Measurement of the isotopic fractionation of $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$ and $^{14}N^{14}N^{18}O$ in the UV photolysis of nitrous oxide

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Abstract. The isotopic analysis of atmospheric nitrous oxide (N_2O) has become a valuable tool in the investigation of its sources, sinks, and its atmospheric cycle. In particular the considerable isotopic enrichment accompanying stratospheric photolysis of N_2O, its dominant atmospheric sink process, provides a key isotope signal in the construction of a global N_2O isotope budget. Here we present the first measurements of the individual fractionation constants for $^{15}N^{14}NO$, $^{15}\varepsilon_1 = 10.9\pm1.7\%o$ and $^{14}N^{15}NO$, $^{15}\varepsilon_2 = 35.7\pm0.5\%o$ during ultraviolet photolysis at 193 nm, along with the ^{18}O fractionation constant, $^{18}\varepsilon = 17.3\pm0.5\%o$. Consistent results were obtained over a wide range of experimental conditions. The observed position-dependent ^{15}N fractionation confirms theoretical predictions and provides a unique signature of N_2O that has been processed in the stratosphere, adding a new dimension to an isotope-based description of the atmospheric N_2O budget.

1. Introduction.

Nitrous oxide (N_2O) is an important atmospheric trace gas because it constitutes the main source of stratospheric NO_x, which contributes significantly to stratospheric ozone destruction [Crutzen, 1970], and because it is a potent greenhouse gas [Yung et al., 1976]. It is produced mainly in the oceans (2-11 Tg/y) [Bange et al., 1996; Nevison and Holland, 1997] and in soils (6-10 Tg/y) [Houghton et al., 1995, and references therein] by microbial nitrification and denitrification processes. The quantification of the atmospheric N_2O budget is difficult because of its extensive sources and its long atmospheric lifetime of about 130 years. Ultraviolet (UV) photolysis (185 to 210 nm) in the stratosphere according to (R1) is the dominant sink for atmospheric N_2O and is responsible for 90% of its removal. The remaining 10% is lost via reaction with $O(^1D)$ (R2 and R3).

$$N_2O + h\nu \rightarrow N_2 + O(^1D) \tag{1}$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \tag{2}$$

$$N_2O + O(^1D) \rightarrow 2NO \tag{3}$$

The UV absorption spectra of the heavy N_2O isotopomers (mainly $^{15}N^{14}NO$, $^{14}N^{15}NO$, $^{14}N^{14}N^{17}O$ and $^{14}N^{14}N^{18}O$), are

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slightly blue-shifted as a result of the lower zero point vibrational energies [Yung and Miller, 1997]. The resulting isotope effects in the photolysis of N_2O are thus wavelength dependent. No fractionation was measured following photolysis at wavelengths near the absorption maximum around 185 nm [Johnston et al., 1995], but in the atmospherically important region at longer wavelengths the heavy N_2O isotopomers are generally photolyzed slightly slower than the main isotopomer $^{14}N^{14}N^{16}O$ [Yung and Miller, 1997]. This has been shown recently in a series of laboratory measurements [Rahn et al., 1998]. Also, isotope measurements of stratospheric N_2O reveal a strong enrichment in all three heavy isotopes, i.e. ^{15}N, ^{17}O and ^{18}O [Cliff et al., 1999; Kim and Craig, 1993; Moore, 1974; Rahn and Wahlen, 1997]. Kim and Craig [1993] proposed that the return flux of this isotopically enriched N_2O into the troposphere provides the important heavy component in the construction of a global N_2O isotope budget, which must be balanced by isotopically depleted sources at the surface. Thus, isotopic analysis of atmospheric N_2O has gained significance as a tool to assess relative N_2O source and sink strengths. In addition to many new data on the ^{15}N and ^{18}O content of N_2O [Dore et al., 1998; Kim and Craig, 1990; Kim and Craig, 1993; Naqvi et al., 1998; Rahn and Wahlen, 1997; Rahn et al., 1998; Wahlen and Yoshinari, 1985; Yoshida, 1988; Yoshida et al., 1989; Yoshinari and Wahlen, 1985], Cliff et al. [1999; 1997] have recently discovered mass independent fractionation in N_2O. This adds a third isotopic signature, i.e. the ^{17}O content, to the set of independent isotopic variables, and the observation of a clear ^{17}O excess in tropospheric and stratospheric N_2O has inspired a search for its atmospheric origin, which is not yet known [Thiemens, 1999].
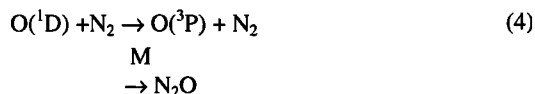
Notwithstanding, there is one isotopic signature that has never been reported on N_2O samples of natural isotopic composition. For the linear NNO molecule with its two non-equivalent nitrogen atoms, it is not only the change in mass due to isotopic substitution that can cause differences in photolysis rates; the actual position of the ^{15}N atom within the molecule also matters. Recent calculations by Yung and Miller [1997] predict that the ^{15}N enrichment during UV photolysis of N_2O should be about a factor of 2 different for the two species $^{15}N^{14}NO$ and $^{14}N^{15}NO$. However, mass spectrometric analysis of N_2O at the ion masses 44, 45 and 46, as conventionally carried out, cannot identify the position of the ^{15}N atom in N_2O and all $\delta^{15}N$ values reported to date represent the average of two distinct isotopic signatures. Using a recently developed technique of isotope ratio mass spectrometry on ion fragments at natural ^{15}N abundance, we have now been able to measure the position dependent ^{15}N fractionation of N_2O during UV photolysis mass spectrometrically.

2. Experimental

To examine the various isotopic fractionation factors of N_2O during UV photolysis, we photolyzed mixtures of N_2O in N_2 at 193 nm with an excimer laser (20 ns pulse duration) under a range of experimental conditions. The 3 photolysis reactors

employed were cylindrical tubes of 10 cm (pure silica), 40 cm (stainless steel) and 50 cm (borosilicate glass) length with a diameter of 4 cm. All cells were equipped with Suprasil™ silica windows at the ends, and the illuminated cylindrical volume had a cross-sectional area of 0.8 cm^2. A table giving the detailed experimental conditions is provided as supplementary material[2].

The N_2 bath gas serves as a quencher for $O(^1D)$ radicals (R4, $k = 2.6 \times 10^{-11} cm^3$ molec.$^{-1}s^{-1}$ at 298K, [DeMore et al., 1997]) which are formed during photolysis (R1) and can otherwise react with N_2O (R2, R3). Note that in R4 a very small product channel leads to the formation of N_2O ($k = 3.5 \times 10^{-37} cm^6$molec.$^{-2}s^{-1}$ at 298K, [DeMore et al., 1997]). This reaction is negligible under the present experimental conditions.

$$O(^1D) + N_2 \rightarrow O(^3P) + N_2 \qquad (4)$$
$$M$$
$$\rightarrow N_2O$$

The reactions of $O(^1D)$ with N_2O (R2 and R3) must be suppressed for two reasons: 1) The accompanying isotopic fractionation is likely to be different from the one during photolysis and thus will lead to erroneous results, and 2) the NO product formed in reaction R3 may initiate undesirable NO_x chemistry. To examine possible NO_x chemistry, some samples were analyzed after photolysis by optical absorption spectroscopy (310-470 nm). This was carried out in situ using a diode array camera/monochromator set up with a halogen lamp as analytic light source. Tests performed at a high mixing ratio of 2.5% N_2O in N_2 (atmospheric pressure) indeed indicated significant formation of NO_2 on the order of 10 ppm under these conditions, probably resulting from NO formation via R3 followed by R5.

$$O + NO \rightarrow NO_2 \qquad (5)$$

The concomitant interference at mass 46 in the isotope ratio mass spectrometer (see below) precluded an accurate ^{18}O analysis in these tests. For the mixing ratios employed in the photolysis experiments, i.e. 0.11%, 0.37% and 0.67% N_2O in N_2, no traces of NO_x could be detected. Furthermore, in this concentration range the ^{18}O isotope data do not show a dependence on mixing ratio, which shows that NO_2 levels are not only below the detection limit of the optical apparatus of ≈0.5 ppm, but that NO_2 does not interfere with the isotope analysis in our experiments.

After photolysis, the remaining N_2O was extracted using a high efficiency cryogenic trap [Brenninkmeijer and Röckmann, 1996], and the extent of photolysis was determined manometrically. The conventional measurement of N_2O isotope ratios at mass 44, 45 and 46 was performed on a Finnigan MAT 252 isotope ratio mass spectrometer (Finnigan, Bremen). It is well known that CO_2 is a serious interference in the precise isotopic analysis of N_2O (and vice-versa), because both have the same isotope masses, but with strongly differing abundance. The standard method of monitoring the CO_2 interference at mass 12 (resulting from the C^+ fragment that is formed in the ion source) was applied to make a corresponding correction on the order of 1‰ to the measured isotope values [Tanaka et al., 1995]. The linear correlation between observed isotope shifts in aliquots of our mass spectrometer N_2O reference gas doped with small amounts of CO_2, and the measured signals at mass 12, was used to establish the precise correction formula.

As mentioned above, the ^{15}N fractionation obtained in the measurement of the molecular ion masses 44, 45 and 46 is the

average of two distinct isotopic ^{15}N fractionations at the two non-equivalent positions in the NNO molecule. These individual isotopic fractionations will in the following be distinguished by the terms "position-1" fractionation for the first, or terminal, N atom and "position-2" fractionation for the second, or central, N atom.

To determine the position-2 fractionation independently, we measured the mass 31 to mass 30 ratio of the NO^+ ion fragment using a VG-PRISM mass spectrometer with adjustable collectors (Micromass, Manchester). Both instruments gave identical ^{15}N and ^{18}O values for N_2O. The principle of the method is that during the fragmentation of N_2O in the ion source the NO^+ fragment should ideally retain the N atom that was originally attached to the oxygen, i.e. $^{15}NO^+$ should originate from $^{14}N^{15}NO$. Precise calibration reveals that the NO^+ fragment indeed contains 91.5% of the position-2 N atom. The isotope scrambling of 8.5% in the ion source could be accurately established using mixtures of N_2O specifically labeled at the individual positions, and a corresponding correction is applied [Brenninkmeijer and Röckmann, 1999]. In contrast, the N^+ fragment appears to be heavily scrambled and is also affected by double ionized NO^{++} ions at the rare mass 15. This precludes the direct measurement of the position-1 fractionation, which is therefore derived as the isotopic difference between the ^{15}N content of the NO fragment and the N_2O molecule. Note that these results depend on the initial intramolecular distribution of ^{15}N in the N_2O molecule, represented by the parameter $f = ^{15}N^{14}NO / (^{15}N^{14}NO + ^{14}N^{15}NO)$, which is not known precisely to date. The ion current ratio of mass 31 : mass 30 = 0.39% (i.e. close to the average ^{15}N abundance) measured on the MS suggests that f is close to the statistical average of f = 0.5. A deviation of f from this value can cause a systematic error, and the errors reported below include a variation of f over the range 0.47 to 0.53, i.e. a ^{15}N difference at the two positions of about 12%. The statistical error of a single measurement is only about 0.2‰. Further details can be found in Brenninkmeijer and Röckmann [1999].

We recently found out that fragment ion analysis of N_2O had been employed for artificially enriched N_2O as early as 1950 by Friedman and Bigeleisen [1950] and was later adapted for biological ^{15}N tracer studies [Garber and Hollocher, 1982]. At the time of submission of this paper we also learned about the independent development of such a technique by Toyoda and Yoshida [1999].

3. Results and discussion

The results for the average ^{15}N enrichment and the individual isotopic enrichments of $^{15}N^{14}NO$ and $^{14}N^{15}NO$ in N_2O samples that were photolyzed at 193 nm are shown in figure 1. Both heavy isotopomers in the remaining N_2O fraction show the expected increase with progression of photolysis. However, the fractionation for $^{14}N^{15}NO$ is more than three times stronger than the one for $^{15}N^{14}NO$. The corresponding fractionation constants derived from the slopes of the linear fits are $^{15}\varepsilon_1 = 10.9 \pm 1.7‰$ for $^{15}N^{14}NO$, $^{15}\varepsilon_2 = 35.7 \pm 0.5‰$ for $^{14}N^{15}NO$ and $^{15}\varepsilon_{mean} = 23.3 \pm 0.5‰$ for the molecular average. Here, ε represents the relative difference of the photolysis rates of $^{14}N^{14}N^{16}O$ and the respective heavy isotopomers. These results provide the experimental evidence that the isotopic signature of N_2O which has been subjected to photolysis in the $X(^1\Sigma^+) \rightarrow B(^1\Delta)$ band, as it happens in the stratosphere, contains much more information than can be derived from conventional $\delta^{15}N$ analyses. The observed ratio $^{15}\varepsilon_2/^{15}\varepsilon_1 = 3.3$ for photolysis at 193 nm is even higher than calculated by Yung and Miller [1997], but is expected to be wavelength dependent. Considering also that the model
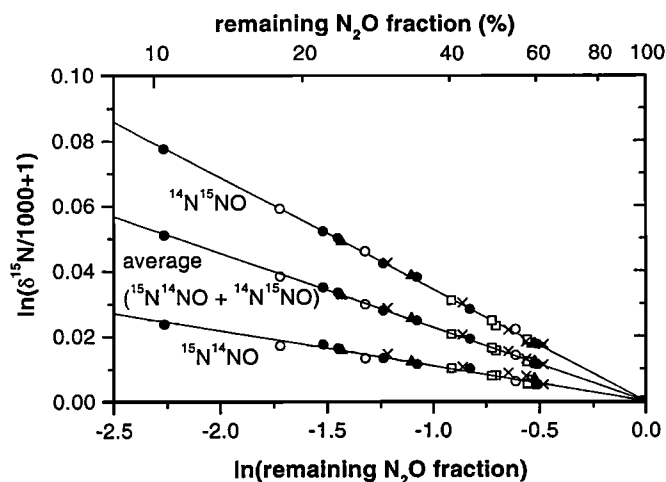
Figure 1. The observed isotopic fractionation at position 2 ($^{14}N^{15}NO$) and total ^{15}N fractionation ($^{15}N^{14}NO + ^{14}N^{15}NO$), and the derived values for position 1 ($^{15}N^{14}NO$), for N_2O samples subjected to photolysis at 193 nm. The δ-value gives the per mil enrichment of the $^{15}N/^{14}N$ ratio in a photolyzed sample (SA) relative to the starting gas (ST), which is cylinder N_2O with an ^{15}N content close to that of air nitrogen, $\delta^{15}N(^{15}N^{14}NO) =$ $((^{15}N^{14}NO/NNO)_{SA}/(^{15}N^{14}NO/NNO)_{ST} - 1) \times 1000‰$. Linear fits are applied to the data. The statistical measurement errors lie within the symbols shown, which are grouped according to the following experimental conditions: Solid circles: pressure ~ 100kPa, N_2O mixing ratio (MR) = 0.37%; open circles: pressure 400 - 600kPa; open squares: pressure ~ 30kPa; solid triangles: MR 0.67%; crosses: MR 0.10%. Three different photolysis reactors were used, the laser fluence was varied from 5 mJ/cm² to 60 mJ/cm² per pulse and the repetition rate between 3 and 20 Hz, without significant deviations from the overall trend.

calculations involve approximations and neglect small structures in the absorption spectrum [*Selwyn and Johnston*, 1981] the agreement is satisfactory.

Thus, the stratospheric ^{15}N fractionation factors that have been reported hitherto are indeed an average of two very different isotope signals, $^{15}\varepsilon_1$ and $^{15}\varepsilon_2$, which are the specific isotopic fingerprint of the fractionation during photolysis of N_2O. As the wavelength distribution of the photolyzing radiation changes with altitude, the position-1 and position-2 fractionation constants, and their ratio $\varepsilon_2/\varepsilon_1$, are expected to vary throughout the stratosphere. These variations are potentially useful as tracers for stratospheric N_2O chemistry and transport, which are both closely coupled to the stratospheric ozone budget.

In figure 2, the conventional, i.e., average ^{15}N fractionation and the ^{18}O fractionation determined in our experiments are compared to the results from *Rahn et al.* [1998]. Our values of $^{15}\varepsilon_{mean} = 23.3 \pm 0.5‰$ and $^{18}\varepsilon = 17.3 \pm 0.5‰$ are 5‰ and 3‰ higher, respectively, than their values of $^{15}\varepsilon_{mean} = 18.7‰$ and $^{18}\varepsilon = 14.7‰$. Many diagnostics experiments were performed to investigate the cause of the difference. A total of 20 samples from the three different photolysis reactors, with varying N_2O mixing ratios and total pressures were processed without photolysis and established a N_2O recovery from the cells of 99.7 ± 1.0%, without variation in the isotope ratios. As described above, also the experimental conditions during photolysis were varied considerably, most parameters by more than one order of magnitude. The results we obtain appear to be very robust, as they do not depend on the material or size of the reactor, the total pressure, the N_2O mixing ratio, the total N_2O sample size, or the

laser fluence or repetition rate. Furthermore, mass spectrometric and optical analysis showed no indications of potentially interfering compounds, apart from the above mentioned small CO_2 interference that was corrected for.

One set of experiments deserves further discussion: Close inspection of the results from *Rahn et al.* [1998] reveals that their data for very low degrees of photolysis are in good agreement with our results (figure 2). For higher degrees of photolysis their data appear to become progressively lower than our results, which leads to the observed discrepancy if a linear fit is applied to their data. All of their data points with relatively high conversion (however, also some of the ones with low conversion) were obtained with a laser repetition rate of 100 Hz, which is not possible with our laser system. In such fast experiments, the N_2O photolysis within the illuminated volume may be of the same order or even faster than diffusion from other parts of the reactor into this area. This can in principle lead to a dilution of the actual isotope signals via mixing of the sample gas in the illuminated volume, which is strongly photolyzed and fractionated, with sample gas outside the illuminated volume, which is only slightly photolyzed and fractionated. To simulate this scenario with our equipment, we increased the total pressure to 600 kPa, thus reducing the diffusion speed into the illuminated volume. However, again the results confirm our average fractionation constant, and the process of inhomogeneity described above is unlikely to be able to reconcile the two experimental data sets. A possible slight difference in the exact photolysis wavelengths could be important, as the fractionation is sensitive to the exact wavelength in the 193 nm region [*Selwyn and Johnston*, 1981].

Whereas the source of the difference in the average ^{15}N fractionation and the ^{18}O fractionation between the two similar experiments remains uncertain, the deconvolution of the ^{15}N signal into its two individual components provides the last missing variable for isotope research on atmospheric N_2O. One now has the full set of 4 independent isotope signatures available, i.e. the ^{15}N content at both positions in the molecule, and the ^{17}O and ^{18}O content. This enables interesting and useful new research. The present work presents the first important application, i.e., the site dependence of the ^{15}N fractionation during photolysis of N_2O in the relevant UV region could be established. Of course, it will be important to further examine photolysis at other wavelengths, and to measure in detail the effect in the atmosphere, i.e. to
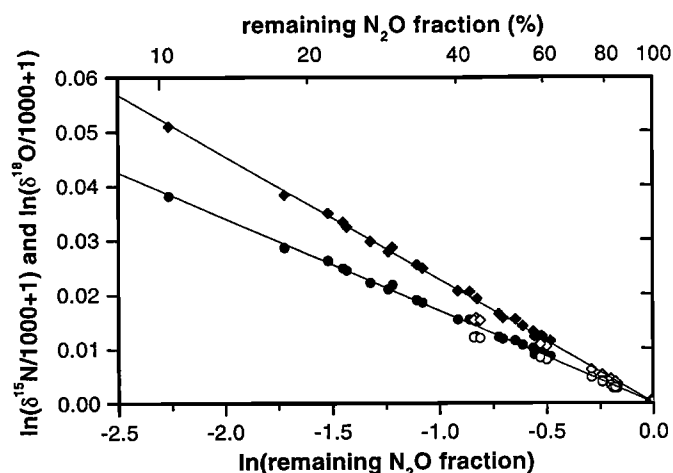

Figure 2. Results for the average ^{15}N fractionation (diamonds) and the ^{18}O fractionation (circles) after photolysis of N_2O at 193 nm, determined in this work (solid symbols) and by *Rahn et al* [1998] (open symbols). For clarity the classification of the individual experimental conditions by different symbols as in figure 1 is left out.

determine the precise intramolecular distribution of ^{15}N in tropospheric and stratospheric N_2O, as well as the individual $^{15}N^{14}NO$ and $^{14}N^{15}NO$ signatures of N_2O emitted from soils and oceans. Regarding the poorly known atmospheric budget of N_2O, the total of 4 isotopic budgets should lead to an improved quantification of the global N_2O cycle.

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