

## ARTICLE

 $O_2(^1\Delta_g)$  Deactivation on  $O_2$ -adsorbed Metal Surfaces

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A flow system was set up to measure the quenching probability  $\gamma$  of  $O_2(^1\Delta_g)$  on various  $O_2$ -adsorbed metal surfaces including Cu, Cr, Ni, and Ag.  $\gamma$  increased with both the duration of the experiment and the  $O_2(^1\Delta_g)$  concentration. After several hours evacuation to a few Pa,  $\gamma$  can return to its original value. A deactivation mechanism of  $O_2(^1\Delta_g)$  is suggested by considering first the weak chemisorption of  $O_2(^1\Delta_g)$  on the surface adsorption sites, followed by the near resonant energy transfer between the gas phase  $O_2(^1\Delta_g)$  and surface  $O_2(^3\Sigma_g^-)$ . A phenomenological model in accord with the experimental fact has been proposed together with relevant kinetic equations.

**Key words:** Singlet oxygen, Surface quenching, Deactivation probability

## I. INTRODUCTION

Molecular  $O_2(^1\Delta_g)$  is the lowest singlet metastable oxygen, which plays an essential role in natural photochemical, photophysical, atmospheric, and biological processes. Therefore, its physical and chemical properties are attractive topics to scientists [1–3] at all times. Because of its unique electronic configuration, the  $O_2(^1\Delta_g \rightarrow ^3\Sigma_g^-)$  transition of  $O_2(^1\Delta_g)$  to its ground state  $O_2(^3\Sigma_g^-)$  is highly forbidden including singlet to triplet, g to g,  $\Delta$  to  $\Sigma$ , so that its radiative lifetime of  $O_2(^1\Delta_g)$  is as long as 65 min [4]. However, due to the spin-orbit coupling as a result of its collision with various molecules in gas and liquid phase, the lifetime can vary from a few microseconds to a few hundred milliseconds. The main quenching mechanism has been well established to be the transfer from  $O_2(^1\Delta_g)$  electronic energy to the vibrational and rotational energy of the quenchers [5–7]. Unfortunately, until now we have not found in the literature the regime of  $O_2(^1\Delta_g)$  deactivation with a pure metal surface. The lifetime measured by different authors may differ from each other appreciably (sometimes the difference may exceed one order of magnitude) [8–14]. We think this is due to the complexity of the surface, which can form very different structures and often adsorb various gases on the surface (besides those by heating or some special treatment in ultrahigh vacuum). Nevertheless, the investigation of  $O_2(^1\Delta_g)$  quenching on the gas-adsorbed metal surfaces can still be important in some fields, *e.g.*, catalysis and chemical oxygen iodine laser (COIL). In the 1980s, Ryskin *et al.* reported that for Au, Pt,

and silica the quenching probability  $\gamma$  increases with temperature rise and diminishes due to CO,  $H_2O$ , and  $NH_3$  adsorption. They even found some hysteresis effects. They suggested a chemisorption mechanism of  $O_2(^1\Delta_g)$  deactivation on active surface sites [15, 16]. Klopovskiy *et al.* studied  $O_2(^1\Delta_g)$  quenching on quartz walls and proposed a model of active surface complexes by chemisorbed O atoms and physisorbed  $O_2$  [17], interpreting the higher  $O_2(^1\Delta_g)$  quenching rate in pure oxygen by a quasi-resonant transfer of  $O_2(^1\Delta_g)$  electronic energy to the physisorbed  $O_2$ .

In this work, we have measured the  $\gamma$  of  $O_2$ -adsorbed metal surface including Cu, Cr, Ni, and Ag at room temperature. We found that  $\gamma$  increases with the experiment time under constant  $O_2(^1\Delta_g)$  concentration and increases with  $O_2(^1\Delta_g)$  concentration rise.  $\gamma$  can return to its original initial value after evacuation for a few hours. These phenomena can be well explained by the weak chemisorption of  $O_2(^1\Delta_g)$  and the near resonant energy transfer between the gas phase  $O_2(^1\Delta_g)$  and surface  $O_2(^3\Sigma_g^-)$ . A phenomenological model was proposed, which may help us understand the deactivation mechanism.

## II. EXPERIMENTS

$O_2(^1\Delta_g)$  is generated by microwave discharge of high purity  $O_2$  gas (>99.99%), in which a small amount of Hg vapor is introduced to remove traces of O and  $O_3$  possibly generated by discharge together with  $O_2(^1\Delta_g)$  [18]. The metal samples for  $O_2(^1\Delta_g)$  deactivation experiments are electroplated with pure Cr, Ag, Ni, and Cu on both sides of a 46.5 cm  $\times$  0.8 cm  $\times$  0.01 cm Cu strip. The purity of metal surface is examined by X-ray photoelectron spectroscopy (XPS) instrument (VJESCALAD MK2 X-ray photoelectron spectroscopy). It shows that

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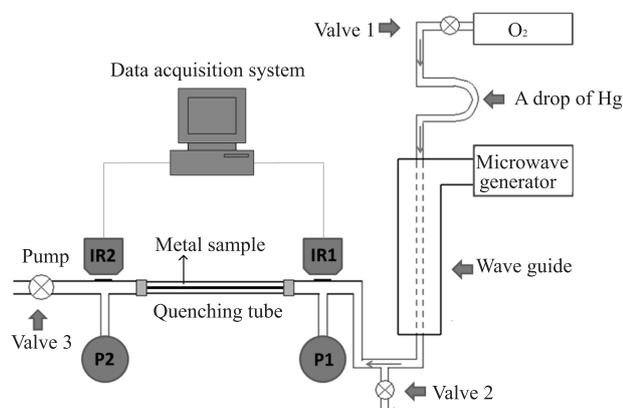
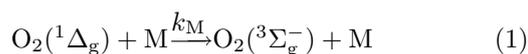


FIG. 1 An experimental setup for studying the deactivation of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) on metal surface. IR refers to infrared detector and P is gas pressure gauge. The metal sample and P is fixed in the middle of the quenching tube. A secondary gas in the binary gas mixture experiments was injected into the flow after the microwave discharge through valve 2.

there is no impurity other than the adsorbed O and C. The sample is fixed along the axis of a glass quenching tube as shown in Fig.1. Two infrared detectors (J160-M204-R05M-60 Judson) are fixed right at the front and at the back of the quenching tube to measure the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub><sup>-</sup> → <sup>3</sup>Σ<sub>g</sub><sup>-</sup>) emission at 1270 nm, then the signal is amplified by a lock-in amplifier (SR830 DSP SRS) and recorded by a data acquisition system. The quenching probability was calculated by comparing the IR emission intensity before and after deactivation. Gas pressure is measured by two gauges P1 and P2 respectively. All the experiments were conducted at room temperature (about 22 °C) and under a pressure ranging from 200 Pa to 500 Pa. For studying the influence of other gases (Ar, He, N<sub>2</sub>, and O<sub>2</sub>) on the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) deactivation, each secondary gas is injected into the system from valve 2 and mixed with the oxygen flow ahead of the quenching tube.

### III. RESULTS

The quenching process of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) can be described by



where M represents the metal surface, and  $k_M$  is the quenching rate constant. Since the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) deactivation efficiency by metal surfaces is much higher than gaseous O<sub>2</sub>, the latter can usually be neglected. Therefore, the ratio of the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration before and after quenching can be expressed as

$$\frac{C}{C_0} = \exp(-k_M\tau) \quad (2)$$

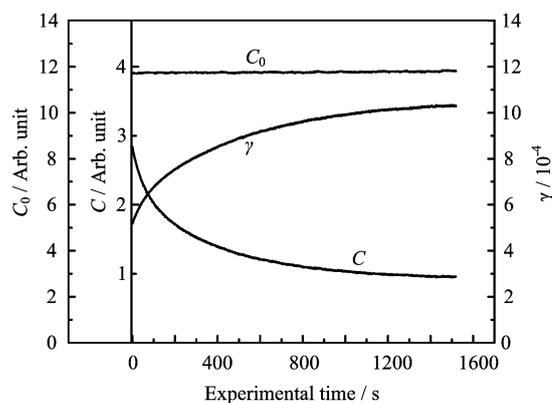


FIG. 2 O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) deactivation on Cu Surface.

where  $C_0$  and  $C$  represent the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration at the entrance and exit of the quenching tube, and  $\tau$  is the residence time of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) in the quenching tube. The relation between  $k_M$  and  $\gamma$  can be described by Eq.(3) [6],

$$k_M = \frac{1}{4} \gamma \sigma \bar{u}_T \quad (3)$$

$$\sigma = \frac{A}{V} \quad (4)$$

where  $\gamma$  is the quenching probability of a O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) molecule during a single collision with the surface,  $\bar{u}_T$  is the average velocity of oxygen molecules under temperature  $T$ ,  $\sigma$  is the specific surface area of the quenching surface,  $A$  the total metal surface area, and  $V$  the gas volume in the quenching tube. From Eqs.(2) and (3),  $\gamma$  can be calculated by Eq.(5).

$$\gamma = \frac{4 \ln(C_0/C)}{\sigma \bar{u}_T \tau} \quad (5)$$

In the experiments of Cr, Ag, Cu, and Ni, we found that while the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration at the entrance of the quenching tube  $C_0$  maintained constant, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration at the exit of the quenching tube  $C$  decreased continually as the experiment proceeds, as shown in Fig.2, and the corresponding  $\gamma$  was increasing during about the first half hour and gradually attained some steady value in a few hours.

This phenomenon indicates that the surface state is changing continually during the experiment, which is obviously due to the adsorption of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) on the surface. Then the system was evacuated to a few Pa and left to stay there for several hours to remove the adsorbed gases on the surface. We found that at the beginning of the next experiment  $C$  will get back to its original initial level. The result indicates that it is a reversible physical adsorption or some type of weak chemical adsorption. In order to make sure if the ground state oxygen molecules could affect  $\gamma$  in a similar way,

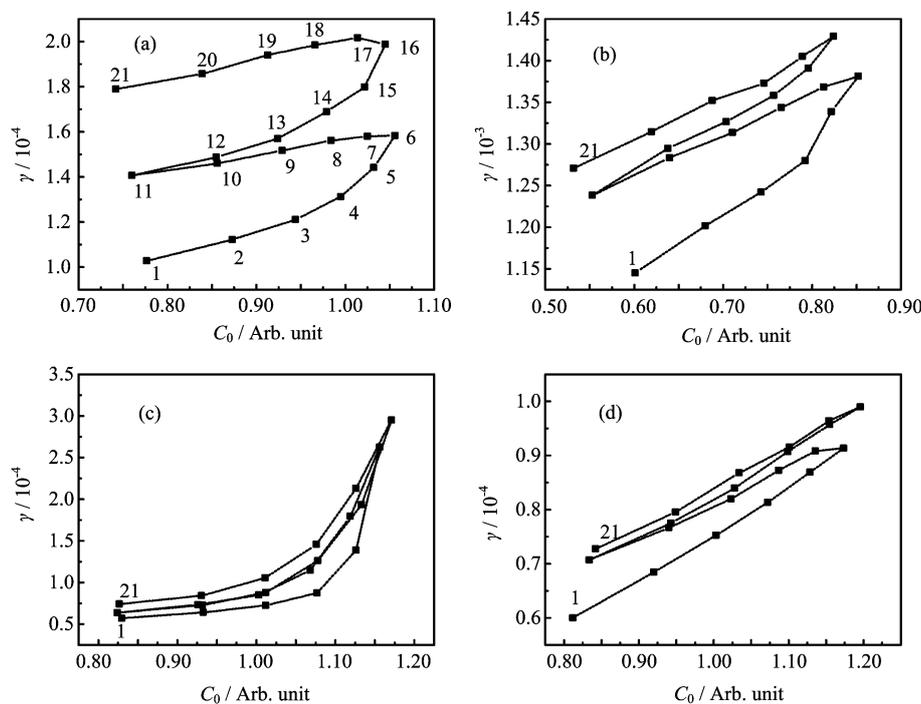


FIG. 3 Quenching probability  $\gamma$  as a function of  $O_2(^1\Delta_g)$  concentration  $C_0$  on Cr (a), Cu (b), Ag (c), and Ni (d). The numbers marked on the curve represent the sequence of experiments. An experiment started at number 1 and closed at number 21 along the curve.

a special experiment was conducted in which the microwave discharge was turned off and only high purity oxygen was allowed to pass through the system for over 20 h and the result showed that no influence on  $\gamma$  was found. Besides the time effect, we found  $\gamma$  increases with the increase of  $C_0$  as shown in Fig.3. In Fig.3(a) for Cr, the numbers 1 to 21 represent the sequence of  $\gamma$  measurement, number 1 refers to the first measurement, number 2 the next measurement at higher  $C_0$  (the time interval is about 5 min, bringing change in the  $O_2(^1\Delta_g)$  concentration). We see that from number 1 to 6,  $\gamma$  rises exponentially with increase of  $C_0$ , which implies that the Cr surface has adsorbed a larger amount of oxygen in this stage. But from number 6 to 11 when we gradually decrease  $C_0$ , the corresponding  $\gamma$  falls only slightly, which means the  $O_2(^1\Delta_g)$  desorbs from the surface being much slower. From number 11 to 16 and to 21, the similar phenomenon appears, albeit at higher  $\gamma$  levels. So we see at last (the  $\gamma$  value at number 21) is much higher than that of number 1 although their  $C_0$  are nearly the same. This experiment demonstrates further that the  $O_2$ -adsorbed Cr surface is an efficient quencher of  $O_2(^1\Delta_g)$ . For Cu (Fig.3(b)), Ag (Fig.3(c)), and Ni (Fig.3(d)), the phenomena are similar although each has its own feature due to the different adsorbing/desorbing rate.

To demonstrate how important the role of  $O_2$ -adsorbed metal surface is on the  $O_2(^1\Delta_g)$  deactivation, we have proceeded a few special experiments by intro-

ducing some secondary gases including Ar (Fig.4(a)), He (Fig.4(b)),  $N_2$  (Fig.4(c)), and  $O_2$  (Fig.4(d)) into the  $O_2(^1\Delta_g)$ - $O_2$  flow through the valve 2. At point 1, the valve opens and we see  $C_0$  drops due to the  $O_2(^1\Delta_g)$  concentration decrease. On the contrary,  $C$  (for Fig.4 (a), (b), and (c)) gradually ascends, and consequently decreases. Obviously this is due to the desorption of  $O_2$  by colliding with Ar, He, or  $N_2$  molecules. At point 2, the valve closed and  $C_0$  returned to near the original value, we see the simultaneous  $C$  rise, followed by slow descending. This should be owing to the  $O_2$  re-adsorption which induced higher  $\gamma$  as shown in Fig.4. But interestingly, when secondary  $O_2$  is introduced as in Fig.4(d), there is no rise of  $C$ . This indicates that  $O_2$  collision on the surface does not induce  $O_2$  desorption. Possibly only  $O_2$ - $O_2$  interchange occurs in the latter case.

#### IV. DISCUSSION

The STM image of our electroplating metal sample shows that the surface consists of a large number of micro poly-crystals with sizes from a few tens to hundreds nm. So there are many defects and adsorbed sites (figure not shown). As soon as the sample is exposed to the air, its surface must be covered by a strongly chemisorbed monomolecular oxygen layer which can not be removed by evacuating to a few Pa at room temperature as shown by the XPS view. In this work we

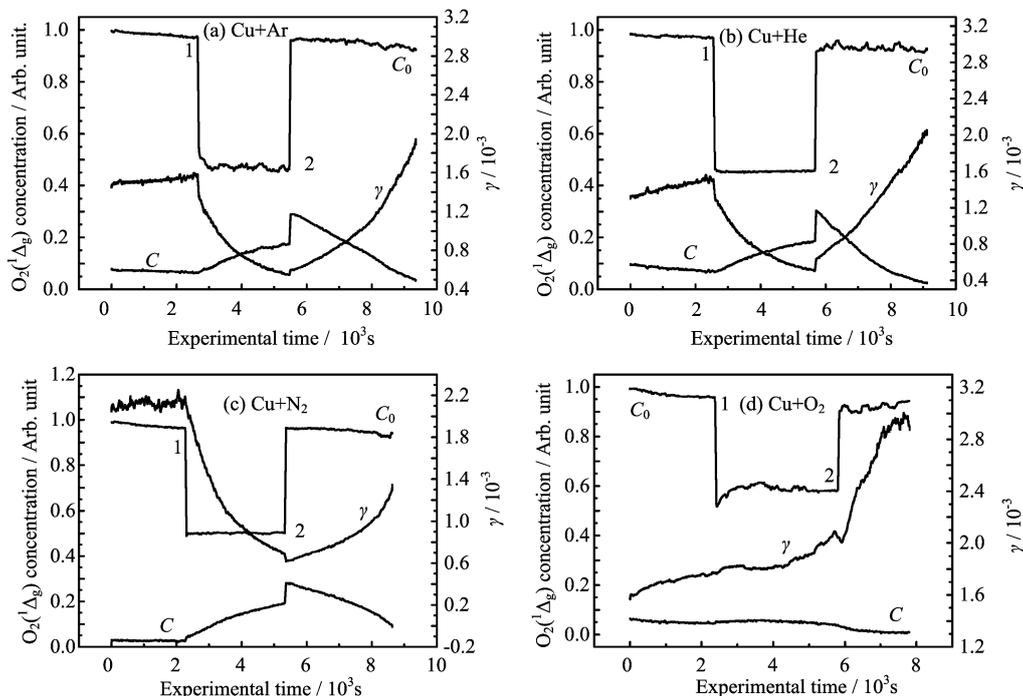


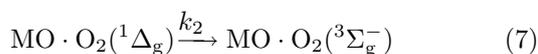
FIG. 4 Deactivation on Cu surface of binary gaseous mixtures containing O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>). The concentration change of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) before (C<sub>0</sub>) and after (C) surface quenching when Ar (a), He (b), N<sub>2</sub> (c), or O<sub>2</sub> (d) as a secondary gas was injected into the O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>)-O<sub>2</sub> flow through valve 2 respectively.

use MO to represent these adsorbed sites and propose a phenomenological model to explain the observed experimental phenomena. Altogether, four consecutive processes are assumed to take place:

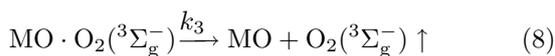
(i) Gas phase O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) molecules striking on MO to form weak chemisorbed O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>)



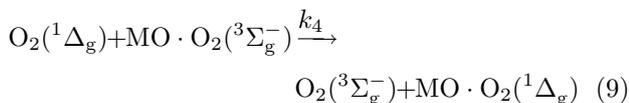
(ii) Very fast relaxation of MO·O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) to form MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) by electron interchange between π<sub>g</sub> electron in O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) and free electron in metal. As estimated by Ryskin *et al.*, the relaxation rate of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) should be value of 10<sup>7</sup>–10<sup>9</sup> s<sup>-1</sup> [16].



(iii) Desorption of O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) from the surface



(iv) As suggested by Klopovskiy *et al.* in their study of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) quenching on the quartz surface [17], a near resonant energy transfer between O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) on the surface and O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) in the gas phase can happen efficiently,



Because γ of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) is proportional to the amount of MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) sites on the surface as we see in the above experiments, so we may write a kinetic equation of MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) to show the time variation of γ as:

$$\frac{d[\text{MO} \cdot \text{O}_2(^3\Sigma_g^-)]}{dt} = k_1[\text{O}_2(^1\Delta_g)][\text{MO}] - k_3[\text{MO} \cdot \text{O}_2(^3\Sigma_g^-)] \quad (10)$$

where [MO]=[MO]<sub>0</sub>−[MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>)], and [MO]<sub>0</sub> represents the initial amount of MO sites. It should be noted here that in Eq.(10) the reaction (9) has been neglected because we consider that its product MO·O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) converts to MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) very rapidly as shown in Eq.(7). From Eq.(10) we can see that at the initial experimental stage, [MO] is large and [MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>)] small, so γ increases with duration of the experiment. Then, as [MO] is converting to MO·O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>), the rate of γ rise goes down. At last, a steady state is reached, *i.e.*, when

$$\frac{d[\text{MO} \cdot \text{O}_2(^3\Sigma_g^-)]}{dt} = 0 \quad (11)$$

we get:

$$[\text{MO} \cdot \text{O}_2(^3\Sigma_g^-)] = \frac{k_1[\text{O}_2(^1\Delta_g)][\text{MO}]_0}{k_1[\text{O}_2(^1\Delta_g)] + k_3} \quad (12)$$

Eq.(12) may explain that γ increases with increasing O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) concentration. For the metal surface with larger amount of [MO]<sub>0</sub> sites, γ value will be larger, this may explain why γ for Cu is larger.

## V. ACKNOWLEDGMENTS

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