

## Fractionation of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ During Photolysis at 213 nm

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**Abstract.** Motivated by *Yung and Miller's* suggestion [1997] that  $\text{N}_2\text{O}$  is isotopically fractionated during UV photolysis in the stratosphere, we have studied the photolysis rates of the  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  structural isotopomers. In this study, we follow the concentrations of these compounds with FTIR spectroscopy during photolysis at 213 nm. Our results show that, as *Yung and Miller* predicted, the photolysis rate of  $^{15}\text{N}^{14}\text{NO}$  is faster than  $^{14}\text{N}^{15}\text{NO}$  at this wavelength. When fitted to a Rayleigh fractionation model, the observations yield single-stage enrichment factors of  $\epsilon(^{14}\text{N}^{15}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O}) = -73 \pm 5$  per mil and  $\epsilon(^{15}\text{N}^{14}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O}) = -41 \pm 10$  per mil. Comparisons are provided with theoretical calculation and previous measurements.

## Introduction

Nitrous oxide, N<sub>2</sub>O, is an important trace gas in Earth's atmosphere. It is an efficient greenhouse gas and the major source of the nitrogen oxide radicals that destroy stratospheric ozone [Houghton, *et al.*, 1995; WMO, 1995]. N<sub>2</sub>O is produced primarily by biological nitrification and denitrification processes occurring in soils and the oceans, and lost through UV photolysis and reaction with O(<sup>1</sup>D) in the stratosphere. It has been established that the present concentration of N<sub>2</sub>O in the atmosphere is 8% higher than the pre-industrial value and that it is increasing at a yearly rate of about 0.25%. N<sub>2</sub>O is targeted by the 1997 Kyoto Protocol on Climate Change for regulation. This is a difficult task, however, because the global budget for N<sub>2</sub>O is poorly quantified. The strength of the sources identified to date can only account for approximately two-thirds of the sum of the well-established sinks and the accumulation in the atmosphere. Efforts to determine the global budget of N<sub>2</sub>O and to identify the cause of its continuing increase in the atmosphere are therefore in order.

Stable isotope analyses can provide useful constraints on the strength of the sources and sinks for atmospheric species. Efforts have been made to investigate the isotopic fractionation of N<sub>2</sub>O in various production and loss processes [Wahlen and Yoshinari, 1985; Yoshinari and Wahlen, 1985; Yoshida, 1988; Kim and Craig, 1990; Kim and Craig, 1993; Yoshinari, *et al.*, 1997; Cliff and Thiemens, 1997; Rahn and Wahlen, 1997; Naqvi, *et al.*, 1998]. These measurements reveal that, relative to tropospheric N<sub>2</sub>O, the major biological sources of N<sub>2</sub>O are light in both <sup>15</sup>N and <sup>18</sup>O, while stratospheric N<sub>2</sub>O is found to be isotopically heavy. To utilize these isotopic data to characterize the N<sub>2</sub>O global budget, one must understand the fractionation induced by biological processing and photolysis in the atmosphere. In an effort to explain the heavy stratospheric N<sub>2</sub>O, Yung and Miller [1997] (YM97) proposed a wavelength-dependent enrichment mechanism during UV photolysis. They suggested that the difference in the zero point vibrational energy (ZPE) for the heavier N<sub>2</sub>O isotopomers causes a blue-shift in the UV cross section, that, when convolved with the spectral characteristics of the actinic flux, results in fractionation. Experiments using laser photolysis and mass spectrometry have been conducted to test one aspect of this theory [Rahn, *et al.*, 1998]. It has been shown that UV photolysis of N<sub>2</sub>O at 207 nm and 193 nm results in significant enrichment in both <sup>15</sup>N and <sup>18</sup>O with larger fractionations at longer wavelengths. This is consistent with YM97, though the observed enrichment factor is more than that predicted by the simple ZPE calculations [Rahn, *et al.*, 1998].

The ZPE-induced fractionation theory also predicts that there should be a differential fractionation between the two structural isotopomers <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O during UV photolysis. In this paper, we use the Fourier Transform Infrared (FTIR) spectroscopy in conjunction with laser photolysis to study the fractionation between <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O at 213 nm.

## Experimental

Figure 1 presents a schematic of our experimental set up. UV photons are generated by a Nd:YAG laser, while IR spectra are collected with an FTIR spectrometer. The general experimental procedure is to photolyze the N<sub>2</sub>O sample continuously while taking IR spectra to monitor the concentration of the isotopomers.

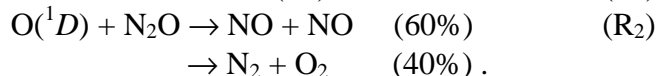
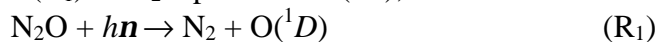
The photolysis is conducted at 212.8 nm (abbreviated as 213 nm hereafter) using the 5<sup>th</sup> harmonic of a Coherent Infinity pulsed Nd:YAG laser. The YAG laser's 532 nm output is doubled using one 2-mm thick  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> (BBO) crystal. In a second thin BBO crystal, 266 nm light is then mixed with the residual 1064 nm radiation to generate 213 nm pulses. The two crystals are cut for type I phase matched 4<sup>th</sup> and 5<sup>th</sup> harmonic generation of the 1064 nm fundamental. A single quartz Pellin Broca prism is used to separate 213 nm from other wavelengths, which are intercepted by beam stops.

After a 45° mirror (M<sub>1</sub>), the photolysis beam enters the FTIR spectrometer (Magna-IR 560 from Nicolet) through a quartz window (W<sub>1</sub>). It passes into the sample compartment aperture at a steep angle and is redirected by a 0° mirror (M<sub>2</sub>) towards a 45° mirror (M<sub>3</sub>). Mirror M<sub>3</sub> and another 0° mirror (M<sub>4</sub>) together pass the UV beam through the sample cell twice and then dump it on the edge of the M<sub>3</sub> mount. All four mirrors (M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub>) are 213 nm high reflectors from Coherent. The spectrometer is oriented so that reflective losses of the photolysis beam on the windows are minimized. During the experiment, the stability of the UV power was monitored with a photodetector (UDT-555UV) through the reflection off window W<sub>1</sub>.

The sample cell is made of thick-wall Pyrex glass. It has an inner diameter of 4 cm and a length of 15 cm. CaF<sub>2</sub> was chosen as the window material because it is transparent in both the IR and UV. The two windows are glued on to the cell with Torr Seal (Varian) at slightly different wedge angles to minimize etaloning.

Three isotopically labeled N<sub>2</sub>O samples were used. A pure N<sub>2</sub>O sample with natural isotopic abundance was used for <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O (99%+). Separate samples of <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O (98%+) and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O (98%+) mixed with N<sub>2</sub> (99.999%) at an N<sub>2</sub>:N<sub>2</sub>O ratio of 40 were purchased from Cambridge Isotopes. The different sample mixtures used in the three photolysis experiments are listed in Table 1. All the experiments are conducted at total pressure of approximately 760 torr and at room temperature.

Photolysis (R<sub>1</sub>) of N<sub>2</sub>O produces O(<sup>1</sup>D), which reacts with N<sub>2</sub>O (R<sub>2</sub>):



Because the occurrence of R<sub>2</sub> confounds the analysis, O(<sup>1</sup>D) quenching by N<sub>2</sub> or CO<sub>2</sub> is necessary:



In Exp. II and III, only one rare N<sub>2</sub>O isotopomer sample is involved and N<sub>2</sub> serves the quenching gas. For an N<sub>2</sub>:N<sub>2</sub>O ratio of 75, less than 3% of O(<sup>1</sup>D) atoms are expected to undergo reaction R<sub>2</sub> due to quenching by N<sub>2</sub> (R<sub>3</sub>) (*DeMore, et al.*, 1997). In Exp. I, N<sub>2</sub> quenching is limited by the total cell pressure and the N<sub>2</sub>:N<sub>2</sub>O ratio of 40 in both the <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O samples. In this case, CO<sub>2</sub>, which is four times more efficient than N<sub>2</sub> at quenching O(<sup>1</sup>D), is used in addition.

The concentration of N<sub>2</sub>O is monitored via the Q-branch of the  $\nu_2+\nu_3$  combination band, which lies at 2798 cm<sup>-1</sup> for <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O. Shown in Figure 2 are the  $\nu_2+\nu_3$  spectra of the three N<sub>2</sub>O isotopomers. They are taken at 0.5 cm<sup>-1</sup> resolution with an MCT-A liquid nitrogen cooled detector. This band is chosen for several reasons. First, it sits in a region free of interference from ambient H<sub>2</sub>O and CO<sub>2</sub> absorption (the spectrometer is nitrogen purged). Second, the peaks for the isotopomers are shifted with respect to each other by 30 cm<sup>-1</sup> and the small amount of cross interference among them can be easily accounted for. Third, at one atmosphere pressure, the Q-branch is collision-broadened and is fully resolved at 0.5 cm<sup>-1</sup> resolution. This leads to linear Beer's Law behavior, which was demonstrated in this apparatus by preparing N<sub>2</sub>O samples of known concentration using manometry. At 0.5 cm<sup>-1</sup> resolution, a high SNR can be achieved in approximately 30 minutes (see below for an explanation of the photolysis time scale). For example, in Exp. II, the S/N is more than 100 for the initial spectrum. The signal is picked at the center of the Q-branch for <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O, while the noise is the root-mean-square (RMS) noise in the baseline between 2850 and 2900 cm<sup>-1</sup>. Similar SNRs are achieved in the other two experiments.

Approximately 60 mW (2 mj at 30 Hz pulse repetitive rate) of 213 nm are used. In 11 hours, 70% of the initial N<sub>2</sub>O is removed. FTIR spectra are co-added, producing one data point every 30 minutes. In addition, spectra are taken before the photolysis to test the spectral processing protocol and data fitting. In order to monitor any post-photolysis processes, IR spectra are recorded after the photolysis laser is turned off. For the background, spectra of the same pressure of N<sub>2</sub> (in Exp. II and III) or the same mixture of N<sub>2</sub> and CO<sub>2</sub> (in Exp. I) are acquired.

The concentration of the isotopomers is derived by first normalizing the co-added spectra against the background. The integrated absorbance of the Q-branches is determined and the retrieved signal is corrected for the small amount of absorption from the other isotopomers.

## Results and Discussion

Figure 3 illustrates the observed fractionation. The slope of the linear fit to the data gives the fractionation factor in a Rayleigh model [*Fritz and Fontes*, 1980]. The results from the three experiments are as follows:  $\epsilon(^{14}\text{N}^{15}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O}) = -73 \pm 5$  per mil and  $\epsilon(^{15}\text{N}^{14}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O}) = -41 \pm 10$  per mil. The uncertainty results primarily from systematic error introduced in defining the spectral baseline during data processing. The N<sub>2</sub>O band is on a sloping region of the IR intensity as shown in Figure 2. An NO<sub>2</sub> band, discussed below, is superimposed nearby on the short-wavelength side of the N<sub>2</sub>O  $\nu_2+\nu_3$  band. These complicate the spectral analysis. Different techniques for inferring the baseline were performed and various reasonable assumptions produced the assigned uncertainty.

The arithmetic average of  $\epsilon(^{14}\text{N}^{15}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O})$  and  $\epsilon(^{15}\text{N}^{14}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O})$  gives  $-57 \pm 15$  per mil for  $\epsilon(^{15}\text{N} / ^{14}\text{N})$  at 213 nm. This result is consistent with the results reported by *Rahn, et al.* [1998]. They observed -18.4 per mil at 193 nm and -48.7 per mil at 207 nm.

We have assumed that all N<sub>2</sub>O loss is due to R<sub>1</sub>; processes other than R<sub>1</sub> that destroy N<sub>2</sub>O would affect our interpretation. One possible interference is R<sub>2</sub>, the reaction of O(<sup>1</sup>D) with N<sub>2</sub>O producing NO. The NO can undergo further conversion to NO<sub>2</sub> in the cell. We have observed the formation of small amounts of NO and NO<sub>2</sub> in each of the three

experiments. NO is monitored via its absorption band near  $1875\text{ cm}^{-1}$ ,  $\text{NO}_2$  is monitored at  $2907\text{ cm}^{-1}$  and  $1617\text{ cm}^{-1}$ . The photolysis of  $\text{NO}_2$ , whose cross section at  $213\text{ nm}$  is more than 1000 times larger than that of  $\text{N}_2\text{O}$  [DeMore, *et al.*, 1997], keeps its concentration low during the experiment. However, once the photolysis beam is turned off, NO is converted into  $\text{NO}_2$  on the time scale of a few hours. Post-photolysis spectra reveal that the conversion of NO into  $\text{NO}_2$  is close to unity. By comparing the photolysis spectra with reference spectra of NO and  $\text{NO}_2$ , we determine that less than 2% of the  $\text{N}_2\text{O}$  destroyed in our cell occurs via  $\text{R}_2$ . This is consistent with the expected quenching rates. Other processes that form  $\text{N}_2\text{O}$  are also taken into consideration. Among them, the three-body reaction of  $\text{N}_2 + \text{O}(^1\text{D})$  to re-form  $\text{N}_2\text{O}$  is extremely slow [DeMore, *et al.*, 1997]. Exp. II and III provide a test to whether the photolysis of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  produces  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and vice versa. At over 70% photolysis yield, no formation of  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  is observed from the photolysis of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and vice versa.

The fractionation found in this experiment (and that by [Rahn *et al.*, 1998]) is significantly larger than that predicted by YM97. It appears that the ZPE model is too simple to fully account for the observed fractionation. There are a number of reasons why this might be the case. At  $298\text{ K}$ , close to 90% of the  $\text{N}_2\text{O}$  is in the ground vibrational state (000) mode while about 10% is in the first excited bending mode (010). Photodissociation dynamics studies [Neyer, *et al.*, 1999 and refs therein] have shown that the photolysis of  $\text{N}_2\text{O}$  ( $\text{R}_1$ ) occurs mainly via an orbitally forbidden but vibronically allowed transition through a bent excited state. Therefore, the vibrationally excited bending states of  $\text{N}_2\text{O}$  have much larger Franck-Condon overlap with the dissociative state than does the (000) mode. This is corroborated by the large observed temperature dependence of the  $\text{N}_2\text{O}$  cross section [Merienne, *et al.*, 1990 and refs therein]. By deconvolving the cross section data at  $225$  and  $296\text{ K}$  [Selwyn, *et al.*, 1977] into contributions from the (000) and (010) modes, we found that the  $213\text{ nm}$  cross section of the (010) mode is approximately 15 times larger than that of (000). This implies that at  $213\text{ nm}$  and at  $298\text{ K}$ , more than 50% of the photolysis occurs from the excited vibrational states. The differences in the potential energy surface for different  $\text{N}_2\text{O}$  isotopomers are different for the two vibrational modes, which leads to different wavelength shifts of cross sections according to YM97. Therefore, including the vibrationally “hot” molecules in the fractionation calculation is a more appropriate approach.

The preceding argument implicitly assumes that the photodissociation of  $\text{N}_2\text{O}$  is via the repulsive  $\text{B}(^1\Delta)$  electronic state, as YM97 did in light of the available data at that time. As Neyer, *et al.* [1999] demonstrate, however, the dynamics of this photodissociation is more complex than previously thought, with more than one electronic state involved in the excitation / dissociation. It is possible that the two different ground state modes may have different coupling with the upper states, which will further complicate the spectroscopy.

In conclusion, this study supports YM97’s suggestion that the different photolysis rates of the various  $\text{N}_2\text{O}$  isotopomers appear to be the predominant mechanism responsible for the observed fractionation in the stratosphere. A fully quantitative test of this theory, however, requires accurate wavelength and temperature dependent differential cross sections for these compounds; the use of simple theoretical models for prediction of these cross sections has been ruled out by this study and previous work of Rahn *et al.* [1998]. The difference in the cross sections of the isotopomers examined here is large enough that a classical Beer’s law study of the isotopomers (which are available commercially in high purity) can provide the required spectroscopic data.

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(Received X X, 1999; Revised X X, X;  
 Accepted X X, X;)

**Table 1.** Gas mixtures used in the photolysis experiments.

Exp.	$^{14}\text{N}^{14}\text{NO}$ (torr)	$^{14}\text{N}^{15}\text{NO}$ (torr)	$^{15}\text{N}^{14}\text{NO}$ (torr)	Quenching Gas (torr)
I	5	6	5.5	460 ( $\text{N}_2$ ) 280 ( $\text{CO}_2$ )
II	6	4	-	750 ( $\text{N}_2$ )
III	6	-	5	750 ( $\text{N}_2$ )

**Figure 1.** Light from an Nd:YAG laser is directed into the sample compartment of an FTIR spectrometer via a side port. Gas samples are located inside the cell.

**Figure 2.** FTIR spectra of the three  $\text{N}_2\text{O}$  isotopomers, taken between  $2650\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$  at  $0.5\text{ cm}^{-1}$  resolution.

**Figure 3.** The fractionation data from 213 nm photolysis, fitted with Rayleigh fractionation model.  $\delta = (R_i / R_{std} - 1) \times 1000$ , where R's are the slow-to-fast photolysis isotopic ratio.  $R_{std}$  is for the pre-photolysis samples and  $R_i$  is for the photolyzed samples.  $f$  is the fraction of  $\text{N}_2\text{O}$  remaining.  $\epsilon(^{15}\text{N}^{14}\text{N}^{16}\text{O}) = \epsilon(^{15}\text{N}^{14}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O})$  and  $\epsilon(^{14}\text{N}^{15}\text{N}^{16}\text{O}) = \epsilon(^{14}\text{N}^{15}\text{N}^{16}\text{O} / ^{14}\text{N}^{14}\text{N}^{16}\text{O})$ .

ZHANG ET AL.: FRACTIONATION OF  $\text{N}_2\text{O}$  DURING PHOTOLYSIS AT 213 NM

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