Efficient Decomposition of NO_2 into N_2 and O_2 by 193-nm ArF Laser in N_2 Atmosphere

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Decomposition of NO_2 in N_2 by 193-nm ArF excimer laser was studied at atmospheric pressure. The NO_2 conversion was 86% and the formation ratios of N_2, O_2, and NO were 32, 75, and 22%, respectively, at a low NO_2 concentration of 200 ppm. The lower NO yield than that predicted from simple $NO_2 \rightarrow NO + O$ photolysis was explained as the second absorption of 193-nm light by NO ($X^2\Pi{:}v'' > 0$) followed by N + O predissociation and subsequent secondary reactions leading to N_2 and O_2.

We have recently initiated development of a photochemical method as a new promising removal method of NO_x at atmospheric pressure. An advantage of photochemical method is that more selective decomposition is possible than electric discharge method, where energetic electrons are main energy carrier. We have recently succeeded in efficient decomposition of N_2O into N_2 and O_2 by using 193-nm ArF excimer laser in N_2 and air at atmospheric pressure.[1] In the present study, decomposition of NO_2 by 193-nm laser was investigated. We have found for the first time that the product distribution in ArF laser photolysis of NO_2 strongly depends on the concentration of NO_2 and that the NO yield can be greatly suppressed at a low NO_2 concentration of 200 ppm.

N_2O photolysis chamber used in this study was identical to that reported previously[1] except for the use of higher sensitive analytical systems of products. Light from an unfocused ArF excimer laser (Lambda Physik, COMPex102) was used to decompose NO_2 at a room temperature. The laser pulses had a duration of 15 ns and delivered an output energy of 80 mJ per pulse at a repletion rate of 5 Hz. All experiments were carried out in a closed batch system. The total pressure was kept at atmospheric pressure and the NO_2 concentration diluted in N_2 was 200 ppm or 5% (v/v).

After 10–180-s laser irradiation, products were analyzed by using HORIBA gas analysis system (FG-100) equipped with an FTIR spectrometer and ANELVA gas analysis system (M-200GA-DTS) equipped with a quadrupole mass spectrometer. We determined the NO_2 conversion, $1\text{-}[NO_2]/[NO_2]_0$, and the formation ratios of N_2, O_2, and NO, defined as $[N_2]/[NO_2]_0$, $[O_2]/[NO_2]_0$, and $[NO]/[NO_2]_0$, respectively, from gas analyses. Here, $[NO_2]_0$ is an initial concentration of NO_2.

Figure 1 shows the dependence of NO_2 conversion and the formation ratios of N_2, O_2, and NO on the irradiation time of ArF laser at a NO_2 concentration of 200 ppm. The NO_2 conversion and the formation ratios of N_2, O_2, and NO increase to 83, 31, 72, and 21%, respectively, in the 0–90 s range and level off above that. The maximum conversion of NO_2 is 86% and the maximum formation ratios of N_2, O_2, and NO are 32, 75, and 22% at 180 s, respectively.

The observed data are compared with calculated values from a kinetic model, which was similar to that used for the decomposition of N_2O by 193-nm laser light.[1] Four photolysis processes and ten two-body and six three-body reactions are taken into account in the simulation.[2] Among them, 11 major photolysis and subsequent reaction processes are given in Table 1. Photolysis of NO_2 by 193-nm ArF laser starts from process (1) leading to $NO + O(^3P,^1D)$ with a large absorption cross section.

The observed NO_2 conversion below 90 s is higher than calculated values, while it is lower than that in the 90–180 s region. It should be noted that there are significant discrepancies between the observed and calculated values for the formation ratios of N_2, O_2, and NO. According to the model calculation, the formation ratio of NO is nearly equal to the NO_2 conversion and no N_2 formation is expected. This is explained by the fact that the major reaction pathway of NO_2 under 193-nm laser light is simple photolysis of NO_2 into $NO + O(^3P,^1D)$ followed by reactions of $O(^3P,^1D)$ atoms with NO_2 and NO.

When NO_2 in a high concentration of 5% was decomposed by 193-nm ArF laser, NO_2 conversion was only 27%, and the formation ratios of N_2, O_2, and NO were 3, 16, and 21%, respectively, after laser irradiation for 30 min. These results indicate that the branching ratio of N_2 decreases, while that of NO increases and it is close to the NO_2 conversion. This result is consistent with the above simple decomposition model. The low conversion at the high NO_2 concentration is attributed to the contribution of oxidation of NO via processes (5) and (9).

An outstanding finding of this study that the decomposition of NO_2 under 193-nm ArF laser depends strongly on the NO_2

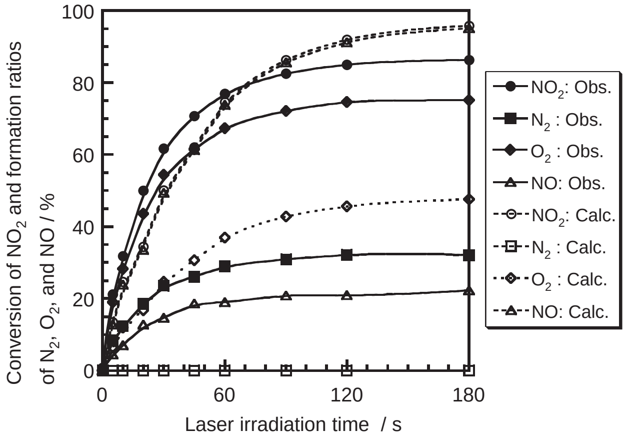

Figure 1. Dependence of NO_2 conversion and the formation ratios of N_2, O_2, and NO on the laser irradiation time at a NO_2 concentration of 200 ppm.

Table 1. Major photolysis and subsequent reaction processes under 193-nm ArF excimer laser irradiation

Processes	Number	Coefficients (Refs. 3–6)
$NO_2 + h\nu \rightarrow NO + O\ (^3P)$	(1a)	1.6×10^{-19}
$\rightarrow NO + O\ (^1D)$	(1b)	1.3×10^{-19}
$N_2O + h\nu \rightarrow O\ (^1D) + N_2$	(2)	8.95×10^{-20}
$O\ (^3P) + NO_2 \rightarrow NO + O_2$	(3)	6.5×10^{-12}
$O\ (^1D) + NO_2 \rightarrow NO + O_2$	(4a)	3.0×10^{-10}
$\rightarrow O\ (^3P) + NO_2$	(4b)	1.5×10^{-10}
$O\ (^3P) + NO + N_2 \rightarrow NO_2 + N_2$	(5)	1.0×10^{-31}
$O\ (^1D) + NO \rightarrow O\ (^3P) + NO$	(6a)	4.0×10^{-11}
$\rightarrow N\ (^4S) + O_2$	(6b)	1.2×10^{-10}
$O\ (^1D) + N_2 \rightarrow O\ (^3P) + N_2$	(7)	2.6×10^{-11}
$O\ (^3P) + O\ (^3P) + N_2 \rightarrow O_2 + N_2$	(8)	2.98×10^{-33}
$2NO + O_2 \rightarrow 2NO_2$	(9)	1.93×10^{-38}
$N\ (^4S) + NO \rightarrow N_2 + O\ (^3P)$	(10)	2.9×10^{-11}
$N\ (^4S) + NO_2 \rightarrow N_2O + O\ (^3P)$	(11)	1.21×10^{-11}

Units of coefficients are cm^2 $molecule^{-1}$ for (1) and (2), cm^3 $molecule^{-1}$ s^{-1} for two-body reactions and cm^6 $molecule^{-2}$ s^{-1} for three-body reactions.

concentration and that it does not follow a simple decomposition model at a low NO_2 concentration of 200 ppm. The observed formation ratios of N_2 and O_2 are much larger than calculated values, while the formation ratio of NO is much smaller than the calculated value. These results suggest that NO produced from photolysis of NO_2 is further efficiently converted into N_2 and O_2 at the low NO_2 level through some processes, which are not included in our model calculation.

It is known that NO ($X^2\Pi{:}\nu'' = 0$) molecules are selectively excited into the excited NO ($B^2\Pi{:}\nu' = 7$) states under 193-nm ArF laser excitation.[7] On the other hand, photoexcitation of NO ($X^2\Pi$) in the vibrationally excited levels gives emitting excited states of NO ($D^2\Sigma^+$, $E^2\Sigma^+$) in the photolysis study of N_2O by 193-nm ArF laser.[8] Similar NO emissions from NO ($A^2\Sigma^+$, $D^2\Sigma^+$, $E^2\Sigma^+$) have been observed by Haak and Stuhl[9] in the NO_2 photolysis by 193-nm ArF laser at the maximum energy of 150 mJ/pulse. These excited states must be also produced by second absorption of 193-nm ArF laser light by NO ($X^2\Pi{:}\nu'' > 0$), because Gong et al.[10] detected NO ($X^2\Pi{:}\nu'' =$ 1–6) after 193-nm ArF laser photolysis of NO_2 by using FTIR spectrometer. In addition to initial photolysis of NO_2, such subsequent secondary reactions as processes (3), (4a), and (6a) will provide NO ($X^2\Pi{:}\nu'' > 0$) levels. The above experimental observation and our detailed model calculation[2] lead us to conclude that some NO ($X^2\Pi{:}\nu'' > 0$) molecules produced from photolysis (1a) and (1b) absorb a second photon within a laser pulse width of 15 ns. On the other hand, those produced from (3), (4a), and (6a) absorb subsequent laser photons, because collisional relaxation of NO ($X^2\Pi{:}\nu'' > 0$) by N_2 is slow at a low NO_2 concentration.[11] For example, V–V transfer rate of NO ($X^2\Pi{:}\nu'' = 1$) for N_2 is slower than that for NO_2 by a factor of 2300.[11] After a second absorption of 193-nm ArF laser light, the NO ($X^2\Pi{:}\nu'' > 0$) molecules are excited to high energy states above dissociation limit of N–O.

$$\begin{aligned} &NO\ (X^2\Pi{:}\nu'' > 0) + h\nu\ (193\,nm) \\ &\quad \rightarrow NO\ (A^2\Sigma^+, D^2\Sigma^+, E^2\Sigma^+) \end{aligned} \tag{12}$$

Not only radiative process, but also predissociation into N + O will occur significantly in such high states, as known for high vibrationally excited states of NO (A, C, D) states.[12,13]

$$NO\ (A, D, E) \rightarrow NO\ (X, A) + h\nu \quad \text{(radiative decay)} \tag{13a}$$

$$\rightarrow N + O \quad \text{(predissociation)} \tag{13b}$$

Subsequent fast reactions of N atoms with NO and NO_2, (10) and (11), give N_2 and N_2O. N_2O is selectively decomposed into $N_2 + O\ (^1D)$ by 193-nm light.[1,8] On the basis of above facts, it is reasonable to assume that efficient decompostion of NO and NO_2 into N_2 and O_2 observed here at the low NO_2 concentration results fom the N (^4S) producton via predissociation (13b).

It is known that vibratinal relaxation is fast for excited states of NO ($X{:}\nu'' > 0$) by collisions with NO_2.[11] Thus, at a high NO_2 concetration of 5%, vibrational relaxtion by collisions with NO_2 becomes significant before second laser absorption. In such a case, excitation into high-energy predissociation states becomes insignificant and the product distribution reflects simple photolysis of NO_2 into NO + O.

In summary, NO_2 photolysis at 193-nm ArF laser was studied. At a low NO_2 concentration of 200 ppm, NO_2 was decomposed into N_2, O_2, and NO. The high formation ratios of N_2 and O_2 and low formation ratio of NO than those expected from known absorption and kinetic data were explained as the second absorption of laser light by NO ($X^2\Pi{:}\nu'' > 0$) leading to N + O via predissociation. Actual NO_2 emission in the industrial process occurs at low level below 1000 ppm. Thus, the photolysis by 193-nm ArF laser is effective for the decomposition of NO_2 into N_2 and O_2. A further detailed study for NO_2 photolysis by 193-nm ArF laser in N_2 and air, including process (13b) in the model calculation, is in progress in order to obtain optimum experimental conditions for NO_2 removal.

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