

**ISOTOPOMER FRACTIONATION DURING PHOTOLYSIS OF  
NITROUS OXIDE BY ULTRAVIOLET OF 206 TO 210 nm**

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**Abstract.** Nitrous oxide ( $\text{N}_2\text{O}$ ) is an important trace gas in the stratospheric chemistry as well as in the tropospheric radiative balance. Although there have been observations on the distribution of  $\text{N}_2\text{O}$  in the atmosphere and its flux from individual sources, the global  $\text{N}_2\text{O}$  budget is not fully understood. The isotopic information of  $\text{N}_2\text{O}$  has been useful for constraining the  $\text{N}_2\text{O}$  cycle since each source and sink has its own isotopic signature and isotope fractionation that is unique to the process. We have recently developed a method to determine isotopomers of  $\text{N}_2\text{O}$  and showed that intramolecular distribution of  $^{15}\text{N}$  is a parameter that has more fundamental and sensitive information than bulk  $^{15}\text{N}$  abundance for constraining the atmospheric  $\text{N}_2\text{O}$  budget. Here, we report the fractionation of isotopomers during ultraviolet photolysis of  $\text{N}_2\text{O}$  in a 206 to 210 nm region. The fractionation factors are different among isotopomers and the site preference between two nitrogen isotopomers becomes larger along with the photolysis. The isotopomer fractionation factors of this representative wavelength are close to the apparent fractionation factors observed in the stratosphere indicating ultraviolet photolysis in the stratosphere is the dominant sink of  $\text{N}_2\text{O}$ . Sources of atmospheric  $\text{N}_2\text{O}$  including terrestrial and oceanic biological processes, agricultural activities, industrial formation and fossil fuel combustion are expected to be characterized to better constrain the global budget of  $\text{N}_2\text{O}$ .

## 1. INTRODUCTION

Nitrous oxide is an important trace gas in the atmosphere. Although its abundance in the troposphere is about 316 ppb, it has a global warming potential as well as carbon dioxide and methane and is increasing by about  $0.3\% \text{yr}^{-1}$  [1]. In the stratosphere,  $\text{N}_2\text{O}$  is decomposed by ultraviolet photolysis and photo-oxidation with an excited oxygen atom, and the reactive decomposition products are incorporated into ozone depleting reactions [2]. Sources of atmospheric  $\text{N}_2\text{O}$  exist in the troposphere and include terrestrial and oceanic biological processes such as nitrification and denitrification, industrial formation as a byproduct in nylon production, fossil fuel combustion, and so on [1]. However, the global  $\text{N}_2\text{O}$  budget is not fully understood.

Natural isotope abundance in  $\text{N}_2\text{O}$  can be used to constrain the  $\text{N}_2\text{O}$  cycle [3,4], as similar manner that applied to carbon dioxide, methane, and so on. Previous studies revealed that  $\text{N}_2\text{O}$  in the stratosphere is enriched in  $^{15}\text{N}$  and  $^{18}\text{O}$  [4,5], and the back flux of such heavy  $\text{N}_2\text{O}$

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from the stratosphere into the troposphere is considered an important key to estimate the magnitude of surface natural and industrial source of N<sub>2</sub>O. We have developed a mass-spectroscopic method to determine isotopomers of nitrous oxide [6] and found that the enrichment in <sup>15</sup>N at the center position of the asymmetric NNO molecule is larger than at the end position for the tropospheric N<sub>2</sub>O, and that the difference is increases in the stratosphere [7]. Almost concurrently, other researchers have also reported similar site-specific enrichment in <sup>15</sup>N of N<sub>2</sub>O in the stratosphere by similar manner as ours [8] or infrared absorption spectroscopy [9].

The mechanism of the heavy-isotope enrichment of N<sub>2</sub>O was first supplied by the theoretical calculation in Ref. [10], which showed that the shift of N<sub>2</sub>O absorption spectrum due to the difference in zero-point energy of each isotopomers causes the fractionation. They predicted the difference of the <sup>15</sup>N enrichment at the two intra-molecular sites and wavelength dependence of the enrichment, which turned to be generally in accordance with recent laboratory experiments [11-13] and stratospheric observations [9,14].

However, recent laboratory photolysis experiments showed disagreement with the theoretical calculation in the magnitude of the enrichment. In addition, apparent enrichment factors obtained from stratospheric observations are variable with altitude [14] presumably because the actual photolysis occurs by variable spectrum of the sun instead of monochromatic light.

In this paper, we intend to estimate the fractionation factors of isotopomers of N<sub>2</sub>O in the stratospheric sink processes by simulating the photolysis, to discuss about wavelength dependence of the fractionation factor and compare the results with other simulation experiments and theoretical calculations, and to compare the results with stratospheric observations and discuss about N<sub>2</sub>O behavior in the stratosphere.

## 2. NOMENCLATURE

We define an isotopomer as one of the set of molecules that are isotopically substituted. Since N<sub>2</sub>O has an asymmetric structure, and nitrogen and oxygen have two and three stable isotopes, respectively, following five isotopomers are significant at natural abundance level: <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O, <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>14</sup>N<sup>17</sup>O and <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O. If we name the center and end positions of the nitrogen atom  $\alpha$  and  $\beta$ , respectively, we can define isotopomer ratio for each position, and express it as a permil deviation from the reference material [6]:

$$\delta^{15}\text{N}^{\alpha} = \{ {}^{15}R^{\alpha} / {}^{15}R(\text{std}) - 1 \} \times 1000 \quad (1)$$

$$\delta^{15}\text{N}^{\beta} = \{ {}^{15}R^{\beta} / {}^{15}R(\text{std}) - 1 \} \times 1000 \quad (2)$$

where <sup>15</sup>R denotes the ratio of <sup>15</sup>N to <sup>14</sup>N and <sup>15</sup>R(std) is the ratio for atmospheric N<sub>2</sub>, the standard material for nitrogen isotope ratio.

Conventional “nitrogen isotope ratio in N<sub>2</sub>O” equals the average of two isotopomer ratios since it does not distinguish these two isotopomers:

$$\begin{aligned} \delta^{15}\text{N}^{\text{bulk}} &= \{ {}^{15}R^{\text{bulk}} / {}^{15}R^{\text{bulk}}(\text{std}) - 1 \} \times 1000 \\ &= (\delta^{15}\text{N}^{\alpha} + \delta^{15}\text{N}^{\beta}) / 2. \end{aligned} \quad (3)$$

Oxygen isotope ratios are expressed by conventional notation:

$$\delta^{17}\text{O} = \{^{17}R / ^{17}R(\text{std}) - 1\} \times 1000 \quad (4)$$

$$\delta^{18}\text{O} = \{^{18}R / ^{18}R(\text{std}) - 1\} \times 1000 \quad (5)$$

where  $^{17}R$  and  $^{18}R$  are the ratio of  $^{17}\text{O}$  and  $^{18}\text{O}$  to  $^{16}\text{O}$ , respectively, and standard material is standard mean ocean water (SMOW).

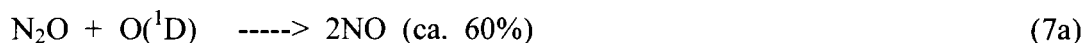
### 3. EXPERIMENTAL

#### 3.1. Photolysis experiments

Since nitrous oxide has an absorption band in a 170 to 230 nm region that overlaps with the so-called "atmospheric window" ranging between 200-210 nm in the stratosphere, it is photolyzed to molecular nitrogen and excited oxygen atom [15]:



One more reaction known as  $\text{N}_2\text{O}$  sink is oxidation by  $\text{O}({}^1\text{D})$  produced mainly by the photolysis of ozone [15]:



When integrated over the whole stratosphere, relative contributions of these reactions are 90 and 10%, respectively [16], so we first concentrated on the photolysis in this study. To avoid the possible side reaction with  $\text{O}({}^1\text{D})$  produced by the photolysis of  $\text{N}_2\text{O}$ , we quenched the excited oxygen by nitrogen gas [17, 18] and checked its effectiveness by changing mixing ratio of  $\text{N}_2$  and  $\text{N}_2\text{O}$ .

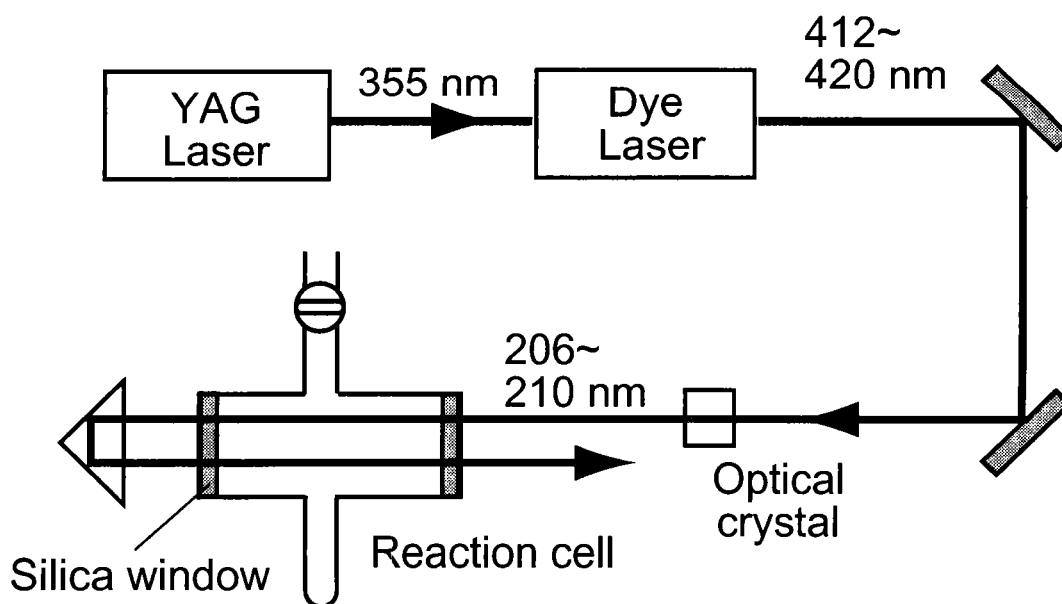


FIG. 1. Apparatus used for photolysis of  $\text{N}_2\text{O}$ .

Figure 1 shows a schematic diagram of our experimental setup for photolysis. We used a dye laser (Lambda Physik, SCANMATE2) pumped by the third harmonic of a Nd:YAG laser (Continuum, Powerlite 8000) to generate the light of between 412 and 420 nm, and obtained the second harmonics of 206.1, 207.1, 209.1 and 210.1 nm through a BBO-A crystal. The light source operates at a repetition rate of 10 Hz with a 206-210 nm pulse energy of ~0.4 mJ, pulse duration of 10 ns and resolution of 0.2 cm<sup>-1</sup>. The wavelengths of 412 and 414 nm were obtained through Exalite 411 (Exciton, INC., dissolved in p-dioxane, approximately 7×10<sup>-4</sup> mol/l), and those of 418 and 420 nm were obtained through Exalite 416. Calibration of the wavelength was carried out by measuring opto-galvanic spectra of Ne.

An aliquot (~2.5 cm<sup>3</sup>STP) of N<sub>2</sub>O ( $\delta^{15}\text{N}^{\text{bulk}} = -1.59\text{‰}$ ,  $\delta^{15}\text{N}^{\alpha} = -3.61\text{‰}$ ,  $\delta^{15}\text{N}^{\beta} = 0.42\text{‰}$  and  $\delta^{18}\text{O} = 21.70\text{‰}$ , determined by our N<sub>2</sub>O isotopomer standard that were calibrated against atmospheric N<sub>2</sub> and SMOW [6]) was introduced to a Pyrex glass cell of 4 cm inside diameter and 24 cm length (approximately 300 cm<sup>3</sup> volume). The cell was equipped with UV-transparent silica windows of 2 mm thickness at both ends, and optically illuminated area was estimated at about 0.2 cm<sup>2</sup>.

For the quenching of O(<sup>1</sup>D), ultra pure N<sub>2</sub> (>99.9998%, Nippon Sanso Co., Ltd.) was added. Mixing ratio of N<sub>2</sub> to N<sub>2</sub>O was typically set to be 150 after the similar photolysis experiment of Ref. [18], but in the experiment at 207 nm, the ratio of 50, 100, and 200 was also tested. Total pressure of the sample mixture was 4.3×10<sup>4</sup> ~ 1.3×10<sup>5</sup> Pa (320 ~ 1000 Torr).

After the sample mixture was irradiated at room temperature for 3 to 10 hours, residual N<sub>2</sub>O was collected at 77 K and purified through cold bath at ~200 K (for drying) and Ascarite (Thomas Scientific, for removing trace CO<sub>2</sub>). Amount of the N<sub>2</sub>O was measured manometrically.

### 3.2. Mass spectrometric analysis

Isotopomer ratios of the photolyzed samples are measured relative to non-photolyzed N<sub>2</sub>O on a modified Finnigan MAT 252 mass spectrometer (Thermoquest K.K.) using a conventional dual inlet. Experimental details are given elsewhere [6]. Briefly, intramolecular distribution of <sup>15</sup>N was determined by analyzing molecular and fragment ions of N<sub>2</sub>O produced by electron impact ionization. NO<sup>+</sup> contains α nitrogen only, while N<sub>2</sub>O<sup>+</sup> contains both α and β nitrogen, so that we can deduce the isotope ratio in nitrogen for both α and β site. When converting measured ratios to isotopomer ratios, we applied experimentally determined correction factor for scrambling of nitrogen atom during ionization, and assumed the mass-dependent relationship between abundance of <sup>17</sup>O and <sup>18</sup>O [17].

## 4. RESULTS AND DISCUSSION

To analyze the isotopomer data, we assume that the photolysis is irreversible reaction and that isotope fractionation factor is constant during the reaction. Then, the isotopomer ratios should satisfy Rayleigh equation and we can obtain the enrichment factor ε from relationship between isotopomer ratios and residual fraction of N<sub>2</sub>O [18].

$$\delta - \delta_0 = \epsilon \ln f \quad (8)$$

where

δ is isotopomer ratio (‰),

ε is the enrichment factor (‰),

f is the remaining fraction of N<sub>2</sub>O ( $=[\text{N}_2\text{O}]/[\text{N}_2\text{O}]_0$ ),

and parameters with subscript zero correspond to the values before photolysis.

Figure 2 shows Rayleigh plots obtained at 207.1 nm. It is clear that all isotopomer ratios are getting higher with the progress of the photolysis, and enrichment in  $^{15}\text{N}$  is higher at  $\alpha$  site than at  $\beta$  site.

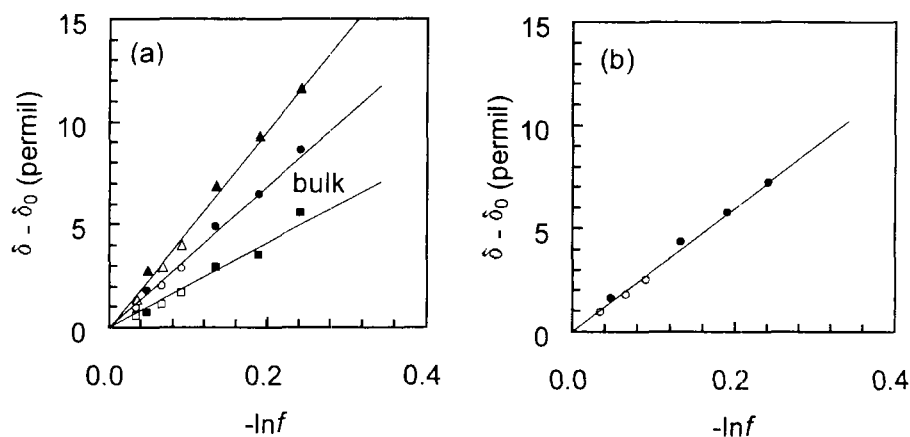


FIG. 2. Rayleigh plots for photolysis of  $\text{N}_2\text{O}$  at 207.1 nm for  $^{15}\text{N}$ -containing isotopomers (a) and  $^{18}\text{O}$ -containing isotopomers (b).

Three open symbols in each plot in Fig. 2 were obtained when the mixing ratio of  $\text{N}_2$  and  $\text{N}_2\text{O}$  were 200, 50, and 100, although irradiation time is also different. We can see that the quenching of excited oxygen atom was effective and hence contribution of photo-oxidation was negligible.

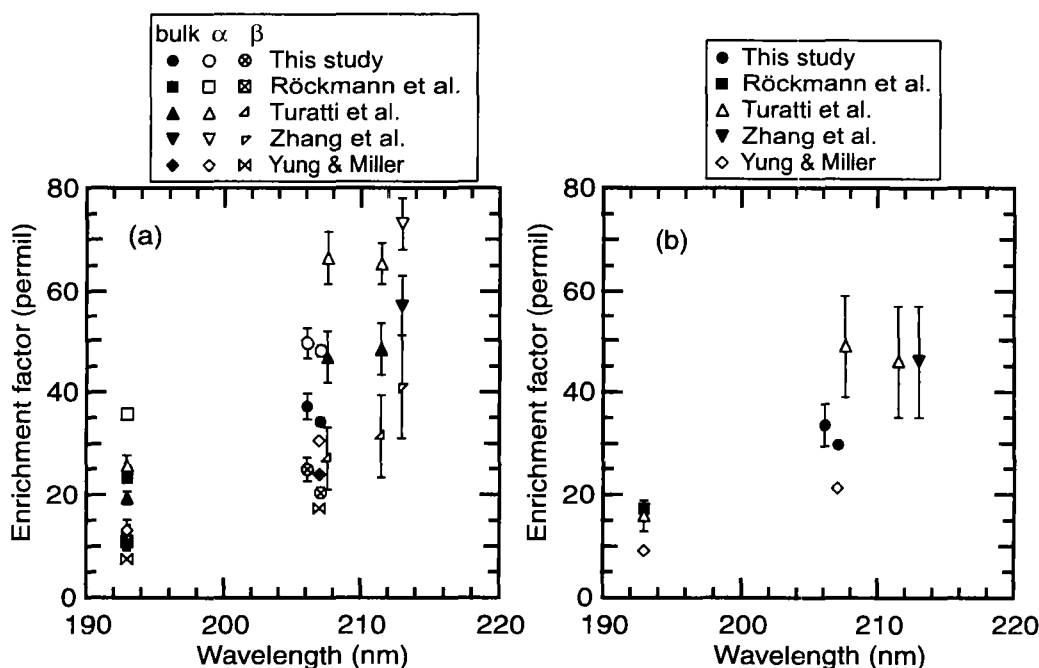


FIG. 3. Enrichment factors during photolysis at various wavelengths experimentally obtained in this study and others [11,12,13], and theoretically calculated value of Ref. [10,19]. For the convenience for comparison, enrichment factors are shown by positive value, although they are negative in our definition using Eq (8) in text. Error bars show the standard deviations of the regression slopes.

In Fig. 3 shown are the enrichment factors obtained at 206.1 and 207.1 nm together with the similar experimental data reported in Ref. [11-13] and theoretical calculation in Ref. [19]. The photolysis at 209 and 210 nm was not successful because the BBO crystal was gradually degraded during the experiments at shorter wavelengths. Nitrous oxide was decomposed only by 8% after 15-hour irradiation and we were able to obtain only three and two data points at 209 and 210 nm, respectively. Thus, the data at 209 and 210 nm were found to give larger errors or offsets when we fit the data by linear regression and calculate the slope (not shown).

Our results at 206.1 and 207.1 nm show smaller values than the experimental data in Ref. [12] at 207.6 nm for each isotopomers. The difference seems to have been caused by some difference of experimental details including analysis of the isotopomers (FTIR absorption spectroscopy was used in Ref. [12]) and/or the dependency of enrichment factor on wavelength though we cannot resolve the effect of these factors at present. However, it is clear that the enrichment factors increase with wavelength when we compare the existing data at 193 nm [11,12] and at 211 [12] and 213 nm [13]. This is in accordance with the prediction in Ref. [10] and we can confirm that their theoretical treatment is generally appropriate. However, a closer look at the experimental and theoretical enrichment factors reveals that the former is higher than the latter for the whole wavelength range and for the all isotopomers. An explanation of this discrepancy has been recently proposed by Ref. [13] that the simple approximation of the model does not consider the dissociation of initially excited N<sub>2</sub>O molecule. Our results support such suggestion that further revision should be needed in theoretical calculation.

Next, we compared the enrichment factors of simulation experiments with those of stratospheric observations. We have observed the vertical profiles of N<sub>2</sub>O isotopomers over Japan using a balloon-borne cryogenic air sampler [14]. Although the apparent enrichment factor obtained by applying Rayleigh model was not constant throughout the stratosphere, we found it constant if we divide the stratosphere into the higher and lower region at the altitude of about 24 km. The shaded area in Fig. 4 indicates the apparent enrichment factor with estimated error in regression analysis.

In Fig. 4, the slope of the wavelength dependence of the photolysis enrichment factor shows a positive correlation with the difference of stratospheric apparent enrichment factors between higher and lower region, so that the wavelength at the crossing point of the regression line and shaded area is almost same for all isotopomers. If we assume the fractionation of N<sub>2</sub>O is solely caused by photolysis, this may indicate that in the higher region, the contribution of longer wavelength is larger than in the lower region.

In fact, the stratospheric *in situ* enrichment factor during photolysis ( $\epsilon_{\text{photo}}^*$ ) is weighted mean of enrichment factors in photolysis at wavelength  $\lambda$  ( $\epsilon_{\text{photo}}(\lambda)$ ) over the whole wavelength range, where the product of actinic flux ( $I$ ) and absorption cross section ( $\sigma$ ) is taken as a weight. Therefore, if we define effective wavelength ( $\lambda_{\text{eff}}$ ) at which  $\epsilon_{\text{photo}}$  equals the  $\epsilon_{\text{photo}}^*$ , it is possibly dependent on altitude, latitude, seasons, and so on [14]:

$$\begin{aligned}\epsilon_{\text{photo}}^* &= \int \epsilon_{\text{photo}}(\lambda) I(\lambda) \sigma(\lambda) d\lambda / \int I(\lambda) \sigma(\lambda) d\lambda \\ &= \epsilon_{\text{photo}}(\lambda_{\text{eff}}).\end{aligned}\tag{9}$$

This may explain the difference of stratospheric enrichment factor between higher and lower region and suggests that there would be variation in  $\epsilon_{\text{photo}}^*$  with respect to time and space.

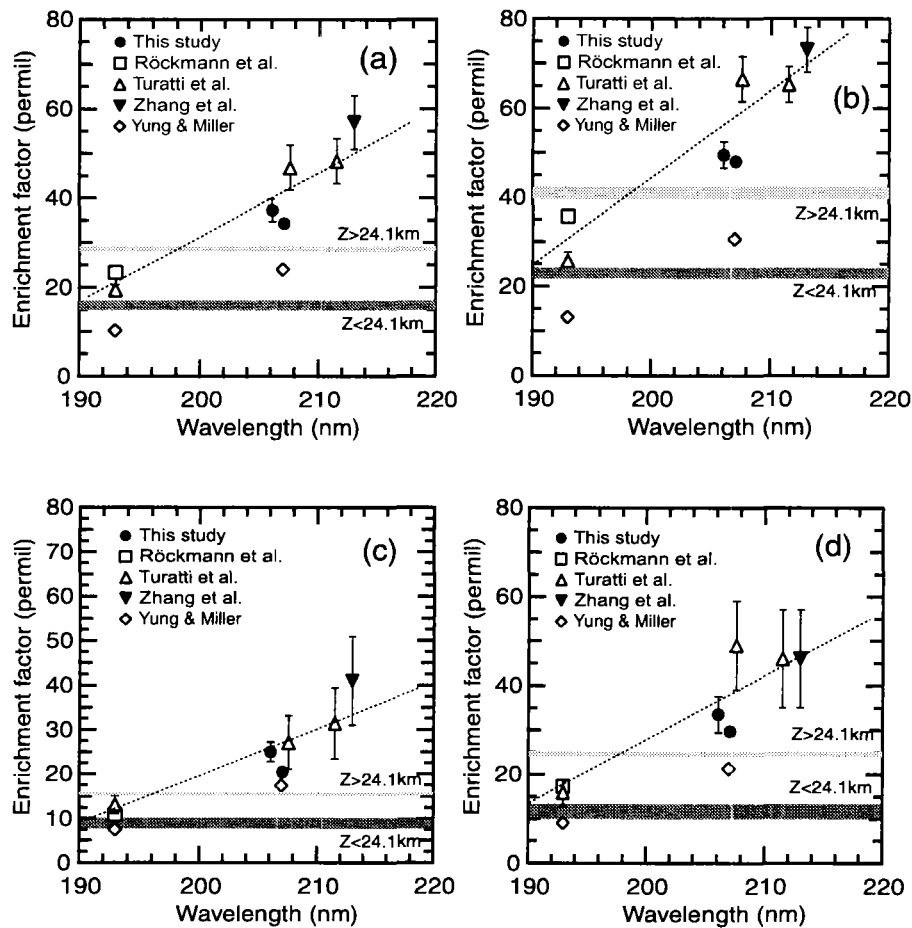


FIG. 4. Comparison of apparent enrichment factors observed in the stratosphere over Japan [14, shaded area] and photolysis enrichment factors obtained in laboratory experiments for (a), bulk nitrogen; (b),  $\alpha$  nitrogen; (c),  $\beta$  nitrogen; (d) oxygen. Dotted lines are regression lines for the photolysis data.

Another factor that can affect the apparent enrichment is mixing of  $N_2O$  that has been decomposed in different extent. This can occur during transportation of  $N_2O$  in the stratosphere. Authors of Ref. [18] showed that a simple one-dimensional diffusion model gives the apparent enrichment factor reduced by about 50% and it can explain the difference of enrichment factors between Ref. [10] and their observations for bulk N and O in the lower stratosphere [5].

One more possible factor is contribution of photo-oxidation, Eqs (7a) and (7b). According to Ref. [17], enrichment in oxygen isotope of  $N_2O$  is less in photo-oxidation than in photolysis. Although there are no data respect to bulk and site-specific nitrogen isotope ratio, contribution of this sink reaction may decrease the apparent enrichment factor. From the higher to the lower altitudes, actinic flux contributing photolysis of  $N_2O$  becomes weaker exponentially because of the absorption by ozone, while the production rate of  $O(^1D)$  does not decrease as rapidly [15]. Therefore, the lower enrichment in the lower region of the stratosphere may indicate that in the lower stratosphere contribution of photo-oxidation to  $N_2O$  destruction is larger than 10%, that is currently estimated value for whole stratosphere based on a two-dimensional photochemical model [16]. Our estimation based on observations and available data of laboratory experiments indicated that the contribution of photo-oxidation could be up to 60% in the lower stratosphere [14].

## 5. CONCLUDING REMARKS

Enrichment of heavy isotopomers of N<sub>2</sub>O during photolysis at 206 and 207 nm was different between each isotopomers, which is in accordance with other simulation experiments, theoretical calculation, and stratospheric observations. Magnitude of the enrichment is higher than that of the theoretical calculation, suggesting that the simple model of the latter should be revised. Comparison with other experiments conducted at different wavelength ascertains that the enrichment factor depends on the wavelength. *In situ* enrichment factors obtained from stratospheric observations suggest that the effective wavelength in photolysis would be variable between 190 and 200 nm when compared to those of photolysis experiments, but factors other than photolysis should also be investigated.

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