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# Determination of Nitrogen Isotopomers of Nitrous Oxide on a Modified Isotope Ratio Mass Spectrometer

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**A new method for the determination of the nitrogen isotopomers (intramolecular distribution of the nitrogen isotopes) of nitrous oxide has been developed. The method makes use of mass analyses of the molecular ( $\text{N}_2\text{O}^+$ ) and fragment ( $\text{NO}^+$ ) ions of  $\text{N}_2\text{O}$  on an isotope-ratio mass spectrometer equipped with a special ion collector system. The fragmentation of  $\text{N}_2\text{O}$  in the electron impact ion source is fairly stable, and the precision of isotope ratio measurements of the fragment ion relative to the reference gas is better than 0.1‰ for pure  $\text{N}_2\text{O}$  samples introduced from a conventional dual-inlet system. Although it is found that the observed isotope ratio of the fragment ion is affected by rearrangement reactions in the ion source, a correction can be applied using an experimentally determined rearrangement fraction. Calibration of the standard  $\text{N}_2\text{O}$  for isotopomer measurements is performed by two procedures: (1) preparation of an  $\text{N}_2\text{O}$  standard by thermal decomposition of  $\text{NH}_4\text{NO}_3$ , (2) relative measurements with pure  $\text{NO}$ .**

Nitrous oxide ( $\text{N}_2\text{O}$ ) is a trace gas in the atmosphere that plays an important role in the tropospheric greenhouse effect and stratospheric chemistry, which regulates the ozone layer. Although its tropospheric concentration is increasing by 0.2–0.3% per year,<sup>1</sup> the global budget and/or cycle of  $\text{N}_2\text{O}$  has not been well-understood because  $\text{N}_2\text{O}$  has a variety of sources (both natural and anthropogenic) and sinks. Nitrogen and oxygen isotope ratios of  $\text{N}_2\text{O}$  for several environments have been reported, and they are considered to be useful parameters for examining the source–sink relationship.<sup>2–13</sup>

Previous studies of isotopic characterization of  $\text{N}_2\text{O}$  have been based on the elements contained in the molecule, i.e., nitrogen and/or oxygen. Additional information, however, would be obtained if the intramolecular distribution of nitrogen isotopes could be determined, since the  $\text{N}_2\text{O}$  molecule has an asymmetric linear structure ( $\text{N}–\text{N}–\text{O}$ ), and thus, site preference of nitrogen isotopes in naturally occurring fractionation processes is expected. For example, Yung and Miller<sup>14</sup> estimated that  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  have different fractionation factors in the stratospheric photodissociation based on a theoretical calculation. Hence, determination of isotopomers of  $\text{N}_2\text{O}$  in the environment and those incorporated in processes simulated in the laboratory has the potential to reveal the contribution of sources and sinks of  $\text{N}_2\text{O}$ , either recognized or proposed ones.

Here we develop an effective method for the determination of isotopomers of  $\text{N}_2\text{O}$  using a conventional isotope-ratio mass spectrometer. The essence of the method is mass analysis of the fragment ion formed by the electron impact of  $\text{N}_2\text{O}$  to obtain the nitrogen isotope ratio at the center position of the molecule. The definition and notation of the isotopomers of  $\text{N}_2\text{O}$  is first described, and then experimental procedures and applicability are shown.

**Definition of the Isotopomers of  $\text{N}_2\text{O}$ .** We define an isotopomer as one of the set of molecules that are isotopically substituted, usually with stable isotopes. The number of isotopomers of a certain compound depends on the number of elements that make up the compound, the number of isotopes of each element, and the symmetry of the molecular structure. In the case of  $\text{N}_2\text{O}$ , 12 isotopomers can theoretically exist since it contains nitrogen (stable isotopes are  $^{14}\text{N}$  and  $^{15}\text{N}$ ) and oxygen ( $^{16}\text{O}$ ,  $^{17}\text{O}$ , and  $^{18}\text{O}$ ) and is an asymmetric linear three-atom molecule ( $2 \times 2 \times 3 = 12$ ). However, only the following five isotopomers have a significant natural abundance level:  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{14}\text{N}^{17}\text{O}$ , and  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$ .

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To distinguish the two kinds of nitrogen atoms in the  $\text{N}_2\text{O}$  molecule, let us name the center and end positions of the molecule  $\alpha$  and  $\beta$ , respectively. If atomic fractions of  $^{15}\text{N}$  at positions  $\alpha$  and  $\beta$  are  $x_\alpha$  and  $x_\beta$ , respectively, the isotope ratio  $^{15}R$  of  $^{15}\text{N}$  to  $^{14}\text{N}$  for each position is expressed as follows:

$$^{15}R^\alpha = x_\alpha / (1 - x_\alpha) \quad (1)$$

$$^{15}R^\beta = x_\beta / (1 - x_\beta) \quad (2)$$

If the atomic fractions of  $^{18}\text{O}$  and  $^{17}\text{O}$  are  $x_{18}$  and  $x_{17}$ , respectively,  $x_\alpha(1 - x_\beta)(1 - x_{18} - x_{17})$  and  $x_\beta(1 - x_\alpha)(1 - x_{18} - x_{17})$  are equal to the molar fractions of the isotopomers of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ , respectively. Hence, multiplying both numerator and denominator of eqs 1 and 2 by  $(1 - x_i)(1 - x_{18} - x_{17})$  (where  $i$  is  $\beta$  for eq 1 and  $\alpha$  for eq 2) leads to the fact that the "isotope ratio" is identical to the "isotopomer ratio":

$$^{15}R^\alpha = [^{14}\text{N}^{15}\text{N}^{16}\text{O}] / [^{14}\text{N}^{14}\text{N}^{16}\text{O}] \quad (3)$$

$$^{15}R^\beta = [^{15}\text{N}^{14}\text{N}^{16}\text{O}] / [^{14}\text{N}^{14}\text{N}^{16}\text{O}] \quad (4)$$

For the oxygen isotope ratio

$$^{17}R = [^{14}\text{N}^{14}\text{N}^{17}\text{O}] / [^{14}\text{N}^{14}\text{N}^{16}\text{O}] \quad (5)$$

$$^{18}R = [^{14}\text{N}^{14}\text{N}^{18}\text{O}] / [^{14}\text{N}^{14}\text{N}^{16}\text{O}] \quad (6)$$

Square brackets denote the quantity or concentration of each isotopomer. It may be noteworthy that the nitrogen isotopomer ratio is not dependent on the oxygen isotopomer ratio and vice versa.

In conventional delta notation

$$\delta^{15}\text{N}^\alpha = \{^{15}R^\alpha / ^{15}R^\alpha(\text{std}) - 1\} \times 1000 \quad (7)$$

$$\delta^{15}\text{N}^\beta = \{^{15}R^\beta / ^{15}R^\beta(\text{std}) - 1\} \times 1000 \quad (8)$$

$$\delta^{17}\text{O} = \{^{17}R / ^{17}R(\text{std}) - 1\} \times 1000 \quad (9)$$

$$\delta^{18}\text{O} = \{^{18}R / ^{18}R(\text{std}) - 1\} \times 1000 \quad (10)$$

where  $R(\text{std})$  is the isotope ratio for the standard material ( $\text{N}_2\text{O}$ ).

Since the conventional nitrogen isotope ratio of  $\text{N}_2\text{O}$  does not distinguish isotopomers that contain  $^{15}\text{N}$ , it corresponds to the average of the two isotopomer ratios:

$$^{15}R^{\text{bulk}} = \{ [^{14}\text{N}^{15}\text{N}^{16}\text{O}] + [^{15}\text{N}^{14}\text{N}^{16}\text{O}] \} / 2 [^{14}\text{N}^{14}\text{N}^{16}\text{O}] = ( ^{15}R^\alpha + ^{15}R^\beta ) / 2 \quad (11)$$

By substituting eq 11 into the definition of the conventional nitrogen isotope ratio, we obtain:

$$\begin{aligned} \delta^{15}\text{N}^{\text{bulk}} &= \{ ^{15}R^{\text{bulk}} / ^{15}R^{\text{bulk}}(\text{std}) - 1 \} \times 1000 = \\ &= \{ ( ^{15}R^\alpha + ^{15}R^\beta ) / ( ^{15}R^\alpha(\text{std}) + ^{15}R^\beta(\text{std}) ) - 1 \} \times 1000 = \\ &= \{ ^{15}R^\alpha(\text{std}) \delta^{15}\text{N}^\alpha + ^{15}R^\beta(\text{std}) \delta^{15}\text{N}^\beta \} / \{ ^{15}R^\alpha(\text{std}) + ^{15}R^\beta(\text{std}) \} \quad (12) \end{aligned}$$

If  $\delta$  values are expressed relative to atmospheric dinitrogen ( $\text{N}_2$ ), the international standard for the nitrogen isotope ratio, then  $^{15}R^\alpha(\text{std})$  and  $^{15}R^\beta(\text{std})$  are substituted by  $^{15}R$  of air  $\text{N}_2$ , and eq 12 takes the simpler form:

$$\delta^{15}\text{N}^{\text{bulk}}_{\text{air}} = ( \delta^{15}\text{N}^\alpha_{\text{air}} + \delta^{15}\text{N}^\beta_{\text{air}} ) / 2 \quad (13)$$

On the other hand, the conventional "oxygen isotope ratio" is not changed by the isotopomer-ratio definition because the  $\text{N}_2\text{O}$  molecule contains only one oxygen atom.

It should be noted that the definition of isotopomers presented here is applicable to other molecules such as organic compounds that contain a number of carbon atoms.

## EXPERIMENTAL SECTION

**Natural and  $^{15}\text{N}$  labeled  $\text{N}_2\text{O}$ .** Commercial  $\text{N}_2\text{O}$  (Showa Denko Co., Ltd., purity >99.999%, 7.5 kg in a 10-L cylinder) is used as the working standard gas without further purification. The conventional nitrogen and oxygen isotope ratios for the material are determined by converting it to  $\text{N}_2$  and  $\text{CO}_2$  in the presence of graphitic carbon (after Yoshinari<sup>15</sup>):  $\delta^{15}\text{N}^{\text{bulk}} = -2.2\text{‰}$ ,  $\delta^{18}\text{O} = 23.3\text{‰}$ , standards for nitrogen and oxygen are atmospheric  $\text{N}_2$  and SMOW (standard mean ocean water), respectively. Since gaseous  $\text{N}_2\text{O}$  condenses at high pressure, some isotope fractionation may occur in the cylinder on long-term usage; however, during the period of the experiment performed here, an isotope shift is not detectable.

Labeled  $\text{N}_2\text{O}$  samples  $^{15}\text{N}^{14}\text{NO}$  and  $^{14}\text{N}^{15}\text{NO}$ , whose stated purity of  $^{15}\text{N}$  is > 99% and 0.37% (natural abundance level) at the labeled and unlabeled positions, respectively, are purchased from Icon Services Inc., USA. Three samples that have different  $^{15}\text{N}$  concentrations at the labeled position are prepared by diluting each of the purchased samples in order to check the stability of the ionization reactions and/or isotope fractionation in the ion source of the mass spectrometer. An aliquot of the purchased sample is transferred to a 100-mL glass flask using an all-stainless-steel vacuum line equipped with a capacitance manometer (Barocel type 600AB, range 0–100 Torr, Edwards High Vacuum International, USA). Then the working standard gas is added to the flask so that the final pressure will become about 760 Torr by the use of another vacuum line equipped with a manometer of 0–1000 Torr range. The final  $^{15}\text{N}$  concentration of the labeled position is calculated from the measured pressure of the gas, inner volume of the flask and vacuum line, and room temperature: 0.582, 0.758, and 1.06% by atomic fraction for  $\alpha$ -labeled  $\text{N}_2\text{O}$  and 0.524, 0.749, and 1.09% for the  $\beta$ -labeled species. Accuracy is estimated to be better than 1% (relative error against calculated  $^{15}\text{N}$  concentration), though uncertainty of the  $^{15}\text{N}$  content of the working standard gas is not included because it is canceled out in the relative measurement between labeled and working standard gas.

**Modified Mass Spectrometer.** A sector-type, isotope-ratio mass spectrometer (Finnigan MAT 252, Thermo Quest K. K.) is used throughout the experiments. The default multicollector system is specially designed and modified so that isotope ratios can be measured for both molecular and fragment ions of  $\text{N}_2\text{O}$  without changing the Faraday collector cup config-

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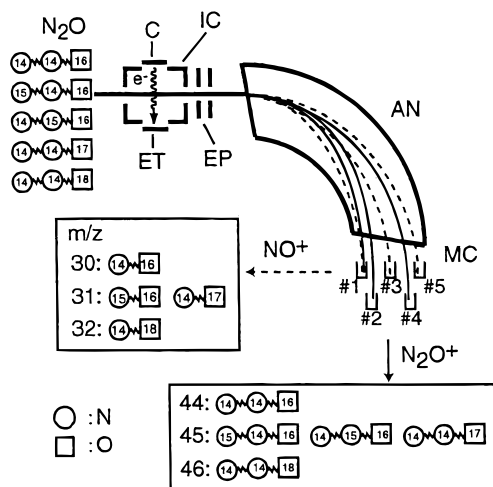


Figure 1. Schematic diagram of the measurement of  $\text{N}_2\text{O}$  isotopomers on a mass spectrometer. IC, ionization chamber; C, cathode; ET, electron trap; EP, extraction plate; AN, analyzer; MC, multi collector system.

uration and the amplifiers associated with the cups (Figure 1). The modified system consists of 5 cups, three of which (cups no. 1, 3, and 5) have wider collector slits than that of the standard cup in order to allow the measurement of other gases such as  $\text{N}_2$ ,  $\text{O}_2$ , and so on, as well as  $\text{N}_2\text{O}$  and  $\text{NO}$ . In the  $\text{N}_2\text{O}$ -measuring mode, cups no. 1, 2, and 4 are used to monitor ions of  $m/z$  44, 45, and 46, respectively, and in the  $\text{NO}$ -measuring mode, cups no. 1, 3, and 5 monitor  $m/z$  30, 31, and 32, respectively.

Experimental parameters of the mass spectrometer are optimized so that both high linearity (isotope ratio is not dependent on sample gas pressure in the ionization chamber) and high sensitivity can be obtained. In some experiments, however, the extraction plate voltage (potential difference between the ionization chamber and the extraction plate outside it) and electron energy (potential difference between the filament and the ionization chamber) are changed to study the effect of these parameters on the isotope ratio measurements.

The effect of the pressure in the ionization chamber is investigated by introducing He continuously using the interface which is supplied by the manufacturer for isotope-ratio-monitoring gas chromatography/mass spectrometry. The vacuum is  $5 \times 10^{-6}$  and  $(3-5) \times 10^{-8}$  Torr with and without He, respectively.

#### Conversion of Measured Ratios into Isotopomer Ratios.

Taking into account the isotopomers of  $\text{N}_2\text{O}$  that contribute to the mass-44, -45 and -46 molecular ion beams and the mass-30, -31 and -32 fragment ion beams in the mass spectrometer, the  $^{45}R$ ,  $^{46}R$ ,  $^{31}R$ , and  $^{32}R$  are given by

$$^{45}R = ^{15}R^\alpha + ^{15}R^\beta + ^{17}R \quad (14)$$

$$^{46}R = ^{18}R + (^{15}R^\alpha + ^{15}R^\beta) ^{17}R + ^{15}R^\alpha ^{15}R^\beta \quad (15)$$

$$^{31}R = ^{15}R^\alpha + ^{17}R \quad (16)$$

$$^{32}R = ^{18}R + ^{15}R^\alpha ^{17}R \quad (17)$$

where  $^iR$  represents the ion beam intensity ratio for species of mass  $i$  to the most abundant species.

Mathematically, we can obtain  $^{15}R^\alpha$ ,  $^{15}R^\beta$ ,  $^{17}R$ , and  $^{18}R$  by substituting observed data into eqs 14–17. The observed repro-

ducibility of  $^{32}R$ , however, is much worse than the other ratios, probably because of an unstable instrumental background level of  $\text{O}_2$  and the  $\text{O}_2^+$  formed in the ionizing reactions of  $\text{N}_2\text{O}$ . Therefore, we assume the mass-dependent fractionation of oxygen contained in sample  $\text{N}_2\text{O}$  and replace eq 17 with the following equation:<sup>16</sup>

$$^{18}R/^{18}R(\text{std}) = \{^{17}R/^{17}R(\text{std})\}^2 \quad (18)$$

Although Cliff and Thiemens<sup>10,17</sup> reported a mass-independent oxygen isotope anomaly in stratospheric and tropospheric  $\text{N}_2\text{O}$ , the magnitude of the anomaly is about 1‰ for  $\delta^{17}\text{O}$ . Hence, the assumption of eq 18 causes only a slight difference (overestimate of about 0.1 and 0.05‰ for  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$ , respectively).

The isotope ratios  $^{45}R$ ,  $^{46}R$ , and  $^{31}R$  of the sample are calculated from those of the working standard gas and the measured  $\delta^{45}$ ,  $\delta^{46}$ , and  $\delta^{31}$  values. Then we obtain  $^{15}R^\alpha$ ,  $^{15}R^\beta$ ,  $^{17}R$ , and  $^{18}R$  by iterative calculation starting from the condition that  $^{17}R$  is equal to that of the working standard gas.<sup>18</sup> The  $\delta$  value is tentatively expressed using the working standard as reference ( $\delta_{x-w}$ ), which is related to the  $\delta$  value relative to the international standard ( $\delta_{x-s}$ ) by the following equation

$$\delta_{x-s} = \delta_{x-w} + \delta_{w-s} + \delta_{x-w} \delta_{w-s}/1000 \quad (19)$$

where  $\delta_{w-s}$  is the  $\delta$  value for the working standard against the international standard.

**Preparation of  $\text{N}_2\text{O}$  Isotopomer Standards from Ammonium Nitrate.** For the calibration of the working standard on an isotopomer basis,  $\text{N}_2\text{O}$  is synthesized by thermal decomposition of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) whose nitrogen isotope ratio is determined independently for  $\text{NH}_4^+$  and  $\text{NO}_3^-$ . The advantage of this reaction is that the nitrogen atom at the  $\alpha$ - (center) position of product  $\text{N}_2\text{O}$  originates from the nitrate ion while the  $\beta$ - (end) nitrogen comes from the ammonium ion.<sup>19</sup>

About 20 mg of  $\text{NH}_4\text{NO}_3$  (special grade, Wako Pure Chemical Industries, Ltd., Japan) is measured in a Pyrex glass tube (9 mm outer diameter, 15-cm-long), which is sealed by a torch after the gas phase is evacuated. During evacuation, the tube is cooled by a dry ice/ethanol bath to add a small amount of water, which is necessary to initiate the decomposition.<sup>19</sup> The sealed tubes are sunk into an oil bath and heated for 4–5 days at 225–230 °C.<sup>20</sup> Since the reaction has the potential hazard of producing an explosion, the experimental scale is determined so that the inner pressure of the tube should not exceed 7 atm when all the reactants are converted to gases. Products are separated into  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$ , and byproduct gases that are noncondensable at liquid nitrogen temperature (major components are  $\text{N}_2$  and  $\text{O}_2$ ) by the use of a vacuum line, cold baths, and molecular sieve traps cooled with liquid nitrogen.

The nitrogen isotope ratio for the ammonium ion and the nitrate ion of  $\text{NH}_4\text{NO}_3$  is determined by the conventional method.<sup>21,22</sup>

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(20) Yoshida, N., Doctoral Dissertation, Tokyo Institute of Technology, Tokyo, Japan, 1984.



Ten milliliters of  $1 \times 10^{-2}$  M solution of  $\text{NH}_4\text{NO}_3$  is distilled with water vapor after 10 mL of 10 M KOH solution is added. The distilled ammonia is absorbed into 10 mL of 0.05 M  $\text{H}_2\text{SO}_4$  solution until the total amount of the solution becomes about 30 mL. Then, 0.5 g of Devarda's alloy is added to the residual solution, and nitrate ion is reduced to ammonium ion at about 70 °C. After the reaction is complete, the resulting ammonia is collected in the same manner as described above. The ammonium ion solutions are concentrated at about 80 °C on a hot plate to reduce the amount into ~10 mL and oxidized to  $\text{N}_2$  by adding 5 mL of KOBr (0.8 M, prepared by addition of  $\text{Br}_2$  to KOH solution) on a vacuum line. The isotope ratio of the  $\text{N}_2$  collected on molecular sieves 5A at liquid nitrogen temperature is determined on a mass spectrometer relative to the working standard gas whose  $\delta^{15}\text{N}_{\text{air}}$  is  $-1.0\text{‰}$ .

**Calibration of  $\text{N}_2\text{O}$  Isotopomer Standard by Comparison with Pure NO.** The calibration of the working standard is tested by another method. Pure NO gas with known  $\delta^{15}\text{N}$  can be compared with the fragment  $\text{NO}^+$  of  $\text{N}_2\text{O}$  to determine  $\delta^{15}\text{N}^\alpha$ . Commercial nitric oxide (Nippon Sanso Co., Ltd., purity > 99%) is purified by the use of a molecular sieve trap, liquid nitrogen, and a 2-methylbutane/liquid nitrogen cold bath.<sup>23</sup> About a 4-mL aliquot of the purified NO is reduced to  $\text{N}_2$  over hot Cu (about 400 °C) and  $\delta^{15}\text{N}$  is determined.

The relative isotope ratio of  $\text{NO}^+$  is measured between the purified NO and the  $\text{N}_2\text{O}$  working standard on a mass spectrometer in the NO measuring mode.

## RESULTS AND DISCUSSION

**Fragment Pattern of  $\text{N}_2\text{O}$ .** Nitrogen and/or oxygen isotope analyses of  $\text{N}_2\text{O}$  by mass spectrometry have been performed by converting the nitrogen to  $\text{N}_2$  and oxygen to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , or  $\text{O}_2$ .<sup>2,4,6,7,15,24</sup> In recent years, many researchers have measured both the nitrogen and the oxygen isotope ratios simultaneously by injecting  $\text{N}_2\text{O}$  directly into an isotope-ratio mass spectrometer.<sup>9,12,18,25</sup> This technique avoids the problem of contamination and/or subreaction during the conversion of  $\text{N}_2\text{O}$  and requires less time and labor than the previous method, although special care is needed to eliminate contamination by isobaric  $\text{CO}_2$ . Electron-impact ionization processes of  $\text{N}_2\text{O}$ , however, are not simple because of its asymmetric molecular structure. Table 1 shows the measured fragment pattern for  $\text{N}_2\text{O}$ . Although more than 75% of the ionized species are molecular ion ( $\text{N}_2\text{O}^+$ ), significant amounts of fragment ions (fraction of  $\text{NO}^+$  to  $\text{N}_2\text{O}^+$  is about 0.3, and those of  $\text{N}_2^+$ ,  $\text{N}^+$ , and  $\text{O}^+$  are about 0.1, 0.07, and 0.03, respectively, not shown in Table 1) are formed in the ion source of the mass spectrometer. Hence, it must be confirmed that the fragment pattern and isotope fractionation in the cracking reaction are constant in a series of measurements in which two samples are introduced alternately into the ion source. We have checked the stability of the fragmentation in three ways: (1) by testing the dependency of the fragment pattern on experimental conditions, (2) by comparing the reproducibility of the isotope

Table 1. Fragment Pattern of  $\text{N}_2\text{O}$

instrumental conditions	electron energy/eV	fragment pattern <sup>a</sup>		no. of measurements <sup>d</sup>
		avg	variation <sup>c</sup>	
normal	49.0	0.3051	0.0007	$n = 2$
	86.6	0.3027	0.0005	$n = 3$
	147.0	0.3108	0.0008	$n = 2$
with He	49.0	0.3136	0.0002	$n = 2$
	86.6	0.3026	0.0002	$n = 3$
	147.0	0.3329	0.0004	$n = 2$

<sup>a</sup> Ion beam intensity ratio of  $m/z$  30 to 44. <sup>b</sup>  $\text{N}_2\text{O}$  is introduced via the conventional dual inlet system. Pressure in the ionization chamber is  $(3-5) \times 10^{-8}$  Torr under normal conditions, while it is  $5 \times 10^{-6}$  Torr when He flows into the chamber through the continuous-flow interface designed for the on-line GC/MS measurement. <sup>c</sup> Standard deviation of three measurements or difference of two measurements. <sup>d</sup> Number of measurements conducted within 10 hours.

ratio measurements with that of the other gases which produce less fragment ions in the ion source than  $\text{N}_2\text{O}$  (e.g.,  $\text{CO}_2$ ,  $\text{N}_2$ ), (3) by conducting experiments changing the  $^{15}\text{N}$  content of the samples.

The results are: (1) the variation of the fragment pattern is within  $\pm 0.2\%$  (relative to the ratio) when experimental conditions are kept constant (Table 1), (2) reproducibility of the isotope ratio measurement of the molecular ion is nearly equal to that of the other gases (standard deviation is better than 0.05‰ for 10 measurements<sup>26</sup>), although in the case of the fragment ion ( $\text{NO}^+$ ) it becomes a little worse (better than 0.08‰<sup>26</sup>) because the beam intensity is weaker than that of the molecular ion, (3) the observed isotope ratios of the molecular and fragment ions are proportional to the  $^{15}\text{N}$  content of the samples.

**Evaluation of Rearrangement Reaction of  $\text{N}_2\text{O}$ .** Analytical precision of the  $\delta$  value (standard deviation for an analytical run of 10 repeated measurements) of the  $^{15}\text{N}$ -labeled samples is nearly equal to that of the samples containing  $^{15}\text{N}$  at a natural level for both the molecular ion ( $\delta 45$  and  $\delta 46$ ) and the fragment ion ( $\delta 31$ ) as has already been shown. In the case of the samples labeled at the  $\alpha$  position, however, precision is decreased to about 0.2–1.2‰ in the fragment-ion-monitoring mode, which is positively correlated with the  $^{15}\text{N}$  concentration (500–1600‰) of the  $\alpha$  nitrogen. This seems to be caused by the well-known “mixing effect” between sample and reference gas because their isotope ratios approach each other during an analytical run, and the precision is improved by a factor of 3 when the measurement is carried out with He flow.

Observed  $\delta$  values of the six samples are compared with those calculated from the  $^{15}\text{N}$  content of the original labeled gas and dilution factor. Figure 2a shows excellent agreement between observed and calculated  $\delta^{15}\text{N}^{\text{bulk}}$  (analytical errors and uncertainties of calculated values based on purity of the reagents and experimental error in the diluting procedure are smaller than the size of the symbols). This indicates that there is no isotope fractionation in sample preparation, and the fractionation factor of the ionization process that forms  $\text{N}_2\text{O}^+$  is constant within a range of 1000‰. The relationship between the observed  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$  and the calculated  $\delta^{15}\text{N}$  of the labeled (or concentrated)

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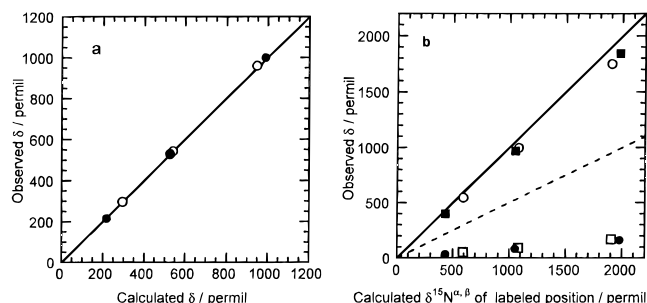


Figure 2. Relationship between observed nitrogen isotope/isotopomer ratio of  $\text{N}_2\text{O}$  and calculated value: (a) bulk isotope ratios of  $\alpha$ -labeled ( $\circ$ ) and  $\beta$ -labeled ( $\bullet$ )  $\text{N}_2\text{O}$ ; (b) isotopomer ratios of  $\alpha$ -labeled ( $\delta^{15}\text{N}^{\alpha}:\text{O}$ ,  $\square$ ) and  $\beta$ -labeled ( $\delta^{15}\text{N}^{\alpha}:\text{O}$ ,  $\bullet$ ;  $\delta^{15}\text{N}^{\beta}:\text{O}$ ,  $\blacksquare$ )  $\text{N}_2\text{O}$ . Calculated values refer to the labeled position. Solid line and horizontal axis show the value of labeled and unlabeled position, respectively, with rearrangement fraction  $y = 0$ . Broken line indicates the value of both labeled and unlabeled position with  $y = 0.5$ .

position is plotted in Figure 2b. Although the observed data show a linear correlation with the calculated values for both labeled and unlabeled positions, their trend is not consistent with our expectation indicated by the solid line and horizontal axis in Figure 2b:  $\delta^{15}\text{N}$  is smaller than the calculated  $\delta$  at the labeled position and is not zero at the unlabeled position.

These results can be explained in two ways: the nitrogen isotope fractionation and/or rearrangement (or scrambling) occur (1) in the synthesis of labeled  $\text{N}_2\text{O}$ , or (2) in the analysis on a mass spectrometer.

The labeled  $\text{N}_2\text{O}$  gases are synthesized by the thermal decomposition of  $^{15}\text{N}$ -labeled ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), assuming that the ammonium N is converted to  $\beta$  N of  $\text{N}_2\text{O}$  and nitrate N to  $\alpha$  N. If the observed results were solely attributed to erroneous specification in the purchased materials, the  $^{15}\text{N}$  fraction of the labeled and unlabeled positions would be calculated to be 90 and 9%, respectively. However, rearrangement of the nitrogen atoms in the thermal decomposition reaction was not observed by microwave spectroscopy,<sup>27</sup> and isotope fractionation of 23000‰ (calculated by  $(9/0.37 - 1) \times 1000$ ) is hardly probable. In addition, the materials used in this study were characterized by near-infrared absorption spectroscopy, and the  $^{15}\text{N}$  purity of the labeled position is higher than 99% for both  $^{15}\text{NNO}$  and  $\text{N}^{15}\text{NO}$  samples.<sup>28</sup>

On the other hand, a rearrangement reaction of  $\text{N}_2\text{O}$  in electron impact ionization<sup>19,29</sup> and photoionization<sup>30</sup> has been reported by several authors who analyzed the mass of  $\text{NO}^+$  formed from  $\alpha$ - and/or  $\beta$ -labeled  $\text{N}_2\text{O}$  ( $^{15}\text{N}$  content was higher than that of the present study). Although the mechanism of the rearrangement reaction has not been clearly explained, it is considered to be possible that activated triangular ions are formed and yield  $\text{NO}^+$  ions that contain either  $\alpha$  or  $\beta$  nitrogen by the breaking of two bonds.<sup>29</sup>

If we define “rearrangement fraction”  $y$  as the fraction of  $\text{NO}^+$  bearing  $\beta$  nitrogen of the initial  $\text{N}_2\text{O}$  to total  $\text{NO}^+$  formed, the observed isotope ratio of  $\text{NO}^+$  can be expressed by the following equation

$$^{15}R_{\text{obs}}^{\alpha} = (1 - y)^{15}R^{\alpha} + y^{15}R^{\beta} \quad (20)$$

Equations 7, 11, and 20 lead to

$$\delta^{15}\text{N}_{\text{obs}}^{\alpha} = \{ (1 - 2y)\delta^{15}\text{N}^{\alpha} + 2yA^{-1}\delta^{15}\text{N}^{\text{bulk}} \} / (1 - 2y + 2yA^{-1}) \quad (21)$$

where

$$A \equiv (^{15}R^{\alpha}/^{15}R^{\text{bulk}})_{\text{std}} \quad (22)$$

The parameter  $A$  is a constant that depends on the isotope ratio of the standard gas. In this study,  $A$  is determined to be 0.998 by the calibration of the working standard described later.

Solving eq 21 for  $y$ , we obtain:

$$y = A (\delta^{15}\text{N}^{\alpha} - \delta^{15}\text{N}_{\text{obs}}^{\alpha}) / [2\{ (1 - A)\delta^{15}\text{N}_{\text{obs}}^{\alpha} - \delta^{15}\text{N}^{\text{bulk}} + A\delta^{15}\text{N}^{\alpha} \}] \quad (23)$$

Table 2 lists  $y$  values calculated by eq 23 under several different experimental conditions.

Two important characteristics of  $y$  allow us to quantitatively estimate, or reconstruct, nitrogen isotopic information on the  $\alpha$  and  $\beta$  positions with high precision.

First, the value of  $y$  is about 0.08, which means about 8% of the observed  $\text{NO}^+$  ions have the  $\beta$ -nitrogen atoms of the parent molecules. In other words, about 92% of  $\alpha$ -nitrogen atoms remain in the fragment ions. If  $y = 0.5$ , the isotope ratio of  $\text{NO}^+$  has no more information than the averaged (= bulk) nitrogen isotope ratio as shown in Figure 2b by a broken line.

Second,  $y$  shows very little variation (relative standard deviation is better than 1%) under typical conditions, even when He flows into the ion source. Uncertainty of the calculation of  $y$ , which arises from error in the observed  $\delta$  values and uncertainty of  $^{15}\text{N}$  concentration of the sample analyzed, is estimated to be smaller than the observed variation. In addition, it is also found that  $y$  is almost independent of electron energy and  $^{15}\text{N}$  concentration. Hence, it is safely concluded that  $y$  is constant on an instrument under standard ion source conditions.

Once the rearrangement fraction is determined, the nitrogen isotopomer ratio of a sample can be calculated from the observed ratio by rearranging eq 21:

$$\delta^{15}\text{N}^{\alpha} = \delta^{15}\text{N}_{\text{obs}}^{\alpha} + 2y(\delta^{15}\text{N}_{\text{obs}}^{\alpha} - \delta^{15}\text{N}^{\text{bulk}}) / \{ A(1 - 2y) \} \quad (24)$$

From the relationship expressed in eq 12, we obtain:

$$\delta^{15}\text{N}^{\beta} = \delta^{15}\text{N}^{\text{bulk}} + A(\delta^{15}\text{N}^{\text{bulk}} - \delta^{15}\text{N}^{\alpha}) / (2 - A) \quad (25)$$

Estimated errors for each of the parameters on the right-hand sides of eqs 24 and 25 indicate that systematic errors of  $\delta^{15}\text{N}^{\alpha}$  and  $\delta^{15}\text{N}^{\beta}$  depend mainly on analytical errors of the observed  $\delta$ -values as long as the uncertainties in  $A$  and  $y$  are less than 1%

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Table 2. Reproducibility of the Rearrangement Fraction  $y$ 

experiment	ion source parameters <sup>a</sup>			variation of $y$			notes
	extraction <sup>b</sup>	electron energy (eV)	trap (V) <sup>c</sup>	typical <sup>d</sup>	controlled		
1	4.64	66.9	54.9	0.0803	0.0805 <i>(0.521 at. %)</i>	0.0800 <i>(1.08 at. %)</i>	Effect of <sup>15</sup> N concentration is tested.
2	2.46	86.6	37.4	0.0810	0.0821 <i>low (49.0)</i>	0.0809 <i>high (147.0)</i>	Effect of electron energy conditions is tested.
3	2.46	86.6	37.4	0.0813	0.0817 <i>low (49.0)</i>	0.0805 <i>high (147.0)</i>	Sample is introduced with He. Effect of electron energy conditions is tested.
4	0.00	86.5	50.0	0.0813			
5	0.00	86.5	50.0	0.0805			
6	0.00	102.1	50.0	0.0812			
				0.0823			
				0.0811	±0.0006		average and standard deviation of the data obtained under standard conditions ( $n = 7$ )

<sup>a</sup> These parameters are optimized so that both high linearity and high sensitivity can be obtained, but optimum values are different from day to day probably because conditions of ion source gradually changed due to absorption and/or desorption of trace amount of gases, ions, radicals, and so on. <sup>b</sup> Label of the potentiometer. Larger number corresponds to lower potential difference between the ionization chamber and the extraction plate. <sup>c</sup> Potential difference between the ionization chamber and the electron trap. <sup>d</sup> Sample is  $\beta$ -labeled gas (<sup>15</sup>N<sup>14</sup>NO, <sup>15</sup>N = 0.744 at. %).

Table 3. Isotopomer Calibration of the Working Standard Gas by Relative Measurement with N<sub>2</sub>O Prepared by Decomposition of NH<sub>4</sub>NO<sub>3</sub><sup>a</sup>

sample	yield of the decomposition (%) <sup>b</sup>		$\delta^{15}\text{N}_{\text{air}}^{\text{c}}$ of N <sub>2</sub> (‰)	calculated isotopomer ratios of the synthesized N <sub>2</sub> O		observed isotopomer ratios of the working standard relative to the synthesized N <sub>2</sub> O <sup>d</sup>		calibrated isotopomer ratios of the working standard	
	N <sub>2</sub> O	N <sub>2</sub>		$\delta^{15}\text{N}_{\text{air}}^{\alpha}$ (‰)	$\delta^{15}\text{N}_{\text{air}}^{\beta}$ (‰)	$\delta^{15}\text{N}_{\text{syn}}^{\alpha}$ (‰)	$\delta^{15}\text{N}_{\text{syn}}^{\beta}$ (‰)	$\delta^{15}\text{N}_{\text{air}}^{\alpha}$ (‰)	$\delta^{15}\text{N}_{\text{air}}^{\beta}$ (‰)
1	95.2	10.3	-0.94	-3.63	-5.72	0.05	6.86	-3.57	1.09
2	86.8	10.3	2.13	-4.34	-6.64	0.07	6.34	-4.27	-0.34
3	88.3	10.4	1.65	-4.21	-6.47	0.14	6.31	-4.07	-0.20
							average <sup>e</sup>	-4.0	0.2
								±0.4	±0.8

<sup>a</sup> Nitrogen isotope ratios of NH<sub>4</sub>NO<sub>3</sub> are  $-5.54 \pm 0.23$  ( $n = 7$ ) and  $-3.55 \pm 0.04$  ( $n = 4$ ) for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, respectively. <sup>b</sup> Calculated from the amount of the reactant (NH<sub>4</sub>NO<sub>3</sub>) and product gases. Amount of N<sub>2</sub> is obtained by subtracting that of O<sub>2</sub> from that of the gases which are condensable at liquid nitrogen temperature. <sup>c</sup> Relative to atmospheric N<sub>2</sub>. <sup>d</sup> After the correction for the rearrangement reaction. <sup>e</sup> Standard deviations are shown.

(relative error). Therefore, the analytical precision of the isotopomer ratios is as high as that of the conventional isotope ratio.

**Isotopomer Calibration of the Working Standard Gas.** The following four procedures are considered for the calibration of the working standard gas on an isotopomer basis: (1) relative measurement with N<sub>2</sub>O prepared by decomposition of NH<sub>4</sub>NO<sub>3</sub>, (2) relative measurement with pure NO, (3) relative measurement with N<sub>2</sub>O prepared by mixing <sup>15</sup>N-labeled N<sub>2</sub>O samples, (4) calibrating by another analytical method. In this paper, results of procedures (1) and (2) are described.

Procedure (3) requires labeled samples of <sup>14</sup>N<sup>15</sup>NO ( $\alpha$ -labeled), <sup>15</sup>N<sup>14</sup>NO ( $\beta$ -labeled), and <sup>14</sup>N<sup>14</sup>NO (<sup>14</sup>N-concentrated sample). However, the accuracy of the <sup>15</sup>N and/or <sup>14</sup>N purity of commercially available samples is not so high that calculated isotopomer ratios of the prepared standard sample would have larger uncertainty.

It is necessary to confirm the accuracy of the mass spectrometric measurement by conducting procedure (4). Near-infrared absorption spectroscopy is a possible candidate, since the oxygen isotope ratio of N<sub>2</sub>O has been successfully determined by this method.<sup>4</sup>

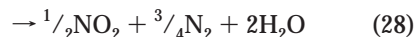
**(1) Relative Measurement with N<sub>2</sub>O Prepared by Decomposition of NH<sub>4</sub>NO<sub>3</sub>.** The nitrogen isotope ratios of ammonium

and nitrate N of NH<sub>4</sub>NO<sub>3</sub> are listed in Table 3. It is important to determine whether these values are preserved to  $\beta$  and  $\alpha$  nitrogen of the product N<sub>2</sub>O in the decomposition reaction.

The reaction mechanism suggested by Friedman and Bigeleisen<sup>19</sup> is that the dehydration of NH<sub>4</sub>NO<sub>3</sub> forms an N–N bond (nitramide), which then generates N<sub>2</sub>O, releasing H<sub>2</sub>O. They reported that 98% of the product gas was N<sub>2</sub>O, but the yield of the product relative to reactant was not described. In this study, the yield was calculated from the amount of the reactant and the product (Table 3). Possible byproducts are N<sub>2</sub>, NO, NO<sub>2</sub>, and O<sub>2</sub>, but the following pairs of compounds are not separated because of similarity in vapor pressure: N<sub>2</sub> (boiling point, -195.8 °C) and O<sub>2</sub> (-182.3 °C), N<sub>2</sub>O (-88.6 °C) and NO (-151.8 °C), NO<sub>2</sub> (21.3 °C) and H<sub>2</sub>O.

The presence of NO is examined by immersing the coldfinger in a 2-methylbutane/liquid nitrogen bath (-160 °C) after trapping the gases that are noncondensable at -72 °C and condensable at -195.8 °C. The vapor pressure of pure NO is about 300 Torr at -160 °C, but the observed pressure is nearly equal to that of N<sub>2</sub>O (about 0.04 Torr), which indicates that the amount of NO formed in the reaction is negligible. The oxygen content of the gases collected by the molecular sieve trap at -195.8 °C is estimated from the beam intensity ratio of mass-32 to -28 using the mass

spectrometer. Assuming that the nitrogen-containing products and byproducts are N<sub>2</sub>O, N<sub>2</sub>, and NO<sub>2</sub>, and they are formed by the following reactions, we can estimate the amount of NO<sub>2</sub> from that of N<sub>2</sub>O, N<sub>2</sub>, and O<sub>2</sub> by stoichiometry:



The estimated amount of NO<sub>2</sub> is less than 5% of the total nitrogen-containing gas by mole fraction, which means nitrogen converted to NO<sub>2</sub> is less than 2.5% of total reacted nitrogen by atomic fraction. Hence, we can neglect reaction 28 and calculate the  $\delta$  values of the produced N<sub>2</sub>O on the basis of the following mass balance equations:

$$m(\text{NH}_4\text{NO}_3) = m(\text{N}_2\text{O}) + m(\text{N}_2) \quad (29)$$

$$\delta^{15}\text{N}(\text{NO}_3^-)m(\text{NH}_4\text{NO}_3) = \delta^{15}\text{N}^\alpha(\text{N}_2\text{O})m(\text{N}_2\text{O}) + \delta^{15}\text{N}(\text{N}_2)m(\text{N}_2) \quad (30)$$

$$\delta^{15}\text{N}(\text{NH}_4^+)m(\text{NH}_4\text{NO}_3) = \delta^{15}\text{N}^\beta(\text{N}_2\text{O})m(\text{N}_2\text{O}) + \delta^{15}\text{N}(\text{N}_2)m(\text{N}_2) \quad (31)$$

The parameter  $m(\text{X})$  denotes the amount of substance X. It is postulated that the nitrogen atoms of the N<sub>2</sub> molecule originate equally from the ammonium ion and the nitrate ion, and that  $\delta^{15}\text{N}$  of the NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions converted to N<sub>2</sub> are equal. This assumption for N<sub>2</sub> formation, especially for the isotope ratio, makes a minor contribution to the calculated  $\delta^{15}\text{N}^\alpha(\text{N}_2\text{O})$  and  $\delta^{15}\text{N}^\beta(\text{N}_2\text{O})$  because the magnitudes of the second terms on the right-hand sides of eqs 30 and 31 are smaller than those of the other terms, and the  $\delta^{15}\text{N}$  difference between the ammonium ion and the nitrate ion happens to be small.

Calibrated results of the working standard relative to the synthesized N<sub>2</sub>O are listed in Table 3, after correction for the rearrangement reaction that has been described.

The isotope ratio for bulk nitrogen calculated from  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$  ((-4.0 + 0.2)/2 = -1.9‰) can be compared with  $\delta^{15}\text{N}^{\text{bulk}}$  determined by converting N<sub>2</sub>O to N<sub>2</sub> (-2.2‰). The difference of about 0.3‰ is slightly larger than the experimental error, which may be caused by the fractionation of the decomposition reaction since the amount and isotope ratios of residual NH<sub>4</sub>NO<sub>3</sub> are neglected in eqs 30 and 31.

**(2) Relative Measurement with pure NO.** The calibration procedure with pure nitric oxide gas is found to have some experimental difficulties.

First, pure NO shows the adsorptive property in the ion source of the mass spectrometer, e.g., it takes a longer time to evacuate and/or introduce NO into the ion source than N<sub>2</sub>O. Hence, the isotope ratio of NO<sup>+</sup> is affected by a mixing effect when relative measurements are performed between pure NO and N<sub>2</sub>O. This problem is resolved to a certain extent by increasing the conductance of the ion source to the evacuating system, which is adjustable by a knob attached to the ion source, and by increasing

Table 4. Isotopomer Calibration of the Working Standard Gas by Relative Measurement with Pure NO

parameters	‰	notes
(1) $\delta^{15}\text{N}_{\text{air}}$ of NO	$1.91 \pm 0.05^a$	measured by reduction of NO to N <sub>2</sub> ( $n = 2$ )
(2) $\delta^{15}\text{N}^\alpha$ of N <sub>2</sub> O relative to NO	$-31 \pm 2^b$	after the correction for rearrangement of N <sub>2</sub> O
(3) $\delta^{15}\text{N}_{\text{air}}^\alpha$	$-29 \pm 2$	obtained by (1) + (2)
(4) $\delta^{15}\text{N}^{\text{bulk}}_{\text{air}}$	$-2.2 \pm 0.6^a$	determined by conversion of N <sub>2</sub> O to N <sub>2</sub> ( $n = 6$ )
(5) $\delta^{15}\text{N}^\beta_{\text{air}}$	$25 \pm 2$	obtained by (4) $\times$ (2) - (3)

<sup>a</sup> Error is standard deviation of analysis of independent samples.

<sup>b</sup> Uncertainty of the relative measurement between fragment and molecular ion estimated from experimental results, although uncertainty caused by dependency on electron energy is not included.

the time for evacuating the previous sample before introducing the next sample. However, reproducibility of the measurement is about 0.2‰, which is worse than that of the relative measurements among N<sub>2</sub>O samples.

Second, some NO<sup>+</sup> formed from N<sub>2</sub>O contains the  $\beta$ -nitrogen of the parent molecule while that formed from NO has no relation to a rearrangement reaction. In this case, uncertainty of the rearrangement fraction has more effect on the correction to the observed results than in the case of N<sub>2</sub>O vs N<sub>2</sub>O measurement since the error in  $y$  is canceled out in the latter case.

Another problem is whether it is appropriate to assume that the isotope fractionation factors for the formation of NO<sup>+</sup> from N<sub>2</sub>O and the NO molecule are equivalent. This is questionable because preliminary experiments show that the observed  $\delta^{31}$  of N<sub>2</sub>O relative to NO increases by about 9‰ when the electron energy is raised from 49 to 147 eV, which results from an increase of the isotope ratio of fragment (N<sub>2</sub>O-derived) NO<sup>+</sup> and a decrease of the ratio of molecular (NO-derived) NO<sup>+</sup>. In fact, calibration results are not consistent with those obtained by decomposition of NH<sub>4</sub>NO<sub>3</sub> (Table 4). Hence, we consider that this calibration procedure is less reliable than the decomposition method.

It is meaningful, however, to estimate the ratio between the fractionation factor of dissociative and that of direct ionization in which NO<sup>+</sup> is formed in order to understand the process occurring in the ion source. Using the isotopomer standard prepared from NH<sub>4</sub>NO<sub>3</sub>, we can calculate the ratio of overall fractionation of each species as follows:

Let the apparent fractionation factors of N<sub>2</sub>O and NO be defined by:

$$f_{\text{N}_2\text{O}} \equiv ({}^{15}R_{\text{obs}}^\alpha / {}^{15}R^\alpha)_{\text{N}_2\text{O}} \text{ and } f_{\text{NO}} \equiv ({}^{15}R_{\text{obs}} / {}^{15}R)_{\text{NO}} \quad (32)$$

Then the ratio of  $f_{\text{N}_2\text{O}}$  to  $f_{\text{NO}}$  is expressed using the  $\delta$ -value for the relative measurement between N<sub>2</sub>O and NO:

$$f_{\text{N}_2\text{O}}/f_{\text{NO}} = \{ {}^{15}R_{\text{obs}}^\alpha(\text{N}_2\text{O}) / {}^{15}R_{\text{obs}}(\text{NO}) \} / \{ {}^{15}R^\alpha(\text{N}_2\text{O}) / {}^{15}R(\text{NO}) \} \cong \{ \delta^{15}\text{N}(\text{N}_2\text{O relative to NO}) + 1000 \} / [ \{ \delta^{15}\text{N}^\alpha(\text{N}_2\text{O}) - \delta^{15}\text{N}(\text{NO}) \} + 1000 ] \quad (33)$$

The value of  $\delta^{15}\text{N}(\text{N}_2\text{O relative to NO})$  is calculated to be between -25 and -34‰ from the data obtained at 49–147 eV of



electron energy and rearrangement fraction  $y = 0.081$ , while  $\delta^{15}\text{N}^\alpha$  ( $\text{N}_2\text{O}$ ) and  $\delta^{15}\text{N}(\text{NO})$  are  $-4.0\text{‰}$  and  $1.9\text{‰}$ , respectively (Tables 3 and 4). Then we obtain  $0.971\text{--}0.981$  for the apparent fractionation factor ratio. This means that the isotopically light  $\text{NO}^+$  is formed more from the  $\text{N}_2\text{O}$  molecule than from the  $\text{NO}$  molecule by electron impact ionization, although the apparent fractionation factor ratio depends not only on the ionization process but also on other processes such as diffusion of the gases. Consequently, the rate-determining step in the formation of the  $\text{NO}^+$  fragment from  $\text{N}_2\text{O}$  seems to be cleavage of the N–N bond.

## CONCLUSION

Measurement of isotopomer abundance of  $\text{N}_2\text{O}$  has been made possible with a precision better than  $0.1\text{‰}$  by the method developed in this study. This new technique is expected to become a useful tool for studying mechanisms of production and consumption and the global budget of  $\text{N}_2\text{O}$ . Analytical methods for

applying this technique to various environmental samples are now under investigation.<sup>26</sup> Although one of the simplest molecules is treated in the present work, application of molecular fragmentation to the determination of isotopomers is possible for some other molecules.

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