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Wavelength dependence of isotope fractionation in N₂O photolysis

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Abstract. In previous reports on isotopic fractionation in the ultraviolet photolysis of nitrous oxide (N₂O) only enrichments of heavy isotopes in the remaining N₂O fraction have been found. However, most direct photolysis experiments have been performed at wavelengths far from the absorption maximum at 182 nm. Here we present high-precision measurements of the ¹⁵N and ¹⁸O fractionation constants (ϵ) in photolysis at 185 nm. Small, but statistically robust depletions of heavy isotopes for the terminal atoms in the linear N₂O molecule are found. This means that the absorption cross sections $\sigma(^{15}\text{N } ^{14}\text{N } ^{16}\text{O})$ and $\sigma(^{14}\text{N}_2 \ ^{18}\text{O})$ are larger than $\sigma(^{14}\text{N}_2 \ ^{16}\text{O})$ at this specific wavelength. In contrast, the central N atom becomes enriched in ¹⁵N. The corresponding fractionation constants (± 1 standard deviation) are

$$^{15}\epsilon_1 = \sigma(^{15}\text{N } ^{14}\text{N } ^{16}\text{O})/\sigma(^{14}\text{N}_2 \ ^{16}\text{O}) - 1 = (3.7 \pm 0.2) \text{‰}$$

$$^{18}\epsilon = \sigma(^{14}\text{N}_2 \ ^{18}\text{O})/\sigma(^{14}\text{N}_2 \ ^{16}\text{O}) - 1 = (4.5 \pm 0.2) \text{‰} \text{ and}$$

$$^{15}\epsilon_2 = \sigma(^{14}\text{N } ^{15}\text{N } ^{16}\text{O})/\sigma(^{14}\text{N}_2 \ ^{16}\text{O}) - 1 = (-18.6 \pm 0.5) \text{‰}$$

To our knowledge, this is the first documented case of such a heavy isotope depletion in the photolysis of N₂O which supports theoretical models and pioneering vacuum ultraviolet spectroscopic measurements of ¹⁵N substituted N₂O species that predict fluctuations of ϵ around zero in this spectral region (Selwyn and Johnston, 1981). Such a variability in isotopic fractionation could have consequences for atmospheric models of N₂O isotopes since actinic flux varies also strongly over narrow wavelength regions between 175 and 200 nm due to the Schumann-Runge bands of oxygen. However, the spacing between maxima and minima of the fractionation constants and of the actinic flux differ by two orders of magnitude in the wavelength domain. The wavelength dependence of fractionation constants in N₂O photolysis can thus be approximated by a linear fit with negligible consequences on the actual value of the spectrally averaged fractionation constant. In order to establish this linear fit, additional measurements at wavelengths other than 185 nm were made using broadband light sources, namely D₂, Hg/Xe and Sb lamps. The latter lamp was used in conjunction with various interference filters to shift the

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peak photolysis rate to longer wavelengths. From these experiments and existing data in the literature, a comprehensive picture of the wavelength dependence of N₂O photolysis near room-temperature is created.

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