

# N<sub>2</sub>O removal in N<sub>2</sub> or air by ArF excimer laser photolysis at atmospheric pressure

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## Abstract

A photochemical process is proposed as a new efficient N<sub>2</sub>O removal technique in N<sub>2</sub> or air at atmospheric pressure and room temperature without using any catalysts. N<sub>2</sub>O diluted in N<sub>2</sub> or air was decomposed into N<sub>2</sub>, O<sub>2</sub>, and NO by using a 193 nm ArF excimer laser. The maximum conversion of N<sub>2</sub>O in N<sub>2</sub>O/N<sub>2</sub> or N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures was 93% at a laser power of 136 mJ, a repetition frequency of 5 Hz, and an irradiation time of 30 min. The formation ratios of N<sub>2</sub>:O<sub>2</sub>:NO in N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures were 64:31:5.1% and 60:27:13%, respectively. The decomposition mechanism of N<sub>2</sub>O under 193 nm photolysis was discussed by comparing experimental data with calculated model using known photochemical and gas kinetic data.

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**Keywords:** N<sub>2</sub>O removal; Photochemical process; ArF excimer laser; Gas kinetics

## 1. Introduction

Nitrous oxide (N<sub>2</sub>O) in the Earth's atmosphere, 47.5% of which arises from combustion processes in 1999 [1], is a major contributor to the greenhouse effect, because it has 270 times the greenhouse potential of CO<sub>2</sub> due to its long residence time of about 150 years. Furthermore, N<sub>2</sub>O also plays a significant role in the destruction of the ozone layer due to its relatively large energy absorption capacity per molecule. The ozone layer is broken down in the stratosphere by photolysis and oxidation and initiates a chain of cyclic reactions leading to stratospheric ozone destruction. Catalytic removal of N<sub>2</sub>O has been studied using several supported precious metals or transition metal oxides such as Fe-ZSM-5, Pd/Fe-ZSM-5, Cu/ZSM-5, Co/ZSM-5, Cu/ZrO<sub>2</sub>, and Rh/ZrO<sub>2</sub> [2–6]. There are some critical items necessary to apply these catalysts to practical processes. (1) Catalysts must be active at low reaction temperatures, even in the presence of components such as O<sub>2</sub>, H<sub>2</sub>O, and NO<sub>x</sub>

usually present in the exhausted gases. (2) Catalysts must be resistant to deactivation by SO<sub>2</sub>. Recent studies on catalytic removal of N<sub>2</sub>O demonstrated that Fe-based catalysts show activity for N<sub>2</sub>O destruction combined with resistance against SO<sub>2</sub>, while Co and in particular Cu based catalysts are sensitive for SO<sub>2</sub> [3–6]. Recently, N<sub>2</sub>O removal has also been studied using pulsed corona and microwave discharges [7–11]. When discharge is used for the decomposition of N<sub>2</sub>O in air at atmospheric pressure, NO<sub>x</sub> is generally emitted due to reactions of decomposition products of N<sub>2</sub> and O<sub>2</sub>: e.g., N(<sup>2</sup>D, <sup>2</sup>P) + O<sub>2</sub> → NO + O reactions. Such an NO<sub>x</sub> emission must be suppressed during the decomposition of N<sub>2</sub>O in discharge of air.

We have recently studied decomposition of N<sub>2</sub>O by a microwave discharge of N<sub>2</sub>O/He, N<sub>2</sub>O/Ar, and N<sub>2</sub>O/N<sub>2</sub> mixtures [7–9]. A high decomposition efficiency of N<sub>2</sub>O (≥94%) was obtained in N<sub>2</sub>O/Ar and N<sub>2</sub>O/N<sub>2</sub> mixtures at atmospheric pressure. NO formation ratio in the products was low in N<sub>2</sub>O/Ar and N<sub>2</sub>O/N<sub>2</sub> mixtures. When a small amount of O<sub>2</sub> was added to N<sub>2</sub>O/Ar and N<sub>2</sub>O/N<sub>2</sub> mixtures, N<sub>2</sub>O conversion decreased significantly, while a great increase in the NO formation ratio was observed. Since discharge processes are generally unselective for atoms and

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molecules, excitation, ionization, and dissociation occur simultaneously for  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$  by fast electron impact. Therefore, decomposition of  $\text{N}_2\text{O}$  in air is generally difficult by using discharge methods. In order to remove  $\text{N}_2\text{O}$  in air at atmospheric pressure, a new technique must be developed. An efficient and selective decomposition of  $\text{N}_2\text{O}$  in  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures is required for the new  $\text{N}_2\text{O}$  removal technique to suppress NO emission. An ideal method proposed here is a photochemical process where a high selective removal of  $\text{N}_2\text{O}$  is expected to be achieved by using photons with an appropriate wavelength. Fortunately, there are significant differences in dependence of absorption coefficients of  $\text{N}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$  on the wavelength of photons [12]. We noticed that absorption coefficient of  $\text{N}_2\text{O}$  is large only for  $\text{N}_2\text{O}$  at 193 nm in  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures. Under 193 nm irradiation,  $\text{N}_2\text{O}$  is selectively decomposed into  $\text{N}_2 + \text{O}(^1\text{D})$  [12–14]. Thus, an efficient and selective removal of  $\text{N}_2\text{O}$  by 193 nm ArF excimer laser photolysis is expected in air.

In this paper, we report the results of  $\text{N}_2\text{O}$  removal in  $\text{N}_2$  and air at atmospheric pressure by 193 nm ArF excimer laser photolysis at a room temperature without using any catalysts. The  $\text{N}_2\text{O}$  conversion and the formation ratios of products were measured as a function of the irradiation time of laser, laser power, and partial pressure of  $\text{N}_2\text{O}$  in order to determine optimum decomposition conditions. The decomposition mechanism of  $\text{N}_2\text{O}$  was discussed by comparing experimental data with those predicted from reported photochemical and gas kinetic data.

## 2. Experimental

Fig. 1 shows the reaction chamber used for the photolysis of  $\text{N}_2\text{O}$  diluted in  $\text{N}_2$  or air by a 193 nm ArF excimer laser. A cylindrical reaction chamber was 2.5 cm in internal di-

ameter and 55 cm length. Light from an unfocused ArF excimer laser (Lambda Physik, COMPex102) was used to decompose  $\text{N}_2\text{O}$  at a room temperature. The laser pulses had a duration of 15 ns and delivered output energy of 50–136 mJ per pulse at a repetition rate of 5 Hz. It is known that there is no absorption of  $\text{N}_2$  at 193 nm [12]. Therefore, the reaction chamber was filled with  $\text{N}_2$  gas at atmospheric pressure, when the laser power was monitored from the outside of the decomposition chamber using a laser power monitor. The reaction chamber was evacuated using an oil rotary pump, before  $\text{N}_2\text{O}$  diluted in  $\text{N}_2$  or air was introduced into it. A mixture of  $\text{N}_2\text{O}/\text{N}_2$  or  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  was kept at a constant flow using mass flow meters and fed into the reaction chamber. The  $\text{N}_2\text{O}:\text{N}_2$  ratios in  $\text{N}_2\text{O}/\text{N}_2$  mixtures were 10–50:500, respectively, and  $\text{N}_2\text{O}:\text{N}_2:\text{O}_2$  ratios were 50:500:100 in  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures. Thus, the  $\text{N}_2\text{O}$  concentration in  $\text{N}_2\text{O}/\text{N}_2$  or  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures was 2.0–9.1% (v/v). The total pressure, monitored by a capacitance pressure gauge, was kept at atmospheric pressure using a needle valve. When laser was irradiated into a flow system of  $\text{N}_2\text{O}/\text{N}_2$  or  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures, the  $\text{N}_2\text{O}$  conversion was less than 10%. Therefore, all experiments reported here were carried out in a closed batch system. After 1–30 min laser irradiation into the reaction chamber, products were analyzed through a sampling orifice by using a quadrupole mass spectrometer (ULVAC QMS 400). The relative sensitivity of QMS for  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and NO was calibrated using standard gases. The flow rate of the buffer  $\text{N}_2$  gas was larger than the  $\text{N}_2$  production from  $\text{N}_2\text{O}$  by factors of >10. Therefore, it was difficult to isolate the  $\text{N}_2$  production signal from the strong signal from the buffer  $\text{N}_2$  gas.

The  $\text{N}_2\text{O}$  conversion,  $1 - [\text{N}_2\text{O}]/[\text{N}_2\text{O}]_0$ , was estimated from the reduction of intensity of the  $\text{N}_2\text{O}^+$  peak, while the formation ratios of  $\text{O}_2$  and NO, defined as  $[\text{O}_2]/[\text{N}_2\text{O}]_0$  and  $[\text{NO}]/[\text{N}_2\text{O}]_0$ , respectively, were determined from the intensities of the  $\text{O}_2^+$  and  $\text{NO}^+$  peaks, taking the

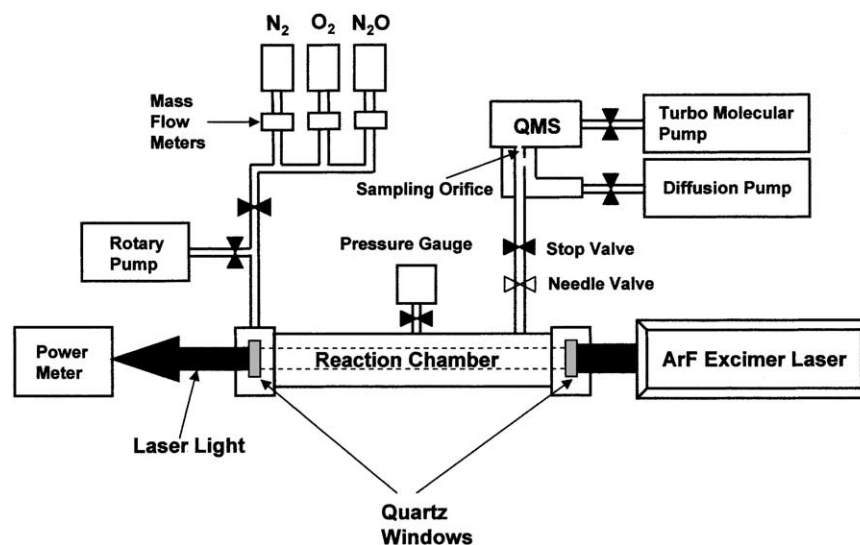


Fig. 1. Decomposition chamber of  $\text{N}_2\text{O}$  by a 193 nm ArF excimer laser in  $\text{N}_2$  or air.

contribution of  $\text{NO}^+$  from electron-impact dissociative ionization of  $\text{N}_2\text{O}$  into consideration. Here,  $[\text{N}_2\text{O}]_0$  is an initial concentration of  $\text{N}_2\text{O}$ . The  $[\text{N}_2]/[\text{N}_2\text{O}]_0$  ratio was estimated from the N balance between the reagent  $\text{N}_2\text{O}$  and products  $\text{N}_2$  and  $\text{NO}$ , because no other products containing N atom could be observed in our conditions.

### 3. Results and discussion

#### 3.1. $\text{N}_2\text{O}$ removal in $\text{N}_2\text{O}/\text{N}_2$ mixture

At first, we studied decomposition of  $\text{N}_2\text{O}$  in an  $\text{N}_2\text{O}/\text{N}_2$  mixture by 193 nm excimer laser photolysis. Fig. 2(a) and (b) show typical mass spectra of the  $\text{N}_2\text{O}/\text{N}_2$  mixture before and after laser irradiation, respectively. A strong  $\text{N}_2^+$  peak ( $m/z = 28$ ) and weak  $\text{N}_2\text{O}^+$  ( $m/z = 44$ ) and  $\text{NO}^+$  ( $m/z = 28$ ) peaks are observed in Fig. 2(a). The  $\text{NO}^+$  peak results from electron-impact dissociative ionization of  $\text{N}_2\text{O}$ . After 5 min laser irradiation, the  $\text{N}_2\text{O}^+$  and  $\text{NO}^+$  peaks reduce their intensities to 26 and 59%, respectively, and an  $\text{O}_2^+$  peak ( $m/z = 32$ ) appears, as shown in Fig. 2(b). No other products such as  $\text{NO}_2^+$  ( $m/z = 46$ ) are detected after laser irradiation. These results and nitrogen balance between reactant and products indicate that  $\text{N}_2\text{O}$  is decomposed into  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  by 193 nm laser irradiation under the present experimental conditions. Thus, the overall decomposition scheme under 193 nm laser irradiation is given by:

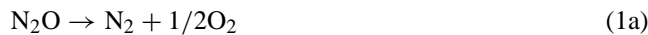


Fig. 3 shows the dependence of  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  on the irradiation time of ArF excimer laser. Dotted lines are calculated values from kinetic model, which will be shown in Section 3.3. The  $\text{N}_2\text{O}$  conversion and the formation ratios of  $\text{N}_2$  and  $\text{O}_2$

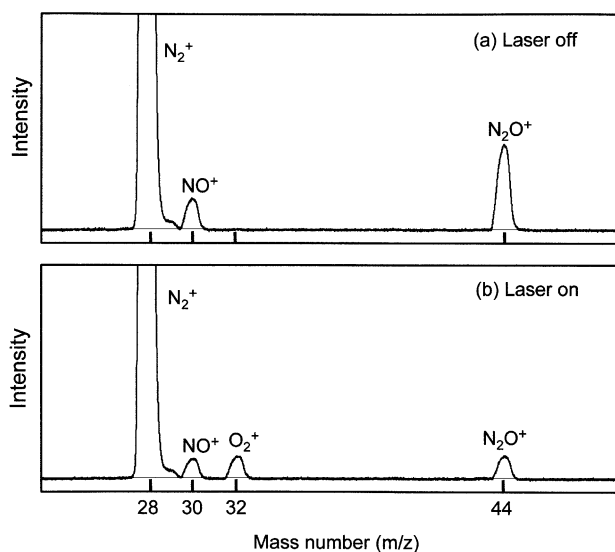


Fig. 2. Mass spectra of  $\text{N}_2\text{O}/\text{N}_2$  mixture (a) before and (b) 5 min after laser irradiation at a total pressure of 101.3 kPa, an initial  $[\text{N}_2\text{O}]:[\text{N}_2]$  ratios of 1:10, and a laser energy of 136 mJ. Spectra are not corrected for relative sensitivity.

rapidly increase to about 85, 80, and 35%, respectively, in the 0–10 min range and level off above that. The maximum conversion of  $\text{N}_2\text{O}$  is 93% at 30 min. The maximum formation ratios of  $\text{N}_2$  and  $\text{O}_2$  are 90 and 43% at 30 min, respectively. Although the formation ratio of  $\text{NO}$  increases from zero to 18% in the 0–5 min range, it decreases from 18 to 7% in the 5–30 min range.

Fig. 4 shows the dependence of  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  on the laser power at an irradiation time of 5 min. The  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  increase almost linearly with increasing the laser power in the 50–114 mJ range. These results indicate that decomposition of  $\text{N}_2\text{O}$  proceeds through one photon process, or one absorption step is

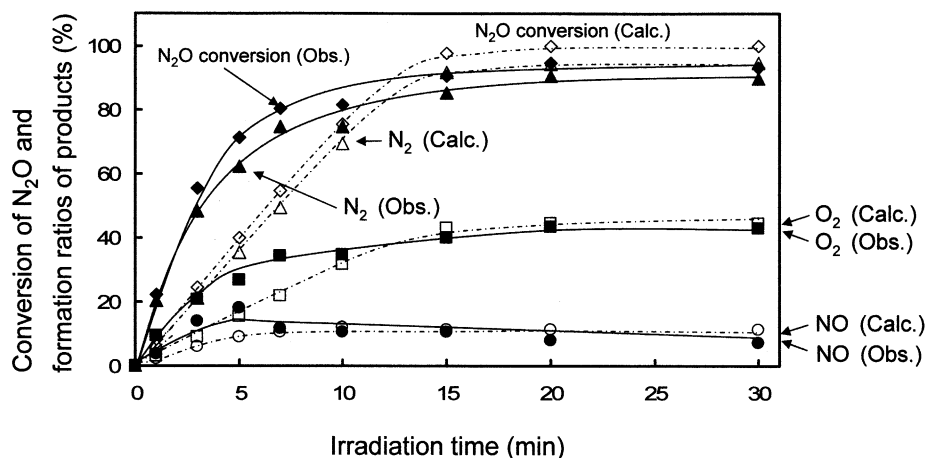


Fig. 3. Dependence of  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  in an  $\text{N}_2/\text{N}_2\text{O}$  mixture on the irradiation time at a total pressure of 101.3 kPa, an initial  $[\text{N}_2\text{O}]:[\text{N}_2]$  ratios of 1:10, and a laser energy of 136 mJ. (◆)  $\text{N}_2\text{O}$  conversion (Obs.), (◇)  $\text{N}_2\text{O}$  conversion (Calc.), (▲)  $\text{N}_2$  (Obs.), (△)  $\text{N}_2$  (Calc.), (■)  $\text{O}_2$  (Obs.), (□)  $\text{O}_2$  (Calc.), (●)  $\text{NO}$  (Obs.), and (○)  $\text{NO}$  (Calc.).

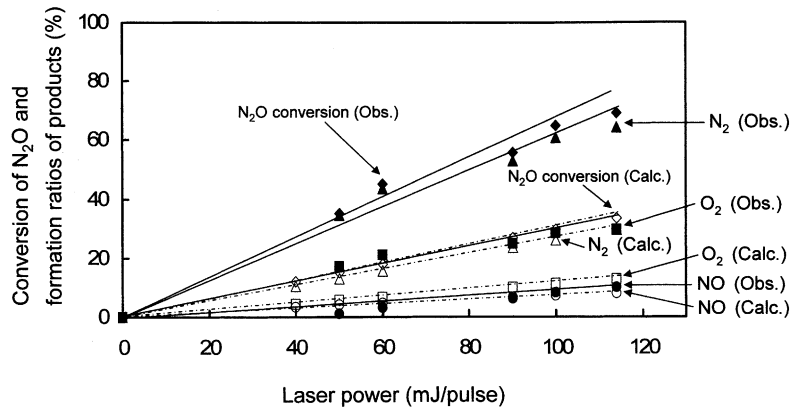


Fig. 4. Dependence of N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub>, O<sub>2</sub>, and NO in an N<sub>2</sub>/N<sub>2</sub>O mixture on the laser power at a total pressure of 101.3 kPa, an initial [N<sub>2</sub>O]:[N<sub>2</sub>] ratios of 1:10, and a laser irradiation time of 5 min (1500 shots).

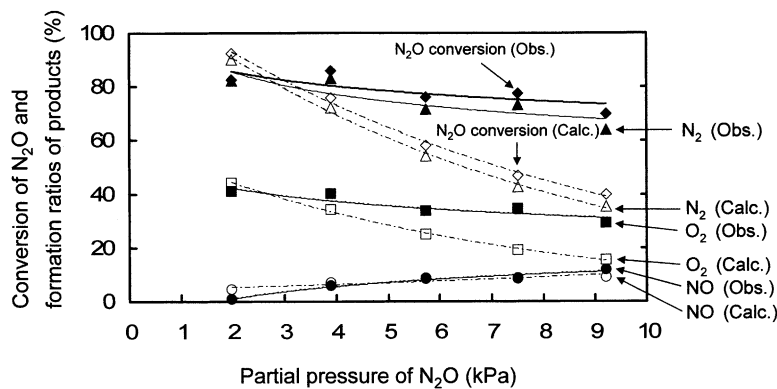


Fig. 5. Dependence of N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub>, O<sub>2</sub>, and NO in an N<sub>2</sub>/N<sub>2</sub>O mixture on the partial pressure of N<sub>2</sub>O at a total pressure of 101.3 kPa, a laser energy of 136 mJ, and laser irradiation time of 5 min (1500 shots).

saturated in two-photon excitation processes under our experimental conditions.

Fig. 5 shows the dependence of N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub>, O<sub>2</sub>, and NO on the partial pressure of N<sub>2</sub>O at an irradiation time of 5 min. The N<sub>2</sub>O conversion decreases from 85 to 70% with increasing the partial pressure of N<sub>2</sub>O from 2 to 9.2 kPa corresponding to N<sub>2</sub>O concentrations of 2.0–9.1% (v/v). The formation ratios of N<sub>2</sub> and O<sub>2</sub> also decrease from 82 to 64% and 41 to 29%, respectively, with increasing the partial pressure of N<sub>2</sub>O from 2 to 9.2 kPa. It should be noted that the formation ratio of NO increases from 1 to 12% in the same partial pressure range of N<sub>2</sub>O.

### 3.2. N<sub>2</sub>O removal in N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture

In order to examine the effects of O<sub>2</sub>, decomposition of N<sub>2</sub>O in an N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture was studied. Fig. 6(a) and (b) show typical mass spectra of the N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture before and after laser irradiation, respectively. A strong N<sub>2</sub><sup>+</sup> peak and weak N<sub>2</sub>O<sup>+</sup>, NO<sup>+</sup>, and O<sub>2</sub><sup>+</sup> peaks are observed in Fig. 6(a). After 5 min laser irradiation, the N<sub>2</sub>O<sup>+</sup> and NO<sup>+</sup> peaks reduce their intensities to 31 and 61%, respectively, while the O<sub>2</sub><sup>+</sup> peak becomes strong by a factor of 24%, as shown in Fig. 6(b). No significant enhancement of NO<sup>+</sup>

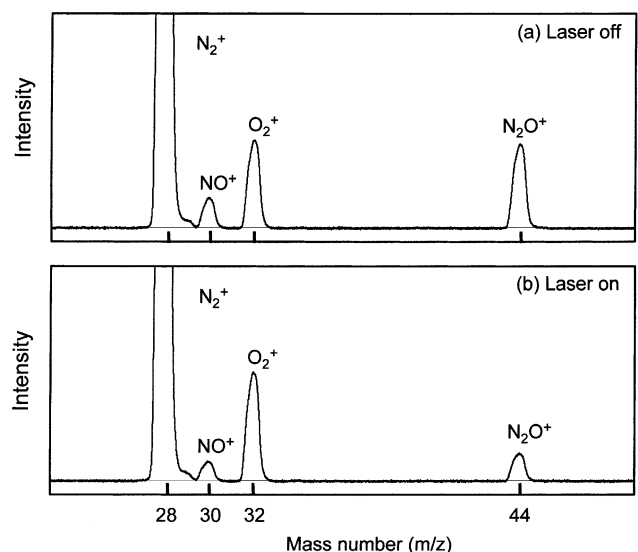


Fig. 6. Mass spectra of N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture (a) before and (b) 5 min after laser irradiation at a total pressure of 101.3 kPa, initial [N<sub>2</sub>O]:[N<sub>2</sub>]:[O<sub>2</sub>] ratios of 1:10:2, and a laser energy of 136 mJ. Spectra are not corrected for relative sensitivity.

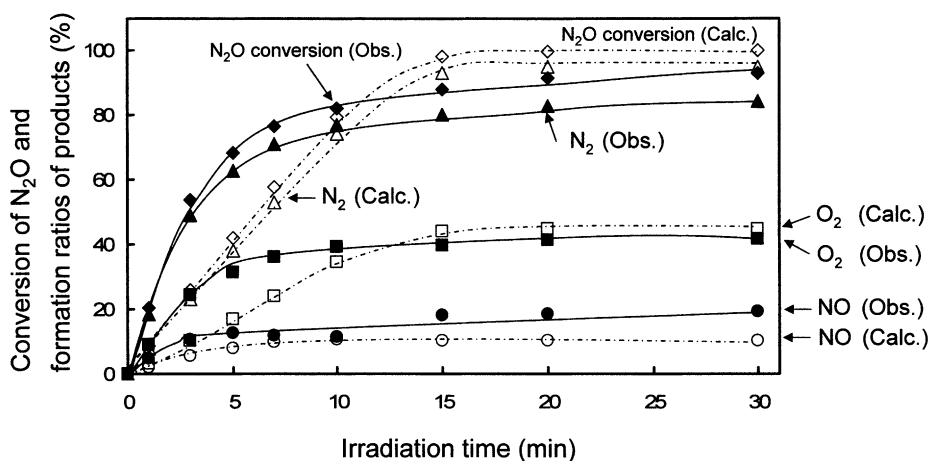


Fig. 7. Dependence of  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  in an  $\text{N}_2/\text{N}_2\text{O}/\text{O}_2$  mixture on the irradiation time at a total pressure of 101.3 kPa, initial  $[\text{N}_2\text{O}]:[\text{N}_2]:[\text{O}_2]$  ratios of 1:10:2, and a laser energy of 136 mJ.

peak intensity is observed by the addition of  $\text{O}_2$ , indicating that the present technique is useful for the selective  $\text{N}_2\text{O}$  removal in air.

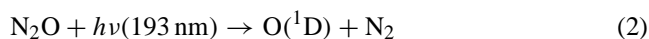
Fig. 7 shows the dependence of  $\text{N}_2\text{O}$  conversion and formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  on the irradiation time in the  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixture. The dependence of  $\text{N}_2\text{O}$  conversion on the irradiation time is very similar to that in the  $\text{N}_2\text{O}/\text{N}_2$  mixture. The  $\text{N}_2\text{O}$  conversion rapidly increases from zero to 82% in the 0–10 min range and levels off above that. The maximum conversion of  $\text{N}_2\text{O}$  is 93% at 30 min, which is identical to that in the  $\text{N}_2\text{O}/\text{N}_2$  mixture. The formation ratios of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  also increase from zero to about 77, 36, and 10%, respectively, in the 0–10 min range. The maximum formation ratios of  $\text{N}_2$  and  $\text{O}_2$  are 84 and 38%, respectively, at 30 min. The formation ratios of  $\text{N}_2$  and  $\text{O}_2$  at 30 min are smaller than those in the  $\text{N}_2\text{O}/\text{N}_2$  mixture by 5–6%. The formation ratio of  $\text{NO}$  in the  $\text{N}_2\text{O}/\text{N}_2$  mixture increases from zero to 18% in the 0–5 min range, and then decreases from 18 to 7% in the 5–30 min range. On the other hand, the formation ratio of  $\text{NO}$  in the  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixture increases from zero to 16% in the 0–15 min range and levels off above that. Summarizing above results, decomposition of  $\text{N}_2\text{O}$  in the  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixture is similar to that in the  $\text{N}_2\text{O}/\text{N}_2$  mixture except for a higher formation ratio of  $\text{NO}$  by factors 1.5–2.4 in the 15–30 min range. In a laser energy of 136 mJ, about 80% of  $\text{N}_2\text{O}$  is decomposed at a laser irradiation time of 10 min. On the basis of this finding, laser radiant energy required for decomposition of 1 mol  $\text{N}_2\text{O}$  was estimated to be about 500 kJ.

### 3.3. Decomposition mechanism of $\text{N}_2\text{O}$ in $\text{N}_2\text{O}/\text{N}_2$ or $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$ mixtures by ArF excimer laser

It is known that there is no absorption at 193 nm for  $\text{N}_2$ , while  $\text{O}_2$  and  $\text{NO}$  are excited to the  $\text{O}_2(\text{B}^3\Sigma_u^-; v' = 4)$  and  $\text{NO}(\text{B}^2\Pi; v' = 7)$  states by the 193 nm ArF laser excitation, leading to  $\text{O}_2(\text{B}^3\Sigma_u^- - \text{X}^3\Sigma_g^-)$  and  $\text{NO}(\text{B}^2\Pi - \text{X}^2\Pi)$  emissions, respectively [15,16]. In order to obtain information on

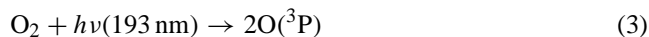
the 193 nm photolysis of  $\text{N}_2\text{O}$  in  $\text{N}_2\text{O}/\text{N}_2$  and  $\text{N}_2\text{O}/\text{N}_2/\text{O}_2$  mixtures, ArF excimer laser was irradiated into 1:1 mixtures of  $\text{N}_2/\text{O}_2$  and  $\text{N}_2/\text{NO}$  at 101.3 kPa (=760 Torr), and products were monitored. Only  $\text{N}_2^+$  and  $\text{O}_2^+$  peaks were observed in the  $\text{N}_2/\text{O}_2$  mixture, and  $\text{N}_2^+$  and  $\text{NO}^+$  were found in the  $\text{N}_2/\text{NO}$  mixture. The relative intensities of  $\text{N}_2^+$  and  $\text{O}_2^+$  peaks in the  $\text{N}_2/\text{O}_2$  mixture and those of  $\text{N}_2^+$  and  $\text{NO}^+$  in the  $\text{N}_2/\text{NO}$  mixture were independent of the irradiation time in the 0–30 min range. It was, therefore, concluded that formation and destruction of  $\text{NO}_x$  do not occur by ArF excimer laser photolysis of 1:1 mixtures of  $\text{N}_2/\text{O}_2$  and  $\text{N}_2/\text{NO}$  under our experimental conditions.

On the basis of the above findings and known  $\text{N}_2\text{O}$  photolysis under 193 nm [12–14], it was concluded that  $\text{N}_2\text{O}$  decomposition diluted in  $\text{N}_2$  initiates from selective one-photon-excitation of  $\text{N}_2\text{O}$  followed by dissociation into  $\text{O} (^1\text{D})$  and  $\text{N}_2$ :

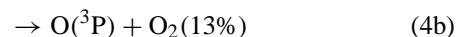
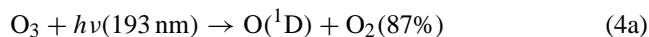


$$\sigma_2 = 8.95 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1} [14]$$

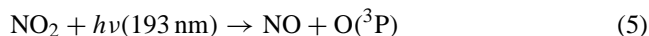
The quantum yield of  $\text{O} (^1\text{D})$  in photodissociation process (2) has been known to be 1.0 [12–14]. In the presence of  $\text{O}_2$ ,  $\text{O}_3$ , and  $\text{NO}_2$ , the following photodissociation processes occur simultaneously under 193 nm laser irradiation.



$$\sigma_2 = 3.2 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1} [17]$$



$$\sigma_4 = 4.34 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} [14]$$



$$\sigma_5 = 2.9 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1} [18]$$

Since there is a large discrepancy for the reported  $\sigma_2$  values of process (3),  $3.2 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$  [17] and  $\sim 2 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$  [19], it was measured by filling

up 20 kPa of O<sub>2</sub> in the reaction chamber. The value obtained agreed well with the former smaller value in our condition. Therefore, we used the former value in the model calculation.

The laser energy absorbed by N<sub>2</sub>O, O<sub>2</sub>, O<sub>3</sub>, or NO<sub>2</sub> during passing through the decomposition chamber,  $E_i$ , after irradiation of a laser pulse was calculated from the relation:

$$E_i = E_0 - E_0 \exp(-\sigma_i N_i l) \quad (6)$$

where,  $E_0$ ,  $N_i$ , and  $l$ , are an energy of incident laser light, the number of N<sub>2</sub>O, O<sub>2</sub>, O<sub>3</sub>, or NO<sub>2</sub> molecule per cm<sup>3</sup> and the length of decomposition chamber, respectively. One photon energy of 193 nm laser light,  $E_{193}$ , is calculated to be  $1.03 \times 10^{-18}$  J from the relation:

$$E_{193} = h\nu = \frac{hc}{\lambda} \quad (7)$$

Number of photons absorbed by a molecule M in an  $i$ th laser pulse,  $n_{Pi}(M)$  was estimated from the relation:

$$n_{Pi}(M) = \frac{E_i}{E_{193}}, \quad M = \text{N}_2\text{O}, \text{O}_2, \text{O}_3, \text{ or NO}_2 \quad (8)$$

Since quantum yield of N<sub>2</sub>O at 193 nm is 1.0 [12–14], the following relation holds between mol numbers of  $n_{Pi}(\text{N}_2\text{O})$  and those of O(<sup>1</sup>D) and N<sub>2</sub> produced through photodissociation process (2) in an  $i$ th laser pulse:

$$n_{Pi}(\text{N}_2\text{O}) = n_{Pi}(\text{O}^1\text{D}) = n_{Pi}(\text{N}_2) \quad (9)$$

After irradiation of laser pulse for 10 ns various two- and three-body reactions of O(<sup>1</sup>D), O(<sup>3</sup>P), and N(<sup>4</sup>S) atoms with atoms or molecules and the O<sub>3</sub>/NO reaction occur in the reaction chamber. Possible secondary reactions and their rate coefficients are listed in Table 1. It should be noted that in addition to photolysis process (2), N<sub>2</sub>O is decomposed by the O(<sup>1</sup>D)/N<sub>2</sub>O reaction (10a) and (10b), leading to N<sub>2</sub>, O<sub>2</sub>, and NO. In our conditions, subsequent chemical reactions (10)–(25) are completed and no reactive O(<sup>1</sup>D), O(<sup>3</sup>P), and N(<sup>4</sup>S) atoms remain before irradiation of next laser pulse. Under such a condition, molar fraction of N<sub>2</sub>O decomposed by photolysis (2) and reaction (10),  $x_i(\text{N}_2\text{O})$ , and molar fractions of N<sub>2</sub>, O<sub>2</sub>, NO, O<sub>3</sub>, and NO<sub>2</sub> produced by photolysis (2)–(5) and subsequent reactions (10)–(25),  $y_i(M)$ , by an  $i$ th laser pulse are calculated. Finally, N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub>, O<sub>2</sub>, NO, O<sub>3</sub>, and NO<sub>2</sub>,  $Y(N)$  are obtained by summing up  $x_i(\text{N}_2\text{O})$  and  $y_i(M)$  over number of laser pulse  $i$ :

$$X(\text{N}_2\text{O}) = \sum_i x_i(\text{N}_2\text{O}) \quad (25a)$$

$$Y(N) = \sum_i y_i(N) \quad (25b)$$

In order to examine the validity of the above reaction scheme, the N<sub>2</sub>O conversion and the formation ratios of N<sub>2</sub>, NO, O<sub>2</sub>, O<sub>3</sub>, and NO<sub>2</sub> were calculated after various laser shots. Calculated  $X(\text{N}_2\text{O})$ ,  $Y(\text{N}_2)$ ,  $Y(\text{O}_2)$ , and  $Y(\text{NO})$  values

Table 1

Possible reactions of O(<sup>1</sup>D,<sup>3</sup>P) and N(<sup>4</sup>S) with atoms and molecules induced by 193 nm photolysis of N<sub>2</sub>O

Reactants and products	Reaction number	Rate coefficients (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) [20,21]
O( <sup>1</sup> D) + N <sub>2</sub> O → N <sub>2</sub> + O <sub>2</sub>	(10a)	4.4 × 10 <sup>-11</sup>
→ 2NO	(10b)	7.2 × 10 <sup>-11</sup>
O( <sup>1</sup> D) + N <sub>2</sub> → O( <sup>3</sup> P) + N <sub>2</sub>	(11)	2.6 × 10 <sup>-11</sup>
O( <sup>1</sup> D) + O <sub>2</sub> → O( <sup>3</sup> P) + O <sub>2</sub>	(12)	4.0 × 10 <sup>-11</sup>
O( <sup>1</sup> D) + NO → O( <sup>3</sup> P) + NO	(13a)	4.0 × 10 <sup>-11</sup>
→ N( <sup>4</sup> S) + O <sub>2</sub>	(13b)	1.2 × 10 <sup>-11</sup>
O( <sup>1</sup> D) + O <sub>3</sub> → 2O <sub>2</sub>	(14a)	2.4 × 10 <sup>-11</sup>
→ O <sub>2</sub> + 2O( <sup>3</sup> P)	(14b)	1.2 × 10 <sup>-11</sup>
O( <sup>1</sup> D) + NO <sub>2</sub> → NO + O <sub>2</sub>	(15a)	3.01 × 10 <sup>-11</sup>
→ NO <sub>2</sub> + O( <sup>3</sup> P)	(15b)	1.6 × 10 <sup>-11</sup>
O( <sup>3</sup> P) + O <sub>2</sub> + N <sub>2</sub> → O <sub>3</sub> + N <sub>2</sub>	(16)	5.7 × 10 <sup>-34</sup> [N <sub>2</sub> ]
O( <sup>3</sup> P) + O <sub>2</sub> + O <sub>2</sub> → O <sub>3</sub> + O <sub>2</sub>	(17)	6.2 × 10 <sup>-34</sup> [O <sub>2</sub> ]
O( <sup>3</sup> P) + O( <sup>3</sup> P) + N <sub>2</sub> → O <sub>2</sub> + N <sub>2</sub>	(18)	4.82 × 10 <sup>-33</sup> [N <sub>2</sub> ]
O( <sup>3</sup> P) + NO + N <sub>2</sub> → NO <sub>2</sub> + N <sub>2</sub>	(19)	1.0 × 10 <sup>-31</sup> [N <sub>2</sub> ]
O( <sup>3</sup> P) + NO + O <sub>2</sub> → NO <sub>2</sub> + O <sub>2</sub>	(20)	8.6 × 10 <sup>-32</sup> [O <sub>2</sub> ]
O( <sup>3</sup> P) + O <sub>3</sub> → 2O <sub>2</sub>	(21)	8.0 × 10 <sup>-15</sup>
O( <sup>3</sup> P) + NO <sub>2</sub> → NO + O <sub>2</sub>	(22)	1.05 × 10 <sup>-11</sup>
O <sub>3</sub> + NO → NO <sub>2</sub> + O <sub>2</sub>	(23)	1.8 × 10 <sup>-14</sup>
N( <sup>4</sup> S) + NO → N <sub>2</sub> + O( <sup>3</sup> P)	(24)	2.9 × 10 <sup>-11</sup>
N( <sup>4</sup> S) + NO <sub>2</sub> → N <sub>2</sub> O + O( <sup>3</sup> P)	(25)	1.21 × 10 <sup>-11</sup>

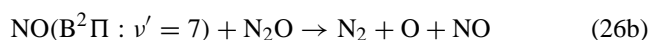
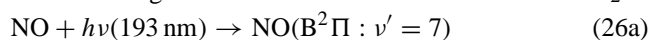
from the above model at various conditions are shown in Figs. 3–5 and 7 by dotted lines. Since calculated  $Y(\text{O}_3)$  and  $Y(\text{NO}_2)$  are negligibly small, they are not shown in these figures. On the basis of model calculations, the decomposition of N<sub>2</sub>O at 136 mJ is completed at about 15 min for both the N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures as shown in Figs. 3 and 7. A major initial difference between the N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures is the presence of a high concentration of O<sub>2</sub> in the N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture. Under such a condition, higher formation ratios of O<sub>3</sub> and NO<sub>2</sub> are expected in the N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture via processes (16), (17), (19), and (20) due to higher concentrations of O(<sup>3</sup>P) and O<sub>2</sub>. However, no significant difference is found for calculated values between Figs. 3 and 7 because the formation ratios of O<sub>3</sub> and NO<sub>2</sub> are negligibly small in both N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures. The low O<sub>3</sub> and NO<sub>2</sub> yields in both mixtures can be explained by the large absorption coefficients of O<sub>3</sub> and NO<sub>2</sub> at 193 nm, so that these molecules are destroyed nearly completely by the subsequent laser pulses. No experimental evidence for the formation of O<sub>3</sub> and NO<sub>2</sub> obtained in this work was consistent with our model calculation. A great advantage of the present photolysis process of N<sub>2</sub>O in N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures is a high conversion of N<sub>2</sub>O into N<sub>2</sub> and O<sub>2</sub> without formation of O<sub>3</sub> and NO<sub>2</sub> at room temperature.

In Fig. 3, there is a reasonable agreement between observed and calculated values for the formation ratios of O<sub>2</sub> and NO in the long irradiation time range of 15–30 min, though the observed N<sub>2</sub>O conversion and the formation ratio of N<sub>2</sub> are smaller than calculated values by 4–7%. It should be noted that there are significant differences in the N<sub>2</sub>O

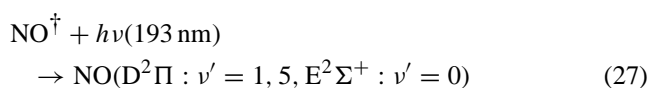
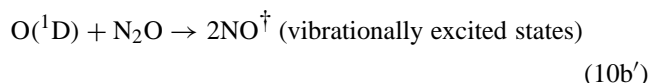
conversion and formation ratios of each product between the observed and calculated values in the short irradiation time range of 0–15 min. The observed N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub> increase more rapidly than the calculated ones with increasing the irradiation time. In the laser power dependence (Fig. 4), measured at a short irradiation time of 5 min, significant discrepancies between the observed and calculated values is also found for the N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub>. In the partial pressure dependence of N<sub>2</sub>O (Fig. 5), there is a reasonable agreement between the observed and calculated values for the NO formation ratio. The observed N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub> are much larger than the calculated values at high partial N<sub>2</sub>O pressure range of 5.7–9.2 kPa. However, discrepancy becomes small with decreasing the partial N<sub>2</sub>O pressure, and a good agreement between observed and calculated values is found for the N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub> at a partial N<sub>2</sub>O pressure of about 3 kPa.

The observed high N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub> in comparison with calculated values in the short irradiation time range of 0–15 min suggest that additional processes contribute to the decomposition of N<sub>2</sub>O at high partial pressure range of N<sub>2</sub>O in the N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures. It is clear from Figs. 3 and 7 that there are similar large discrepancy between the observed and calculated values of the N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub> in both N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures. This led us to conclude that such oxygen species as O(<sup>3</sup>P, <sup>1</sup>D), O<sub>2</sub>, and O<sub>3</sub> do not play a significant role in additional decomposition processes of N<sub>2</sub>O below 15 min.

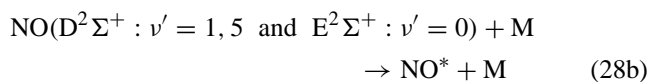
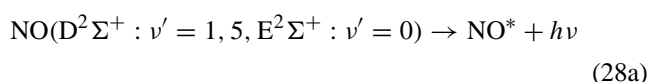
It is known that NO and O<sub>2</sub> molecules are excited into the excited NO(B<sup>2</sup>Π:ν' = 7) and O<sub>2</sub>(B<sup>3</sup>Σ<sub>u</sub><sup>-</sup>:ν' = 4) states under 193 nm ArF laser excitation [15,16]. The lifetime of NO(B<sup>2</sup>Π:ν' = 7) was measured to be 330 ± 30 ns, while that of O<sub>2</sub>(B<sup>3</sup>Σ<sub>u</sub><sup>-</sup>:ν' = 4) was estimated to be 1 ps from the linewidth [15]. Although the latter state is too short to cause further energy transfer reactions, the former state has a sufficient long lifetime to cause further collisions with N<sub>2</sub>O:



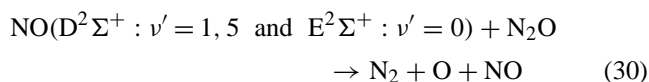
Since dissociation energy of N<sub>2</sub>–O is only 1.73 eV [22], NO(B<sup>2</sup>Π:ν' = 7) with an energy of 6.4 eV has a sufficient energy to decompose N<sub>2</sub>O into N<sub>2</sub> and O. Secondary process (26b) occurs via single photon process, being consistent with the experimental observation. Thus, process (26b) may be an important secondary process for the enhancement of N<sub>2</sub>O decomposition and formation of N<sub>2</sub> and O<sub>2</sub> in the short irradiation time range of 0–15 min. It is known that NO produced from reaction (10b) is vibrationally excited and further absorbs 193 nm laser light leading to NO(D<sup>2</sup>Π:ν' = 1.5, E<sup>2</sup>Σ<sup>+</sup>:ν' = 0) [13]:



It is known that predissociation into N + O compete with radiative decay for NO(D<sup>2</sup>Σ<sup>+</sup>:ν' ≥ 0) with radiative lifetimes of 18–19 ns due to a rotational on heterogeneous interaction (gyroscopic) with NO(C<sup>2</sup>Π) [23]. To the best of our knowledge, we have no information whether predissociation competes with radiative decay for the NO(E<sup>2</sup>Σ<sup>+</sup>:ν' = 0) state with a lifetime of 40 ± 3 ns [23]. Radiative decay of NO(D<sup>2</sup>Σ<sup>+</sup>:ν' = 1.5 and E<sup>2</sup>Σ<sup>+</sup>:ν' = 0), process (28a), probably competes with collisional quenching to lower states, process (28b), from which predissociation into N + O (29b) will occur, as reported for the NO(C<sup>2</sup>Π:ν' = 0, D<sup>2</sup>Σ<sup>+</sup>:ν' = 0) state [24]:

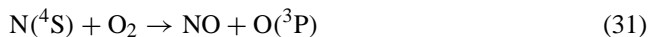


Zavelovich et al. [13] studied VUV fluorescence following photodissociation of N<sub>2</sub>O at 193 nm with an output energy of ~80 mJ per pulse in the N<sub>2</sub>O pressure range of 133–26,600 Pa. They found that the dependence of the fluorescence intensity of NO emissions on laser intensity was linear even under unfocused conditions. Since at least two photons are necessary to generate fluorescence, the linear dependence implied saturation of the second photoexcitation process (27). The absorption cross section of this process was estimated to be σ ≥ 1 × 10<sup>-15</sup> cm<sup>2</sup> molecule<sup>-1</sup>, which is larger than that of the first process (2) by four orders of magnitude. Since laser power used in this work (136 mJ per pulse) is higher than that in their study, similar secondary excitation steps are expected to occur more significantly. NO(D<sup>2</sup>Σ<sup>+</sup>:ν' = 1.5 and E<sup>2</sup>Σ<sup>+</sup>:ν' = 0) with excitation energies of 7.5–8.0 eV have enough energies to decompose N<sub>2</sub>O into N<sub>2</sub> and O (1.73 eV). It is thus, highly likely that the secondary reaction of NO(D<sup>2</sup>Σ<sup>+</sup>:ν' = 1.5 and E<sup>2</sup>Σ<sup>+</sup>:ν' = 0) with N<sub>2</sub>O is also responsible for the additional decomposition of N<sub>2</sub>O under 193 nm laser excitation:



The ground-state N(<sup>4</sup>S) atoms produced via predissociation reacts with NO leading to N<sub>2</sub> and O via process (24). Fast reaction (24) could explain the low formation ratio of NO and high formation ratios of N<sub>2</sub> and O<sub>2</sub> observed in the present experiments. It was found that the formation ratio

of NO becomes large in the presence of O<sub>2</sub>. It is known that rate coefficient of the N(<sup>4</sup>S) atoms with O<sub>2</sub> is very small:



$$k_{31} = 9.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad [20,21]$$

Thus, reaction (31) for the vibrational ground state of O<sub>2</sub> could not explain the enhancement of the NO formation in the N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture. However, it is known that the O<sub>2</sub>(X<sup>3</sup>Σ<sub>g</sub><sup>-</sup> : v'' = 1–13, 15) states are preferentially formed due to O<sub>2</sub>(B:v' = 4) → O<sub>2</sub>(X:v'') emission under 193 nm excitation of O<sub>2</sub> [15]. The reaction (31) for the vibrationally excited states of O<sub>2</sub> will be much faster than that for the vibrational ground state. Under such a condition, reaction (31) in the N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixture will be enhanced.

#### 4. Conclusion

In conclusion, photochemical N<sub>2</sub>O removal was studied in N<sub>2</sub>O/N<sub>2</sub> and N<sub>2</sub>O/N<sub>2</sub>/O<sub>2</sub> mixtures at atmospheric pressure and room temperature. ArF excimer laser was used as an excitation source. The conversion of N<sub>2</sub>O was >90% at a laser energy of 136 mJ. Under typical conditions, laser radiant energy required for decomposition of 1 mol N<sub>2</sub>O was estimated to be about 500 kJ. We found that N<sub>2</sub>O is efficiently decomposed by one photon decomposition at 193 nm. Thus, a low power cw lamp at 193 nm will also be useful for the selective removal of N<sub>2</sub>O in air at atmospheric pressure. If cheap UV or VUV lamps are available as light sources, practical application of this photochemical process for N<sub>2</sub>O removal may be possible. The N<sub>2</sub>O conversion and formation ratios of N<sub>2</sub> and O<sub>2</sub>, calculated from simple decomposition of N<sub>2</sub>O into O(<sup>1</sup>D) + N<sub>2</sub> followed by chemical reactions are significantly lower than the experimental observations. This discrepancy may be due to the contribution of such secondary reactions as NO(B<sup>2</sup>Π:v' = 7, D<sup>2</sup>Σ<sup>+</sup>:v' = 1, 5 and E<sup>2</sup>Σ<sup>+</sup>:v' = 0) + N<sub>2</sub>O, which are not included in the present model calculation. Further detailed experimental data and model calculations, including kinetic data for electronically or vibrationally excited NO and O<sub>2</sub> states, are required in order to clarify the decomposition mechanism of N<sub>2</sub>O in N<sub>2</sub> or air under 193 nm laser excitation.

We proposed here a photochemical removal method as a new method for the selective decomposition of N<sub>2</sub>O in air without using any catalysts at room temperature. However, more work remains to be done before this method can be applied in any real case. In this experiment, N<sub>2</sub>O destruction was studied at relatively high N<sub>2</sub>O concentrations above 2.0–9.1% (v/v) because of low detection sensitivity of mass spectrometer used in this study at low N<sub>2</sub>O concentrations below 2%. However, actual N<sub>2</sub>O emission occurs at much lower levels below 2000 ppmv. According to model calculation, most of all N<sub>2</sub>O can be decomposed into N<sub>2</sub> and O<sub>2</sub> at low concentrations of N<sub>2</sub>O without formation of NO, be-

cause relative importance of photochemical process (2) to that of reaction (10) increases with decreasing the N<sub>2</sub>O concentration. In order to confirm our prediction, further detailed experimental study at low concentrations of N<sub>2</sub>O will be necessary. Moreover, effects of other emitting species such as NO, SO<sub>2</sub>, CO, CO<sub>2</sub>, hydrocarbons, H<sub>2</sub>O, and dust in the photolysis of N<sub>2</sub>O must be examined for the practical application of this technique.

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