Water Aerosol Formation upon Irradiation of Air Using KrF Laser at 248 nm

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We report water aerosol formation upon irradiation of wet air with a KrF laser at 248 nm. It occurred at temperatures ranging from 0 to 50 °C and at relative humidity values from ca. 10% to 100%. Aerosols were detected either by light scattering or by differential mobility analyses, and particle growth from 10 nm to sub-micrometers was observed. Photodissociation of oxygen was proposed as the initial step of the reactions leading to formation of the final stable molecule of hydrogen peroxide as a nucleus with a low vapor pressure. Simulations of the chemical kinetics by considering wet air revealed that the amount of the final product could be controlled by laser operational conditions such as laser repetition rates and pulse energies. KrF laser light can reach a few kilometers in the atmosphere owing to a small absorption cross section of oxygen and yet can produce water aerosol.

Water condensation is one of the most important issues in atmospheric science and human life. Under atmospheric conditions, a low-vapor pressure material as a nucleus for condensation is often produced by complicated photochemical and thermochemical reaction chains.¹ Much effort has been devoted to the artificial control of precipitation through techniques such as spraying chemicals (e.g., silver iodide) or dropping coolant materials like dry ice into the air.

We previously reported the photochemical formation of water droplets/aerosols in response to the irradiation of wet air by UV light using either a low pressure Hg lamp (185 nm) or an ArF laser (193 nm).^{2,3} Additionally, we proposed a reaction mechanism for this water condensation. Specifically, the chemical reaction started by photodissociation of oxygen and further sequential reactions produced hydrogen peroxide (H₂O₂) as a final stable product with a low vapor pressure, and nucleation occurred. The chemical intermediates hydroperoxy radical (HO₂) and ozone (O₃) were observed in situ and were successfully simulated by the chemical kinetic model.²

In the 1970s, photoinduced nucleation of water vapor with helium or hydrogen as a carrier gas was reported following continuous VUV or UV irradiation;^{4,5} however, this did not receive considerable attention from atmospheric scientists. More recently, water droplet formation in both the laboratory and atmospheric air was reported following application of ionized filaments generated by intense ultrafast laser pulses.^{6,7}

Here, we report water-aerosol formation upon irradiation of air with a KrF laser at 248 nm. It was observed in the laboratory by light scattering and by differential mobility analyses under very wide temperature and relative humidity (RH) conditions. Simulation of the chemical kinetics revealed that formation of the final product, hydrogen peroxide, could be controlled by the operating conditions of the laser, namely pulse energies and repetition rates. The wavelength of 248 nm is much longer than that used in our previous study. It is worth noting that at this wavelength, a laser beam can reach long distances into the air owing to the small absorption cross section of oxygen and yet can produce aerosols if there is no scattering by other materials such as dust or clouds.

Experimental

Two types of reaction vessels were made; a flow vessel for particle-velocity measurements and a batch cell for laser scattering experiment. The former was a $55 \text{ cm} \times 31 \text{ cm} \times$ 31 cm (53 L) box with two quartz windows for laser incident and exit directions. The batch cell was a hollow quartz tube with a diameter of 15 cm and height of 15 cm (2.6 L). Particle formation was observed by light scattering with a laser pointer (green light), which was stretched to 2D by a cylindrical lens. For excitation, we used a pulsed KrF laser (Lambda Physik, Complex 110F or Coherent, LPX Pro 210) (0.05–0.8 J/pulse at 248 nm; laser cross section, 1.2 cm \times 2.3 cm) at 5–100 Hz without focusing.

Particle-size distributions (10–1000 nm in diameter) were analyzed using a differential mobility analyzer (DMA) (MSP, 1000XP). The peak size-distribution values were given in the $dN/d \log D_p$ value of size distribution (D_p is the particle diameter and N is the particle number cm⁻³). The laboratory air before laser irradiation was much below 10³ cm⁻³ after passing through two water bubblers and a 10-cm tube filled with wet fibers. Based on the measurement time of the particle-size distribution histogram, the system has a time resolution of about 60 s.

To check for possible effects of laser ablation of the quartz windows and formation of small particles, we removed them



Figure 1. Particle size distribution and dynamics upon excitation of air (24 °C, relative humidity of 28%) by KrF laser (0.4 J/pulse, 10 Hz, 30 s) observed by the differential mobility analyses (DMA). a) Observed distribution at 0 min (right after the termination of laser irradiation), b) a distribution at 15 min (ordinate is magnified by 5 times), and c) a distribution at 29 min (ordinate is magnified by 20 times).



Figure 2. Particle size distribution and dynamics upon excitation of air (50 °C, relative humidity of 12%) by KrF laser (0.4 J/pulse, 10 Hz, 30 s) observed by DMA. a) Observed distribution at 0 min (right after laser irradiation), b) a distribution at 3 min (ordinate is magnified by 2 times), and c) a distribution at 23 min (ordinate is magnified by 25 times).

and placed holes in the wall of the reaction vessel so that the laser beam could pass through without surface interaction. The results of particle-size distribution by the DMA measurement were the same with or without quartz windows. Thus, most of the experiments were performed using windows.

Ambient air was used for most of the experiments. The temperature and relative humidity were measured using a semiconductor detector (SATO, SK-LHII α -2 and T&D, Thermo Recorder TR-72U).

Results

Figure 1 shows the particle-size distributions in the reaction vessel at 24 °C with an RH of 28% upon excitation with a 0.4 J laser pulse at a repetition rate of 10 Hz for 30 s. The obtained initial peak of distribution gave approximately 1×10^6 in the $dN/d \log D_p$ value, particles cm⁻³, with a peak diameter of ≤ 20 nm (Figure 1a). Small particle growth with time was observed at the peak position, and some larger particles of ≥ 100 nm were detected (Figures 1b and 1c). The peak number decreased with time as a result of diffusion to the cell wall and evaporation as well as growth to larger particles.

Figure 2 shows the results obtained under extreme conditions of high temperature and low RH (50 °C and RH 12%). Excitation at 0.4 J/pulse, 10 Hz, and 30 s gave particle numbers as large as 4×10^6 in the $dN/d \log D_p$ value with a peak distribution of ca. 10 nm in diameter. After 3 min, the particles grew to ca. 30 nm with an approximately threefold decrease in the peak height (Figure 2b). At 23 min particle size had further increased (ca. 40 nm), and some distributions toward larger particles sizes (\geq 100 nm) were again recognized (Figure 2c).

Figure 3 shows the light scattering observed at right angles from aerosols produced upon excitation at 0.04 J/pulse and 20 Hz for 25 s. The sample chamber was maintained at 22 °C and RH 88% during analysis. Light scattering was only observed on the laser incident side (right) because penetration of light further to the left was limited as a result of scattering. According to the Mie light-scattering theory, the scattering intensity of small particles by green light ($\lambda = 0.5 \,\mu$ m) peaks at 1 µm in diameter and then gradually decreases as the diameters decrease, besides the contributions of larger particles.⁸ In the present study, particles of several tenths of a micron contributed to the scattering. Such particles are certainly reflected in the DMA size-distribution measurements shown in Figures 1b, 1c, 2b, and 2c.

Discussion

Reaction Mechanism. In a previous study, we proposed a reaction scheme based on observation of the reaction intermediates and final product in accordance with excellent agreements of the results of chemical kinetics simulation.² This scheme is briefly described in five major steps here.



Figure 3. Light scattering of aerosol observed at right angles when sample chamber was at 22 °C, relative humidity of 88%. KrF laser was operated at 40 mJ 20 Hz for 25 s. The green laser-pointer light could penetrate only the right half of the incident direction due to scattering. The horizontal frame of the picture is 10 cm.

The photochemical reaction of oxygen induces ozone via the following two reactions:^{1,8,9}

$$O_2 + h\nu \to 2O(^3P) \tag{1}$$

$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
⁽²⁾

Ozone has a very strong absorption at 248 nm and dissociates photochemically to an active oxygen atom $O(^{1}D)$ and oxygen molecule as follows:

$$O_3 + h\nu \to O_2 + O(^1D) \tag{3}$$

This atom efficiently reacts with H₂O to produce OH radicals:

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
(4)

The OH then reacts with ozone to produce a radical HO₂:

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{5}$$

Finally, two HO₂ radicals form hydrogen peroxide (H_2O_2) and O_2 :

$$\mathrm{HO}_2 + \mathrm{HO}_2 \to \mathrm{H}_2\mathrm{O}_2 + \mathrm{O}_2 \tag{6}$$

We apply this model to the present experiment with proper considerations of the properties of KrF laser light and oxygen absorption. Table 1 shows the 25 associated elementary reactions that were used in the present simulation. These include radical quenching reactions, association of radicals with water, and photochemical reactions of intermediates. Hydrogen peroxide (H₂O₂) is a stable hygroscopic molecule, and its vapor pressure is nearly two orders of magnitude smaller than that of water. Therefore, we proposed that it has a high capture rate of water molecules and becomes a nucleus for the formation of aerosols.² In the present study we did not simulate particle formation induced by the gas-phase chemical reactions. Direct connection of the gas-phase reaction and particle formation would be a future problem.

The optical absorption and photochemistry of oxygen at 248 nm occurs for several reasons. The wavelength of 248 nm is in a tail of the absorption band of the Herzberg I ($A^3\Sigma_u^+ - X^3\Sigma_g^-$) system. There is currently no complete consensus

Table 1. Reactions Included in the Calculation

$O_2 + h\nu \rightarrow O + O$	$O + O_3 \rightarrow O_2 + O_2$
$O + O_2 \rightarrow O_3$	$O(^{1}D) + O_{2} \rightarrow O + O_{2}$
$O_3 + h\nu \rightarrow O$	$O(^{1}D) + O_{3} \rightarrow O_{2} + O_{2}$
$O_3 + h\nu \rightarrow O(^1D)$	$O(^{1}D) + O_{3} \rightarrow O_{2} + O + O$
$\rm O + OH \rightarrow O_2 + H$	$O(^{1}D) + H_{2}O \rightarrow OH + OH$
$H + O_2 \rightarrow HO_2$	$O + HO_2 \rightarrow OH + O_2$
$O_3 + OH \rightarrow HO_2 + O_2$	$OH + OH \rightarrow H_2O + O$
$\rm OH + OH + M \rightarrow H_2O_2 + M$	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$OH + HO_2 \rightarrow H_2O + O_2$	$H_2O_2 + h\nu \rightarrow OH + OH$
$OH + H_2O_2 \rightarrow H_2O + HO_2$	$\mathrm{HO}_2 + \mathrm{O}_3 \rightarrow \mathrm{OH} + \mathrm{O}_2 + \mathrm{O}_2$
$H + O_3 \rightarrow OH + O_2$	$HO_2 + h\nu \rightarrow OH + O(^1D)$
$HO_2 + H_2O \rightarrow HO_2-H_2O$	$HO_2 + HO_2 - H_2O_2$
	\rightarrow complex
$HO_2-H_2O + HO_2-H_2O_2$	
\rightarrow complex	

regarding the value of the absorption cross section at this wavelength, but it will be between 3×10^{-24} and 2×10^{-25} cm².¹⁰ Since the experimental data were scattered, we adopted an absorption cross section of 1×10^{-24} cm² for the following chemical kinetic simulation.

Ozone has a very strong absorption with a cross section of 1×10^{-17} cm² at 248 nm. If the concentration of ozone is 10 ppb, the absorbance will be ca. 0.24 at long distances such as 1 km (1 atm, 300 K). In principle the reactions starting from reactions (1) and (3) may coexist in the present scheme for this long distance, about a few kilometers. In the laboratory, the absorbance is negligible owing to the short distances in the reaction chamber. We observed experimentally that very high concentrations (about 1 ppm) of ozone were needed to detect particles.¹⁴

The dissociation threshold of oxygen has long been known to be 242.4 nm.⁹ However, the formation of ozone by irradiation of oxygen at 248 nm has recently been reported. The possible mechanism for absorption and reaction at this wavelength has been discussed on the basis of a hot band absorption and absorption by oxygen dimer.^{15,16}

Let us compare the mechanism identified in the present study with that observed in an investigation that employed a femtosecond laser filament.^{6,7} In the present study, the onephoton dissociation of oxygen and ozone, and consecutive radical reactions produced the final product as a nucleus. The single-photon nature is even more evident when the fact that irradiation with a very weak steady-state mercury lamp (a pentype lamp with only a few watts electric input) was sufficient to produce particles is considered.² This mechanism is very different from that obtained using an intense ultrafast filament laser beam. In the present experiment, the laser intensity was estimated to be $1 \times 10^6 \,\mathrm{W \, cm^{-2}}$ (0.1 J/pulse, pulse duration 25 ns). On the other hand, in the femtosecond filament experiment, the laser intensity was $5 \times 10^{15} \,\mathrm{W \, cm^{-2.7}}$ This significant difference of more than nine orders of magnitude of the peak power induced the alternative reaction mechanism. It was proposed that ionization as well as dissociation of oxygen and nitrogen occurred during high intensity reactions and that the subsequent dark reactions lead to the formation of nitric acid as a nucleus.⁷

Table 2. Quantum Yield of Photochemical Reactions

Reaction	Absorption cross section/cm ² at 248 nm	Quantum yield
$O_2 + h\nu \rightarrow 2O(^{3}P)$	1.0×10^{-24}	1.0
$O_3 + h\nu \rightarrow O(^{3}P)$	$1.0 imes 10^{-17}$	0.1
$O_3 + h\nu \rightarrow O(^1D)$	$1.0 imes 10^{-17}$	0.9
$HO_2 + h\nu \rightarrow OH + O(^1D)$	3.0×10^{-19}	1.0
$H_2O_2 + h\nu \rightarrow 2OH$	7.0×10^{-20}	1.0

Simulation of Reactions. In the preceding study, we simulated the reaction kinetics according to the general scheme described above and obtained an excellent match between the calculated and observed values of the reaction intermediates.² Table 1 provides the reactions used in the present scheme. The kinetic parameters used for simulation are listed in the references.^{2,17–19} The CHEMKIN II program was adopted to solve the differential eqs.²⁰ We also considered the complex formation of intermediate HO₂ radicals and water (Table 1).¹⁸

In the present scheme, five photochemical reactions were taken into account for the simulation (Table 2). The kinetic equation was as follows:

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = I\sigma\phi[M] \tag{7}$$

Here, Y_i is the molar fraction of *i*-th chemical species, *I* is the photon flux, σ is the absorption cross section, ϕ is the quantum yield, and [*M*] is the concentration of photochemically active molecules. The photon flux was 1.3×10^{17} per pulse at 0.1 J with a pulse width of 25 ns. The σ and ϕ values used are listed in Table 2. We examine the effect of operational conditions at idealized conditions of using pure air and obtained the effect of laser power and pulse repetition rates.

Figures 4a and 4b show the simulated time courses of the reaction intermediates and the final products at rather extremely different conditions of temperature, RH, laser power, and repetition rates. The ordinate in log scale indicates the mole fractions of the reaction intermediates and final product. Nitrogen, oxygen, and water are not shown in this scale. Figure 4a is an example of low pulse-repetition rate and low RH, namely, RH 20% and high temperature 318 K conditions with excitation at 0.4 J/pulse, 10 Hz for 30 s. The dynamics of O₃, H₂O₂, OH, HO₂, $O(^{3}P)$, and $O(^{1}D)$ are shown. These atomic oxygens are formed and consumed very rapidly. The HO2 radicals decayed relatively slowly, while the OH radicals decayed much quicker upon termination of irradiation, but O₃ and H₂O₂ remained as stable species. Although the direct comparison between the gasphase simulation data and the results of DMA experiment is difficult, we can make some qualitative arguments. At such low RH conditions (ca. 20%, Figure 4a) the production of H_2O_2 is rather low, and we usually observe the peak particle number is limited and the peak particle diameter stops growing at about 20-30 nm (Figure 1). Figure 4b shows the results of high-energy of 1 J and high-repetition rate irradiation of 100 Hz for short excitation time of 5 s with an ordinary temperature of 293 K and RH of 100%. Under these conditions, it is interesting to note that the obtained mole fraction of H₂O₂ became greater than O₃ and the rise time of hydrogen peroxide and ozone also become as fast as a couple of seconds.



Figure 4. Simulation of reactions upon excitation of air at 248 nm. The ordinate in log scale indicates mole fractions of species. a) Irradiation at 0.4 J 10 Hz for 30 s with relative humidity of 20%, 45 °C, b) at 1 J 100 Hz for 5 s with relative humidity of 100%, 27 °C.

To compare the effects of the pulse energy and repetition rate on production, the total input energy should be kept equivalent (Figure 5, left). Therefore, we examined the formation of H₂O₂ and O₃ by balancing the repetition rate and irradiation time, namely, 10 Hz, 50 s and 100 Hz, 5 s, at each laser energy level. The results revealed that the laser repetition rate had a significant effect on the formation process. The molar fraction of H₂O₂ increased much more rapidly under high repetition-rate conditions and overcame the O₃ molar fraction (Figure 5, left (a)). Conversely, at low repetition rates, H_2O_2 never exceeded O3 under the given conditions (Figure 5, left (b)). Figure 5 right more directly shows the effects of the pulse repetition rate. The molar fraction of H₂O₂ exceeded that of O₃ at higher repetition rates. Taken together, the results presented here indicate that photoproducts are controllable by irradiation conditions such as pulse energies and pulse repetition rates. The significant effects of the repetition rates of laser pulses on the product ratio are primarily a result of the intermediate reaction HO₂ + $h\nu \rightarrow$ OH + O(¹D) (Table 1). The photon is used to recreate OH and O(¹D) and enhance the final product formation at the middle of the scheme. If we compare the ratio of hydrogen peroxide formation upon the ArF-laser to



Figure 5. Comparison of pulse energy and repetition rate on formation of H_2O_2 and O_3 at 300 K. Left: Pulse energy (J) dependence (a) at high repetition rate (100 Hz) with a short irradiation time 5 s (total 500 laser shots). (b) at low repetition rate (10 Hz) with a long irradiation time 50 s (total 500 laser shots). Right: Repetition rate dependence on product formation at pulse energy of 0.1 J/pulse.

KrF-laser excitation, the former is greater by about two orders of magnitude. This can be explained by the ratio of the products of absorption cross sections of oxygen and ozone at two different wavelengths. The reach of ArF light in the atmosphere, however, is significantly shorter than that of KrF light due to the difference of absorption cross section of oxygen.

Concluding Remarks

We have demonstrated that water aerosols were formed in air upon irradiation by light from a KrF laser at 248 nm. They were observed either by light scattering or by the differentialmobility analyses, and the time courses of particle growth were measured. Photodissociation of oxygen was proposed to be the initial step in the reactions leading to formation of low-vapor pressure substances as nucleus. Particles were produced under a wide range of relative humidity (12-100%) and temperature (0-50 °C). Simulation of the chemical kinetics showed that production of the final product and intermediates could be controlled by the operational conditions of the laser-pulse energies and repetition rates. We indicated that the KrF laser light can reach a few kilometers into the air and yet produce aerosols. The present experiment may offer an opportunity to apply this method to achieve local *albedo* control, namely a control of reflectivity of the earth surface, and hence address the problem of global warming associated with a negative radiative forcing of water particles.

The authors appreciate valuable discussions with the late Professor N. Fukuta of the University of Utah, Professor M. Kawasaki of Kyoto University, and Dr. M. Murakami of Meteorological Research Institute as well as encouragement by Dr. K. Akihama of Toyota Central R & D Laboratories. We also thank Mr. Y. Hattori of TCRDL, Professor T. Taira and Mr. T. Yamanaka of the Institute for Molecular Science for their assistance with the experiments.

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