Determination of N_2O isotopomers with quantum cascade laser based absorption spectroscopy

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Abstract: We present an analytical technique based on direct absorption laser spectroscopy for high precision and simultaneous determination of the mixing ratios of the most abundant nitrous oxide isotopic species: $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$ and $^{14}N_2^{16}O$. A precision of 0.5 ‰ was achieved for the site specific isotope ratios of N_2O at 90 ppm using an averaging time of 300 s.

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1. Introduction

Nitrous oxide (N_2O) is a stratospheric ozone depleting substance and exerts the fourth largest radiative forcing. The predominant sources of N_2O on a global scale are microbial production in fertilized agricultural lands as well as biomass and fossil fuel burning. While the major sink, stratospheric destruction, is well quantified, the strength of N_2O sources remains largely uncertain, due to the complexity of pathways involved [1].

Important information about the geochemical cycle of N_2O can be obtained by measuring the intramolecular distribution of ^{15}N within atmospheric N_2O [2]. Being a linear, non-symmetric molecule (N–N–O), with one nitrogen atom at the center (α site) and one at the end (β site), there are two isotopomers containing one heavy isotope of nitrogen, namely $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, referred to as $^{15}N^{\alpha}$ and $^{15}N^{\beta}$, respectively. The corresponding isotope ratios are usually reported in the δ-notation, where $\delta^{15}N$ denotes the relative difference in per mil (‰) of the $^{15}N/^{14}N$ ratio of the sample versus the reference material (atmospheric N_2), thus $\delta^{15}N^{\beta}$ for example denotes the site specific ratio of $^{15}N^{14}N^{16}O$ vs. $^{14}N^{14}N^{16}O$.

Currently, the only analytical technique for N_2O isotope measurements at ambient concentrations is the laboratory-based isotope-ratio mass-spectrometry (IRMS). Unfortunately, isotopomers such as $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$, cannot directly be distinguished by IRMS, as they have identical molecular mass. The determination of site-selective isotopic composition involves the complex analysis of the NO^+ and N_2O^+ ions [3, 4] and the adopted methods lead to an unresolved discrepancy of almost 30 ‰ for the absolute intramolecular distribution of ^{15}N in N_2O. The difference seems partly be due to differences in calibration strategies [5]. These limitations might be avoided by the development of more direct and independent analytical approaches. Moreover, continuous measurements under field conditions would open a completely new field of applications for N_2O isotopomer studies.

This motivates the development of an alternative analytical technique based on direct absorption laser spectroscopy. In contrast to IRMS, laser spectroscopy offers the inherent advantage of site selectivity combined with high sensitivity and time resolution. So far, the published spectroscopic measurements of N_2O isotope ratios were mostly done in pure N_2O and suffered from limited precision [6-8]. In this paper, we demonstrate the precise and simultaneous determination of the site specific isotope abundance ratios of N_2O at concentrations as low as 9 ppm with a pulsed quantum cascade laser based spectrometer. This instrument is adequate to determine the isotopic signature of major biogenic and technical processes where the concentrations of the emitted N_2O can increase up to several tens of ppm [9-10]. Furthermore, isotopic analysis at ambient concentrations would be accessible by coupling the laser spectrometer to a preconcentration unit.

2. Experimental

2.1 Instrumental setup and data analysis

Figure 1(a) shows the experimental setup employing a single-mode, pulsed quantum cascade laser (QCL) emitting at 4.6 µm, a multipass absorption cell and a detection system. The spectrometer is an improved version of an instrument built by Aerodyne Research Inc. [11-12]. Briefly, the laser (Alpes Lasers SA, CH) operates at quasi-room temperature with 10 ns pulses at a repetition rate of 1 MHz and it is frequency tuned with a sweep rate of 8 kHz by a sub-threshold current ramp that rapidly modulates its temperature. The tuning rate of the laser is determined using the fringe spectrum of a solid state Ge-etalon with a free spectral range of 0.0485 cm^{-1}. The laser beam passes through a wedged BaF_2 beamsplitter and is then coupled

into the multipass cell with an optical path length of 56 m in a volume of 0.5 L (Aerodyne Research Inc., USA). The outcoming beam is focused on a thermoelectrically cooled detector (PDI-2TE-5, Vigo System SA, PL). The fraction of light that has been reflected by the beamsplitter is directly coupled into the same detector. Due to the large path length difference between reference and sample pulse, the former reaches the detector 150 ns earlier than the pulse exiting the multipass cell. Since the detector is fast enough ($\tau = 60$ ns) it can temporally resolve these two pulses. Normalizing the sample pulse with the reference pulse reduces the effect of pulse-to-pulse fluctuations and, therefore, significantly improves the signal-to-noise ratio [11].

The mixing ratios are obtained by simultaneously fitting a low-order polynomial to the spectral baseline and a Gaussian-convoluted Voigt profile to the observed absorption lines, taking into account the measured path length, gas temperature (~ 306 K), pressure (8 kPa) and laser line width (0.014 cm^{-1}).
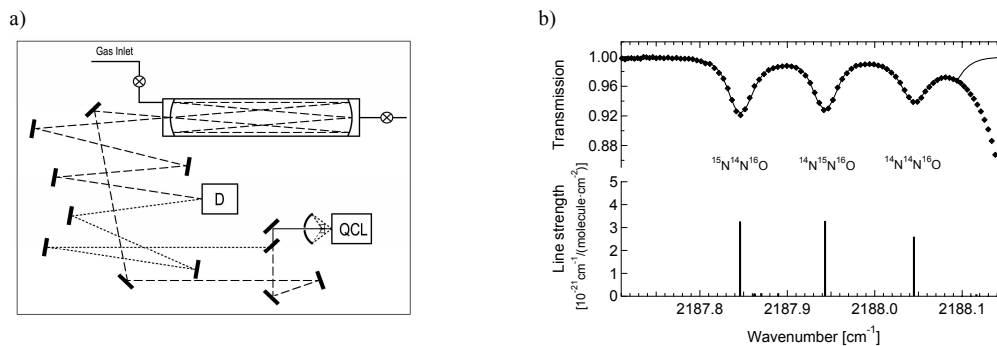

Fig. 1. (a). Schematic of the optical layout (QCL: quantum cascade laser, D: detector). (b) Measured (dots) and fitted spectrum (solid line) of the N_2O isotopes (top) and the corresponding line strengths (bottom). The tail of a strong absorption line of $^{14}N^{14}N^{16}O$ (2188.19 cm^{-1}) is clearly visible and was considered in the fit up to 2188.1 cm^{-1}.

The selected absorption lines for this study are shown in Fig. 1(b). They are located within the scanning range of the laser and have sufficiently strong line strength with similar absorbance for each isotopic species. This, however, also implies considerable differences in the lower state energies (E") of the selected absorption lines and results in a pronounced temperature sensitivity. With E" = 1205.9 cm^{-1} the absorption line of the main isotope has a significantly different E" than the two other isotopomers $^{14}N^{15}N^{16}O$ (65.4 cm^{-1}) and $^{15}N^{14}N^{16}O$ (110.1 cm^{-1}). These differences translate into a temperature sensitivity of 17.3 ‰ K^{-1} and 16.6 ‰ K^{-1} for $\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$, respectively. To account for this, the gas temperature is controlled to 0.1 K and measured with a precision of one mK using a calibrated 10 kΩ thermistor in the absorption cell. As discussed in [8], these absorption lines are essentially interference-free at ambient concentrations. For field applications with large changes in H_2O, CO or CO_2 we would, nevertheless, consider using specific adsorbing or drying agents.

2.2 Preparation of isotopic standards

A set of gas mixtures with distinct N_2O isotopomer compositions was prepared in two steps. First, isotopically pure (> 98 %) $^{15}N^{14}N^{16}O$ and $^{14}N^{15}N^{16}O$ (Cambridge Isotope Laboratories, USA) were diluted with high purity synthetic air (> 99.999 %, 20.5 % O_2, Messer, CH) and their exact mixing ratio determined gravimetrically. The gas cylinders contained 359 ± 3 ppm ($^{15}N^{\alpha}$) and 353 ± 3 ppm ($^{15}N^{\beta}$) of N_2O, respectively. Additionally, the isotopic purity of both tanks was determined by the quantification of $^{14}N_2^{16}O$ (< 2 ppm) using laser spectroscopy. Secondly, in order to span the δ-scale, five calibration gases were produced in 50 L stainless steel cylinders. These were first filled with known volumes of medical N_2O (> 98 %, Messer, CH), supplemented with exact amounts of isotopic pure N_2O ($^{15}N^{\alpha}$ and / or $^{15}N^{\beta}$) and diluted with a defined volume of high purity synthetic air (Table 1). The exact amounts of added N_2O

were determined using a high precision flow measurement device (molbox1, DH Instruments Inc., USA), and the dilution with synthetic air was controlled gravimetrically. Calibration gas concentrations were assigned using laser spectroscopy, referenced to a certified standard (92.0 ± 0.2 ppm N_2O in synthetic air, Messer, CH). Similarly to the use of atmospheric N_2 for IRMS, isotopomer specific ratios here are reported relative to medical N_2O in synthetic air which is used as reference to calculate the δ-values from the isotope ratios.

Table 1. N_2O concentrations and δ-values of calibration gases with ±σ (δ reference point: medical N_2O)

Cylinder code	Description	N_2O [ppm]	$\delta^{15}N^{\alpha}$ [‰]	$\delta^{15}N^{\beta}$ [‰]
Ref	medical N_2O	91.1 ± 0.8	0[a]	0[a]
α50	med. N_2O + $^{15}N^{\alpha}$	90.8 ± 0.8	51.5 ± 0.7	0
αβ25	med. N_2O + $^{15}N^{\alpha}$ + $^{15}N^{\beta}$	90.8 ± 0.8	25.4 ± 0.6	25.4 ± 0.8
β50	med. N_2O + $^{15}N^{\beta}$	91.6 ± 0.8	0	50.5 ± 0.9
β100	med. N_2O + $^{15}N^{\beta}$	91.4 ± 0.8	0	101.1 ± 1.2

[a]by definition

3. Results and discussion

3.1 Precision and long-term stability

The spectrometer's performance regarding precision and stability was characterized using the Allan variance technique [13]. At a concentration of 90 ppm N_2O, a short term precision (1 Hz) of 6.1 ‰ for the $^{15}N^{\beta}/^{14}N$ ratio was obtained, while the Allan variance reached its minimum at an integration time of 300 s, corresponding to a precision of 0.46 ‰ (see Fig. 2). Similar results were obtained for the $^{15}N^{\alpha}/^{14}N$ ratio (data not shown). The isotopomer concentrations reported here are weighted by the isotopic abundance as given in the HITRAN database [14]. The $^{15}N^{\beta}/^{15}N^{\alpha}$ ratio measurement had a comparable precision (0.67 ‰ @ 300 s), which indicates that temperature fluctuations do not limit instrumental precision. At 9 ppm, the precision was 5 to 10 times lower than at 90 ppm (see Fig. 2).
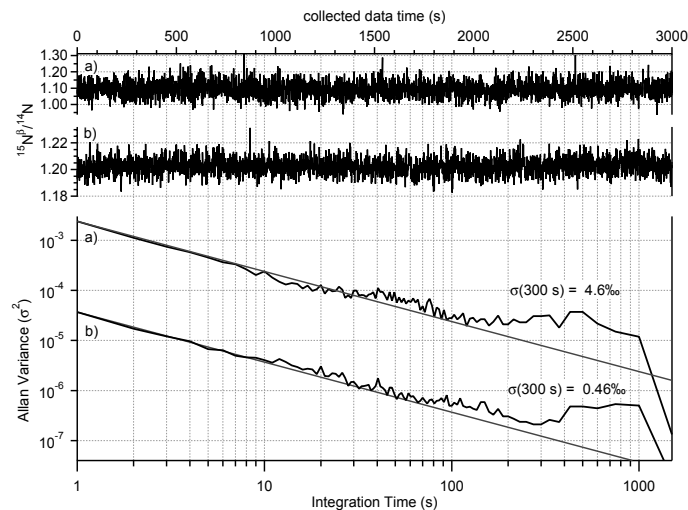

Fig. 2. Allan variance of the normalized isotope ratio $^{15}N^{\beta}/^{14}N$ (see text) at 9 ppm (a) and 90 ppm (b) of N_2O.

The long-term stability of the instrument was assessed by performing an unattended measurement over several days while alternating every 10 minutes between sample gas (α50) and reference N_2O (Ref). A small vacuum pump continuously drew the gas through the absorption cell, while a manually adjusted metering valve maintained a gas flow of 0.15 L/min. During these measurements, a slight drift in gas pressure ($\Delta P = 0.3$ kPa) and temperature ($\Delta T = 0.1°C$) was observed. The pressure dependence of the analytical procedure had previously been determined experimentally as 4 ‰/kPa. Hence, the changes in these parameters can not explain the shift of 80 ‰ observed in the derived isotope ratio illustrated in Fig 3(a). The drift was due to an unusually large change in laser intensity of 11 % during the measurement period. Moreover, the overall spectral range (0.43 cm^{-1}) shifted by 4% towards higher wavenumbers. About 90 % of this took place in the first 15 hours after turning on the instrument, i.e. in a situation when thermal equilibrium of the whole system was not achieved yet. However, even in such extreme situations the average $\delta^{15}N^{\beta}$ of the sample gas could be determined with a standard deviation of 0.7 ‰ (see Fig. 3(b)). For $\delta^{15}N^{\alpha}$ a standard deviation of 0.5 ‰ was achieved, which is similar to the precision obtained by the Allan variance technique. This clearly demonstrates the necessity of a frequent calibration procedure.
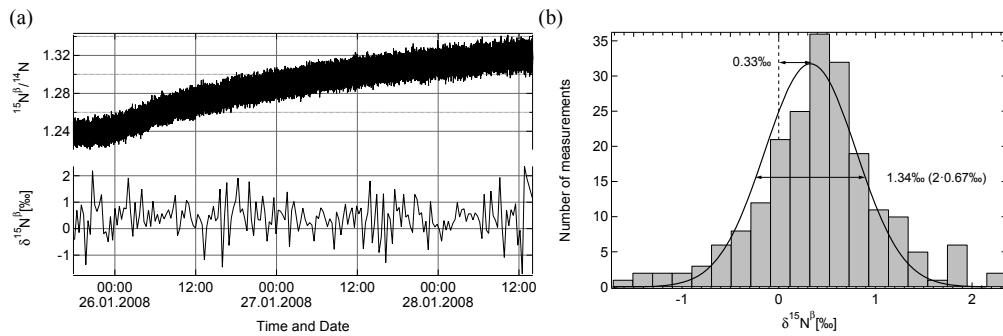

Fig. 3. Repeated measurements of a gas cylinder (α50). (a) Time series of the $^{15}N^{\beta}/^{14}N$ ratio and the drift corrected averaged $\delta^{15}N^{\beta}$ values (10 min) during 2.5 days. (b) After drift correction averaged $\delta^{15}N^{\beta}$ values (10 min) were plotted as a histogram with a 0.2 ‰ bin width. The distribution is nearly Gaussian with a standard deviation of 0.7 ‰ and a shift of 0.3 ‰ with respect to the expected δ-value.

3.2 Calibration procedure

Direct absorption spectroscopy is an absolute method that, in principle, allows for a straightforward determination of the concentration, and hence the calculation of isotope ratios from the measured signals. In practice, however, the accuracy of this calculation depends on many parameters, such as the laser line width and shape, and the quality of the molecular line parameters. Additionally, instrumental nonlinearity and drifts will bias the retrieved isotope ratios. To account for this, the instrument needs to be equipped with a calibration system.

The retrieved isotope ratios showed an accentuated dependence on the N_2O concentration, which is consistent with observations from measurements of CO_2 isotopologues [15]. This dependence on total N_2O was characterized by dynamically diluting various calibration gases with N_2O-free synthetic air. The experimental results for $\delta^{15}N^{\beta}$ are well described by a linear interpolation. The very slight deviations in the slope values for individual dilution curves are probably due to instrumental drifts. Their average value of 0.28 ‰ ppm^{-1} is an excellent approximation to account for the dependence on total N_2O for all δ–values, as shown in Fig. 4(a). Based on this linear interpolation, the expected δ-values of the calibration gases were plotted against the spectroscopically measured isotope ratios which were normalized to an arbitrarily selected N_2O concentration (60 ppm in this case). This yielded a calibration function that links the measured isotope ratio values to the δ-scale (Fig. 4(b)). The linearity

and potential accuracy of the instrument can be assessed from the residual of the linear interpolation, which has a 1σ standard deviation of 0.34 ‰. Given the linear behavior depicted in Fig. 4, the entire calibration of the spectrometer can in principle be performed by single-point measurements of three adequate reference gases. Two are needed to determine the dependency of isotope ratios on the N_2O concentration and a third one to define the calibration function that links the normalized isotope ratio values to the δ-scale. The same procedure can be applied to $\delta^{15}N^{\alpha}$.

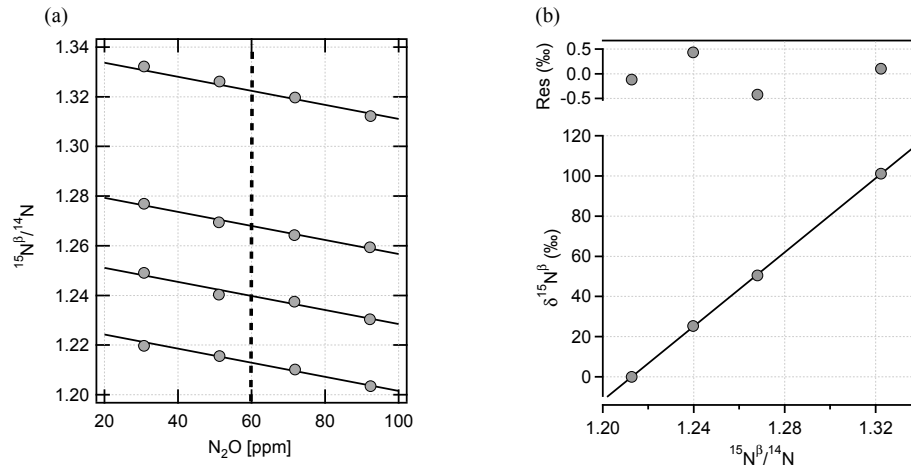Fig. 4. (a). The isotopomer specific $^{15}N^{\beta}/^{14}N$ ratio measured for different N_2O concentrations. (b) The linear relationship between $\delta^{15}N^{\beta}$ of the calibration gases and the interpolated $^{15}N^{\beta}/^{14}N$ ratios determined by laser spectroscopy.

4. Conclusions and outlook

A versatile analytical method for high precision, continuous and simultaneous determination of the site specific isotope abundance ratios of N_2O at trace level is presented. In contrast to IRMS, this optical technique offers a direct way to investigate the intramolecular isotope distribution of nitrogen without any sample pretreatment. The instrument achieves a precision of 0.5 ‰ with 300 s averaging time for 90 ppm of N_2O which is more than one order of magnitude better than previously reported values. Measurements of various, isotopically enriched gas samples showed a linear instrumental response to changing δ-values. This allows for a straightforward calibration of the system.

The precision and sensitivity of the current spectrometer is adequate for example to differentiate between the most important biogenic N_2O emitting processes, nitrification and denitrification, where differences in the site preference ($\delta^{15}N^{\alpha}$ - $\delta^{15}N^{\beta}$) exceed 30 ‰ and concentrations are in the ppm-range [16]. Other field applications, such as source characterization of anthropogenic N_2O emissions, are also directly accessible. For atmospheric applications, further improvements are needed. A significant step forward would be the use of a high power, continuous wave QCL that should soon be available. Further enhancements may be obtained by the latest generation of TE-cooled detectors or the implementation of a reference cell as demonstrated for CO_2 isotope measurements [16]. At the current state of laser spectroscopy, the most promising way to reach excellent precision at ambient N_2O concentration may be the addition of an automated preconcentration unit.