

Stable Isotope Fractionation during Ultraviolet Photolysis of N₂O

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Abstract. The biogeochemical cycling of nitrous oxide plays an important role in greenhouse forcing and ozone regulation. Laboratory studies of N₂O:N₂ mixtures irradiated between 193-207 nm reveal a significant enrichment of the residual heavy nitrous oxide isotopomers. The isotopic signatures resulting from photolysis are well modeled by an irreversible Rayleigh distillation process, with large enrichment factors of $\epsilon_{15,18}(193 \text{ nm}) = -18.4, -14.5$ per mil and $\epsilon_{15,18}(207 \text{ nm}) = -48.7, -46.0$ per mil. These results, when combined with diffusive mixing processes, have the potential to explain the stratospheric enrichments previously observed.

Introduction

Nitrous oxide is a trace gas that is produced during microbial energy exchange reactions involving both reduced (NH₃) and oxidized (NO₃⁻) forms of nitrogen. These nitrification and denitrification processes are widespread in soils and in the world's oceans. A portion of the N₂O that is produced as an intermediate escapes to the troposphere where it is chemically inert. Eventually nitrous oxide ascends to the stratosphere, where it is photolyzed by ultraviolet radiation, oxidized by excited atomic oxygen, or returned to the troposphere during stratosphere/troposphere exchange processes. While in the atmosphere, N₂O actively absorbs infrared radiation and thereby contributes to greenhouse warming. A portion of the N₂O destroyed by the reaction with O(¹D) provides the principle natural source of NO, which initiates the catalytic NO_x cycling of stratospheric ozone. The current tropospheric concentration is about 313 ppbv [R. Weiss, personal comm.] and is increasing at a rate of ~0.25% per

year. Its contribution to the greenhouse effect, its effect on stratospheric ozone chemistry, and the observed rate of increase in the atmosphere make nitrous oxide a trace gas of significant research interest.

Estimates of the natural sources of N₂O range from 1.4 to 5.2 Tg N/yr for oceanic sources and 2.7 to 7.7 Tg N/yr from tropical and temperate soils [WMO, 1995; for more recent, somewhat higher oceanic flux estimates see Bange, *et al.*, 1996]. The atmospheric increase is considered to arise primarily from application of fertilizers to cultivated soils, but animal waste, biomass burning, fuel combustion, and industrial processes also contribute. The estimated range of the sum of various anthropogenic sources is 2.1 to 6.3 Tg N/yr [WMO, 1995]. In an effort to reduce the error in these estimates and balance the N₂O budget, investigations of the stable isotopic signatures of the various sources and sinks have been carried out by several research groups [Moore, 1974; Yoshida and Matsuo, 1983; Wahlen and Yoshinari, 1985; Yoshinari and Wahlen, 1985; Kim and Craig, 1990; Kim and Craig, 1993; Yoshinari, *et al.*, 1997; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997; Naqvi, *et al.*, 1998].

Two of these studies [Moore, 1974; Kim and Craig, 1993] showed that N₂O collected from the lower stratosphere was substantially enriched in ¹⁵N and ¹⁸O, but only three samples in total were isotopically analyzed. We expanded this lower stratosphere database with seven additional samples which revealed a coherent trend with concentration that was consistent with a single stage Rayleigh distillation model [Rahn and Wahlen, 1997] (hereafter RW97).

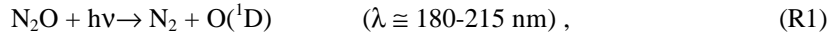
Rayleigh distillation describes an irreversible sink with the resulting isotopic enrichment related to the fraction remaining by the expression

$$\frac{R}{R_0} = f^{[\alpha-1]}, \quad (1)$$

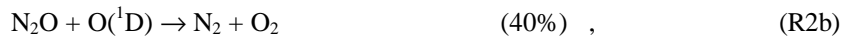
where R and R₀ are the residual and initial heavy-to-light isotope ratios, f is the fraction of N₂O remaining (i.e. the stratospheric concentration divided by the tropospheric concentration), and α is the ratio of the heavy-to-light reaction or photolysis rates. This relationship can be approximated by $\delta \cong \delta_0 + \epsilon \times \ln(f)$, where the slope, $\epsilon = 1000(\alpha - 1)$, is the enrichment factor expressed in per mil. The δ and δ₀ terms, also expressed in per mil, are the residual and initial delta values, with $\delta_i = (R_i/R_{std}-1)*1000$, where R_i and R_{std} are the heavy-to-light isotopic ratios

in the sample and in the standard. The enrichment factors determined from the stratospheric flask samples were $\epsilon = -14.5$ per mil and -12.9 per mil for ^{15}N and ^{18}O , respectively.

The isotopic enrichments observed in the stratosphere have lead to speculation about the validity of the currently accepted conceptual model of N_2O stratospheric chemistry. Standard theory holds that 90% of the N_2O loss in the stratosphere occurs via the photolytic reaction



that 10% is lost via the two branches of the reaction with excited atomic oxygen;



and that there are no significant atmospheric sources of nitrous oxide. Laboratory tests by Johnston et al. [1995] (hereafter JCT95) found negligible ^{18}O fractionation during reaction R1 and a $\epsilon_{18} = -6$ per mil enrichment for the photo-oxidation reactions R2a and R2b, begging the question of what could be responsible for the observed enrichment. This led a number of researchers to propose a variety of source reactions with ostensibly large enrichment factors [McElroy and Jones, 1996; Prasad, 1997; Prasad, *et al.*, 1997]. On the other hand, the more recent data of RW97 are compatible with a single stage loss process, indicating that the mechanism responsible for the observed enrichment is most likely a sink.

An explanation for the apparent incompatibility of observations and laboratory results has been proposed by Yung and Miller [1997] (hereafter YM97). The photolysis experiments of JCT95 were performed with a mercury arc lamp source at 184.9 nm, near the peak of the N_2O absorption continuum. Citing the small shifts in the N_2O UV cross sections with isotopic substitution observed by Selwyn and Johnston [1981], JCT95 concluded that fractionation should be inconsequential when averaged across the continuum. However, as pointed out by Froidevaux and Yung [1982] and Minschwaner et al. [1993], while the N_2O cross section does indeed peak at ~ 182 nm, the photolysis in the stratosphere occurs principally at longer wavelengths, specifically in the 190-210 nm window defined by the O_2 Schumann-Runge bands to the blue and O_2 Herzberg continuum plus ozone Hartley and Huggins band absorption to the red.

Mindful of this, YM97 proposed a wavelength-dependent mechanism for the photolytic fractionation of N_2O based on subtle shifts in the zero point energy with isotopic substitution. For example, substituting ^{18}O for ^{16}O

results in a calculated zero point energy blue shift for the heavier isotopomer of only -27.5 cm^{-1} . While the cross sections are essentially identical at the absorption peak, a clear separation is manifest on both shoulders. Analogous to determining the kinetic fractionation for a chemical reaction, the photolysis fractionation factor will be equal to the ratio of the heavy-to-light photolysis rates and thus to the ratio of the cross sections. For N_2O , the theoretical enrichment factors can be calculated analytically as a function of wavelength using the spectral function recommended by Selwyn *et al.* [1977]. At wavelengths shorter than $\sim 182 \text{ nm}$, ϵ is initially positive, but passes through zero at the cross section maximum and gets progressively more negative with increasing wavelength. At 185 nm , for example, the predicted fractionation factor for the ^{18}O substituted species is $\epsilon_{18} = -2.9$ per mil while at 207 nm , $\epsilon_{18} = -21.3$ per mil. Similar constructs can be developed for the remaining isotopomers, which exhibit analogous behavior but of varying magnitude.

We have performed a series of photolysis experiments at 193 and 207 nm followed by mass spectrometry to investigate the validity of the YM97 theory. While we do indeed observe significant enrichment of the heavy isotopic species in the residual N_2O , the magnitude of the enrichment is approximately double that predicted.

Experimental and Results

Aliquots of our isotopic standard nitrous oxide working-gas (SNOW) were introduced to a jacketed glass cell of 4 cm inside diameter and 25 cm length (approximately 300 cm^3 volume) fitted with ports for sample inlet and vacuum lines. The cell was equipped with UV-transparent fused silica windows of half inch diameter and 2 mm thickness, with an optically illuminated area estimated at 0.8 cm^2 . The jacketed outer layer was equipped with ports for fluid circulation to facilitate temperature control. Tunable UV radiation between $205\text{--}225 \text{ nm}$ was generated by a frequency doubled type II beta-barium borate ($\beta\text{-BaB}_2\text{O}_4$ or BBO) optical parametric oscillator (OPO) pumped by the third harmonic of a Coherent Infinity Nd:YAG laser. The OPO has been described in detail elsewhere [Wu, *et al.*, 1997]. The light source operates at repetition rates up to 100 Hz with a $205\text{--}220 \text{ nm}$ pulse energy of $\sim 1\text{--}2 \text{ mJ}$, a line width of $\sim 1.5\text{--}2.5 \text{ cm}^{-1}$, and a pulse duration of $\sim 2 \text{ ns}$. At 193 nm , the output of a Lambda Physik LPX 120i excimer laser was used, which has a somewhat longer pulse duration of $\sim 17\text{--}20 \text{ ns}$ and a line width of $\sim 400 \text{ cm}^{-1}$. Pulse energies are recorded in Table 1 and are estimated to be stable within $\pm 1 \text{ mJ}$ over the course of a run. To test for the presence of multi-photon effects, the peak power was varied by factors of $>3\text{--}5$,

and no statistically significant trends were seen. Samples were irradiated for different time periods ranging from a few minutes to several hours.

In order to suppress reaction of the N₂O sample with the O(¹D) formed during photolysis, ultra-high purity N₂ gas was added as a quenching agent, typically at a N₂:N₂O ratio of 150:1. The rate constant for the reaction of O(¹D) and N₂ to form N₂O has been shown to be extremely slow due to an electronic curve crossing [DeMore, *et al.*, 1996]. Production of N₂O via heterogeneous reactions involving N₂ and atomic oxygen are also expected to be negligible relative the sample size [Maric and Burrows, 1992; JCT95]. Varying amounts of N₂ were added to examine the quenching efficiency, and several samples were processed without irradiation in order to verify the gas handling procedures. After each run, samples were bled to a vacuum extraction line where the residual N₂O was trapped cryogenically, tested for photolysis extent by manometry, and collected in flame sealed 6 mm glass tubes for subsequent isotopic analysis on a VG-Prism II mass spectrometer. The methodology for the direct injection of N₂O into the VG triple collector mass spectrometer has been described in RW97 and includes monitoring of peaks at M/z = 12 and 22 for possible CO₂ contamination.

The results of the experimental analyses are recorded in Table 1 and shown graphically in Fig. 1. A number of observations are readily apparent. First and foremost, the data are clearly consistent with a simple Rayleigh fractionation model, and the trend of the heavy isotope enrichment with wavelength is consistent with that predicted by YM97. For example, the ¹⁸O enrichments at 193.0 and 207.6 nm are found to be $\epsilon_{18}(193 \text{ nm}) = -14.5$ per mil and $\epsilon_{18}(207 \text{ nm}) = -46.0$ per mil. Doubling the quenching ratio (sample # 34), varying the laser power (sample #'s 49, 51, 53), or varying the laser power and pulse frequency/irradiation period (sample #'s 59, 61, 62, 63), had no additional effect on the isotopic signature. These results virtually rule out any significant production of N₂O by reaction with atomic oxygen, in either third body or heterogeneous reactions, as any production would be expected to have a dependence both on the reactant concentrations and on reaction rates. Therefore, the observed fractionation should be that due to photolysis alone. Interestingly, the enrichment factors measured here are more than twice that predicted by YM97, for which $\epsilon_{18}(\text{YM97}) = -9.1$ and -21.3 per mil at 193.0 and 207.6 nm, respectively.

The same general observations made for the ¹⁸O data apply to the ¹⁵N data sets with the following caveat. The analyses of the ¹⁵N data are complicated by the fact that there are three additional isotopomers to be accounted

for, $^{14}\text{N}^{15}\text{NO}$, $^{15}\text{N}^{14}\text{NO}$, and $^{14}\text{N}^{14}\text{N}^{17}\text{O}$. The first two of these are not distinguishable with current mass spectrometric analytical methods, and YM97 accounted for this complexity by averaging the enrichment of the two ^{15}N species. We have accounted for the $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ isotopomer in our experimental data by applying a variation of the standard correction [Craig, 1957] which assumes mass dependent enrichment. The theoretical enrichment factors are $\epsilon_{15}(\text{YM97}) = -10.4$ and -24.0 per mil at 193.0 and 207.6 nm. The values obtained from the experimental data are $\epsilon_{15}(193 \text{ nm}) = -18.4$ per mil and $\epsilon_{15}(207 \text{ nm}) = -48.7$ per mil, again roughly double that predicted by the model. Correcting for ^{17}O by assuming mass dependent enrichment is considered valid since any mass independent enrichment on the order of that observed by Cliff and Thiemens [1997] would result in additional corrections which are smaller than the experimental precision reported in Table 1 [see for instance Röckmann, 1998]. It must also be kept in mind that there will be an additional fractionation between the two ^{15}N species which will result in a second order enhancement of the effect.

Atmospheric Implications

The results of this study go a long way toward answering some major questions regarding the isotopic budget of nitrous oxide but, as is often the case, new and intriguing questions are also raised. Most important is the verification that UV photolysis of N_2O , at least at certain wavelengths, results in significant isotopic enrichment in the residual gas. Furthermore, we observe that a comparison of the enrichments of ^{15}N to ^{18}O yields ratios of slightly greater than unity at wavelengths close to the effective, or mean, stratospheric photolysis wavelength of 205 nm. This is nearly identical to the ratio of the enrichments observed in RW97 and close to that predicted by YM97, and supports the hypothesis that photolysis is *the* mechanism responsible for the observed stratospheric enrichments and that the standard model of stratospheric N_2O chemistry is essentially complete. While the absolute magnitude of the fractionation observed in the laboratory is significantly different from that predicted by YM97, the general concept of enrichment being caused by a spectral shift with isotopic substitution is still a valid and highly likely mechanism. It is possible that a more rigorous treatment of the zero point energy shifts proposed by YM97, including non-Born-Oppenheimer effects and dipole moment surface variations, might yield better quantitative agreement.

The large absolute magnitude of the laboratory enrichments are problematic at first glance, however. For the longer wavelengths investigated here, the fractionation is more than three times that observed in the

stratosphere. To determine how stratospheric mixing processes might influence the observed isotopic enrichment factors for a tracer which has a decay constant λ_A and no *in situ* production, we consider the one-dimensional (1D) diffusion-limited case where the steady state continuity equation for trace species A is reduced to

$$K_D \frac{\partial^2[A]}{\partial z^2} - \lambda_A[A] = 0 \quad , \quad (2)$$

K_D being the eddy diffusion coefficient and z being the height above the tropopause. With the boundary conditions $A = A_0$ at $z(0)$ and $A = 0$ at $z(\infty)$, Eq. 2 has the solution

$$A = A_0 \exp\left(-z \sqrt{\frac{\lambda_A}{K_D}}\right) \quad .$$

If B is the isotopically substituted species, then $R = \frac{B}{A}$ and

$$\frac{R}{R_0} = \exp\left[-z \left(\frac{\sqrt{\lambda_B} - \sqrt{\lambda_A}}{\sqrt{K_D}}\right)\right] \quad . \quad (3)$$

Recognizing that $f = \frac{A}{A_0}$ and $\ln(f) = -z \sqrt{\frac{\lambda_A}{K_D}}$, Eq. 3 yields

$$\ln \frac{R}{R_0} = \left(\sqrt{\frac{\lambda_B}{\lambda_A}} - 1\right) \ln(f) \quad \text{and, finally,} \quad \frac{R}{R_0} = f^{\left(\sqrt{\frac{\lambda_B}{\lambda_A}} - 1\right)}$$

which is of the form of Eq. 1. Since α is equal to the ratio of the heavy-to-light reaction rates, it is apparent that the effective fractionation in this 1D diffusive system is

$$\alpha_{\text{eff}} = \sqrt{\frac{\lambda_B}{\lambda_A}} \quad , \text{ or } \quad \alpha_{\text{eff}} = \sqrt{\alpha} \quad ;$$

and, since $\alpha = (1 + \epsilon/1000)$, $\epsilon_{\text{eff}} \sim \epsilon/2$ [see also, Eriksson, 1965]. If we consider the fractionation at 205 nm to be representative of the integrated stratospheric fractionation (as in YM97) and further assume a linear dependence between the laboratory results at 193 and 207 nm, then the effective enrichment factors are $\epsilon_{15\text{eff}} = -21.8$ per mil and $\epsilon_{18\text{eff}} = -20.4$ per mil, in much closer agreement with the stratospheric measurements of RW97. A choice of 200 nm as the representative wavelength brings the effective enrichments into even closer agreement with $\epsilon_{15\text{eff}} = -16.7$

per mil and $\epsilon_{18\text{eff}} = -15.1$ per mil. In either case, the laboratory fractionation (α) far exceeds the observed *in situ* fractionation as it must in order to be able to account for diffusive mixing processes in the stratosphere.

In regard to the wavelength which is chosen to be representative of the integrated stratospheric fractionation; it is important to note that the stratospheric isotopic signature is the result of the mid-stratosphere radiation field integrated over the range of N_2O UV absorption and that the polynomial expression used by YM97 for the cross section spectral dependence is only an approximation. Indeed, there is actually a significant amount of vibrational structure in the cross section at wavelengths below 190 nm [Selwyn and Johnston, 1981] which will result in multiple curve crossings with small spectral shifts. Since the YM97 enrichment factors actually change sign below a cross section maximum, and since there are well defined transmission windows in the Schumann-Runge bands, we postulate that there may be enrichments of opposite sign below 190 nm which compensate for the large negative enrichments at longer wavelengths. The ratio of the measured enrichment factors for ^{15}N and ^{18}O at 193 nm is rather different than those measured at $\lambda > 207$ nm, and may in part be due to the continuation of such vibrational structure, structure that is not accounted for in the spectral function of Selwyn *et al.* [1977] nor in the YM97 model yet which is clearly present in the laboratory cross section data [Selwyn and Johnston, 1981; Yoshino, *et al.*, 1984].

The fact that one of the dominant isotopic signatures in atmospheric nitrous oxide arises from UV photolysis not only obviates the need for “exotic” chemistry, it makes this species a powerful tool for addressing important issues in global climate change. For example, once the isotopic systematics of N_2O UV photolysis are fully characterized in the laboratory, it should provide a unique signature to distinguish between fractionation occurring in the upper atmosphere and that resulting from biological or anthropogenic processes, thereby helping in N_2O budgetary analyses and quantifying stratospheric back-fluxing. Further, because the photolytic isotope fractionation only occurs in the mid- to upper-stratosphere, the extent to which the integrated photolytic fractionation exceeds the *in situ* stratospheric observations may help to determine the degree of mixing between “aged” and “new” stratospheric air. This in turn would lead to quantitative estimates of mass transport in the middle atmosphere, especially when combined with measurements of other trace gases such as carbon dioxide and methane [Boering, *et al.*, 1996]. Finally, a better understanding of atmospheric dynamics would enable models to

better reproduce the observed distribution of various gases and help to predict the atmospheric response to human activities.

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Samp. #	Wavelength	Residual	ln(f)	$\delta^{15}\text{N}$	$\delta^{18}\text{O}$	notes
	nm	Fraction		per mil	per mil	
24	207.6	0.88	-0.13	5.4	5.3	
26	207.8	0.81	-0.21	9.9	9.4	
27	207.8	0.76	-0.27	12.5	11.9	
29	207.4	0.72	-0.33	16.0	15.0	
32	-	1.00	0.00	-0.1	-0.2	np
34	207.4	0.85	-0.16	7.3	6.9	300:1 N ₂ :N ₂ O
49	193.0	0.85	-0.17	3.5	2.7	3 min, 100 Hz, 3.1 mJ
50	193.0	0.61	-0.50	10.4	7.9	6 min, 100 Hz, 3.8 mJ
51	193.0	0.79	-0.24	5.2	4.0	3 min, 100 Hz, 3.8 mJ
52	193.0	0.75	-0.29	6.1	4.7	1.5 min, 100 Hz, 8.0 mJ
53	193.0	0.59	-0.53	10.8	8.3	3 min, 100 Hz, 8.0 mJ
54	193.0	0.43	-0.83	15.7	12.2	5 min, 100 Hz, 8.0 mJ
56	-	1.00	0.00	-0.2	-0.4	np
57	193.0	0.43	-0.84	15.3	12.0	5 min, 100 Hz, 8.4 mJ
58	193.0	0.44	-0.81	15.3	11.9	5 min, 100 Hz, 8.4 mJ
59	193.0	0.82	-0.20	4.4	3.2	60 min, 10 Hz, 1.5 mJ
61	193.0	0.83	-0.19	3.9	2.7	12 min, 10 Hz, 4.5 mJ
62	193.0	0.83	-0.18	3.9	2.8	1.2 min, 100 Hz, 7.0 mJ
63	193.0	0.79	-0.24	5.1	3.8	120 min, 1 Hz, 6.2 mJ
40	-	1.00	0.00	0.2	0.6	np
45	-	1.00	0.00	0.1	0.1	np
46	-	1.00	0.00	0.1	0.2	np

Table 1: Isotopic signatures of N₂O following varying degrees of photolysis at 207 and 193 nm. Results are discussed in the text. Replicate analyses of samples processed with no irradiation (indicated with np = no photolysis) indicate a precision of ± 0.2 and ± 0.4 for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$, respectively, for the combined extraction procedure and mass spectrometric analysis. The extraction procedures allow for a ln(f) precision of ± 3 percent as determined from the yield of the np samples. Isotopic results are reported relative to our standard N₂O working-gas (SNOW). Unless otherwise noted, N₂:N₂O ratios are 150:1.

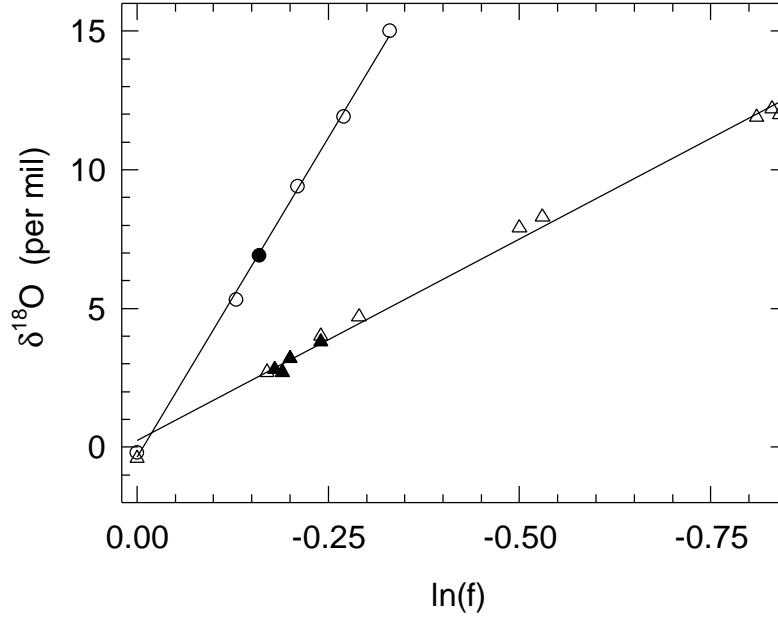


Figure 1: Rayleigh distillation plot of the enrichment of N_2^{18}O during photolysis at 207 and 193 nm. Open circles record the room temperature data at 207 nm for samples with an N_2 quenching ratio of 150:1. Falling almost directly on the 207 nm fitted line is the filled circle, representative of the sample in which the quenching ratio was increased to 300:1. Open triangles record the room temperature data at 193 nm with an N_2 quenching ratio of 150:1 and constant pulse frequency, while the filled triangles indicate samples in which the peak power and pulse frequency were varied to test for multi-photon effects and for secondary production of N_2O . The lines are least squares fits to the open symbol data and yield enrichment factors of $\epsilon_{18}(207 \text{ nm}) = -46.0$ per mil (samples 24-32) and $\epsilon_{18}(193 \text{ nm}) = -14.5$ per mil (samples 49-58). Errors are as described in Table 1.