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THE POSITION DEPENDENT ^{15}N ENRICHMENT OF NITROUS OXIDE IN THE STRATOSPHERE

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The position dependent ^{15}N fractionation of nitrous oxide (N_2O), which cannot be obtained from mass spectrometric analysis on molecular N_2O itself, can be determined with high precision using isotope ratio mass spectrometry on the NO^+ fragment that is formed on electron impact in the source of an isotope ratio mass spectrometer. Laboratory UV photolysis experiments show that strong position dependent ^{15}N fractionations occur in the photolysis of N_2O in the stratosphere, its major atmospheric sink. Measurements on the isotopic composition of stratospheric N_2O indeed confirm the presence of strong isotope enrichments, in particular the difference in the fractionation constants for $^{15}N^{14}NO$ and $^{14}N^{15}NO$. The absolute magnitudes of the fractionation constants found in the stratosphere are much smaller, however, than those found in the lab experiments, demonstrating the importance of dynamical and also additional chemical processes like the reaction of N_2O with $O(^1D)$.

Keywords: Atmospheric chemistry; Nitrous oxide; Isotopic fractionation photolysis

Measurements of the isotopic composition of atmospheric nitrous oxide (N_2O) have been carried out for more than 20 years to derive information about the strengths of its various sources and sinks and thus to constrain its atmospheric budget. In the past, the focus of isotope studies on N_2O

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has been on the ^{15}N fractionation and the ^{18}O fractionation. However, with common isotope ratio mass spectrometric techniques it is not possible to resolve the position of ^{15}N in the linear NNO molecule, *i.e.*, to differentiate between $^{15}N^{14}NO$ and $^{14}N^{15}NO$. Thus, ^{15}N values measured in the past were the average of two distinct fractionation constants, and one independent isotope signature to examine the N_2O budget was not experimentally accessible.

Interest in the possibility to measure the two ^{15}N fractionation constants individually was stirred recently by calculations that showed that the photolysis rates of N_2O in the stratosphere should be largely different for the two ^{15}N substituted isotopomers [1]. This is due to the fact that the zero point energy is lower for $^{14}N^{15}NO$ than for $^{15}N^{14}NO$. Ultraviolet (UV) photolysis in the stratosphere is the main sink for atmospheric N_2O, responsible for 90% of its total removal from the atmosphere. Therefore, the fractionations in N_2O photolysis are important parameters in the construction of a global N_2O isotope budget.

Concurrently to the development of optical techniques that can distinguish the two ^{15}N substituted isotopomers [2, 3], a mass spectrometry based method to differentiate between $^{14}N^{15}NO$ and $^{15}N^{14}NO$ at ambient ^{15}N abundance has recently been developed [4, 5]. When N_2O is admitted into the ion source of an isotope ratio mass spectrometer, the magnitude of the NO^+ fragment beam that is produced at typical electron energies of ~70 eV is about 30% of the N_2O^+ beam. Thus, the fragment beam is sufficiently abundant to determine the ^{15}N content of the NO^+ fragment. The idea is that the nitrogen atom remaining in the NO^+ fragment should be the one that was originally attached to the oxygen atom, and thus the measurement of $\delta^{15}N$ on the NO^+ fragment can be used to determine the ^{15}N fractionation at the central position, denoted as position 2, of the N_2O molecule. Careful calibration using N_2O gases specifically labeled at both positions showed that a small amount (~8.5%) of scrambling occurs in the ion source, *i.e.*, 8.5% of the nitrogen found in the NO^+ fragment originates from position 1, *i.e.*, the terminal position [4]. A similar scrambling was established by Toyoda and Yoshida [5], who developed this technique simultaneously. Note that already in 1950, Friedman and Bigeleisen (1950) distinguished between $^{15}N^{14}NO$ and $^{14}N^{15}NO$ this way (however using strongly enriched N_2O) and found a similar scrambling.

In principle, the two individual ^{15}N fractionation constants can thus be derived from the measurement of the overall ^{15}N fractionation on N_2O^+ and the position-2 ^{15}N fractionation on NO^+. However, because of the scrambling, the isotopic distribution of ^{15}N in the mass spectrometer reference gas must be at least approximately known. Unfortunately, no position dependent isotope standard is available, but measurements have shown that the ^{15}N fractionation of tropospheric N_2O is roughly the same at both positions [5, 6]. Thus the overall fractionation determined on the N_2O^+ ion is actually the average of both fractionations when a reference gas with an isotopic composition close to atmospheric N_2O is used.

Motivated by the predictions by Yung and Miller [1], the new technique was first employed to analyze N_2O that was produced in laboratory UV photolysis experiments at 193 nm [7]. The results from this and other experiments carried out with different techniques and at different photolysis wavelengths [2, 3] confirmed that the resulting enrichments are indeed much larger for $^{14}N^{15}NO$ than for $^{15}N^{14}NO$. However, all these measurements were carried out at single isolated photolysis wavelengths, using the few available UV photolysis sources. To examine the isotope fractionations under conditions representative for the stratosphere, further laboratory measurements were recently carried out using a broadband photolysis lamp [8]. The results again showed strong enrichments of the heavy isotopes, with factionation constants of $^{15}\varepsilon_1 = 16.3 \pm 0.6‰$ for $^{15}N^{14}NO$, $^{15}\varepsilon_2 = 33.4 \pm 1.2‰$ for $^{14}N^{15}NO$ and $^{18}\varepsilon = 21.4 \pm 0.6‰$ for $^{14}N^{14}N^{18}O$. Thus, the position-2 fractionation is about a factor of 2 stronger than the position-1 fractionation.

Having established the fractionation constants in the laboratory, clearly the next step was to determine the isotopic composition of N_2O in the stratosphere. To carry out the fragment analysis on N_2O from the small stratospheric air samples that were available from several balloon launches, the new technique, initially developed using the dual inlet system of an isotope ratio mass spectrometer, was adopted in continuous-flow mode [8]. The results show that in the stratosphere N_2O gets progressively enriched in the heavy isotopes concomitant with decreasing mixing ratio, and indeed the $^{14}N^{15}NO$ fractionation is much larger than the $^{15}N^{14}NO$ fractionation. Quantitative examination reveals that the isotopic fractionation during the removal of N_2O in the stratosphere follows a single-stage Rayleigh fractionation pattern. These fractionation constants are much higher than those established in the laboratory experiments. Furthermore, detailed analysis shows that the fractionation constants, in the lower stratosphere are even further reduced when compared to the middle stratosphere [8]. This trend of lower fractionation constants at lower altitudes has been independently established using balloon-borne FTIR measurements of the N_2O isotopomers [9].

Clearly, the stratosphere is not an isolated photolysis reactor, and dynamic processes like mixing and diffusion all tend to reduce the effective fractionation in the stratosphere [8, 10]. The chemistry in the stratosphere is not constant, either. The second atmospheric sink of N_2O, reaction with $O(^1D)$ in the stratosphere, is responsible for the removal of the remaining 10% N_2O that are not removed by photolysis, and its contribution varies with altitude. Also the isotope effects during N_2O photolysis may vary with altitude because they are wavelength dependent. These chemical effects must be responsible for the fact that the ratio $^{15}\varepsilon_1/^{15}\varepsilon_2$ appears to vary in the stratosphere. Dynamic processes should not significantly affect the ratios of fractionation constants.

To examine all these effects quantitatively, the incorporation of the fractionation constants obtained in the laboratory into stratospheric chemistry and transport models is required. The combination of N_2O mixing and isotope ratios as tracers in these models provides additional observables to test our understanding of stratospheric transport and chemistry.

CONCLUSIONS

A new mass spectrometric technique to determine the position dependent ^{15}N fractionation in atmospheric N_2O has been developed and applied to N_2O samples prepared in laboratory experiments and stratospheric N_2O samples. Results show that strong position dependent fractionations occur in the UV photolysis of N_2O. The resulting distinct fractionation pattern characteristic of N_2O that has been processed in the stratosphere has been clearly established. Although some questions remain open, we now understand important factors determining the isotopic composition of N_2O in the stratosphere. The ability to resolve the ^{15}N fractionation at the two positions within the N_2O molecule adds an additional isotopic dimension to isotope research on N_2O and should also yield interesting information in the study of the various N_2O sources.

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