope ratio mass spectrometry calibrated with the  $\text{N}_2\text{O}$  synthesized by thermal decompositions of isotopically characterized  $\text{NH}_4\text{NO}_3$  were 0.998 [20] and 1.004 [19]. Westley et al. [19], however, reported the value change between 0.848 and 0.998 depending on the calibration approaches since they used the “reference” method. In the present study, we first performed the absolute measurement of the isotopic ratio using cw-CRDS.

## 4 Conclusion

We have determined the spectroscopic parameters and line intensities of  $3\nu_3$  band of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (456) and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (546) using continuous wave cavity ring-down spectroscopy at  $1.5$   $\mu\text{m}$ . Using the line intensities obtained in

the present study, the absolute isotopic ratio of  $N_2O$  in a commercial gas cylinder was determined to be 1.0041(51).

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