

# Photolytic fractionation of seven singly and doubly substituted nitrous oxide isotopocules measured by quantum cascade laser absorption spectroscopy

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## ABSTRACT

There is strong interest in using isotopic analysis to better constrain the budget of atmospheric nitrous oxide ( $\text{N}_2\text{O}$ ). This interest is supported by emerging instruments that allow analysis of multiply substituted species. We have studied fractionation during UV photolysis of singly and doubly isotopically substituted molecules (isotopocules) of  $\text{N}_2\text{O}$ .  $\text{N}_2\text{O}$  was photolyzed in an electropolished stainless-steel reactor using a broadband laser-driven light source with bandpass filters. Isotopocule ratios were quantified at different stages of photolysis using a quantum cascade laser absorption spectroscopy (QCLAS) system. Wavelength-dependent fractionation constants were determined using the Rayleigh distillation model. The fractionation constants for photolysis with 200 nm and 214 nm bandpass filters, respectively, for the seven most abundant isotopocules of  $\text{N}_2\text{O}$  (after  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ ) are:  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  (456):  $(-48.9 \pm 7.4) \text{‰} / (-82.4 \pm 22.3) \text{‰}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  (546):  $(-22.2 \pm 5.3) \text{‰} / (-36.1 \pm 19.6) \text{‰}$ ,  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$  (447):  $(-12.7 \pm 4.5) \text{‰} / (-21.9 \pm 15.7) \text{‰}$ ,  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$  (448):  $(-33.5 \pm 12.0) \text{‰} / (-44.1 \pm 29.8) \text{‰}$ ,  $^{14}\text{N}^{15}\text{N}^{18}\text{O}$  (458):  $(-80.9 \pm 6.5) \text{‰} / (-120.9 \pm 23.7) \text{‰}$ ,  $^{15}\text{N}^{14}\text{N}^{18}\text{O}$  (548):  $(-52.7 \pm 10.8) \text{‰} / (-79.1 \pm 28.5) \text{‰}$ ,  $^{15}\text{N}^{15}\text{N}^{16}\text{O}$  (556):  $(-66.9 \pm 9.8) \text{‰} / (-110.9 \pm 27.5) \text{‰}$ . The fractionation constants determined here for isotopocules 456, 546, 447, 448, and 556 are in agreement with previous theoretical models employed in this study and previous experiments. For 458 and 548, the fractionation constants were determined for the first time, confirming the prediction of more negative fractionation for  $^{15}\text{N}$  substitution in the central position. The effect of stratospheric photolysis on the clumped isotope  $\Delta$  values of tropospheric  $\text{N}_2\text{O}$  was found to be modest with  $\Delta^{458} = (4.0 \pm 1.0) \text{‰}$ ,  $\Delta^{548} = (-4.0 \pm 1.0) \text{‰}$ , and  $\Delta^{556} = (-1.5 \pm 1.0) \text{‰}$  at 9% photolysis. Therefore, atmospheric variations of doubly substituted  $\text{N}_2\text{O}$  isotopocules will likely be dominated by the characteristics of the  $\text{N}_2\text{O}$  sources, which strongly supports their value for source attribution and quantification.

## 1. Introduction

Nitrous oxide ( $\text{N}_2\text{O}$ ) is a potent greenhouse gas with a global warming potential that is 300 times larger than that of  $\text{CO}_2$  on a 100-year time scale (Griffis et al., 2017). In addition,  $\text{N}_2\text{O}$  is the most important anthropogenic ozone-depleting chemical of the twenty-first century (Ravishankara et al., 2009). The mole fraction of atmospheric  $\text{N}_2\text{O}$  has increased from  $270 \text{ nmol mol}^{-1}$  in the pre-industrial era to

$331 \text{ nmol mol}^{-1}$  in 2018 (World Meteorological Organization and Global Atmosphere Watch, 2019). The increase is mainly driven by the rising use of agricultural fertilizer (Griffis et al., 2017; Syakila and Kroeze, 2011), which stimulates nitrification and denitrification, the two main microbial sources of  $\text{N}_2\text{O}$  (Toyoda et al., 2017).

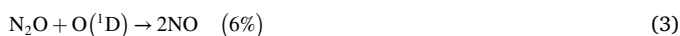
There is significant uncertainty in the atmospheric  $\text{N}_2\text{O}$  budget as the biological sources are diffuse. In contrast to numerous  $\text{N}_2\text{O}$  sources, there are only few sink processes. The main atmospheric loss processes

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are shown in Eq. (1)–(3). Stratospheric photolysis in a narrow range of wavelengths (Eq. (1)) is by far the main removal path, constituting 90% of the total. The remaining 10% is removed by reaction with electronically excited oxygen atoms  $O(^1D)$  (Eq. (2) and Eq. (3)), which are mainly produced in the atmosphere by photolysis of ozone ( $O_3$ ) but also by photolysis of  $N_2O$  (Minschwaner et al., 1993).



The reaction of  $N_2O$  with  $O(^1D)$  is the most important source of stratospheric  $NO_x$  gases which cause catalytic  $O_3$  depletion.

The linear  $N_2O$  molecule (N–N–O) offers 12 different isotopocules, representing all possible combinations of naturally occurring isotopes of N and O ( $^{14}N$ ,  $^{15}N$ ,  $^{16}O$ ,  $^{17}O$ ,  $^{18}O$ ). The abundances of individual isotopocules are often used to characterize sources and sinks of greenhouse gases (Peterson and Fry, 1987; Yu et al., 2020). To ease the isotopocule notation in this work, we make use of the HITRAN notation (Rothman et al., 2013), e.g. the shorthand 446 when referring to the  $^{14}N^{14}N^{16}O$  isotopocule. The abundance of individual isotopocules is reported using the  $\delta$  notation defined as

$$\delta^{xyz} = \frac{R_{\text{sample}}}{R_{\text{ref}}} - 1, \quad (4)$$

where the superscript xyz refers to one of the substituted isotopocules, and  $R$  is the ratio between the fraction of a substituted isotopocule to that of the most abundant species (446) for a sample and a reference (Toyoda and Yoshida, 1999). The  $^{15}N/^{14}N$  ratios of Air- $N_2$  and  $^{18}O/^{16}O$  and  $^{17}O/^{16}O$  ratios of VSMOW are used as the reference scale. As the position of the two nitrogen atoms in the  $N_2O$  molecule is distinguishable, the  $^{15}N$  site preference (SP) parameter is defined as (Toyoda et al., 2017)

$$SP = \delta^{456} - \delta^{546}. \quad (5)$$

“Clumped isotopes” is a collective term used for isotopocules containing more than one heavy isotope (Eiler, 2007). In this work, the three most abundant clumped isotopes in  $N_2O$ , isotopocules 458, 548, and 556, were studied. The isotopic quantities expressing deviation of their abundance from a stochastic (random) distribution, denoted as  $\Delta^{458}$ ,  $\Delta^{548}$ , and  $\Delta^{556}$ , are defined as (Kantnerová et al., 2020)

$$\Delta^{458} = \delta^{458} - \delta^{456} - \delta^{448}, \quad (6)$$

$$\Delta^{548} = \delta^{548} - \delta^{546} - \delta^{448}, \quad (7)$$

$$\Delta^{556} = \delta^{556} - \delta^{456} - \delta^{546}. \quad (8)$$

As with SP, the difference in the abundance of the clumped isotopomers 458 and 548 is defined as (Magyar et al., 2016)

$$SP^{18} = \delta^{458} - \delta^{548}. \quad (9)$$

A kinetic isotope effect describes a change in the rate of a chemical reaction for an isotopocule when its rate is larger or smaller due to isotopic substitution. Such an effect leads to the depletion or enrichment of the relative concentration of isotope or isotopocule in the sample as compared to the starting material. The kinetic isotope effect for an isotopocule xyz is commonly quantified via the fractionation constant  $\epsilon_{xyz}$  or the fractionation factor  $\alpha_{xyz}$  (Kaiser et al., 2003b), which are defined as

$$\alpha_{xyz} = \frac{k_{xyz}}{k_{446}} = 1 + \epsilon_{xyz}, \quad (10)$$

where  $k_{xyz}$  and  $k_{446}$  are reaction rate constants for one of the substituted

isotopocules and the most abundant species, respectively. Since the value of  $\epsilon$  is small, it is usually reported in units of ‰.

The three-isotope exponent  $\beta$  is used to determine whether a process (e.g. photolysis) fractionates  $^{17}O$  and  $^{18}O$  in a mass-dependent way relative to  $^{16}O$  (Kaiser et al., 2004). It is defined as

$$\beta = \frac{\ln(\epsilon_{447} + 1)}{\ln(\epsilon_{448} + 1)}, \quad (11)$$

where  $\epsilon_{447}$  and  $\epsilon_{448}$  are fractionation constants for isotopocules 447 and 448, respectively. A process is regarded to be anomalous in regard to O mass-dependent behavior if  $\beta$  is greater than 0.53 or lower than 0.50 (Schmidt et al., 2011).

The aim of this work is to determine isotopic fractionation of  $N_2O$  during photolysis by UV light. The absorption cross section of  $N_2O$  has its maximum around 180 nm (Selwyn et al., 1977). In the stratosphere, the spectrum of sunlight is highly structured in the range of  $N_2O$  absorption. There is a narrow UV window at roughly 205 nm, in between the absorption of  $O_3$  and the Schumann-Runge band of molecular oxygen ( $O_2$ ). Therefore, most  $N_2O$  is photolyzed on the low-energy shoulder of its absorption peak, in the spectral region 195–215 nm. Because of this alignment, a small shift in the position or intensity of the  $N_2O$  absorption, for example due to isotopic substitution, can have a large effect on the photolysis rate. Stratospheric processing leads to the enrichment of the heavier  $N_2O$  isotopocules in air returning from the stratosphere to the troposphere. This was first noted by Moore (1974) and confirmed later by Rahn and Wahlen (1997) and Kim and Craig (1993).

Experiments performed by Kaiser et al. (2003b) were used to study photolysis around the  $N_2O$  absorption maximum, at 185 nm, using a low-pressure Hg(Ar) light source. The fractionation constants were determined to be  $(-18.6 \pm 0.5) \text{‰}$ ,  $(3.7 \pm 0.2) \text{‰}$ , and  $(4.5 \pm 0.2) \text{‰}$  for 456, 546, and 448, respectively, while the fractionation constants increased to  $(-95 \pm 7) \text{‰}$ ,  $(-43 \pm 3) \text{‰}$ , and  $(-61 \pm 5) \text{‰}$  when photolysis was done with a Sb lamp and a bandpass filter around 220 nm. Other experimental studies of  $N_2O$  photolysis (Johnston et al., 1995; Rahn and Wahlen, 1997; Röckmann et al., 2000, 2001; Turatti et al., 2000; Umemoto, 1999; Zhang et al., 2000; Toyoda et al., 2018) are in qualitative agreement with the findings of Kaiser et al. (2003b). Von Hessberg et al. (2004) determined the temperature-dependent (233 K and 283 K) and wavelength-dependent (181–218 nm) cross section of 446, 546, 456, and 556. The data were used to construct fractionation constants with spectral resolution of 1 nm.

Yung and Miller (1997) introduced the theory that the absorption spectrum of an isotopically substituted species is that of the main component, shifted by the change in the vibrational zero-point energy (ZPE). Heavy isotope substitution shifts the absorption band to higher energy leading to reduced overlap with the stratospheric UV window. However, the ZPE-shift model underestimated isotopic fractionation compared to laboratory photolysis experiments by about a factor of two. Subsequent theoretical investigations by Johnson et al. (2001) and Schmidt et al. (2011) used quantum-mechanical wave packet propagation in connection with ground- and excited-state potential energy surfaces to study  $N_2O$  photolysis. The theoretical fractionation constants were in good agreement with values in the literature (Schmidt et al., 2011), and it was found that vibrational excitation in the bending mode is important for correct determination of the fractionation constants, especially at higher temperatures. Subsequent theoretical studies by Schmidt and Johnson (2015) extended and applied the method to determine fractionation constants for the multiply substituted species 556, 557, 458, 548, 457, and 547. Of these, experimental fractionation constants only exist for the 556 isotopocule (Kaiser et al., 2003a).

Recent development of improved laser spectroscopic (Kantnerová et al., 2019, 2020) and mass spectrometric techniques (Magyar et al., 2016) have enabled the first accurate measurements of low-abundance clumped  $N_2O$  isotopocules. These techniques are able to quantify the most abundant clumped isotopocules together with the singly

substituted and unsubstituted species in the same sample, even though their abundance spans a range of five orders of magnitude. They thus provide access to tracers that constrain the N<sub>2</sub>O biogeochemical cycle. There is significant optimism that the additional information provided by these tracers will resolve critical gaps in our understanding of N<sub>2</sub>O source mechanisms, source strengths, and atmospheric dynamics (Ostrom and Ostrom, 2017; Yu et al., 2020). In order to constrain the global N<sub>2</sub>O budget, isotopic signatures and fractionation factors of the most important source and sink processes are required. It is therefore of paramount importance to determine the clumped isotope fractionation factors. This work presents experimentally determined fractionation constants for UV photolysis of the seven most abundant N<sub>2</sub>O isotopocules (after 446), including, for the first time in one measurement setup, three clumped species, in the region of the stratospheric window.

## 2. Methodology

### 2.1. First principles calculation of photolytic fractionation

Isotopic fractionation constants at the temperature and wavelength of the experiments were derived from state-specific N<sub>2</sub>O cross sections and the vibrational energies of the contributing vibrational states ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ) for the selected isotopocules as described in Schmidt et al. (2011). First, the total absorption cross section  $\sigma_{xyz}$  for an isotopocule  $xyz$  at photolysis wavelength  $\lambda$  and temperature  $T$  (20 °C) was calculated:

$$\sigma_{xyz}(\lambda, T) = \sum_i (w_i(T) \cdot \sigma_i(\lambda)), \quad (12)$$

where

$$w_i(T) = \frac{d_i}{Q(T)} \cdot e^{\frac{-E_i}{k_B T}} \quad (13)$$

is the Boltzmann weighting factor for each vibrational state  $i$  at temperature  $T$ ,  $\sigma_i$  is the state-specific cross section for the isotopocule  $xyz$  at wavelength  $\lambda$ ,  $d_i$  is the degeneracy of state  $i$  ( $d = 1 + \nu_2$ ;  $\nu_2$  is the second vibrational quantum number associated with the N<sub>2</sub>O bending mode),  $E_i$  is the vibrational energy of state  $i$ ,  $k_B$  is Boltzmann's constant, and  $Q$  is the partition function:

$$Q(T) = \sum_i \left( d_i \cdot e^{\frac{-E_i}{k_B T}} \right). \quad (14)$$

The expected fractionation constant  $\varepsilon_{xyz}$  for an isotopocule  $xyz$  was calculated following Eq. (15):

$$\varepsilon_{xyz}(\lambda, T) = \frac{\sigma_{xyz}(\lambda, T)}{\sigma_{446}(\lambda, T)} - 1. \quad (15)$$

The input data for the calculation were acquired from supplementary material related to work by Schmidt et al. (2011) for all species except 458 and 548, for which the data were obtained following personal communication with J. A. Schmidt.

### 2.2. UV photolysis

The photolysis experiments were performed in a custom-made cylindrical stainless-steel reactor with inner diameter of 5.7 cm, base length of 44 cm, and volume of 1.1 L. Both ends of the photoreactor were equipped with uncoated fused-silica windows (Thorlabs, USA) with high transmission in the region 185–2100 nm. The photoreactor was equipped with a pressure gauge (LEO3, 0–1 MPa, Keller AG, Switzerland) to monitor the gas pressure during the experiment. It was filled with a N<sub>2</sub>O gas mixture (high purity N<sub>2</sub>O – 99.999%, PanGas, The Linde Group, Switzerland – diluted with 99.9999% N<sub>2</sub> to 1.70% N<sub>2</sub>O by NPL, Teddington, UK) to a pressure of 300 kPa. The pressure in the photolysis cell decreased gradually during the experiment as samples of the gas were

extracted for analysis, and also due to a minor leak to the ambient air. The pressure in the photoreactor was not allowed to drop below 140 kPa to ensure stable sampling conditions.

Photolysis was driven by a broadband laser-driven Xe-plasma light source (LDLS EQ-99, Energetiq, USA) that produces a stable output in the range of 170–2100 nm. Stratospheric behavior was simulated by illuminating the cell in two regions selected with dielectric bandpass filters (Edmund Optics, USA) placed between the light source and the photoreactor: the bandpass filters were centered at 200 nm and 214 nm with a full width at half maximum (FWHM) of 10 nm and a peak transmission of 18–20%. The light source output was collimated before hitting the bandpass filter. The photolysis experiments were run for around 9 days using the filter at 200 nm and 28 days using the filter at 214 nm (photolysis yields are specified in the Results and Discussion). The experiment with the bandpass filter at 200 nm was duplicated. The progress of the photolysis was traced by measuring concentration of residual N<sub>2</sub>O in the photoreactor by QCLAS.

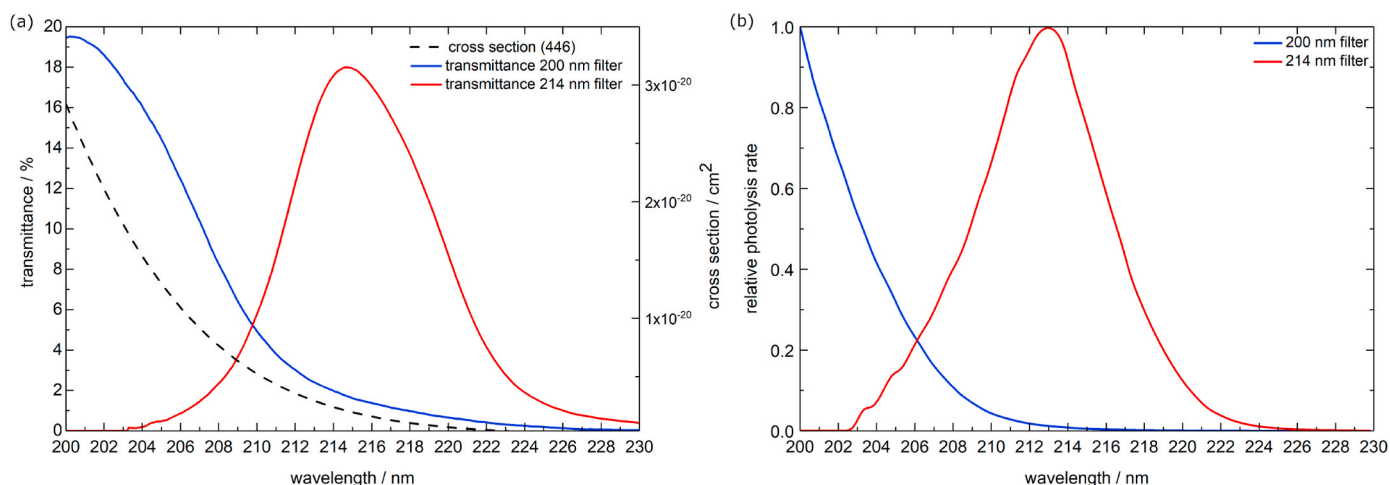
The relative stability of the light source was confirmed to be better than 5% over the full emission spectrum by regular analysis of the light exiting the photoreactor with a UV/NIR spectrometer (Flame-S-XR1-ES, Ocean Optics, USA). Relative spectral photolysis rates shown in Fig. 1b were calculated by combining transmittance curves of the bandpass filters with the cross section of 446 calculated by Schmidt et al. (2011), which are shown in Fig. 1a. The maximum of the relative photolysis rate spectrum is shifted by 1–2 nm relative to the transmittance curves of the corresponding bandpass filters due to the slope of the absorption cross section. Therefore, the theoretical fractionation constants in Table 1 and Table 2 were calculated at the wavelength of the maximum photolysis rate – 198 nm and 213 nm – and not the center of the filter passband. Including the entire band in the calculation of the theoretical fractionation constants changed the results by less than 1 ‰. Therefore, the fractionation constants calculated at the single wavelength of the maximum photolysis rate were directly compared to the fractionation constants obtained using the bandpass filters that transmit a given wavelength region.

#### 2.2.1. Secondary effects

Kaiser et al. (2002b) observed that the apparent fractionation constants decreased in experiments when the degree of photolysis was high. This was explained by the build-up of photolysis products, e.g. NO<sub>2</sub> and O<sub>3</sub>, which led to a secondary source of O(<sup>1</sup>D) in the experiment. Following Kaiser et al. (2002b), a box model was created for this study to estimate the effect of secondary chemistry in the photolysis experiment. According to the model, approximately 6–9% of N<sub>2</sub>O is removed by O(<sup>1</sup>D). Most of this loss is due to O(<sup>1</sup>D) produced directly in N<sub>2</sub>O photolysis.

A blank experiment (without photolysis) was performed for 14 days with sampling every 24 h to test the stability of the instrument and potential secondary effects (e.g. leakage) in the photoreactor over extended periods. We found a subtle decrease of N<sub>2</sub>O concentration during the course of the blank experiment, but no change in the N<sub>2</sub>O isotopic composition, and attributed the N<sub>2</sub>O loss to a possible catalytic decomposition or minor leakage during sampling. This loss was corrected in all experiments, although it was minor. Based on the box model, the rate of this secondary N<sub>2</sub>O loss was determined to be one order of magnitude lower than the photolysis rate at 214 nm and two orders of magnitude lower than the photolysis rate at 200 nm.

The box model was also used to estimate the ratio of N<sub>2</sub>O removed by photolysis itself as shown in Appendix, Fig. A1: 92% and 78% is removed by photolysis in the 200 nm and 214 nm experiments, respectively, and the rest is removed by secondary chemistry. The fractionation constants for the N<sub>2</sub>O + O(<sup>1</sup>D) reaction were determined by Kaiser et al. (2002a) to be (– 2.21 ± 0.12) ‰, (– 8.79 ± 0.14) ‰, and (– 12.23 ± 0.14) ‰ for the isotopocules 456, 546, and 448, respectively. Secondary loss in the 200 nm experiment is < 8% (2% caused by loss



**Fig. 1.** (a) Transmittance of the bandpass filters and 446 absorption cross section from Schmidt et al. (2011). (b) Relative photolysis rates for the bandpass filters. The relative photolysis rate is calculated by multiplying the transmission with the absorption cross section and dividing all values by the value at peak maximum.

**Table 1**

Fractionation constants  $\epsilon$  for photolysis of  $\text{N}_2\text{O}$  with the 200 nm bandpass filter at 20 °C calculated by two different methods (described in the main text) – “mean direct” and “Rayleigh plot”; fractionation constants  $\epsilon$  derived from theoretical absorption cross sections at 20 °C based on Schmidt et al. (2011) (theory); and experimental values of Kaiser et al. (2003b) at room temperature (experiment). The uncertainty is expressed at the 95% confidence interval based on uncertainties of the duplicate experiments. All values are given in ‰.

	“mean direct”	“Rayleigh plot”	theory	experiment
	$\epsilon$	$\epsilon$	intercept	$\epsilon$
$\epsilon_{456}$	$-51.6 \pm 4.8$	$-48.9 \pm 7.4$	$0.3 \pm 0.4$	$-45.6$
$\epsilon_{546}$	$-25.2 \pm 3.8$	$-22.8 \pm 5.3$	$0.2 \pm 0.3$	$-21.0$
$\epsilon_{15\text{bulk}}$	$-38.4 \pm 3.0$	$-35.5 \pm 4.7$	$0.3 \pm 0.2$	$-33.3$
$\epsilon_{447}$	$-11.7 \pm 3.1$	$-12.7 \pm 4.5$	$-0.1 \pm 0.2$	$-15.5$
$\epsilon_{448}$	$-31.1 \pm 8.5$	$-33.5 \pm 12.0$	$0.1 \pm 0.6$	$-29.3$
$\epsilon_{458}$	$-78.8 \pm 4.5$	$-80.9 \pm 6.5$	$-0.1 \pm 0.3$	$-61.2$
$\epsilon_{548}$	$-51.3 \pm 7.3$	$-52.7 \pm 10.8$	$0.1 \pm 0.5$	$-39.5$
$\epsilon_{556}$	$-68.7 \pm 7.6$	$-66.9 \pm 9.8$	$0.4 \pm 0.4$	$-66.7$

**Table 2**

Fractionation constants  $\epsilon$  for photolysis of  $\text{N}_2\text{O}$  with the 214 nm bandpass filter at 20 °C calculated by two different methods (described in the main text) – “mean direct” and “Rayleigh plot”; fractionation constants  $\epsilon$  derived from theoretical absorption cross sections at 20 °C based on Schmidt et al. (2011) (theory); and experimental values of Kaiser et al. (2003b) at room temperature (experiment). The uncertainty is expressed at the 95% confidence interval. All values are given in ‰.

	“mean direct”	“Rayleigh plot”	theory	experiment
	$\epsilon$	$\epsilon$	intercept	$\epsilon$
$\epsilon_{456}$	$-88 \pm 1.7$	$-82.4 \pm 22.3$	$0.2 \pm 0.5$	$-83.5$
$\epsilon_{546}$	$-42.1 \pm 18.7$	$-36.1 \pm 19.6$	$0.3 \pm 0.4$	$-45.2$
$\epsilon_{15\text{bulk}}$	$-65.1 \pm 12.9$	$-59.0 \pm 15.0$	$0.3 \pm 0.3$	$-64.4$
$\epsilon_{447}$	$-29.8 \pm 14.9$	$-21.9 \pm 15.7$	$0.4 \pm 0.3$	$-37.6$
$\epsilon_{448}$	$-48.9 \pm 25.4$	$-44.1 \pm 29.8$	$0.2 \pm 0.6$	$-70.3$
$\epsilon_{458}$	$-130.4 \pm 20.3$	$-120.9 \pm 23.7$	$0.0 \pm 0.5$	$-92.4$
$\epsilon_{548}$	$-81.6 \pm 22.6$	$-79.1 \pm 28.5$	$0.2 \pm 0.6$	$-59.7$
$\epsilon_{556}$	$-112.9 \pm 23.5$	$-110.9 \pm 27.5$	$0.1 \pm 0.6$	$-124.3$

determined from the blank experiment, 6% caused by the  $\text{N}_2\text{O} + \text{O}(^1\text{D})$  reaction), whereas for the 214 nm experiment it is < 22% (13% caused by loss determined from the blank experiment, 9% caused by the  $\text{N}_2\text{O} +$

$\text{O}(^1\text{D})$  reaction; these fractions were determined from the box model). Therefore, the effect of the  $\text{N}_2\text{O} + \text{O}(^1\text{D})$  reaction on the fractionation constant of  $\text{N}_2\text{O}$  photolysis is small (max. 0.2 ‰ for 456, 0.8 ‰ for 546, 1.1 ‰ for 448). Moreover, information regarding the fractionation of the other studied isotopocules for this reaction is not available. Consequently, in this work we assume that the  $\text{O}(^1\text{D})$  loss process and the  $\text{N}_2\text{O}$  loss observed during the blank experiment do not fractionate isotopes (similarly to Kaiser et al., 2003a) and photolysis of  $\text{N}_2\text{O}$  is the only process responsible for the observed isotopic fractionation.

### 2.3. QCLAS analysis

The analytical setup includes a quantum cascade laser absorption spectrometer (QCLAS, Aerodyne Research, Inc., USA; Kantnerová et al., 2020) and a customized automated inlet system (Aerodyne Research, Inc., USA). The QCLAS instrument is equipped with an astigmatic Herriott multi-pass absorption cell (volume 2.5 L, optical path length 204 m). Samples are measured at a pressure of 400 Pa. The inlet system consists of a 16-port VICI rotary valve (VICI Valco Instruments, USA), 10 pneumatically operated bellows valves (BK series, Swagelok, USA), a high-conductance pneumatic valve (Swagelok, USA), a pressure sensor (0–130 kPa Baratron, MKS Instruments, USA), and a turbo-molecular pump station (HiCube 80 Eco, Pfeiffer Vacuum (Schweiz) AG, Switzerland). It is operated by command-based scripts in the TDLWintel software that controls the QCLAS instrument.

The inlet system introduces calibration or sample gas (approx. 10 mL at standard temperature and pressure) into the optical cell of the QCLAS instrument. Pressure in the optical cell is controlled by subsampling of the analyzed gas into an intermediate volume of 50 mL ( $\pm 20$  mL). Prior to filling, the VICI valve and the tubing are purged with the analyzed gas to the pump station. Then, the gas is expanded into the optical cell, the cell is closed, and an absorption spectrum is measured. A measurement cycle consists of analysis of a sample bracketed by analyses of three calibration gases and requires around 40 min. Between the individual measurements, the optical cell and the inlet system are evacuated for 90 s, flushed with nitrogen, and evacuated for another 90 s.

The sampling scheme was adapted to the strongly different photolysis rate at 200 nm and 214 nm. When using the 200 nm bandpass filter, the gas was sampled every 12 h for the full duration of the experiment. For the experiment at 214 nm, sampling took place every 12 h for the first 4 days, then once per week (triplicates) until day 28, when the sample gas analysis was run four times.

Three calibration gases span the concentration range of 1.50–1.85%  $\text{N}_2\text{O}$  in  $\text{N}_2$  (Kantnerová et al., 2020). They share the same isotopic composition:  $\delta^{456} = (-0.11 \pm 0.20) \text{ ‰}$ ,  $\delta^{546} = (0.95 \pm 0.21) \text{ ‰}$ ,



$\delta^{448} = (38 \pm 0.25) \text{ ‰}$ ,  $\Delta^{458} = (-0.06 \pm 0.80) \text{ ‰}$ ,  $\Delta^{548} = (0.49 \pm 0.46) \text{ ‰}$ ,  $\Delta^{556} = (-0.88 \pm 1.76) \text{ ‰}$ . The uncertainties are given at the 95% confidence interval.

## 2.4. Data analysis

The  $\delta^{xyz}$  (Eq. (4)) and  $\Delta^{xyz}$  (Eq. (6)–(8)) values for an isotopocule  $xyz$  were calculated using a mole fraction-calibration scheme described in Kantnerová et al. (2020). The full definitions for the isotopic values can be found therein. The isotopic composition of the calibration gases reported in section 2.3 is used for the calculations.

The time evolution of the  $\delta$  values during photolysis was described by the Rayleigh distillation model following Schmidt et al. (2011) (Eq. (16)) in its linearized form (Eq. (17)):

$$\delta^{xyz} = \left( \frac{R_0^{xyz}}{R_{ref}^{xyz}} \right) \cdot f^{\epsilon_{xyz}} - 1, \quad (16)$$

$$\ln \left( \frac{\delta^{xyz} + 1}{\delta_0^{xyz} + 1} \right) = \epsilon_{xyz} \cdot \ln(f), \quad (17)$$

where  $R_0^{xyz}$  is the initial ratio of the isotopocule  $xyz$  and 446 in the photolyzed gas (represented by  $\delta_0^{xyz}$  in Eq. (17)),  $R_{ref}^{xyz}$  is the ratio of the reference (VSMOW for  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  and Air-N<sub>2</sub> for  $^{15}\text{N}/^{14}\text{N}$ ),  $f$  is the remaining fraction of unphotolyzed isotopocule 446, and  $\epsilon_{xyz}$  is the fractionation constant.

The fractionation constants  $\epsilon$  were calculated by two different strategies, following Kaiser et al. (2003b): 1) “Rayleigh plot” – weighted least-squares regression using Eq. (17) in the form  $y = a \cdot x + b$  assuming an error in both variables (derived from the experimental precision; York et al., 2004); 2) “mean direct” method – only the five last measurements were considered ( $f < 0.093$ ) and the intercept ( $b$ ) was set to zero. The slope  $a$  and the intercept  $b$  of the regression fit were calculated with 95% confidence intervals.

## 3. Results and Discussion

Using the bandpass filter at 200 nm, 8.8% of the initial N<sub>2</sub>O amount was photolyzed during the two 9-day experiments. For the bandpass filter at 214 nm, 4.6% of the initial N<sub>2</sub>O amount was photolyzed in 28 days. Fig. 2 shows an example of the Rayleigh fractionation plots for  $\delta^{458}$  and  $\delta^{15}\text{N}^{\text{bulk}}$  in panel (a), and  $\delta^{556}$  and  $\delta^{447}$  in panel (b). Clearly, the doubly substituted isotopocules undergo stronger photolytic fractionation than the singly substituted isotopocules (Fig. 2). Observed smaller

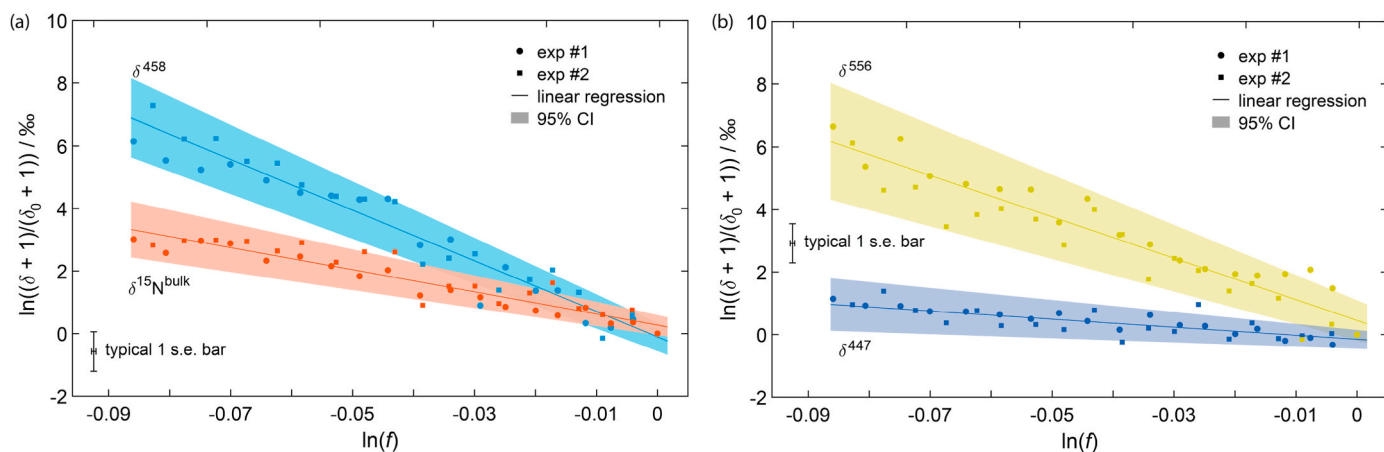
photolysis rates for the heavier isotopocules in comparison with the lighter isotopocules indicate a so-called normal isotope effect.

The fractionation constants determined by the UV photolysis experiments with the 200 nm and 214 nm bandpass filters are shown in Tables 1 and 2, respectively.  $\epsilon$  values for both calculation strategies are in agreement within their uncertainty, which is generally smaller for the “mean direct” approach. The uncertainty for the photolysis experiment at 214 nm is larger than at 200 nm because of the about twofold lower photolysis rate.

Furthermore, Table 1 and Table 2 compare the fractionation constants from our study with those from Kaiser et al. (2003b), both at room temperature, and values calculated using absorption cross sections at 20 °C. Our results agree with the theoretical values for most isotopocules, and for all isotopocules with the values from Kaiser et al. (2003b) within the experimental uncertainty. The fractionation constants of the isotopocule 448 at 214 nm are somewhat smaller than the theoretical values but they agree well with the value by Kaiser et al. (2003b). However, our experimental values for the clumped isotopomers 458 and 548 are consistently larger than the theoretical values, meaning that photolysis of these species is slower than is predicted by the aforementioned theory.

According to Kaiser et al. (2003a), the fractionation constant  $\epsilon_{556}$  must be equal to the sum of the fractionation constants at the central and terminal N positions ( $\epsilon_{456}$  and  $\epsilon_{546}$ , respectively) in order to maintain a statistical isotope distribution. Based on the available experimental evidence, those authors noted that this “additivity rule” seemed to be valid, although the value of  $\epsilon_{556}$  predicted from the sum of  $\epsilon_{456}$  and  $\epsilon_{546}$  obtained experimentally in their work deviated significantly from the observed  $\epsilon_{556}$  at two of the seven data points, by 20–30 %. The remaining five data points were in agreement to within the error of the measurement. In addition, theoretical predictions using the ZPE models (Yung and Miller, 1997) seemed to confirm the additivity rule. However, later theoretical predictions employing more complete models do not obey this rule (Johnson et al., 2001; Schmidt et al., 2011; Schmidt and Johnson, 2015). There is no strong theoretical argument for the additivity rule because many of the underlying processes are nonlinear, including the shift in ZPE with isotopic substitution, and the amplitude of the bending motion, which affects the transition amplitude as the transition dipole changes strongly with the bending angle. Moreover, isotopic substitution influences both the amplitude and the energy of the transition, in addition to changing the populations of the vibrational states, most importantly the bending state (Nanbu and Johnson, 2004).

For completeness, we applied the additive rule to the new species explored in this paper because, as stated in Kaiser et al. (2003a), the additivity rule observed for 556 should apply also to other doubly



**Fig. 2.** Rayleigh fractionation plots of  $\ln((\delta + 1)/(\delta_0 + 1))$  vs.  $\ln(f)$  for photolysis with the 200 nm bandpass filter. (a)  $\delta^{458}$  and  $\delta^{15}\text{N}^{\text{bulk}}$ , (b)  $\delta^{556}$  and  $\delta^{447}$ . The experimental data were fitted by using a linear regression function  $y = a \cdot x + b$ , assuming an error in both variables (typical 1 standard error (s.e.) bar depicted). Shaded areas show the 95% confidence intervals.

substituted isotopocules. Based on the values shown in Tables 1 and 2, the additivity rule is, within the experimental uncertainty, consistent for the experimental results for all three clumped isotopocules and for the theoretical value of  $\epsilon_{556}$ , but not for those of  $\epsilon_{458}$  and  $\epsilon_{548}$ . More work needs to be performed in order to resolve the discrepancy between the experimental and theoretical results for the species 458 and 548. Experimental determination of the absorption cross section of the two species can provide an alternative approach to access the fractionation constant and may likely resolve the discrepancy. The observed discrepancy may be linked to secondary reactions occurring along the photolysis, or possibly the theoretical potential energy surfaces used in Schmidt et al. (2011) could be improved by a higher level of theory and a tighter computational grid.

Experimental values of the three-isotope exponent  $\beta_{\text{exp}}$  were calculated based on Eq. (11) using the “Rayleigh plot”-derived values of  $\epsilon$  in Tables 1 and 2, and compared with theoretical values of  $\beta_{\text{theory}}$ , which are based on the expected values of  $\epsilon$ . The values of  $\beta_{\text{exp}}$  are within their uncertainty intervals (1  $\sigma$ ) in agreement with  $\beta_{\text{theory}}$ :  $\beta_{\text{exp}}(200 \text{ nm}) = 0.46 \pm 0.16$ ,  $\beta_{\text{theory}}(200 \text{ nm}) = 0.52$ ,  $\beta_{\text{exp}}(214 \text{ nm}) = 0.49 \pm 0.25$ ,  $\beta_{\text{theory}}(214 \text{ nm}) = 0.53$ . The obtained larger uncertainty of  $\beta_{\text{exp}}$  prevents stating with confidence that the photolytic fractionation was mass-dependent for  $^{17}\text{O}$  and  $^{18}\text{O}$  relative to  $^{16}\text{O}$ .

During photolysis at both wavelengths, SP and SP<sup>18</sup> show small temporal trends – approx. 2 ‰ for SP and 4 ‰ for SP<sup>18</sup>. This corresponds to larger values of the fractionation constant  $\epsilon$  for the isotopocules 546 and 548 in comparison to 456 and 458, respectively. In other words, the isotopocules 546 and 548 are photolyzed faster than their corresponding isotopomer, causing the gradual change in SP and SP<sup>18</sup>.

The  $\Delta$  values of the clumped isotopocules do not show any significant change in the course of photolysis.  $\Delta^{458}$  is slightly enriched compared to the stochastic distribution, with values up to 4 ‰. On the contrary,  $\Delta^{548}$  has slightly negative values, down to – 4 ‰, similarly to  $\Delta^{556}$ , which is between – 2 and – 1 ‰. The standard uncertainty of the  $\Delta$  values is approx. 1 ‰.

## 4. Conclusion

The experiments simulated the major sink of N<sub>2</sub>O in the stratosphere, where N<sub>2</sub>O is removed by UV light in the transmission window (195–215 nm). The photolysis experiments with the 200 nm and 214 nm bandpass filters allow the determination of fractionation constants of both singly and doubly substituted isotopocules of N<sub>2</sub>O. The photolysis rate at 200 nm is larger than at 214 nm. The fractionation constants,

based on laser spectroscopic measurements of residual N<sub>2</sub>O, indicate slower photolysis progress for the isotopically substituted species in comparison with the lighter species 446, or a so-called normal isotope effect.

Most of the fractionation constants obtained in this study (for isotopocules 456, 546, 447, 448, and 556) show good agreement for both photolysis wavelengths with values calculated from theoretical absorption cross sections by Schmidt et al. (2011) and experimental values for the singly substituted species determined by Kaiser et al. (2003b). Fractionation constants obtained for the clumped isotopomers 458 and 548 show a discrepancy with respect to the theoretical values. This may lead to a refinement of possible secondary chemistry or of theoretical predictions for the clumped isotopes in N<sub>2</sub>O, and ultimately improve the quantification of the importance of UV photolysis in the stratospheric N<sub>2</sub>O budget. Finally, our experiments show that the effect of stratospheric photolysis on the clumped isotope  $\Delta$  values of tropospheric N<sub>2</sub>O is modest, and therefore any variation that is seen will be strongly characteristic of the source and not of atmospheric processes.

## CRediT authorship contribution statement

**Kristýna Kantnerová:** Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Malte F. Jespersen:** Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Stefano M. Bernasconi:** Supervision, Writing - review & editing. **Lukas Emmenegger:** Supervision, Writing - review & editing. **Matthew S. Johnson:** Methodology, Supervision, Writing - review & editing. **Joachim Mohn:** Methodology, Supervision, Writing - review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix

### A. Box model

A box model was created to estimate the effect of secondary chemistry in the photolysis experiment. The starting conditions of the box model are shown in Table A1. The bi- and termolecular reactions included in the model are listed in Table A2. The photolysis rate of N<sub>2</sub>O is estimated by fitting the time evolution of N<sub>2</sub>O to the experimental data as shown in Fig. A2. All other photolysis rates are estimated using the ratio between the absorption cross section of the species and that of N<sub>2</sub>O. The absorption cross sections are shown in Tables A3 and A4, and the photolysis rates in Tables A5 and A6. Radical wall loss is calculated from a 2D-diffusion model, where the diffusion length  $D_l$  of the considered radical species is calculated from Eq. (A1):

$$D_l = \sqrt{4D_x t}, \quad (\text{A1})$$

where  $D_x$  is the diffusion constant and  $t$  is the time. The gas mixture is assumed to be a binary gas mixture with N<sub>2</sub> as the only bath gas. The diffusion constant  $D_x$  is calculated as:

$$D_x = \frac{3}{8p\sigma_x^2} \sqrt{\frac{k_B^3 T^3}{2\pi} \left( \frac{1}{m_x} + \frac{1}{m_{\text{N}_2}} \right)}, \quad (\text{A2})$$

where  $p$  is the pressure,  $\sigma_x$  is the average cross section of the two components, and  $m_x$  and  $m_{\text{N}_2}$  are the molecular masses of the radical and molecular

nitrogen, respectively. The average cross sections are calculated from crude estimates of van der Waals radii obtained by molecular mechanic optimization in the GaussView software. The values of the van der Waals radii are shown in Table A7. The N<sub>2</sub>O removal observed in the blank experiment is included as wall loss in the box model. Experimental and modeled N<sub>2</sub>O loss in the blank experiment are shown in Fig. A3. Loss due to sampling is calculated from an exponential fit to the starting and end pressure and is shown in Tables A8 and A9.

A sensitivity analysis was performed on the box model. Four critical parameters – pressure, photolysis rate, water concentration, and radical wall loss – were selected to test the performance of the box model. The starting pressure and the photolysis rates were varied by  $\pm 10\%$ . The initial water concentrations of 0, 1, 10 and 100  $\mu\text{mol mol}^{-1}$  were tested. The radical wall loss was increased by a factor of 10 and excluded entirely from the model. The results of this analysis are shown in Table A10 and indicate that the uncertainties in the 214 nm experiment are higher than in the 200 nm experiment. In addition, the uncertainty for the determined fraction of N<sub>2</sub>O that reacts by photolysis is lower than  $\pm 1.5\%$ , showing that two major contributions to the secondary chemistry are O(<sup>1</sup>D) directly formed by N<sub>2</sub>O photolysis and the N<sub>2</sub>O loss observed in the blank experiment. The results indicate that secondary chemistry has only a minor effect on the results under the small extent of photolysis obtained in this work, but may become important when higher extents of photolysis are reached. The build-up of photolysis products during the photolysis experiments are shown in Fig. A4 and Fig. A5. The build-up of O<sub>3</sub> and O<sub>2</sub> especially is a potential source of O(<sup>1</sup>D), thereby leading to an increased removal of N<sub>2</sub>O in the experiment.

**Table A1**

Initial concentration of species included in the box model, species not listed in the table have initial concentration of 0 molecules/cm<sup>3</sup>

200 nm	molecules/cm <sup>3</sup>
N <sub>2</sub>	$7.37 \cdot 10^{19}$
N <sub>2</sub> O	$1.26 \cdot 10^{18}$
H <sub>2</sub> O	$7.5 \cdot 10^{14}$
214 nm	molecules/cm <sup>3</sup>
N <sub>2</sub>	$7.50 \cdot 10^{19}$
N <sub>2</sub> O	$1.28 \cdot 10^{18}$
H <sub>2</sub> O	$7.6 \cdot 10^{14}$

**Table A2**

Secondary bi- and termolecular reactions included in the box model

termolecular/(cm <sup>6</sup> s <sup>-1</sup> )	E <sub>a</sub> /(kJ mol <sup>-1</sup> )	reaction	reference
$9.98 \cdot 10^{-32}$	0.00	OH + NO <sub>2</sub> + M → HNO <sub>3</sub> + M	Sander et al. (2011)
$2.61 \cdot 10^{-31}$	0.00	O( <sup>3</sup> P) + NO <sub>2</sub> + M → NO <sub>3</sub> + M	Sander et al. (2011)
$2.86 \cdot 10^{-36}$	0.00	O( <sup>1</sup> D) + N <sub>2</sub> + M → N <sub>2</sub> O + M	Sander et al. (2011)
$9.32 \cdot 10^{-32}$	0.00	O( <sup>3</sup> P) + NO + M → NO <sub>2</sub> + M	Sander et al. (2011)
$4.27 \cdot 10^{-36}$	0.00	H + O <sub>2</sub> + M → HO <sub>2</sub> + M	Sander et al. (2011)
$5.20 \cdot 10^{-35}$	- 7.48	O( <sup>3</sup> P) + O( <sup>3</sup> P) + M → O <sub>2</sub> + M	Tsang and Hampson (1986)
$6.35 \cdot 10^{-34}$	0.00	O <sub>2</sub> + O( <sup>3</sup> P) + M → O <sub>3</sub> + M	Sander et al. (2011)
bimolecular/(cm <sup>3</sup> s <sup>-1</sup> )	E <sub>a</sub> /(kJ mol <sup>-1</sup> )	reaction	reference
$3.12 \cdot 10^{-11}$	- 0.46	O <sub>2</sub> + O( <sup>1</sup> D) → O <sub>2</sub> + O( <sup>3</sup> P)	Sander et al. (2011)
$8.00 \cdot 10^{-12}$	17.13	O <sub>3</sub> + O( <sup>3</sup> P) → 2O <sub>2</sub>	Sander et al. (2011)
$1.20 \cdot 10^{-10}$	0.00	O <sub>3</sub> + O( <sup>1</sup> D) → 2O <sub>2</sub>	Sander et al. (2011)
$1.20 \cdot 10^{-10}$	0.00	O <sub>3</sub> + O( <sup>1</sup> D) → O <sub>2</sub> + 2O( <sup>3</sup> P)	Sander et al. (2011)
$2.15 \cdot 10^{-11}$	- 0.91	O( <sup>1</sup> D) + N <sub>2</sub> → N <sub>2</sub> + O( <sup>3</sup> P)	Sander et al. (2011)
$4.63 \cdot 10^{-11}$	- 0.17	N <sub>2</sub> O + O( <sup>1</sup> D) → N <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
$7.25 \cdot 10^{-11}$	- 0.17	N <sub>2</sub> O + O( <sup>1</sup> D) → 2 NO	Sander et al. (2011)
$5.10 \cdot 10^{-12}$	- 1.75	NO <sub>2</sub> + O( <sup>3</sup> P) → NO + O <sub>2</sub>	Sander et al. (2011)
$1.00 \cdot 10^{-11}$	0.00	O( <sup>3</sup> P) + NO <sub>3</sub> → O <sub>2</sub> + NO <sub>2</sub>	Sander et al. (2011)
$3.00 \cdot 10^{-12}$	12.47	NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
$1.50 \cdot 10^{-11}$	- 1.41	NO + NO <sub>3</sub> → 2 NO <sub>2</sub>	Sander et al. (2011)
$1.20 \cdot 10^{-13}$	20.37	NO <sub>2</sub> + O <sub>3</sub> → NO <sub>3</sub> + O <sub>2</sub>	Sander et al. (2011)
$8.50 \cdot 10^{-13}$	20.37	NO <sub>3</sub> + NO <sub>3</sub> → 2NO <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
$1.44 \cdot 10^{-12}$	0.00	NO <sub>2</sub> + NO <sub>3</sub> → N <sub>2</sub> O <sub>5</sub>	Sander et al. (2011)
$2.00 \cdot 10^{-21}$	0.00	N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O → 2HNO <sub>3</sub>	Sander et al. (2011)
$1.63 \cdot 10^{-10}$	- 0.49	O( <sup>1</sup> D) + H <sub>2</sub> O → 2OH	Sander et al. (2011)
$1.80 \cdot 10^{-11}$	- 1.50	O( <sup>3</sup> P) + OH → O <sub>2</sub> + H	Sander et al. (2011)
$3.00 \cdot 10^{-11}$	- 1.66	O( <sup>3</sup> P) + HO <sub>2</sub> → OH + O <sub>2</sub>	Sander et al. (2011)
$1.40 \cdot 10^{-10}$	3.91	H + O <sub>3</sub> → OH + O <sub>2</sub>	Sander et al. (2011)
$7.20 \cdot 10^{-11}$	0.00	H + HO <sub>2</sub> → 2OH	Sander et al. (2011)
$1.60 \cdot 10^{-12}$	0.00	H + HO <sub>2</sub> → O( <sup>3</sup> P) + H <sub>2</sub> O	Sander et al. (2011)
$6.90 \cdot 10^{-12}$	0.00	H + HO <sub>2</sub> → H <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
$1.70 \cdot 10^{-12}$	7.82	OH + O <sub>3</sub> → HO <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
$2.80 \cdot 10^{-12}$	14.97	OH + H <sub>2</sub> → H <sub>2</sub> O + H	Sander et al. (2011)
$1.80 \cdot 10^{-12}$	0.00	OH + OH → H <sub>2</sub> O + O( <sup>3</sup> P)	Sander et al. (2011)
$2.60 \cdot 10^{-11}$	0.00	OH + OH → H <sub>2</sub> O <sub>2</sub>	Sander et al. (2011)
$4.80 \cdot 10^{-11}$	- 2.08	OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	Sander et al. (2011)
$1.80 \cdot 10^{-12}$	0.00	OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	Sander et al. (2011)
$1.00 \cdot 10^{-14}$	4.07	HO <sub>2</sub> + O <sub>3</sub> → OH + 2O <sub>2</sub>	Sander et al. (2011)

(continued on next page)

**Table A2** (continued)

termolecular/(cm <sup>6</sup> s <sup>-1</sup> )	E <sub>a</sub> /(kJ mol <sup>-1</sup> )	reaction	reference
3.00 · 10 <sup>-13</sup>	– 3.82	HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
1.40 · 10 <sup>-12</sup>	16.63	O( <sup>3</sup> P) + H <sub>2</sub> O <sub>2</sub> → OH + HO <sub>2</sub>	Sander et al. (2011)
3.60 · 10 <sup>-11</sup>	0.00	OH + NO → HONO	Sander et al. (2011)
1.80 · 10 <sup>-11</sup>	3.24	OH + HONO → H <sub>2</sub> O + NO <sub>2</sub>	Sander et al. (2011)
1.64 · 10 <sup>-13</sup>	0.00	OH + HNO <sub>3</sub> → H <sub>2</sub> O + NO <sub>3</sub>	Sander et al. (2011)
2.90 · 10 <sup>-12</sup>	0.00	HO <sub>2</sub> + NO <sub>2</sub> → HO <sub>2</sub> NO <sub>2</sub>	Sander et al. (2011)
5.00 · 10 <sup>-16</sup>	0.00	HO <sub>2</sub> + NO <sub>2</sub> → HONO + O <sub>2</sub>	Sander et al. (2011)
3.50 · 10 <sup>-12</sup>	0.00	HO + NO <sub>3</sub> → OH + NO <sub>2</sub> + O <sub>2</sub>	Sander et al. (2011)
4.00 · 10 <sup>-10</sup>	2.83	H + NO <sub>2</sub> → OH + NO	Sander et al. (2011)
2.20 · 10 <sup>-11</sup>	0.00	OH + NO <sub>3</sub> → NO <sub>2</sub> + HO <sub>2</sub>	Sander et al. (2011)

**Table A3**

Absorption cross sections used in the model for the 200 nm experiment

species	wavelength/nm	cross section/cm <sup>2</sup>	quantum yield	reference
O <sub>3</sub> → O <sub>2</sub> + O( <sup>1</sup> D)	198–202	3.20 · 10 <sup>-19</sup>	1	Sander et al. (2011)
N <sub>2</sub> O → N <sub>2</sub> + O( <sup>1</sup> D)	200–202	3.84 · 10 <sup>-20</sup>	1	Sander et al. (2011)
O <sub>2</sub> → 2O( <sup>3</sup> P)	205	7.25 · 10 <sup>-24</sup>	1	Sander et al. (2011)
N <sub>2</sub> O <sub>5</sub> → NO <sub>3</sub> + NO + O( <sup>3</sup> P)	200	9.10 · 10 <sup>-18</sup>	1	Sander et al. (2011)
NO <sub>3</sub> → NO <sub>2</sub> + O( <sup>1</sup> D)	220	3.4 · 10 <sup>-19</sup>	1	Sander (1986)
HO <sub>2</sub> → OH + O( <sup>1</sup> D)	200	3.68 · 10 <sup>-18</sup>	1	Sander et al. (2011)
H <sub>2</sub> O → OH + H	198	9.00 · 10 <sup>-22</sup>	1	Sander et al. (2011)
H <sub>2</sub> O <sub>2</sub> → 2OH	200	4.75 · 10 <sup>-19</sup>	1	Sander et al. (2011)
HONO → H + NO <sub>2</sub>	200	2.10 · 10 <sup>-18</sup>	1	Sander et al. (2011)
HNO <sub>3</sub> → OH + NO <sub>2</sub>	200	5.88 · 10 <sup>-18</sup>	0.33	Sander et al. (2011)
HNO <sub>3</sub> → HONO + O( <sup>1</sup> D)	200	5.88 · 10 <sup>-18</sup>	0.67	Sander et al. (2011)
HO <sub>2</sub> NO <sub>2</sub> → OH + NO <sub>3</sub>	200	5.63 · 10 <sup>-18</sup>	0.25	Sander et al. (2011)
HO <sub>2</sub> NO <sub>2</sub> → HO <sub>2</sub> + NO <sub>2</sub>	200	5.63 · 10 <sup>-18</sup>	0.75	Sander et al. (2011)

**Table A4**

Absorption cross sections used in the model for the 214 nm experiment

species	wavelength/nm	cross section/cm <sup>2</sup>	quantum yield	reference
O <sub>3</sub> → O <sub>2</sub> + O( <sup>1</sup> D)	212.77–215.05	9.03 · 10 <sup>-19</sup>	1	Sander et al. (2011)
N <sub>2</sub> O → N <sub>2</sub> + O( <sup>1</sup> D)	214	3.42 · 10 <sup>-21</sup>	1	Sander et al. (2011)
O <sub>2</sub> → 2O( <sup>3</sup> P)	214	5.72 · 10 <sup>-24</sup>	1	Sander et al. (2011)
N <sub>2</sub> O <sub>5</sub> → NO <sub>3</sub> + NO + O( <sup>3</sup> P)	214	3.22 · 10 <sup>-18</sup>	1	Sander et al. (2011)
NO <sub>2</sub> → NO + O( <sup>1</sup> D)	214	4.64 · 10 <sup>-19</sup>	1	Bass et al. (1976)
NO <sub>3</sub> → NO <sub>2</sub> + O( <sup>1</sup> D)	220	3.4 · 10 <sup>-19</sup>	1	Sander (1986)
HO <sub>2</sub> → O( <sup>1</sup> D) + OH	215	3.85 · 10 <sup>-18</sup>	1	Sander et al. (2011)
H <sub>2</sub> O <sub>2</sub> → 2 OH	215	3.07 · 10 <sup>-19</sup>	1	Sander et al. (2011)
N <sub>2</sub> O <sub>5</sub> → NO <sub>3</sub> + NO + O( <sup>3</sup> P)	214	3.22 · 10 <sup>-18</sup>	1	Sander et al. (2011)
HONO → H + NO <sub>2</sub>	214	1.93 · 10 <sup>-18</sup>	1	Sander et al. (2011)
HNO <sub>3</sub> → OH + NO <sub>2</sub>	214	4.39 · 10 <sup>-19</sup>	0.33	Sander et al. (2011)
HNO <sub>3</sub> → HONO + O( <sup>1</sup> D)	214	4.39 · 10 <sup>-19</sup>	0.67	Sander et al. (2011)
HO <sub>2</sub> NO <sub>2</sub> → OH + NO <sub>3</sub>	215	1.61 · 10 <sup>-18</sup>	0.25	Sander et al. (2011)
HO <sub>2</sub> NO <sub>2</sub> → HO <sub>2</sub> + NO <sub>2</sub>	215	1.61 · 10 <sup>-18</sup>	0.75	Sander et al. (2011)

**Table A5**Photolysis rates for the 200 nm experiment. Photon flux is determined by fitting the N<sub>2</sub>O concentration to the experimental values.

photolysis rate/s <sup>-1</sup>	reaction
1.11 · 10 <sup>-7</sup>	N <sub>2</sub> O → O( <sup>1</sup> D) + N <sub>2</sub>
8.84 · 10 <sup>-7</sup>	NO <sub>2</sub> → NO + O( <sup>1</sup> D)
7.84 · 10 <sup>-6</sup>	NO <sub>3</sub> → NO <sub>2</sub> + O( <sup>1</sup> D)
9.22 · 10 <sup>-7</sup>	O <sub>3</sub> → O( <sup>1</sup> D) + O <sub>2</sub>
2.62 · 10 <sup>-5</sup>	N <sub>2</sub> O <sub>5</sub> → NO <sub>3</sub> + NO + O( <sup>3</sup> P)
2.09 · 10 <sup>-10</sup>	O <sub>2</sub> → 2O( <sup>3</sup> P)
1.06 · 10 <sup>-5</sup>	HO <sub>2</sub> → O( <sup>1</sup> D) + OH
2.59 · 10 <sup>-9</sup>	H <sub>2</sub> O → OH + H
1.37 · 10 <sup>-6</sup>	H <sub>2</sub> O <sub>2</sub> → 2 OH
6.05 · 10 <sup>-6</sup>	HONO → H + NO <sub>2</sub>
5.65 · 10 <sup>-6</sup>	HNO <sub>3</sub> → OH + NO <sub>2</sub>
1.13 · 10 <sup>-5</sup>	HNO <sub>3</sub> → HONO + O( <sup>1</sup> D)
4.06 · 10 <sup>-6</sup>	HO <sub>2</sub> NO <sub>2</sub> → OH + NO <sub>3</sub>
1.22 · 10 <sup>-5</sup>	HO <sub>2</sub> NO <sub>2</sub> → HO <sub>2</sub> + NO <sub>2</sub>



**Table A6**

Photolysis rates for the 214 nm experiment. Photon flux is determined by fitting the N<sub>2</sub>O concentration to the experimental values.

photolysis rate/s <sup>-1</sup>	reaction
$1.56 \cdot 10^{-8}$	N <sub>2</sub> O → O( <sup>1</sup> D) + N <sub>2</sub>
$1.89 \cdot 10^{-7}$	NO <sub>2</sub> → NO + O( <sup>1</sup> D)
$1.38 \cdot 10^{-7}$	NO <sub>3</sub> → NO <sub>2</sub> + O( <sup>1</sup> D)
$3.68 \cdot 10^{-7}$	O <sub>3</sub> → O( <sup>1</sup> D) + O <sub>2</sub>
$1.31 \cdot 10^{-6}$	N <sub>2</sub> O <sub>5</sub> → NO <sub>3</sub> + NO + O( <sup>3</sup> P)
$2.33 \cdot 10^{-11}$	O <sub>2</sub> → 2O( <sup>3</sup> P)
$1.57 \cdot 10^{-6}$	HO <sub>2</sub> → O( <sup>1</sup> D) + OH
$1.25 \cdot 10^{-7}$	H <sub>2</sub> O <sub>2</sub> → 2 OH
$7.86 \cdot 10^{-7}$	HONO → H + NO <sub>2</sub>
$5.96 \cdot 10^{-8}$	HNO <sub>3</sub> → OH + NO <sub>2</sub>
$1.19 \cdot 10^{-7}$	HNO <sub>3</sub> → HONO + O( <sup>1</sup> D)
$1.64 \cdot 10^{-7}$	HO <sub>2</sub> NO <sub>2</sub> → OH + NO <sub>3</sub>
$4.92 \cdot 10^{-7}$	HO <sub>2</sub> NO <sub>2</sub> → HO <sub>2</sub> + NO <sub>2</sub>

**Table A7**

Wall-loss reactions included in the model, van der Waals radii of the species, and wall-loss rates. Wall loss of N<sub>2</sub>O is estimated from the blank experiment, while the other reactions are calculated as diffusion of a two-component system with N<sub>2</sub> as the only bath gas.

species	radius/10 <sup>-10</sup> m	wall-loss rate/s <sup>-1</sup>
N <sub>2</sub> O → wall·N <sub>2</sub> O		$2.5 \cdot 10^{-9}$
N <sub>2</sub> → wall·N <sub>2</sub>	2.18	0
O( <sup>3</sup> P) → wall·O(P)	1.47	0.253495
NO → wall·NO	2.26	0.210422
NO <sub>2</sub> → wall·NO <sub>2</sub>	4.14	0.168435
NO <sub>3</sub> → wall·NO <sub>3</sub>	4.72	0.157105
HNO <sub>3</sub> → wall·HNO <sub>3</sub>	4.95	0.154357
HO <sub>2</sub> NO <sub>2</sub> → wall·HO <sub>2</sub> NO <sub>2</sub>	5.97	0.142066
HONO → wall·HONO	4.87	0.159151
OH → wall·OH	1.92	0.236884
H → wall·H	1.2	0.473705
H <sub>2</sub> O <sub>2</sub> → wall·H <sub>2</sub> O <sub>2</sub>	4.59	0.179288
HO <sub>2</sub> → wall·HO <sub>2</sub>	3.8	0.214067
N <sub>2</sub> O <sub>5</sub> → wall·N <sub>2</sub> O <sub>5</sub>	6.21	0.137486

**Table A8**

Sampling loss for the 200 nm experiment. The sampling loss is determined from exponential fit to the starting and final pressure in the photoreactor.

sampling loss/s <sup>-1</sup>	reaction
$7.08 \cdot 10^{-7}$	O <sub>3</sub> → loss
$7.08 \cdot 10^{-7}$	O( <sup>1</sup> D) → loss
$7.08 \cdot 10^{-7}$	O <sub>2</sub> → loss
$7.08 \cdot 10^{-7}$	O( <sup>3</sup> P) → loss
$7.08 \cdot 10^{-7}$	N <sub>2</sub> → loss
$7.08 \cdot 10^{-7}$	N <sub>2</sub> O → loss
$7.08 \cdot 10^{-7}$	NO → loss
$7.08 \cdot 10^{-7}$	NO <sub>2</sub> → loss
$7.08 \cdot 10^{-7}$	NO <sub>3</sub> → loss
$7.08 \cdot 10^{-7}$	N <sub>2</sub> O <sub>5</sub> → loss
$7.08 \cdot 10^{-7}$	H → loss
$7.08 \cdot 10^{-7}$	OH → loss
$7.08 \cdot 10^{-7}$	HO <sub>2</sub> → loss
$7.08 \cdot 10^{-7}$	H <sub>2</sub> O <sub>2</sub> → loss
$7.08 \cdot 10^{-7}$	H <sub>2</sub> O → loss
$7.08 \cdot 10^{-7}$	HNO <sub>3</sub> → loss
$7.08 \cdot 10^{-7}$	HONO → loss
$7.08 \cdot 10^{-7}$	HO <sub>2</sub> NO <sub>2</sub> → loss

**Table A9**

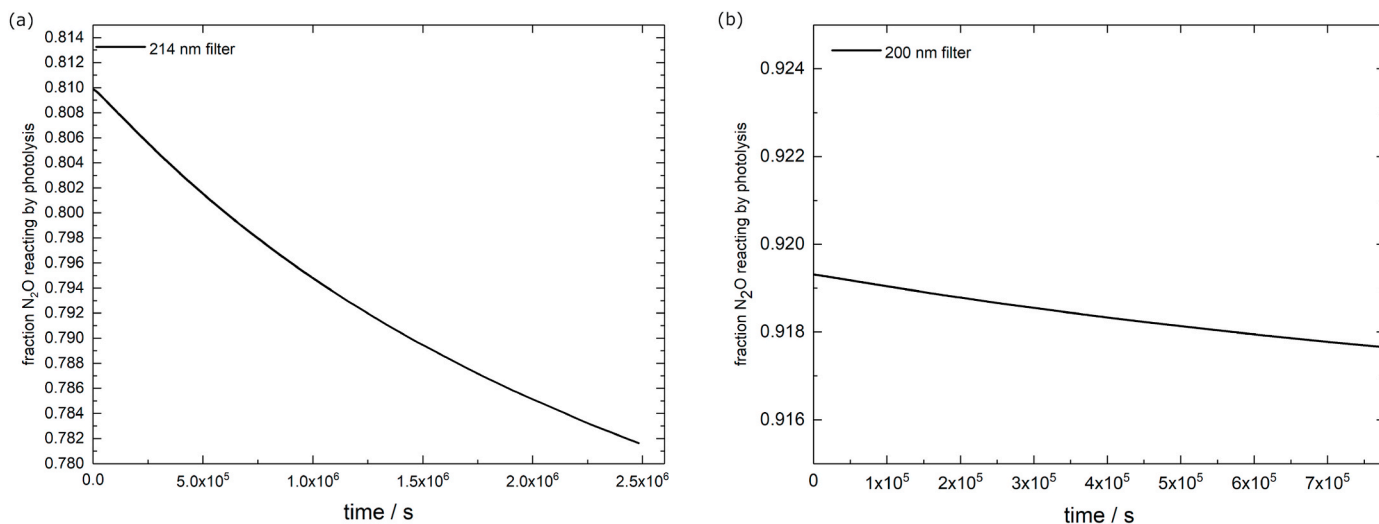
Sampling loss for the 214 nm experiment. The sampling loss is determined from exponential fit, to the starting and final pressure in the photoreactor.

sampling loss/s <sup>-1</sup>	reaction
$3.14 \cdot 10^{-7}$	O <sub>3</sub> → loss
$3.14 \cdot 10^{-7}$	O( <sup>1</sup> D) → loss
$3.14 \cdot 10^{-7}$	O <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	O( <sup>3</sup> P) → loss
$3.14 \cdot 10^{-7}$	N <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	N <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	NO → loss
$3.14 \cdot 10^{-7}$	NO <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	NO <sub>3</sub> → loss
$3.14 \cdot 10^{-7}$	N <sub>2</sub> O <sub>5</sub> → loss
$3.14 \cdot 10^{-7}$	H → loss
$3.14 \cdot 10^{-7}$	OH → loss
$3.14 \cdot 10^{-7}$	HO <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	H <sub>2</sub> O <sub>2</sub> → loss
$3.14 \cdot 10^{-7}$	H <sub>2</sub> O → loss
$3.14 \cdot 10^{-7}$	HNO <sub>3</sub> → loss
$3.14 \cdot 10^{-7}$	HONO → loss
$3.14 \cdot 10^{-7}$	HO <sub>2</sub> NO <sub>2</sub> → loss

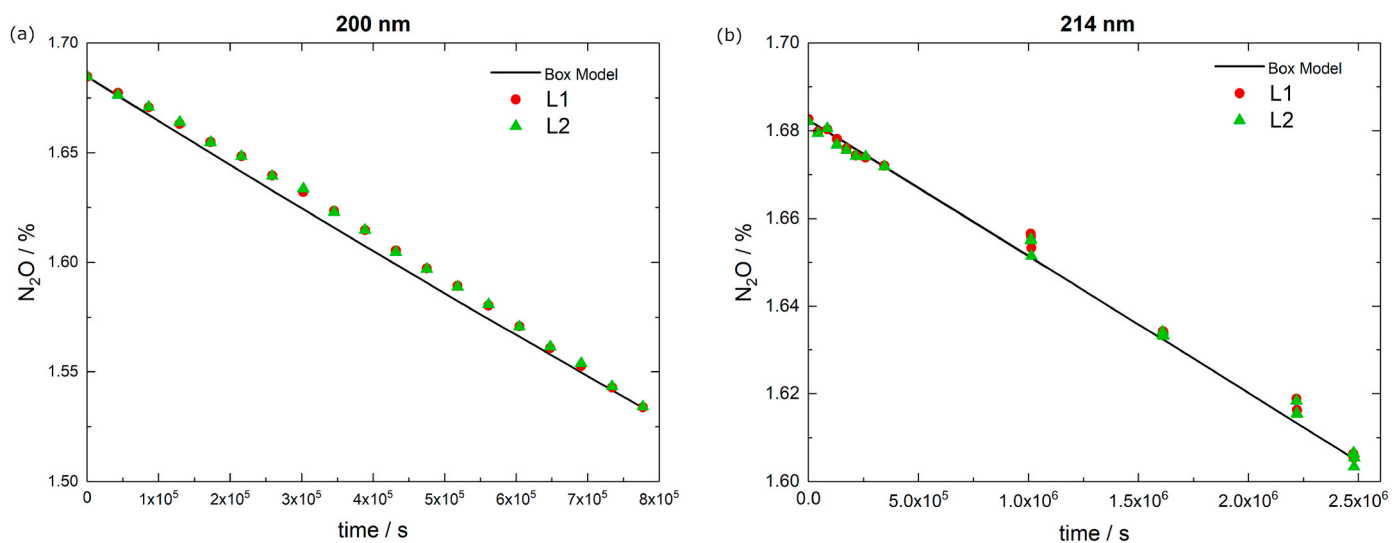
**Table A10**

Sensitivity analysis;  $f$  is the fraction of N<sub>2</sub>O which reacts by photolysis

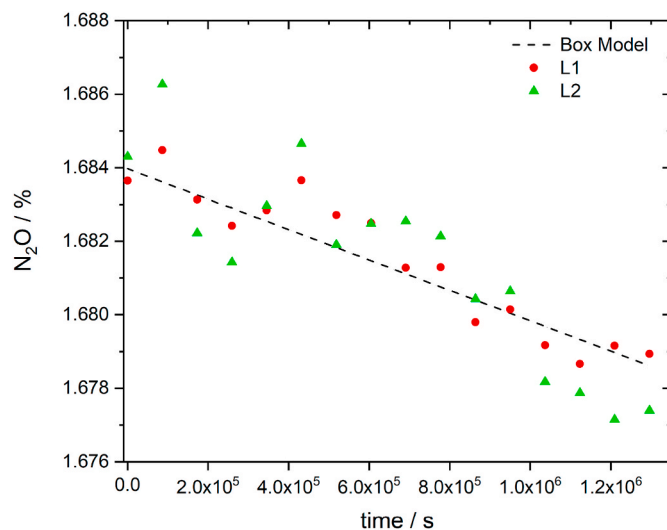
sensitivity analysis	$f$ (200 nm)	error estimate (200 nm)/%	$f$ (214 nm)	error estimate (214 nm)/%
standard model (10 $\mu\text{mol mol}^{-1}$ H <sub>2</sub> O)	0.91757		0.78164	
photolysis 110%	0.91924	0.173	0.78925	0.974
photolysis 90%	0.91569	-0.214	0.77223	-1.204
pressure 110%	0.91759	-0.007	0.7811	-0.069
pressure 90%	0.91772	0.008	0.78226	0.079
radical loss x10	0.91768	0.003	0.78368	0.261
no radical loss	0.91746	-0.021	0.7865	0.622
100 $\mu\text{mol mol}^{-1}$ H <sub>2</sub> O	0.91802	0.040	0.78299	0.173
1 $\mu\text{mol mol}^{-1}$ H <sub>2</sub> O	0.91762	-0.003	0.7815	-0.018
no H <sub>2</sub> O	0.91761	-0.004	0.78148	-0.020



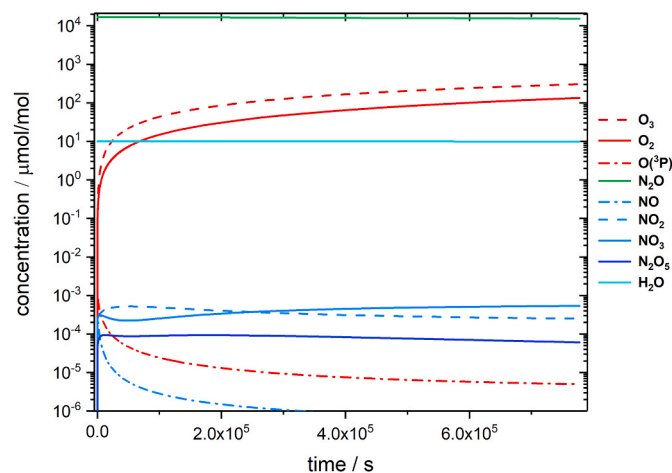
**Fig. A1.** Fraction of N<sub>2</sub>O removed by photolysis in the experiments with (a) the 214 nm filter, (b) the 200 nm filter. The results are obtained from the box model.



**Fig. A2.**  $N_2O$  concentration measured in the experiment and modeled by the box model in the experiment with (a) the 200 nm filter, (b) the 214 nm filter. L1, L2 indicates species 446 measured by laser 1 and laser 2, respectively.



**Fig. A3.**  $N_2O$  concentration in the blank experiment (species 446 measured by laser 1 (L1) and laser 2 (L2)), and the  $N_2O$  concentration from the box model.



**Fig. A4.** Temporal evolution of  $N_2O$  (educt) and the most abundant product species in the box model for the 200 nm experiment.

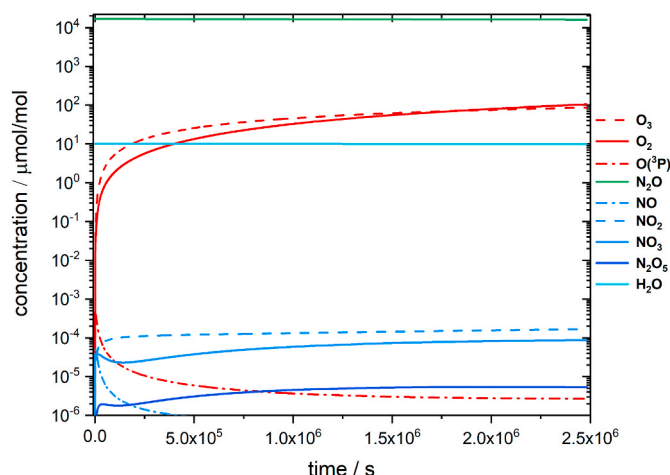


Fig. A5. Temporal evolution of  $\text{N}_2\text{O}$  (educt) and the most abundant product species in the box model for the 214 nm experiment.

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