Positionally dependent ^{15}N fractionation factors in the UV photolysis of N$_2$O determined by high resolution FTIR spectroscopy

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Abstract. Positionally dependent fractionation factors for the photolysis of isotopomers of N$_2$O in natural abundance have been determined by high resolution FTIR spectroscopy at three photolysis wavelengths. Fractionation factors show clear ^{15}N position and photolysis wavelength dependence and are in qualitative agreement with theoretical models but are twice as large. The fractionation factors increase with photolysis wavelength from 193 to 211 nm, with the fractionation factors at 207.6 nm for ^{14}N^{15}N^{16}O, ^{15}N^{14}N^{16}O and ^{14}N^{14}N^{18}O equal to -66.5 ± 5 ‰, -27.1 ± 6 ‰ and -49 ± 10 ‰, respectively.

Introduction

Nitrous oxide (N$_2$O) is an important atmospheric trace gas, because of its role as a major greenhouse gas [Yung et al., 1976] and its involvement in stratospheric ozone destruction through reaction with O(^{1}D) and resultant formation of nitrogen oxides [Crutzen, 1970]. It is a useful tracer for transport because of its long atmospheric lifetime of approximately 150 years [Khalil and Rasmussen, 1992]. Its main sources are bacterial denitrification and nitrification reactions in soils and oceans. Nitrous oxide is also produced in some industrial processes, especially as a by-product in the production of adipic acid [Bouwman et al., 1995]. Its main sink is photolysis in the stratosphere.

Uncertainties in the source and sink budget of atmospheric N$_2$O remain difficult to reduce, due to the relatively small source fluxes that are spread over large surface areas [Bouwman et al., 1995]. Isotopic measurements of nitrous oxide sources have been increasingly carried out to provide additional constraints on the global N$_2$O budget, with the aim of narrowing these uncertainties [Cliff et al., 1999; Dore et al., 1998; Kim and Craig, 1990; Naqvi et al., 1998; Yoshida et al., 1984; Yoshida and Matsuo, 1983; Yoshida et al., 1989; Yoshinari and Wahlen, 1985]. Isotopic measurements are quoted as deviations (δ) from a standard in parts per mil (‰). For example,

$$\delta\ ^{18}O = \left(\frac{R^{18}_{(sample)}}{R^{18}_{(standard)}} - 1 \right) \times 1000 \qquad (1)$$

where R^{18} is the ratio of ^{18}O to ^{16}O. Currently, δ^{15}N and δ^{18}O measurements of N$_2$O are made relative to the ^{15}N/^{14}N and ^{18}O/^{16}O ratios of atmospheric N$_2$ and O$_2$, respectively.

Nitrous oxide is believed to be inert in the troposphere. Photolysis in the stratosphere is responsible for about 90% of its removal via the reaction N$_2$O + hν → N$_2$ + O(^{1}D) (λ ≈ 180-215 nm), the remainder being destroyed by reactions with O(^{1}D) to give either O$_2$ and N$_2$ or alternatively, NO.

Yung and Miller [1997] have suggested the heavy isotopomers of N$_2$O in the stratosphere should be photolysed at slower rates than the parent isotope, ^{14}N^{14}N^{16}O (446), leading to an enrichment of the heavy N$_2$O isotopomers. In particular the two positional isotopomers ^{14}N^{15}N^{16}O (456) and ^{15}N^{14}N^{16}O (546) should have markedly different stratospheric photolysis rates. Differences in the zero point energy (ZPE) of the isotopomers lead to a blue-shift of the UV absorption spectrum for the heavy isotopomers relative to the parent isotope, 446. The blue-shifted UV absorption spectra have lower cross sections in the region of the solar UV spectrum, so that the heavy isotopomers are photolysed more slowly than the parent. To a first approximation the photolysis rates are proportional to the size of the ZPE shift, such that photolysis rates are predicted to increase in the order 446>447>546>448>456. The consequent stratospheric enrichment of the heavy isotopes has been observed for the mean δ^{15}N and δ^{18}O from analysis of stratospheric samples [Kim and Craig, 1993; Rahn and Wahlen, 1997], and laboratory laser-photolysis studies of N$_2$O [Rahn et al., 1998; Röckmann et al., 2000; Zhang et al., 2000]. Measurements by Griffith et al. [2000] of stratospheric N$_2$O vertical profiles by a balloon borne FTIR spectrometer confirm the enrichment of the heavy isotopomers 456, 546 and 448.

If all N$_2$O destruction occurs by photolysis in the stratosphere and is irreversible, it can be described by a Rayleigh distillation model [Rahn and Wahlen, 1997]. In this model the resulting isotopic enrichment is related to the fraction of unphotolysed N$_2$O remaining by:

$$R = R_0 f^{(\alpha-1)} \qquad (2)$$

where R and R_0 are the remaining and initial heavy-to-light isotopic ratios, f is the unphotolysed fraction of N$_2$O and α is the ratio of the heavy to light isotopic photolysis rates. If R and R_0 are close to 1, this relationship can be simplified to:

$$\delta = \delta_0 + \varepsilon \ln(f) \qquad (3)$$

where δ and δ_0 are the residual and initial δ values and the slope ε = 1000(α-1) is the fractionation factor expressed in parts per mil (‰) [Fritz and Fontes, 1980].

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In this paper we present measurements of the fractionation factors (ε) for laboratory-photolysed N_2O samples. We have used high resolution FTIR spectroscopy to measure the positionally dependent ^{15}N photolysis fractionation factors, ε^{456} and ε^{546}, and also ε^{448} in natural abundance at three wavelengths, 193, 211.5 and approximately 207.6 nm.

Experimental

We analysed the same samples of N_2O photolysed at 207.6 nm and 193 nm as described by Rahn *et al.* [1998] in a previous study. Additional N_2O samples photolysed at 211.5 nm were also included. Experimental details for the photolysis procedure are given by Rahn *et al.* [1998]. Briefly, samples of N_2O were introduced to a thermostatted glass cell (approximately 300 mL in volume) and photolysed with laser-generated UV light at 211.5 nm, 207.6 nm or 193 nm with a line width of ≈ 1.5-2.5 cm^{-1}. After photolysis, the unphotolysed N_2O fraction was determined manometrically and then cryogenically collected. We analysed these samples by high resolution FTIR spectroscopy for determination of the positional isotopomers and the photolysis fractionation factors. Rahn *et al.* [1998] used Isotope Ratio Mass Spectrometry (IRMS) to determine the mean $\delta^{15}N$ and $\delta^{18}O$ of these same samples.

Between 6 and 9 μmol of pure photolysed N_2O was introduced via a manifold (≈ 20 mL in volume) into a multiple reflection White cell [White, 1942] of total optical pathlength 2.4 m and volume 120 mL. Both the manifold and the White cell were thermostatted at 25°C. Spectra of the N_2O were acquired using a high resolution Bomen DA8 FTIR spectrometer with globar source, KBr beamsplitter and InSb detector. Each spectrum consisted of 15 coadded scans acquired over 30 minutes at an apodised resolution of 0.012 cm^{-1}. This technique is non-destructive, insensitive to the presence of moderate amounts of impurity gases (including CO_2) and requires no chemical modification of the N_2O sample. Most samples were measured twice, approximately 3 months apart.

Quantitative analysis of the spectrum for each isotopomer was carried out by a Classic Least Squares (CLS) algorithm using calculated reference spectra for each isotopomer. Full details of the method are given by Esler *et al.* [2000a-c] and Griffith [1996]. Under these conditions, most absorbance lines of the main band of the parent $^{14}N^{14}N^{16}O$ isotopomer saturate and are not suitable for CLS analysis. Small regions of the infrared spectrum of N_2O were selected between these strong lines to minimize non-Beer's law behavior. We analysed 80 such "microwindows", each typically less than 1 cm^{-1} wide. These 80 determinations were pooled to give a single result for each isotopomer by taking the weighted mean of the individual determinations.

We calculated δ values relative to the those of the starting N_2O before photolysis, Standard Nitrous Oxide Working gas (SNOW), which has $\delta^{15}N = 1.31$ ‰ and $\delta^{18}O = 18.46$ ‰ relative to atmospheric N_2 and O_2, respectively [Rahn, 1998]. We relate all measurements by reference to a working standard of high purity N_2O (Scott-Marrin), in a tank filled to a pressure which avoids liquification of the N_2O. Measurements of photolysed N_2O were interleaved with measurements of the working standard. Scan to scan variations and drift in the spectrometer on a timescale of about 1 hour are the major limitations to precision with the

current spectrometer. Consecutive replicate measurements of a single N_2O sample provide an estimate of the analytical precision ($\pm 1\sigma$) of approximately 1.6, 2.2 and 4.1 ‰ for δ^{456}, δ^{546} and δ^{448} respectively. Modeling of the instrument performance suggests a precision of 0.3, 0.4 and 0.4 ‰ respectively should be achievable for measurements under the same conditions [Esler *et al.*, 2000a].

Results and Discussion

Figure 1 illustrates the data plotted to a Rayleigh distillation model for N_2O photolysis at 193 nm; plots for photolysis at 211.5 nm and 207.6 nm are similar. In all cases, the data fit the Rayleigh distillation model well, within the scatter. Table 1 summarises the fractionation factors (ε) for the 456, 546 and 448 isotopomers at each wavelength, determined as the slopes of the regressions of δ against $\ln(f)$. The errors quoted are the standard deviations of the slopes from the regressions. The ^{15}N fractionation factors are also given as the mean or bulk $\varepsilon^{15}N = (\varepsilon^{546}+\varepsilon^{456})/2$ for comparison with IRMS measurements, and the difference $\varepsilon^{546-456} = \varepsilon^{546} - \varepsilon^{456}$. As predicted by the theoretical work of Yung and Miller, photolysis rates for the positional N_2O isotopomers $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ are significantly different at all three photolysis wavelengths. The difference in the positional isotopomer fractionation factors ($\varepsilon^{546-456}$) is clearly wavelength dependent, and ranges from 12.6 ± 3 ‰ for 193 nm photolysis to 39.3 ± 7 ‰ for 207.6 nm photolysis. Under the approximation that photolysis rates are proportional to the ZPE shift of the substituted species from that of the parent $^{14}N^{14}N^{16}O$, we expect the $\varepsilon^{456}/\varepsilon^{546}$ ratio to be approximately 1.8 – the ratio of their ZPE shifts. The measured $\varepsilon^{456}/\varepsilon^{546}$ ratios are 2.08 ± 0.5, 2.45 ± 0.6 and 1.96 ± 0.3 for the photolysis wavelengths 211.5 nm, 207.6 nm and 193 nm respectively, qualitatively supporting the Yung and Miller mechanism. However, all measured fractionation factors are nearly twice as large as those predicted by the Yung and Miller theory.

Two recent complementary studies [Röckmann *et al.*, 2000; Zhang *et al.*, 2000] have also determined the
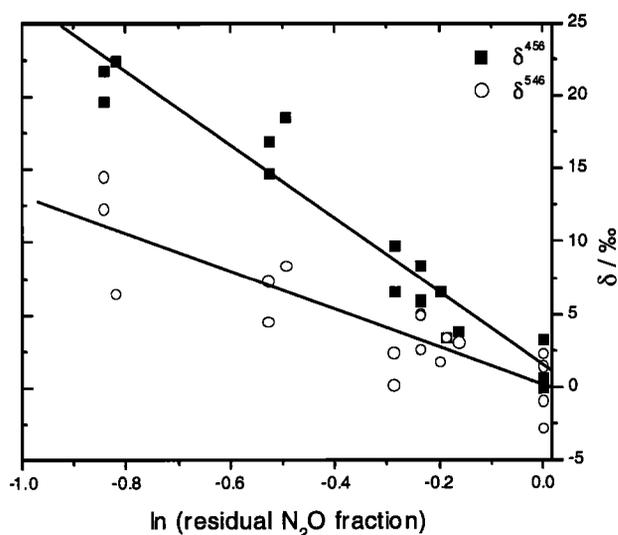

Figure 1. Rayleigh distillation plot for N_2O photolysis at 193 nm.

Table 1. Photolysis fractionation factors of N_2O (this work)

λ (nm)	ε^{456}	ε^{546}	$\varepsilon^{15}N$	$\varepsilon^{546-456}$	ε^{448}
193	-25.7±2	-13.1±2	-19.4± 1.2	12.6±3	-15.9±3
207.6	-66.5±5	-27.1±6	-46.8 ± 5	39.3±7	-49±10
211.5	-65.3±4	-31.4±8	-48.3 ± 5	33.9±9	-46±11

The fractionation factors (ε) are the slopes of regressions of δ against $\ln(f)$ as described in Equation 3. The errors are the standard deviations of the regression slopes. $\varepsilon^{15}N$ is the average of ε^{546} and ε^{456}, and $\varepsilon^{546-456}$ is the difference ε^{546} - ε^{456}.

positionally dependent fractionation factors for laboratory photolysed N_2O. Röckmann et al. [2000] employed a modified isotope ratio mass-spectrometry technique [Brenninkmeijer and Röckmann, 1999; Toyoda and Yoshida, 1999] for measuring positionally dependent fractionation factors during N_2O photolysis at 193 nm. Zhang et al. [2000] measured fractionation factors for laboratory photolysis of equimolar mixtures of pure isotopomers of N_2O at a single wavelength (213 nm), by using low resolution (0.5 cm^{-1}) FTIR spectroscopy to measure the Q-branch of the v_2+v_3 combination band. The original work by Rahn et al. [1998] measured the average ^{15}N fractionation factor, $\varepsilon^{15}N$, by conventional IRMS methods. Figure 2 summarises the fractionation factors $\varepsilon^{15}N$ and $\varepsilon^{546-456}$ and their errors for N_2O photolysis from all laboratory studies reported to date, together with the predictions of Yung and Miller.

In most cases there is good agreement within the error estimates for the $\varepsilon^{15}N$ and $\varepsilon^{546-456}$ fractionation factors. The error estimates in Figure 2 are dominated by random errors. Minor systematic differences may be due to the different calibration methods used in each study. In this work, calibration is based on HITRAN line parameters [Rothman et al., 1998] and the calculation of synthetic spectra, whereas Zhang et al. used laboratory measurements of the pure isotopomer spectra. In the work of Röckmann et al. calibration is dependent on reactions in the ion source, in particular scrambling of the end and central N atoms in N_2O. Since each study reports fractionations relative to the starting N_2O isotopic composition, most systematic errors should cancel, but non-linearities could lead to small systematic discrepancies. With the exception of the measurements at 193 nm, any such systematic differences appear to be smaller than random errors. At 193 nm, the magnitudes of the fractionation factors of Röckmann et al. are significantly larger than those from the other studies, and the cause of this particular discrepancy is unresolved at present. Röckmann et al. suggested a saturation effect in the photolysis experiments of Rahn et al., but the exact cause is as yet unidentified. Further measurements and exchange of calibration standards currently underway should resolve this difference.

In general, all the laboratory measurements are nearly double those predicted by the Yung and Miller theory, the exception being $\varepsilon^{546-456}$ at 193 nm from the study of Röckmann et al. which is nearly five times the Yung and Miller prediction. Whilst the absolute magnitude of this fractionation of the N_2O isotopomers is still in question, it seems that the principle behind the Yung and Miller model of isotopic enrichment is valid. Zhang et al. [2000] and Miller and Yung [2000] discuss the limitations of the theory in more detail.

Enrichment of the heavy isotopomers in N_2O samples from the lower stratosphere was first observed by Moore [1974], followed by Kim and Craig [1993], and more recently confirmed by Rahn and Wahlen [1997]. The measured stratospheric ^{15}N fractionation factors (-14‰ to -18‰) are considerably smaller than the laboratory measurements, but in good agreement with the theory of Yung and Miller. Rahn et al. [1998] invoked diffusive mixing to explain the reduced fractionations compared to laboratory measurements: diffusive mixing of isotopically light N_2O from lower altitudes will reduce the apparent stratospheric fractionation factors. Assuming mixing is also included in the Yung and Miller 2D model, it is not clear why there is agreement with the stratospheric results but a factor of two discrepancy with the laboratory measurements. Very recent measurements of vertical profiles of N_2O isotopomers to 35km altitude indicate fractionation factors in the middle stratosphere (20–35 km) similar to laboratory measurements [Griffith et al., 2000]. Thus, while the Yung and Miller model appears to be qualitatively correct, there are quantitative differences still to be resolved. Direct measurements of the temperature-dependent, pure isotopomer, high resolution UV absorption spectra of N_2O are needed to help resolve the discrepancies. From such spectra the true differences in absorption (and hence fractionation) for the isotopomers can be calculated without need for simplifying ZPE assumptions.

Conclusions

This work presents the first high resolution FTIR measurements of the positionally dependent fractionation
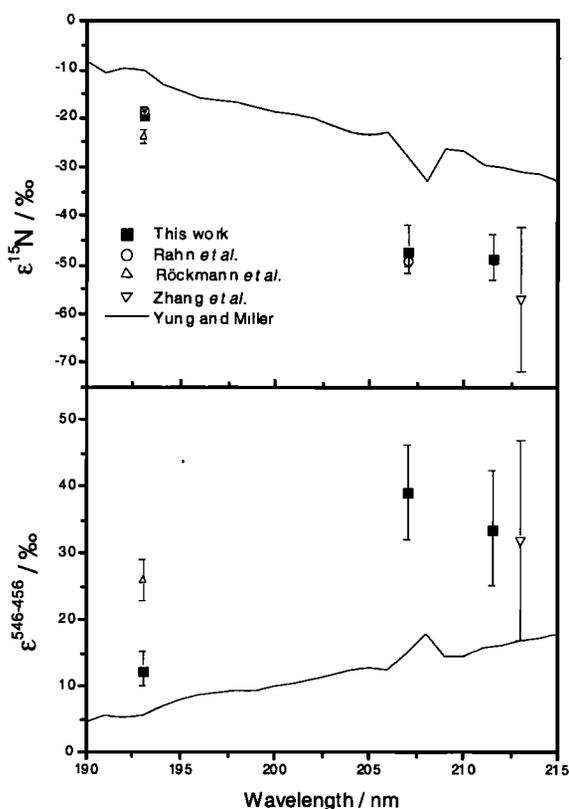

Figure 2. Fractionation factors $\varepsilon^{15}N$ and $\varepsilon^{546-456}$ for the laboratory photolysis of N_2O. Error bars (±1σ) are determined from the scatter in the respective measurements.

factors for the UV photolysis of N_2O in natural isotopomeric abundance. The high resolution FTIR technique complements IRMS techniques for N_2O isotopic analysis. We confirm the positional dependence of the photolysis of N_2O, with $^{14}N^{15}N^{16}O$ being fractionated approximately twice as much as $^{15}N^{14}N^{16}O$. Further, there is a clear wavelength dependence in the fractionation factors, with the differences increasing with photolysis wavelength. Where they can be compared, the FTIR measurements are generally in good agreement with other experimental studies. The measured fractionation factors relative to each other and their wavelength dependence are in qualitative agreement with the Yung and Miller theory, but are consistently nearly double those predicted by the theory. The isotopic fractionation factors are neatly described by a Rayleigh distillation model, consistent with fractionation by an irreversible sink process.

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