Effect of humidity on the production of ozone and other radicals by low-pressure mercury lamps

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Abstract

An ultraviolet (UV) process using a low-pressure mercury lamp is affected by ambient humidity. It is due to strong influence of humidity on the production of ozone and other radicals by the UV light. In this paper, a photochemical reaction model under the irradiation of a low-pressure mercury lamp is developed, and the effect of humidity on the production of ozone and other radicals [O, O(¹D), O₂(^aΔ_g), O₂(^bΣ_g⁺), OH, HO₂, H, and H₂O₂] by a low-pressure mercury lamp is discussed using the reaction model. The validity of the reaction model is confirmed by comparing the ozone densities calculated using the model with experimentally measured ozone densities, and they showed good agreement. The reaction model shows that the ozone density decreases with increasing humidity for three reasons: (i) attenuation of 185 nm light due to absorption by H₂O, leading to a decreased O atom production by O₂ + hν(185 nm) → O + O which is required to produce ozone by O + O₂ + M → O₃ + M; (ii) ozone destruction by O₃ + hν(254 nm) → O(¹D) + O₂(^aΔ_g), where the resulting O(¹D) partly reacts with H₂O before converting back to O₃ after quenching to O; and (iii) an ozone destruction cycle OH + O₃ → HO₂ + O₂ and HO₂ + O₃ → OH + 2O₂. The effect of humidity on the densities of other radicals is also discussed

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using the reaction model.

Keywords: low-pressure mercury lamp, humidity, ozone density, radicals, reaction model

1. Introduction

An ultraviolet (UV) process using a low-pressure mercury lamp is widely used for surface treatment, sterilization, and water treatment. The UV process often utilizes ozone produced by the UV light. In the “UV/O₃ process”, it is empirically known that an increase in humidity reduces the ozone density, which can lower the effect of the UV/O₃ process. This is partially caused by the catalytic ozone destruction cycle involving OH and HO₂ [1, 2]:

The production of OH and HO₂ by a low-pressure mercury lamp was experimentally confirmed using light absorption measurements [1, 3].

In contrast, some UV processes are enhanced by humidification, such as those that use radicals produced in a humid environment (e.g., OH and HO₂). The decomposition of volatile organic compounds (VOCs) using a low-pressure mercury lamp is enhanced by humidity because OH radicals efficiently decompose VOCs [4, 5]. Our group used a low-pressure mercury lamp for the surface treatment of dye-sensitized solar cells and found that the effect of using the lamp is improved by humidification [6]. Furthermore, some UV processes are not significantly influenced by humidity [7, 8]. To understand the effects of humidity on the UV processes, the photochemical reactions occurring under the irradiation of a low-pressure mercury lamp should be investigated.

In this paper, a photochemical reaction model under the irradiation of a low-pressure mercury lamp is developed, and the effect of humidity on the densities of ozone and other radicals [O, O(¹D), O₂(^aΔ_g), O₂(^bΣ_g⁺), OH, HO₂, H, and H₂O₂] produced by the lamp is examined using the reaction model. After the reaction model is described in the next section, the validity of the reaction model is confirmed by comparing the ozone densities calculated using the model with experimentally measured ozone densities. Then, the effect of humidity on the production of ozone and other radicals is dis-

cussed using the reaction model. Particularly, the decrease in ozone density with increasing humidity is discussed in detail.

2. Reaction model

The reaction model under the irradiation of a low-pressure mercury lamp is described in this section. The low-pressure mercury lamp emits radiation at wavelengths of 185 nm and 254 nm. The 185 nm radiation dissociates O_2 into $O(^3P)$:

$O(^3P)$ reacts with O_2 to produce O_3 :

O_3 is dissociated by the 254 nm radiation to produce $O(^1D)$, $O(^3P)$, $O_2(a^1\Delta_g)$, and $O_2(v)$:

where $\phi_3 = 0.9$ [9].

In addition, the 185 nm radiation dissociates H_2O :

Thus, the UV radiation from the low-pressure mercury lamp produces $O(^3P)$, $O(^1D)$, $O_2(a)$, O_3 , OH , and H . These radicals react as shown in reactions R5–R32, which are listed in Table 1 along with their rate coefficients at 298 K. The absorption cross-sections and the rate coefficients of reactions R1–R4 are also shown in Table 1.

The cross-section of R1, σ_1 , is uncertain. It was previously reported that σ_1 of the low-pressure mercury lamp depends on the O_2 column, with values ranging from 0.6×10^{-20} to $1.2 \times 10^{-20} \text{ cm}^2$ [16]. In another study [17], the range of values for σ_1 were reported to be 1.4×10^{-20} to $1.8 \times 10^{-20} \text{ cm}^2$. In our experiment, σ_1 is measured using our lamp, as shown in the next section, and is estimated to be $1.2 \times 10^{-20} \text{ cm}^2$. This σ_1 value is used in our model.

Table 1: Rate coefficients (k [cm³/s]) at 298 K and cross-sections (σ [cm²]) of the reactions considered in the reaction model. The ratios written in R7, R10, R13–R16, and R22 are branching ratios.

	Reactions	k and σ	Refs.
(R1)	$\text{O}_2 + h\nu(185 \text{ nm}) \rightarrow \text{O} + \text{O}$	^{a)} $\sigma_1 = 1.5 \times 10^{-20}$	—
(R2)	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	$k_2 = 6.0 \times 10^{-34}[\text{O}_2]$ $= 5.6 \times 10^{-34}[\text{N}_2]$	[10]
(R3)	$\text{O}_3 + h\nu(254 \text{ nm}) \rightarrow \text{products}$	$\sigma_3 = 1.16 \times 10^{-17}$	[11]
(R4)	$\text{H}_2\text{O} + h\nu(185 \text{ nm}) \rightarrow \text{H} + \text{OH}$	$\sigma_4 = 7.14 \times 10^{-20}$	[10]
(R5)	$\text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2$	$k_5 = 8.0 \times 10^{-15}$	[10]
(R6)	$\text{O}(^1D) + \text{N}_2 \rightarrow \text{O} + \text{N}_2$	$k_6 = 2.6 \times 10^{-11}$	[12]
(R7)	$\text{O}(^1D) + \text{O}_2 \rightarrow \text{O} + \text{O}_2(X, a, b)$	$k_7 = 4.0 \times 10^{-11}$ (15:5:80)	[10]
(R8)	$\text{O}(^1D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$k_8 = 2.2 \times 10^{-10}$	[10]
(R9)	$\text{O}(^1D) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2, \text{O}_2 + \text{O} + \text{O}$	$k_9 = 2.4 \times 10^{-10}$ (1:1)	[10]
(R10)	$\text{O}_2(a) + \text{O}_2 \rightarrow \text{O}_2 + \text{O}_2$	$k_{10} = 1.6 \times 10^{-18}$	[10]
(R11)	$\text{O}_2(a) + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 + \text{O}$	$k_{11} = 3.8 \times 10^{-15}$	[10]
(R12)	$\text{O}_2(a) + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$k_{12} = 5 \times 10^{-18}$	[10]
(R13)	$\text{O}_2(a) + \text{O}_2(a) \rightarrow \text{O}_2(X, b) + \text{O}_2$	$k_{13} = 2.8 \times 10^{-17}$ (1:1)	[13]
(R14)	$\text{O}_2(b) + \text{N}_2 \rightarrow \text{O}_2(X, a) + \text{O}_2$	$k_{14} = 2.1 \times 10^{-15}$ (1:9)	[10, 13]
(R15)	$\text{O}_2(b) + \text{H}_2\text{O} \rightarrow \text{O}_2(X, a) + \text{H}_2\text{O}$	$k_{15} = 4.6 \times 10^{-12}$ (1:9)	[10, 13]
(R16)	$\text{O}_2(b) + \text{O}_3 \rightarrow \text{O}_2(X, a) + \text{O}_3, \text{O} + 2\text{O}_2$	$k_{16} = 2.2 \times 10^{-11}$ (3:27:70)	[10, 13]
(R17)	$\text{OH} + \text{O} \rightarrow \text{O}_2 + \text{H}$	$k_{17} = 3.5 \times 10^{-11}$	[10]
(R18)	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$k_{18} = 5.5 \times 10^{-32}[\text{N}_2]$	[10]
(R19)	$\text{HO}_2 + \text{O} \rightarrow \text{OH} + \text{O}_2$	$k_{19} = 5.8 \times 10^{-11}$	[10]
(R20)	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_{20} = 1.1 \times 10^{-10}$	[10]
(R21)	$\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	$k_{21} = 2.9 \times 10^{-11}$	[14]
(R22)	$\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}, \text{H}_2 + \text{O}_2, \text{H}_2\text{O} + \text{O}$	$k_{22} = 8.0 \times 10^{-11}$ (90:7:3)	[10]
(R23)	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	$k_{23} = 6.9 \times 10^{-31}[\text{N}_2]$ $= 4.4 \times 10^{-30}[\text{H}_2\text{O}]$	[15]
(R24)	$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$k_{24} = 1.5 \times 10^{-12}$	[10]
(R25)	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	^{b)} $k_{25} = 5.2 \times 10^{-12}$	[10]
(R26)	$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$	$k_{26} = 1.7 \times 10^{-12}$	[10]
(R27)	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	$k_{27} = 7.3 \times 10^{-14}$	[10]
(R28)	$\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M}$	^{b, c)} $k_{28}^0 = 2.9 \times 10^{-12}$	[10]
(R29)	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	$k_{29} = 2.0 \times 10^{-15}$	[10]
(R30)	$\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$	$k_{30} = 1.7 \times 10^{-15}$	[10]
(R31)	$\text{H}_2\text{O}_2 + h\nu(185 \text{ nm}) \rightarrow \text{OH} + \text{OH}$	$\sigma_{31} = 8 \times 10^{-19}$	[10]
(R32)	$\text{H}_2\text{O}_2 + h\nu(254 \text{ nm}) \rightarrow \text{OH} + \text{OH}$	$\sigma_{32} = 7.0 \times 10^{-20}$	[10]

^{a)} See text.

^{b)} Calculated using low- and high-pressure limits and broadening factor.

^{c)} $k_{28} = k_{28}^0 \{1 + 1.4 \times 10^{-21} \exp(2200/T)[\text{H}_2\text{O}]\}$

Figure 1: Photo-reaction cell equipped with a low-pressure mercury lamp.

3. Verification of reaction model

For the verification of the reaction model developed in the previous section, the ozone densities calculated using the reaction model are compared with experimentally measured ozone densities. A cylindrical reaction cell equipped with a low-pressure mercury lamp shown in Fig. 1 is used for the verification. The ozone density at the gas outlet of the reaction cell is measured and compared with that calculated using the reaction model. The experiment and simulation are detailed below.

3.1. Experiment

A 36-cm long low-pressure mercury lamp is placed in the cylindrical cell, as shown in Fig. 1. The photo-reaction cell is made from aluminum, and black non-glossy paint is applied to the inner wall of the cell to reduce reflections. The radius of the lamp, r_0 , is 0.9 cm and the length of the cell, L , is 30 cm. The UV lamp emits radiation continuously. Humid air or humid $O_2(50\%)/N_2$ is allowed to flow through the reaction cell. Two conditions of $O_2 = 20\%$ and 50% are used to verify the reaction model for different O_2 concentrations. Temperature and humidity are measured at the gas outlet. After the lamp is switched on, the ozone density increases with time and reaches equilibrium after around 20 min. After equilibrium conditions are reached, the ozone density at the gas outlet is measured using an UV absorption method. A 2-cm quartz absorption cell and 254-nm radiation from another low-pressure mercury lamp are used for the UV absorption. The 254-nm light is absorbed by H_2O_2 as well as ozone (see R32). However, the ozone density measurement is not disturbed by H_2O_2 because the absorption cross section of ozone at 254 nm is two orders of magnitude larger than that of H_2O_2 (Table 1) and

the density of ozone is orders of magnitude higher than that of H_2O_2 (see Fig. 4). To verify the reaction model for different conditions, the gas flow rate is changed between 1.5 and 12 L/min and two sizes of photo-reaction cells are used: $R = 4$ cm and 8 cm where R is the inner radius of the cell. The gas flow rates and the cell sizes are chosen to fix the ozone density into a range of about 2.5×10^{15} to $2.5 \times 10^{16} \text{ cm}^{-3}$ (100 to 1000 ppm), which is typical values for actual UV/ O_3 processes.

The radiation power of the lamp is measured as follows. The lamp is placed outside the photo-reaction cell, and the illuminance of 185 nm and 254 nm radiation is measured at different distances from the lamp surface at the midst of the lamp. The 185 nm and 254 nm light is measured using the illuminometers H9535-172 (Hamamatsu) and UV-M02 (Orc), respectively. H9535-172 is calibrated for 172 nm light but is also sensitive to 185 nm. A spectral response provided on its manual is used for calibration. Then, the illuminance is numerically simulated, and the radiation power is determined by fitting the simulated values to the measured results. In the simulation of the illuminance, the photon flux at the measurement point is volume integrated over the lamp volume. The $\cos \theta$ dependence of the 254-nm illuminometer is not good, and the details of this dependency provided by the manufacturer is considered in the simulation. The radiation power is determined to be 1.9 W for 185 nm and 12.2 W for 254 nm.

In addition, the cross section of R1, σ_1 , is determined by the fitting of measured and simulated 185-nm illuminance. It is determined to be $1.2 \times 10^{-20} \text{ cm}^2$. In the calculation of σ_1 , the absorption of 185 nm by H_2O (see R4) in the presence of humidity, where the 185-nm illuminance was measured, is also considered.

3.2. Simulation

The radical densities in the photo-reaction cell are simulated using the reaction model. The aim of the simulation is to verify the reaction model and not to develop an exhaustive simulation. Therefore, assumptions are made to simplify the modeling.

The cylindrical axis (r, z) shown in Fig. 1 is used in the simulation. The inside of the photo-reaction cell is divided into uniform computational mesh. The densities of short-lived radicals $[\text{O}, \text{O}(^1D), \text{O}_2(a), \text{O}_2(b), \text{OH}, \text{HO}_2, \text{and H}]$ at a point (r, z) are calculated by solving the rate equations obtained from Table 1 under equilibrium conditions (e.g., $d[\text{O}]_{r,z}/dt = 0$). Diffusion is neglected for those radicals. The numbers of the mesh are sufficiently large:

100 for r -direction and 300 for z -direction, respectively. It was confirmed that the calculated radical densities are not affected by the number of the mesh for larger than 100×300 meshes. The photon flux at 185 nm and 254 nm at a point (r, z) is calculated by integrating the photon flux over the lamp volume. The light absorption due to reactions R1, R3, and R4 is considered in the calculation of the photon flux.

For long-lived species (O_3 and H_2O_2), two models are assumed. In “model 1”, it is assumed that O_3 and H_2O_2 diffuse sufficiently and that their densities are uniform in the photo-reaction cell. Under equilibrium conditions, the number of ozone molecules in the reaction cell does not change with time. The number of ozone molecules flowing out from the reaction cell per unit time is $F[\text{O}_3]_0$, where F is the volumetric flow rate of the gas and $[\text{O}_3]_0$ is the ozone density in the reaction cell which is uniform in the cell. Under equilibrium conditions, the value of $F[\text{O}_3]_0$ is equal to the number of ozone molecules produced in the reaction cell per unit time:

$$F[\text{O}_3]_0 = \int_V \left(\frac{d[\text{O}_3]}{dt} \right)_{r,z} dV, \quad (1)$$

where $(d[\text{O}_3]/dt)_{r,z}$ is increase in ozone density at (r, z) by reactions R1–R32 per unit time and the integral is volume integration in the reaction cell. The O_3 density is calculated by solving Eq. (1). The H_2O_2 density is also calculated using the same way.

In model 1, it was assumed that the O_3 and H_2O_2 densities are uniform in the photo-reaction cell. However, their densities must be slightly or much lower at the upstream side (near the inlet of the photo-reaction cell) and higher at the downstream side (near the outlet) because they are accumulated as the gas flows downstream. Accurate calculation of their density distribution requires fluid dynamics model, which is beyond the scope of the present work. Instead, in “model 2”, it is simply assumed that their densities have gradients in the z -direction and uniform in the r -direction with boundary conditions of $[\text{O}_3] = 0$ and $[\text{H}_2\text{O}_2] = 0$ at the inlet of the reaction cell ($z = 0$). The ozone density at z , $[\text{O}_3]_z$, is calculated as follows. In an infinitely short time of Δt , the gas flows by $\Delta z = v_z \Delta t$, where v_z is the average flow velocity of the gas, and the ozone density increases by $(d[\text{O}_3]_z/dz)\Delta z$. At the same time, the increase in ozone density in Δt by reactions R1–R32 at (r, z) can also be written as $(d[\text{O}_3]/dt)_{r,z}\Delta t$. Therefore, the following

equation holds:

$$\begin{aligned} \int_S \frac{d[\text{O}_3]_z}{dz} \Delta z dS &= \int_S \left(\frac{d[\text{O}_3]}{dt} \right)_{r,z} \Delta t dS, \\ \therefore v_z \frac{d[\text{O}_3]_z}{dz} \int_S dS &= \int_S \left(\frac{d[\text{O}_3]}{dt} \right)_{r,z} dS, \end{aligned} \quad (2)$$

where the integral, $\int_S dS = \int_{r_0}^R 2\pi r dr$, is surface integral at z . The ozone density is calculated by solving Eq. (2). The H_2O_2 density is also calculated using the same way.

4. Results and discussion

4.1. Comparison between simulation and experiment

Figure 2 compares the simulated and measured ozone densities under different flow and humidity conditions. In Fig. 2(e), $\text{O}_2(50\%)/\text{N}_2$ gas is used instead of air. The O_3 and H_2O_2 densities are calculated using both models 1 and 2, and their results are shown. Figure 2 shows that the simulation underestimates the ozone density by 30–70% than the measured values for all conditions, but it simulates well the effect of humidity on ozone density. Considering that the rate coefficients listed in Table 1 have generally an uncertainty of 10%–30% [10] and some simplifying assumptions are made in the simulation, the errors of 30–70% are allowable. Thus, it can be concluded that the reaction model is suitable.

The reaction model has been verified. Next, the decrease in ozone density with increasing humidity is discussed using the reaction model. Then, the effect of humidity on the densities of other radicals is examined using the reaction model. These information is important for an efficient use of the UV process with a low-pressure mercury lamp in a humid environment.

4.2. Reduction of O_3 density with increasing humidity

Figure 2 shows that the ozone density is reduced with increasing humidity. There are three reasons for this reduction.

1. Absorption of 185 nm radiation by H_2O : (R4).
2. Consumption of $\text{O}(^1D)$ by H_2O : (R8).
3. Catalytic ozone destruction by OH and HO_2 : (R27) and (R29).

Figure 2: Comparison of the ozone densities obtained from simulation and experiments under different humidity, O_2 concentration, and flow conditions.

Figure 3: Simulation of ozone density versus relative humidity using model 2. Curve 1 is calculated using all reactions R1–R32. Curves 2–6 are calculated by excluding some reactions. Here $R = 4$ cm, $T = 25$ °C, and 1.5 L/min.

Curve 1 in Fig. 3 shows a simulated ozone density calculated using all reactions R1–R32 and curve 2 is calculated excluding the following reactions: R4, R8, R27, and R29. It can be observed that curve 2 is almost independent of humidity, indicating that the ozone reduction by humidity is in fact caused by these three processes. These processes are discussed below in detail.

4.2.1. Absorption of 185 nm radiation by H_2O

The 185 nm radiation from the lamp is absorbed by O_2 and H_2O according to R1 and R4. The ratio of the absorption by O_2 is $\sigma_1[O_2]/(\sigma_1[O_2] + \sigma_4[H_2O])$, which decreases with increasing humidity. As a result, the production of $O(^3P)$ by R1 is reduced with increasing humidity, leading to decreased ozone production by R2. Curve 3 in Fig. 3 is a simulation where R4 is added to the conditions of curve 2. The difference between curves 2 and 3 indicates the ozone reduction caused by the absorption of 185 nm light by H_2O (R4).

4.2.2. Consumption of $O(^1D)$ by H_2O

Ozone is photodissociated by R3 to produce $O(^3P)$ and $O(^1D)$. $O(^3P)$ converts back to O_3 by R2, and $O(^1D)$ also reacts to form O_3 by R2 after

quenching to $O(^3P)$ by N_2 and O_2 as R6 and R7. Because of this regeneration cycle, ozone is not practically decomposed by R3. However, in humid conditions, a part of $O(^1D)$ reacts with H_2O (R8) and does not get converted back to ozone. Because of this branching from the ozone regeneration cycle, ozone is partly decomposed by R3. Curve 5 in Fig. 3 is a simulation obtained by adding R8 to the conditions of curve 2. The difference between curves 2 and 5 indicates the ozone reduction caused by R8 that breaks the ozone regeneration cycle.

4.2.3. Catalytic ozone destruction by OH and HO_2

In humid conditions, ozone is decomposed by the ozone destruction cycle involving OH and HO_2 , as shown in R27 and R29. Curves 4 and 6 in Fig. 3 are the simulations where the ozone destruction cycle, R27 and R29, have been added to the conditions of curves 3 and 5, respectively. In both cases, the ozone density is remarkably reduced by the ozone destruction cycle.

4.3. Other radical densities

The effect of humidity on the densities of other radicals is examined. The radical densities are calculated in the reaction cell of $R = 4$ cm with $T = 25$ °C and $F = 1.5$ L/min conditions as an example. Figure 4 shows the calculated densities under different humidity conditions near the inner wall of the photo-reaction cell ($r = R$) and near the lamp surface ($r = r_0$) at the center cross-section of the photo-reaction cell ($z = L/2$). The densities of $O(^1D)$, $O_2(b)$, and H are not plotted in Fig. 4 because they are too small of the orders of $10^5 \sim 10^6$ cm $^{-3}$, $10^6 \sim 10^7$ cm $^{-3}$, and $10^7 \sim 10^9$ cm $^{-3}$, respectively. Near the inner wall of the reaction cell ($r = R$), the densities of O_3 , $O_2(a)$, H_2O_2 , HO_2 , OH , and O are of the orders of 10^{15} cm $^{-3}$, 10^{13} cm $^{-3}$, 10^{13} cm $^{-3}$, 10^{12} cm $^{-3}$, 10^{11} cm $^{-3}$, and 10^{10} cm $^{-3}$, respectively. Near the lamp surface ($r = r_0$), the radical densities increase because the photon flux from the lamp is larger than that at $r = R$.

Figure 4 shows radical densities and effect of humidity for typical conditions for actual UV/ O_3 process: several cm distance from the lamp surface with O_3 density of the order of 10^{15} cm $^{-3}$. It shows that ozone has the highest density among the radicals. The density of atomic oxygen is 4 to 5 orders of magnitude lower than the ozone density, but its dependence on humidity is approximately the same as the ozone density. Radicals originating from water vapor, OH , HO_2 , and H_2O_2 , are produced in humid environment. But their densities do not necessarily increase with humidity. The densities of

Figure 4: Simulation of the radical densities for different humidity conditions at $(r, z) = (R, L/2)$ and $(r_0, L/2)$. They are calculated using model 2. Here $R = 4$ cm, $T = 25$ °C, and $F = 1.5$ L/min.

HO_2 and H_2O_2 reach maxima at relative humidity of 5–20%. Further increase in humidity decreases their densities. On the other hand, the OH density increases in nearly proportional to humidity. The density of $\text{O}_2(a)$ is almost independent of humidity at $r = R$, while decreases with increasing humidity at $r = r_0$.

The densities of radicals and their dependence on humidity can be obtained from Fig. 4, but only for the limited condition. Next, a simple model is deduced to estimate those radical densities for more general conditions. If the ozone density and illuminance of 185 nm and 254 nm light are known, approximate radical densities can be analytically estimated. For example,

the density of $O(^1D)$ can be approximated by

$$[O(^1D)] \cong \frac{\phi_3 \sigma_3 I_{254} [O_3]}{k_6 [N_2] + k_7 [O_2]} = \Phi_{O(D)} I_{254} [O_3], \quad (3)$$

where I_{254} is the 254-nm illuminance and $\Phi_{O(D)} = \phi_3 \sigma_3 / (k_6 [N_2] + k_7 [O_2])$ is a constant. This approximation is valid because $O(^1D)$ is mostly produced by R3 and predominantly reacts via R6 and R7. If $[O_3]$ and I_{254} are known, $[O(^1D)]$ can be analytically calculated using Eq. (3).

Similarly, for experimental conditions similar to ours, the densities of O, $O_2(a)$, $O_2(b)$, OH, and HO_2 can be approximated as follows:

$$[O] \cong \frac{2\sigma_1 I_{185} [O_2] + \sigma_3 I_{254} [O_3]}{k_2 [O_2]}, \quad (4)$$

$$[O_2(a)] \cong \frac{\phi_3 \sigma_3 I_{254}}{k_{11}}, \quad (5)$$

$$[O_2(b)] \cong \frac{0.8k_7 [O_2]}{k_{15} [H_2O]} \Phi_{O(D)} I_{254} [O_3], \quad (6)$$

$$[OH] \cong \frac{2k_8 \Phi_{O(D)} [H_2O] I_{254} + k_{29} [HO_2]}{k_{20} [HO_2] / [O_3] + k_{27}}, \quad (7)$$

$$[HO_2] \cong \frac{k_{27} [OH] [O_3]}{k_{20} [OH] + k_{29} [O_3]}, \quad (8)$$

where I_{185} is the 185-nm illuminance. $[OH]$ and $[HO_2]$ can be calculated by solving the simultaneous equations (7) and (8). Figure 5 shows the radical densities calculated using the numerical simulation with all reactions R1–R32 and those calculated using the analytical model of equations (3)–(8) with values of $[O_3]$, I_{185} , and I_{254} obtained from the simulation. The difference between the analytical and full reaction models is within a factor of two. The analytical model gives a good approximation of the radical densities.

For the analytical model, the main production and reaction paths of the radicals can be discussed. For example, the main production and reaction paths of $O_2(a)$ are R3 and R11, respectively, as shown in Eq. (5); i.e., $O_2(a)$ is produced by ozone photodissociation (R3) and quenched by reaction with ozone (R11). Similarly, O atoms are mainly produced by the photodissociation of O_2 and O_3 (R1 and R3) and consumed by reaction with O_2 (R2) to produce ozone. The OH radicals are mainly produced by R8 and the catalytic ozone destruction cycle (R29) and consumed by reaction with HO_2 (R20) and

Figure 5: Radical densities calculated using the numerical simulation with all reactions and those calculated using the analytical model for different humidity conditions at $(r, z) = (R, L/2)$ and $(r_0, L/2)$. Here $R = 4$ cm, $T = 25^\circ\text{C}$, and $F = 1.5$ L/min. The numerical simulation used is model 2.

the catalytic ozone destruction cycle (R27). HO_2 is mainly produced by the catalytic ozone destruction cycle (R27) and consumed by reaction with OH (R20) and the catalytic ozone destruction cycle (R29). The radical densities are affected by humidity due to these reactions.

5. Conclusions

The effect of humidity on the densities of ozone and other radicals produced by a low-pressure mercury lamp was examined using a reaction model developed in the present work. After the reaction model was developed, the validity of the reaction model was verified by showing that the simulated ozone densities agreed well with the measured ones for different conditions. It was shown that there are three reasons for the decrease in the ozone density with increasing humidity: (i) decrease in $\text{O}(^3P)$ production (R1) due to

attenuation of 185 nm radiation by H_2O (R4); (ii) O_3 destruction by 254 nm radiation arising from R3 and R8; and (iii) O_3 destruction cycle by OH and HO_2 (R27 and R29). The densities of O, $\text{O}(^1D)$, $\text{O}_2(a^1\Delta_g)$, $\text{O}_2(b^1\Sigma_g^+)$, OH, HO_2 , H, and H_2O_2 were also calculated and the effect of humidity on those densities were discussed. Their main production and reaction paths were discussed based on the reaction model.

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