Measurement and simulation of $\text{O}_2(a^1\Delta_g)$ density under low-pressure mercury lamp irradiation

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Abstract

The density of singlet delta oxygen $\text{O}_2(a^1\Delta_g)$ produced under low-pressure mercury lamp irradiation in an oxygen-nitrogen mixture is measured by infrared optical emission spectroscopy and compared with the results of simulations. A 30-cm-long lamp, whose radiation power is 1.9 W for 185 nm light and 12.2 W for 254 nm light, is irradiated in a cylindrical reactor of 8 cm inner diameter with an $\text{O}_2(1\text{--}20\%)/\text{N}_2$ flow of 3.75–10 L/min. The measurement shows that the $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet is approximately 1–2 ppm under all experimental conditions, regardless of the O_2 concentration and the flow rate. The simulation reproduces the measurement results well and within an error of 50%. On the basis of the simulation model, the $\text{O}_2(a^1\Delta_g)$ density can be simply expressed as $[\text{O}_2(a^1\Delta_g)] = 2.7 \times 10^{-3}I / (1 + 4.2 \times 10^{-4}[\text{O}_2]/[\text{O}_3])$, where I is the illuminance at 254 nm. When $[\text{O}_3]/[\text{O}_2] \gg 4.2 \times 10^{-4}$, $[\text{O}_2(a^1\Delta_g)]$ can be approximated as $2.7 \times 10^{-3}I$, which is independent of parameters other than I , as shown by the measurement. The $\text{O}_2(a^1\Delta_g)$ densities calculated using these

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simple expressions agree with the measured $\text{O}_2(a^1\Delta_g)$ densities within an error of 80%.

Keywords: low-pressure mercury lamp, reaction model, singlet delta oxygen $\text{O}_2(a^1\Delta_g)$, infrared optical emission spectroscopy

1. Introduction

An ultraviolet (UV) process using a low-pressure mercury lamp is widely used for surface treatment, sterilization, and water treatment [1, 2]. A low-pressure mercury lamp emits light at wavelengths of 185 nm and 254 nm. The 185 nm light photodissociates O_2 to produce O atoms, which is followed by ozone production:

Ozone is then photodissociated by the 254 nm light:

where $\phi_3 = 0.9$ [3]. This process is called the “UV/ O_3 process” [1]. It produces various reactive species through the intermediate formation of ozone. In a humid environment, $\text{O}(^1D)$ produced by reaction (R3a) reacts with H_2O to produce OH:

leading to the production of HO_2 and H_2O_2 . The authors previously developed a photochemical reaction model of low-pressure mercury lamp irradiation in a humid air environment and calculated the densities of the reactive

species in the UV/O₃ process [4]. It was shown that various reactive species (O, O₃, O₂(*a*¹Δ_g), O₂(*b*¹Σ_g⁺), O(¹D), OH, H, HO₂, H₂O₂) are produced under low-pressure mercury lamp irradiation.

In the present study, the density of singlet delta oxygen O₂(*a*¹Δ_g) produced under low-pressure mercury lamp irradiation is measured by infrared optical emission spectroscopy in an oxygen-nitrogen mixture and compared with the results of the simulation developed in [4]. O₂(*a*¹Δ_g) is metastable molecular oxygen in the first electronically excited state (0.98 eV) and has a long radiation lifetime (> 75 min) [5]. It causes cellular damage and can be used for cancer treatment [5–9]. It is also used in the synthesis of fine chemicals, the treatment of wastewater, sterilization, insecticides, herbicides, chemical oxygen–iodine lasers (COILs), and the enhancement of combustion [5, 10, 11]. In spite of its importance, the density of O₂(*a*¹Δ_g) in the UV/O₃ process has not been quantified. The absolute density of O₂(*a*¹Δ_g) and the effects of the ambient gas composition on the O₂(*a*¹Δ_g) density are investigated by measurement and simulation.

2. Experiments and simulations

2.1. Experimental setup

The experimental setup is shown in Fig. 1. A 30-cm-long low-pressure mercury lamp is placed in a cylindrical reactor. The reactor is made from aluminum, and black non-glossy paint is applied to its inner wall to reduce reflection. The diameter of the lamp is 1.8 cm. The radiation power of the lamp is 1.9 W for 185 nm light and 12.2 W for 254 nm light, as measured using illuminometers and described in [4]. An O₂/N₂ mixture with an O₂ concentration of 1–20% flows through the reactor.

Figure 1: Cylindrical reactor and setup for infrared optical emission spectroscopy.

The infrared emission of $\text{O}_2(a^1\Delta_g)$ ($\sim 1.27 \mu\text{m}$) emitted from a quartz cell placed downstream of the reactor is measured. The quartz cell is connected to the reactor with a polymer tube of length L and 5 mm inner diameter (Pisco, soft polyolefin tube). The infrared emission is measured using a thermoelectric cooled infrared photomultiplier tube (PMT) unit (H10330B-45, Hamamatsu). The PMT has a spectral response in the range of 950–1400 nm. The PMT unit is equipped with a condenser lens (18 mm diameter, $f = 25.7 \text{ mm}$) that focuses a parallel light onto a photocathode of 1.6 mm diameter. The quartz cell is placed at a distance of 27 cm from the condenser lens. The infrared light from the quartz cell is collected with the condenser lens through a bandpass filter ($1275 \pm 23 \text{ nm}$). The focal point

of the collected light is slightly away from the photocathode because the incident light is not parallel.

The purpose of this measurement is to obtain the $\text{O}_2(a^1\Delta_g)$ density in the cylindrical reactor. However, measurement of the $\text{O}_2(a^1\Delta_g)$ emission in the reactor is difficult because the infrared emission from the low-pressure mercury lamp is much more intense. Therefore, the $\text{O}_2(a^1\Delta_g)$ density is measured in the quartz cell far from the reactor. The $\text{O}_2(a^1\Delta_g)$ density in the reactor is estimated from the measured $\text{O}_2(a^1\Delta_g)$ density while considering the decrease in the $\text{O}_2(a^1\Delta_g)$ density in the polymer tube.

Two types of quartz cell are used. One is a rectangular cell of $2 \times 2.5 \times 1 \text{ cm}^3$ and the other is a quartz tube of 2 mm inner diameter. The rectangular cell has a large volume, gives an intense infrared emission, and is used for almost all the experiments. The tube cell is used only for density calibration with a pinhole of 1.4 mm diameter. The tube cell is suitable for density calibration because all of the infrared emission from the small tube cell with the pinhole reaches the photocathode, while only part of the emission from the rectangular cell reaches the photocathode and the ratio that reaches the photocathode is difficult to determine.

2.2. Infrared optical emission spectroscopy

The electronically excited state $\text{O}_2(a^1\Delta_g)$ emits infrared light of wavelength 1.26–1.29 μm when it transfers to the ground state $\text{O}_2(X^3\Sigma_g^-)$. The bandpass filter transmits approximately 80% of the $\text{O}_2(a^1\Delta_g)$ emission. Since the transition between the $a^1\Delta_g$ and $X^3\Sigma_g^-$ states is forbidden, the infrared $\text{O}_2(a^1\Delta_g)$ emission is very weak. Therefore, the PMT is used in the photon-counting mode. The photon count per unit time is given by

$$P = \frac{\Omega}{4\pi} \eta Q_E (A + A_c) V N, \quad (1)$$

where Ω is the solid angle of light collection, η is the transmittance of the optics including the bandpass filter, Q_E is the quantum efficiency of the PMT, A is the spontaneous emission rate ($= 2.22 \times 10^{-4} \text{ s}^{-1}$ [5]), A_c is the collision-induced emission rate given by [12, 13]

$$A_c = k_{\text{O}_2}^c [\text{O}_2] + k_{\text{N}_2}^c [\text{N}_2], \quad (2)$$

V is the volume of the observed $\text{O}_2(a^1\Delta_g)$, and N is the $\text{O}_2(a^1\Delta_g)$ density in the quartz cell. The collision-induced emission enhances the transition rate at high pressure. In this study, $k_{\text{O}_2}^c = 3.4 \times 10^{-23} \text{ cm}^3/\text{s}$ and $k_{\text{N}_2}^c = 6.6 \times 10^{-24} \text{ cm}^3/\text{s}$ are used [14].

2.3. Ozone density measurement

The ozone density is measured in addition to the $\text{O}_2(a^1\Delta_g)$ density because it is required for analyzing the measured $\text{O}_2(a^1\Delta_g)$ density, as described later. The ozone density is measured using a 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 measurement. The absorption cell is connected to the outlet port of the reactor with a 50-cm-long polymer tube.

2.4. Simulation

The $\text{O}_2(a^1\Delta_g)$ density is calculated using the simulation developed in [4] and compared with the measured $\text{O}_2(a^1\Delta_g)$ density. The simulation was described in detail in [4] and will be mentioned only briefly here. The cylindrical axes (r, z) shown in Fig. 1 are used in the simulation. The inside of the cylindrical reactor is divided into a mesh for computation. The simulation includes 12 reactions and five reactive species $[\text{O}, \text{O}_3, \text{O}(^1D), \text{O}_2(a^1\Delta_g),$

$\text{O}_2(b^1\Sigma_g^+)]$. The densities of short-lived reactive species at each point (r, z) are calculated by solving rate equations under equilibrium conditions. For ozone, which has a long lifetime, its accumulation in the ambient gas is considered. Diffusion is neglected and a laminar flow is assumed in the reactor. The absorption of 185 nm and 254 nm light by O_2 and O_3 , respectively, is considered when the illuminance at (r, z) is calculated.

The $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet placed at $r = 2.8$ cm (Fig. 1) is calculated in the simulation and compared with the measured densities. The simulated $\text{O}_2(a^1\Delta_g)$ density at $r = 2.8$ cm is plotted in Fig. 2 as a function of z for a gas flow rate of 10 L/min. The $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet is approximately 1.7–1.8 ppm and almost independent of the O_2 concentration for $\text{O}_2 = 1\text{--}20\%$. After being emitted from the reactor outlet, $\text{O}_2(a^1\Delta_g)$ flows to the quartz cell through the polymer tube of length L . $\text{O}_2(a^1\Delta_g)$ decays in the tube mainly by the following three processes:

where k_5 and k_6 are rate coefficients and γ is the wall loss probability. The radially averaged rates for wall loss are given by [15]:

$$\nu_w \text{ (s}^{-1}\text{)} \cong \left(\frac{R^2}{2.4^2 D} + \frac{2R}{\gamma \langle v \rangle} \right)^{-1}, \quad (3)$$

where R is the tube radius, D is the diffusion coefficient, and $\langle v \rangle$ is the mean velocity. The $\text{O}_2(a^1\Delta_g)$ density in the quartz cell after passing through the tube of length L is given by

$$N = N_0 \exp \left(-k \frac{L}{v_g} \right), \quad (4)$$

Figure 2: Simulated axial distribution of $\text{O}_2(a^1\Delta_g)$ density in the reactor for $r = 2.8$ cm. An O_2/N_2 mixture flows at 10 L/min with O_2 concentrations of 1% and 20%.

where N_0 is the $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet, v_g is the gas flow velocity in the tube, and k is the decay rate of $\text{O}_2(a^1\Delta_g)$ given by

$$k = k_5[\text{O}_3] + k_6[\text{O}_2] + \nu_w. \quad (5)$$

3. Results

3.1. Infrared emission from $\text{O}_2(a^1\Delta_g)$

Figure 3 shows the time evolution of the infrared emission intensity from the quartz cell when the UV light and O_2 flow are both on and off. An $\text{O}_2(4\%)/\text{N}_2$ mixture flows at 10 L/min (2 L/min of artificial air and 8 L/min of N_2) and the quartz cell is placed at a distance of 50 cm from the reactor ($L = 50$ cm). At 0 s, the lamp is off. The lamp is switched on at 10 s, off again at 35 s, and on again at 50 s. At 65 s, the air flow is stopped and only

Figure 3: Time evolution of $O_2(a^1\Delta_g)$ density when Hg lamp and O_2 flow are both on and off. An $O_2(4\%)/N_2$ mixture flows at 10 L/min. $L = 50$ cm.

the N_2 flows at 8 L/min. Figure 3 shows that the infrared emission is only observed when the lamp is on and the oxygen flows. This ensures that the infrared emission is emitted from $O_2(a^1\Delta_g)$. Since the O_2 concentration in the reactor decreases slowly after the air flow is switched off, it takes more than 100 s for the infrared emission to decrease to zero after the air flow is switched off.

3.2. Decay of $O_2(a^1\Delta_g)$ density in polymer tube

The decay of the $O_2(a^1\Delta_g)$ density in the polymer tube connecting the reactor and the quartz cell is measured for different tube lengths L . Figure 4 shows the results for O_2 concentrations of 1%, 2%, and 4%. In all measurements, the rectangular quartz cell is used. Then, the density calibration is performed using the quartz tube cell for $O_2 = 4\%$ and $L = 50$ cm. The calibration value is used to calibrate all measurement data in the present

Figure 4: Measured $\text{O}_2(a^1\Delta_g)$ densities for different tube lengths L and their fitted lines. The O_2 concentrations are 1%, 2%, and 4%. The gas flow rate is 10 L/min.

work.

Figure 4 shows the single-exponential decay for all O_2 concentrations. The decay rates of the $\text{O}_2(a^1\Delta_g)$ density are determined from the slopes of fitted lines. Table 1 shows the decay rates. The decay rate is also calculated using Eq. (5) and compared with the measurement results. For the calculation, the ozone density and wall loss probability are required. Thus, the ozone density is measured. The measurement results are shown in Fig. 5 with the simulated ozone densities. Figure 5 shows that the simulated ozone density is approximately 60% of the measured density. The underestimation of ozone density by the simulation was previously reported in [4]. The fitted line shown in Fig. 5 (broken line) is used as the ozone density in Eq. (5) when the $\text{O}_2(a^1\Delta_g)$ decay rate is calculated using Eq. (5). The wall loss probability is not known for the polymer tube. If it is assumed to be 2.5×10^{-5} , the calculated and measured decay rates show the best agreement. Here-

Figure 5: Measured and simulated ozone densities for different O₂ concentrations. The simulated densities are those at the outlet of the reactor. The gas flow rate is 10 L/min. The broken line is a fitted curve.

after, $\gamma = 2.5 \times 10^{-5}$ is used for the polymer tube, which is approximately equivalent to those of Pyrex and quartz ($1-5 \times 10^{-5}$ [16]). The decay rates of O₂($a^1\Delta_g$) calculated from Eq. (5) with the measured ozone density and the assumed wall loss probability are shown in Table 1. They agree well with the measured results. The lifetime of O₂($a^1\Delta_g$) in the polymer tube is obtained from the results in Table 1 to be 250 ms for O₂ = 1% and 100 ms for O₂ = 4%.

3.3. Effects of oxygen concentration and gas flow rate

The effect of the oxygen concentration on the O₂($a^1\Delta_g$) density is measured. First, the O₂($a^1\Delta_g$) density is measured at $L = 50$ cm for O₂ concentrations of 1–20% with a flow rate of 10 L/min. Then, the O₂($a^1\Delta_g$) density at the reactor outlet ($L = 0$ cm) is calculated from the measured density at $L = 50$ cm using Eqs. (4) and (5) with $\gamma = 2.5 \times 10^{-5}$. The results are

Table 1: Measured and calculated decay rates of $\text{O}_2(a^1\Delta_g)$ in the polymer tube. The latter is calculated using Eq. (5) with $\gamma = 2.5 \times 10^{-5}$. The gas flow rate is 10 L/min.

O_2 [%]	1	2	4
k [s^{-1}] (measurement)	3.9	6.1	9.4
k [s^{-1}] (calculation)	4.0	5.9	9.6

shown in Fig. 6. In Fig. 6, the simulated $\text{O}_2(a^1\Delta_g)$ density for $L = 0$ cm is also plotted (solid line). The simulation shows that the $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet is 1.7–1.8 ppm and almost independent of the O_2 concentration. The measurement shows a similar tendency: the measured density is 1.7–2.3 ppm and almost independent of the O_2 concentration. This is in contrast to the O_3 density, which is approximately proportional to the O_2 concentration (Fig. 5). The difference between the measured and simulated $\text{O}_2(a^1\Delta_g)$ densities is within only 50%.

Next, the effect of the gas flow rate on the $\text{O}_2(a^1\Delta_g)$ density is measured. Figure 7 shows the measured result for a fixed O_2 concentration of 4%. The $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet ($L = 0$ cm) is calculated from the measured density at $L = 50$ cm using Eqs. (4) and (5) with $\gamma = 2.5 \times 10^{-5}$. The $\text{O}_2(a^1\Delta_g)$ density simulated for $L = 0$ cm is also plotted (solid line). The simulation shows that the $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet is 1.8–2.1 ppm and almost independent of the O_2 concentration. The measurement shows a similar tendency. This is in contrast to the O_3 density, which decays exponentially with increasing flow rate (data not shown). The difference between the measured and simulated $\text{O}_2(a^1\Delta_g)$ densities is within 40%.

Figure 6: Measured and simulated $\text{O}_2(a^1\Delta_g)$ densities for different O_2 concentrations. The $\text{O}_2(a^1\Delta_g)$ density for $L = 0$ cm is calculated from the measured $\text{O}_2(a^1\Delta_g)$ density for $L = 50$ cm. The dotted and broken lines are the $\text{O}_2(a^1\Delta_g)$ densities calculated using Eqs. (7) and (8), respectively. The gas flow rate is 10 L/min.

4. Discussion

It was shown in Figs. 6 and 7 that the difference between the measured and simulated $\text{O}_2(a^1\Delta_g)$ densities at the reactor outlet is within 50%. However, both the measurement and simulation probably have errors of more than 50%. The two errors may cancel and result in a small total error. The sources of the measurement error include the solid angle of light collection, the volume of the observed $\text{O}_2(a^1\Delta_g)$, the collision-induced emission rate, and the misalignment of the optics. These sources of error may result in a total error of more than twofold. The simulation error may also reach more than twofold. For example, the simulation includes an error of at least 60% in the ozone density, as shown in Fig. 5. Since the ozone density measure-

Figure 7: Measured and simulated $\text{O}_2(a^1\Delta_g)$ densities for different gas flow rates with fixed O_2 concentration of 4%. The $\text{O}_2(a^1\Delta_g)$ density for $L = 0$ cm is calculated from the measured $\text{O}_2(a^1\Delta_g)$ density for $L = 50$ cm. The dotted and broken lines are $\text{O}_2(a^1\Delta_g)$ densities calculated using Eqs. (7) and (8), respectively.

ment using UV absorption has a small error (estimated to be 10%), the 60% error is mainly caused by the simulation.

The $\text{O}_2(a^1\Delta_g)$ density can be calculated even without performing a simulation [4]. $\text{O}_2(a^1\Delta_g)$ is mainly produced by reaction (R3a) and decays by reactions (R5) and (R6). The rate equation of the $\text{O}_2(a^1\Delta_g)$ density is given by

$$\frac{d[\text{O}_2(a^1\Delta_g)]}{dt} = \sigma_3\phi_3[\text{O}_3]I_{254} - k_5[\text{O}_3][\text{O}_2(a^1\Delta_g)] - k_6[\text{O}_2][\text{O}_2(a^1\Delta_g)], \quad (6)$$

where $\sigma_3 = 1.16 \times 10^{-17} \text{ cm}^2$ [17] is the cross section of reaction (R3) and I_{254} is the illuminance at 254 nm. Under a steady-state condition, the $\text{O}_2(a^1\Delta_g)$

density is given by

$$[\text{O}_2(a^1\Delta_g)] = \frac{\sigma_3\phi_3 I_{254}[\text{O}_3]}{k_5[\text{O}_3] + k_6[\text{O}_2]} = \frac{2.7 \times 10^{-3} I_{254}}{1 + 4.2 \times 10^{-4} [\text{O}_2]/[\text{O}_3]}. \quad (7)$$

If $[\text{O}_3]/[\text{O}_2] \gg k_6/k_5 = 4.2 \times 10^{-4}$, $[\text{O}_2(a^1\Delta_g)]$ can be rewritten as

$$[\text{O}_2(a^1\Delta_g)] = \frac{\sigma_3\phi_3 I_{254}}{k_5} = 2.7 \times 10^{-3} I_{254}. \quad (8)$$

Equation (8) shows that the $\text{O}_2(a^1\Delta_g)$ density is determined only by the illuminance at 254 nm and is independent of the O_2 and O_3 densities and the flow rate. In all the present experiments, the time constant of the increase in $\text{O}_2(a^1\Delta_g)$ density determined by Eq. (6) is less than 1 s. Since the gas residence time in the reactor is longer than 9 s in the present experiments, the steady-state condition holds at the reactor outlet and the $\text{O}_2(a^1\Delta_g)$ density can be calculated using Eq. (7) or (8). In the present experiments, $[\text{O}_3]/[\text{O}_2] \cong 1.5 \times 10^{-3}$ at the outlet of the reactor, as shown in Fig. 5. Therefore, Eq. (8) can be used for the approximate estimation of the $\text{O}_2(a^1\Delta_g)$ density. The $\text{O}_2(a^1\Delta_g)$ densities calculated using Eqs. (7) and (8) are also plotted in Figs. 6 and 7. They show that Eqs. (7) and (8) give good approximations of the $\text{O}_2(a^1\Delta_g)$ density. In Figs. 6 and 7, the errors of the simulated densities are within 30% and those of the measured densities are within 80%.

5. Conclusions

The density of $\text{O}_2(a^1\Delta_g)$ produced under low-pressure mercury lamp irradiation was measured by infrared optical emission spectroscopy and compared with the results of simulations. The lamp was irradiated in a cylindrical reactor and the $\text{O}_2(a^1\Delta_g)$ density was measured by a quartz cell downstream of the reactor, which was connected to the reactor with a

polymer tube. The measurement showed that the $\text{O}_2(a^1\Delta_g)$ density at the reactor outlet was approximately 1–2 ppm under all experimental conditions, regardless of the O_2 concentration and the flow rate. The simulation could reproduce the measurement results well and within an error of 50%. This result ensures the reliability of the simulations. It was shown that the $\text{O}_2(a^1\Delta_g)$ density can be simply calculated even without performing a simulation using Eqs. (7) and (8). The $\text{O}_2(a^1\Delta_g)$ densities calculated using these simple expressions were in agreement with the measured $\text{O}_2(a^1\Delta_g)$ densities within an error of 80%. The wall loss probability of $\text{O}_2(a^1\Delta_g)$ on the polymer tube was determined to be 2.5×10^{-5} . The lifetime of $\text{O}_2(a^1\Delta_g)$ in the polymer tube of 5 mm inner diameter was 250 ms for $\text{O}_2 = 1\%$ and 100 ms for $\text{O}_2 = 4\%$ at 10 L/min.

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