

Efficient Decomposition of NO₂ into N₂ and O₂ by 193-nm ArF Laser in N₂ Atmosphere

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Decomposition of NO₂ in N₂ by 193-nm ArF excimer laser was studied at atmospheric pressure. The NO₂ conversion was 86% and the formation ratios of N₂, O₂, and NO were 32, 75, and 22%, respectively, at a low NO₂ concentration of 200 ppm. The lower NO yield than that predicted from simple NO₂ → 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 N₂ and O₂.

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 N₂O into N₂ and O₂ by using 193-nm ArF excimer laser in N₂ and air at atmospheric pressure.¹ In the present study, decomposition of NO₂ by 193-nm laser was investigated. We have found for the first time that the product distribution in ArF laser photolysis of NO₂ strongly depends on the concentration of NO₂ and that the NO yield can be greatly suppressed at a low NO₂ concentration of 200 ppm.

N₂O photolysis chamber used in this study was identical to that reported previously¹ 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 NO₂ 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 repetition rate of 5 Hz. All experiments were carried out in a closed batch system. The total pressure was kept at atmospheric pressure and the NO₂ concentration diluted in N₂ 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 NO₂ conversion, $1 - [\text{NO}_2]/[\text{NO}_2]_0$, and the formation ratios of N₂, O₂, and NO, defined as $[\text{N}_2]/[\text{NO}_2]_0$, $[\text{O}_2]/[\text{NO}_2]_0$, and $[\text{NO}]/[\text{NO}_2]_0$, respectively, from gas analyses. Here, $[\text{NO}_2]_0$ is an initial concentration of NO₂.

Figure 1 shows the dependence of NO₂ conversion and the formation ratios of N₂, O₂, and NO on the irradiation time of ArF laser at a NO₂ concentration of 200 ppm. The NO₂ conversion and the formation ratios of N₂, O₂, 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 NO₂ is 86% and the maximum formation ratios of N₂, O₂, 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 N₂O 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 NO₂ by 193-nm ArF laser starts from process (1) leading to NO + O(³P, ¹D) with a large absorption cross section.

The observed NO₂ 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 N₂, O₂, and NO. According to the model calculation, the formation ratio of NO is nearly equal to the NO₂ conversion and no N₂ formation is expected. This is explained by the fact that the major reaction pathway of NO₂ under 193-nm laser light is simple photolysis of NO₂ into NO + O(³P, ¹D) followed by reactions of O(³P, ¹D) atoms with NO₂ and NO.

When NO₂ in a high concentration of 5% was decomposed by 193-nm ArF laser, NO₂ conversion was only 27%, and the formation ratios of N₂, O₂, and NO were 3, 16, and 21%, respectively, after laser irradiation for 30 min. These results indicate that the branching ratio of N₂ decreases, while that of NO increases and it is close to the NO₂ conversion. This result is consistent with the above simple decomposition model. The low conversion at the high NO₂ 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 NO₂ under 193-nm ArF laser depends strongly on the NO₂

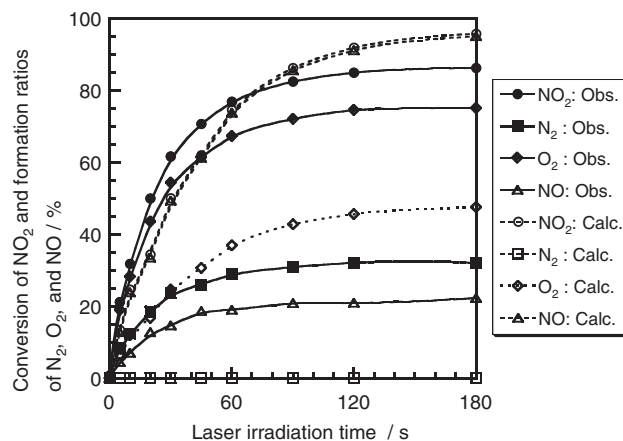


Figure 1. Dependence of NO₂ conversion and the formation ratios of N₂, O₂, and NO on the laser irradiation time at a NO₂ concentration of 200 ppm.

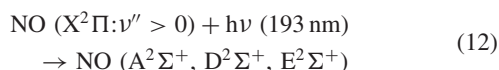
Table 1. Major photolysis and subsequent reaction processes under 193-nm ArF excimer laser irradiation

Processes	Number	Coefficients (Refs. 3–6)
$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} (^3\text{P})$	(1a)	1.6×10^{-19}
$\rightarrow \text{NO} + \text{O} (^1\text{D})$	(1b)	1.3×10^{-19}
$\text{N}_2\text{O} + h\nu \rightarrow \text{O} (^1\text{D}) + \text{N}_2$	(2)	8.95×10^{-20}
$\text{O} (^3\text{P}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	(3)	6.5×10^{-12}
$\text{O} (^1\text{D}) + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	(4a)	3.0×10^{-10}
$\rightarrow \text{O} (^3\text{P}) + \text{NO}_2$	(4b)	1.5×10^{-10}
$\text{O} (^3\text{P}) + \text{NO} + \text{N}_2 \rightarrow \text{NO}_2 + \text{N}_2$	(5)	1.0×10^{-31}
$\text{O} (^1\text{D}) + \text{NO} \rightarrow \text{O} (^3\text{P}) + \text{NO}$	(6a)	4.0×10^{-11}
$\rightarrow \text{N} (^4\text{S}) + \text{O}_2$	(6b)	1.2×10^{-10}
$\text{O} (^1\text{D}) + \text{N}_2 \rightarrow \text{O} (^3\text{P}) + \text{N}_2$	(7)	2.6×10^{-11}
$\text{O} (^3\text{P}) + \text{O} (^3\text{P}) + \text{N}_2 \rightarrow \text{O}_2 + \text{N}_2$	(8)	2.98×10^{-33}
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	(9)	1.93×10^{-38}
$\text{N} (^4\text{S}) + \text{NO} \rightarrow \text{N}_2 + \text{O} (^3\text{P})$	(10)	2.9×10^{-11}
$\text{N} (^4\text{S}) + \text{NO}_2 \rightarrow \text{N}_2\text{O} + \text{O} (^3\text{P})$	(11)	1.21×10^{-11}

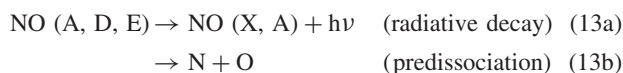
Units of coefficients are $\text{cm}^2 \text{ molecule}^{-1}$ for (1) and (2), $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for two-body reactions and $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ for three-body reactions.

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 ($X^2\Pi; v'' = 0$) molecules are selectively excited into the excited NO ($B^2\Pi; v' = 7$) 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 Stuhl⁹ 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 ($X^2\Pi; v'' > 0$), because Gong et al.¹⁰ detected NO ($X^2\Pi; v'' = 1-6$) 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 ($X^2\Pi; v'' > 0$) levels. The above experimental observation and our detailed model calculation² lead us to conclude that some NO ($X^2\Pi; v'' > 0$) 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 ($X^2\Pi; v'' > 0$) by N_2 is slow at a low NO_2 concentration.¹¹ For example, V–V transfer rate of NO ($X^2\Pi; v'' = 1$) 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 ($X^2\Pi; v'' > 0$) molecules are excited to high energy states above dissociation limit of N–O.



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}



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 $\text{N}_2 + \text{O} (^1\text{D})$ by 193-nm light.^{1,8} On the basis of above facts, it is reasonable to assume that efficient decomposition of NO and NO_2 into N_2 and O_2 observed here at the low NO_2 concentration results from the N (^4S) producton via predissociation (13b).

It is known that vibrational relaxation is fast for excited states of NO ($X; v'' > 0$) by collisions with NO_2 .¹¹ Thus, at a high NO_2 concentration of 5%, vibrational relaxation 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 ($X^2\Pi; v'' > 0$) 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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