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

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Abstract. Positionally dependent fractionation factors for the photolysis of isotomers of N$_2$O in natural abundance have been determined by high resolution FTIR spectroscopy at three photolysis wavelengths. Fractionation factors show clear $^1$S 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 $^{15}$N$^{15}$N$^{16}$O, $^{15}$N$^{14}$N$^{16}$O and $^{14}$N$^{14}$N$^{18}$O equal to -66.5 $\pm$ 5 %, -27.1 $\pm$ 6 % and -49 $\pm$ 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 Masuo, 1983; Yoshida et al., 1989; Yoshinari and Wahlen, 1985]. Isotopic measurements are quoted as deviations ($\delta$) from a standard in parts per mil ($\%\circ$). For example,

$$\delta^{18}\text{O} = \left( \frac{R^{18}_{\text{Sample}}}{R^{18}_{\text{Standard}}} - 1 \right) \times 1000$$

where $R^{18}$ is the ratio of $^{18}$O to $^{16}$O. Currently, $\delta^{15}$N and $\delta^{18}$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 + hv $\rightarrow$ N$_2$ + O($^1$D) ($\lambda =$ 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, $^{15}$N$^{15}$N$^{16}$O (446), leading to an enrichment of the heavy N$_2$O isotopomers. In particular the two positional isotopomers $^{15}$N$^{15}$N$^{16}$O (456) and $^{15}$N$^{14}$N$^{18}$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 $\delta^{15}$N and $\delta^{18}$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; Rottmann 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:

$$R = R_0 \cdot f^{(a-1)}$$

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 $a$ 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:

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

where $\delta$ and $\delta_0$ are the residual and initial $\delta$ values and the slope $\varepsilon = 1000(a-1)$ is the fractionation factor expressed in parts per mil ($\%\circ$) [Fritz and Fontes, 1980].

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2 Now at the Australian Wine Research Institute, Waite Rd Urrbrae, SA 5064 Australia.
In this paper we present measurements of the fractionation factors (ε) for laboratory-photolysed N₂O samples. We have used high resolution FTIR spectroscopy to measure the positionally dependent ¹⁵N photolysis fractionation factors, ε⁴⁴₆ and ε⁵₄₆, and also ε⁴₄₈ in natural abundance at three wavelengths, 193, 211.5 and approximately 207.6 nm.

**Experimental**

We analysed the same samples of N₂O photolysed at 207.6 nm and 193 nm as described by Rahn et al. [1998] in a previous study. Additional N₂O 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 N₂O 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 N₂O 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 δ₁⁵N and δ₁⁸O of these same samples.

Between 6 and 9 μmol of pure photolysed N₂O 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 N₂O 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 CO₂) and requires no chemical modification of the N₂O 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 ¹⁴N¹⁴N¹⁶O isotopomer saturate and are not suitable for CLS analysis. Small regions of the infrared spectrum of N₂O 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 N₂O before photolysis, Standard Nitrous Oxide Working gas (SNOW), which has δ¹⁵N = 1.31 ‰ and δ¹⁸O = 18.46 ‰ relative to atmospheric N₂ and O₂, respectively [Rahn, 1998]. We relate all measurements by reference to a working standard of high purity N₂O (Scott-Marrin), in a tank filled to a pressure which avoids liquefaction of the N₂O. Measurements of photolysed N₂O 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 N₂O sample provide an estimate of the analytical precision (±1 σ₀) of approximately 1.6, 2.2 and 4.1 %₀ for δ⁴⁴₆, δ⁵₄₆ and δ⁴₄₈ respectively. Modeling of the instrument performance suggests a precision of 0.3, 0.4 and 0.4 %₀ 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 N₂O 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 ¹⁵N fractionation factors are also given as the mean or bulk ε¹⁵N = (ε⁴⁴₆ + ε⁵₄₆)/2 for comparison with IRMS measurements, and the difference ε⁴⁴₆-ε⁵₄₆ = ε⁵₄₆ - ε⁴⁶₅. As predicted by the theoretical work of Yung and Miller, photolysis rates for the positional N₂O isotopomers ¹⁴N¹⁴N¹⁶O and ¹⁵N¹⁴N¹⁶O are significantly different at all three photolysis wavelengths. The difference in the positional isotopomer fractionation factors (ε⁴⁴₆-ε⁵₄₆) is clearly wavelength dependent, and ranges from 12.6 ± 3 %₀ for 193 nm photolysis to 39.3 ± 7 %₀ 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 ¹⁴N¹⁴N¹⁶O, we expect the ε⁴⁴₆/ε⁵₄₆ ratio to be approximately 1.8 - the ratio of their ZPE shifts. The measured ε⁴⁴₆/ε⁵₄₆ 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 [Rückmann et al., 2000; Zhang et al., 2000] have also determined the
The fractionation factors ($\epsilon$) are the slopes of regressions of $\delta$ against $\ln(\delta)$ as described in Equation 3. The errors are the standard deviations of the regression slopes. $\epsilon^{15}\text{N}$ is the average of $\epsilon^{456}$ and $\epsilon^{546}$, and $\epsilon^{546-456}$ is the difference $\epsilon^{546} - \epsilon^{456}$.

Positionally dependent fractionation factors for laboratory photolyzed $\text{N}_2\text{O}$. Rockmann et al. [2000] employed a modified isotope ratio mass-spectrometry technique [Brenninkmeijer and Rockmann, 1999; Toyoda and Yoshida, 1999] for measuring positionally dependent fractionation factors during $\text{N}_2\text{O}$ photolysis at 193 nm. Zhang et al. [2000] measured fractionation factors for laboratory photolysis of equimolar mixtures of pure isotopomers of $\text{N}_2\text{O}$ 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 $^{15}\text{N}$ fractionation factor, $\epsilon^{15}\text{N}$, by conventional IRMS methods. Figure 2 summarises the fractionation factors $\epsilon^{15}\text{N}$ and $\epsilon^{546-456}$ and their errors for $\text{N}_2\text{O}$ 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 $\epsilon^{15}\text{N}$ and $\epsilon^{546-456}$ fractionation factors. The error estimates in Figure 2 are dominated by random errors. Minor systematic differences may be due to 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 Rockmann et al., calibration is dependent on reactions in the ion source, in particular scrambling of the end and central N atoms in $\text{N}_2\text{O}$. Since each study reports fractionations relative to the starting $\text{N}_2\text{O}$ 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 Rockmann et al. are significantly larger than those from the other studies, and the cause of this particular discrepancy is unresolved at present. Rockmann et al. suggested a saturation effect in the photolysis experiments of Rahn et al., but the exact cause is 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 $\epsilon^{546-456}$ at 193 nm from the study of Rockmann et al. which is nearly five times the Yung and Miller prediction. Whilst the absolute magnitude of this fractionation of the $\text{N}_2\text{O}$ 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.

Table 1. Photolysis fractionation factors of $\text{N}_2\text{O}$ (this work)

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\epsilon^{456}$</th>
<th>$\epsilon^{546}$</th>
<th>$\epsilon^{546} - \epsilon^{456}$</th>
<th>$\epsilon^{546-456}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>-25.7±2</td>
<td>-13.1±2</td>
<td>-19.4±1.2</td>
<td>12.6±3</td>
</tr>
<tr>
<td>207.6</td>
<td>-66.5±5</td>
<td>-27.1±6</td>
<td>-46.8±5</td>
<td>39.3±7</td>
</tr>
<tr>
<td>211.5</td>
<td>-65.3±4</td>
<td>-31.4±8</td>
<td>-48.3±5</td>
<td>33.9±9</td>
</tr>
</tbody>
</table>

Figure 2. Fractionation factors $\epsilon^{15}\text{N}$ and $\epsilon^{546-456}$ for the laboratory photolysis of $\text{N}_2\text{O}$. Error bars ($\pm1\sigma$) are determined from the scatter in the respective measurements.

Conclusions

This work presents the first high resolution FTIR measurements of the positionally dependent fractionation factors during $\text{N}_2\text{O}$ photolysis at 193 nm. Zhang et al. [2000] measured the average $^{15}\text{N}$ fractionation factor, $\epsilon^{15}\text{N}$, by conventional IRMS methods. Figure 2 summarises the fractionation factors $\epsilon^{15}\text{N}$ and $\epsilon^{546-456}$ and their errors for $\text{N}_2\text{O}$ photolysis from all laboratory studies reported to date, together with the predictions of Yung and Miller. 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 Rockmann et al., calibration is dependent on reactions in the ion source, in particular scrambling of the end and central N atoms in $\text{N}_2\text{O}$. Since each study reports fractionations relative to the starting $\text{N}_2\text{O}$ 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 Rockmann et al. are significantly larger than those from the other studies, and the cause of this particular discrepancy is unresolved at present. Rockmann et al. suggested a saturation effect in the photolysis experiments of Rahn et al., but the exact cause is yet unidentified. Further measurements and exchange of calibration standards currently underway should resolve this difference.

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factors for the UV photolysis of N₂O in natural isotopomeric abundance. The high resolution FTIR technique complements IRMS techniques for N₂O isotopic analysis. We confirm the positional dependence of the photolysis of N₂O, with ¹⁵N₄N₆O being fractionated approximately twice as much as ¹⁴N₄N₆O. 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.

References


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(Turatti et al.: Positionally Dependent Fractionation Factors)