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ELECTRON STIMULATED O<sup>-</sup> DESORPTION FROM O<sub>2</sub> CONDENSED ON

A RARE-GAS FILM: EVIDENCE FOR AN INDIRECT "BOUNCE" TRAJECTORY

By

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**Electron-stimulated O<sup>-</sup> Desorption from O<sub>2</sub> Condensed on a Rare-gas Film: Evidence for an Indirect "bounce" trajectory.**

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**1. INTRODUCTION**

The electron-stimulated dissociation of O<sub>2</sub> gas is well understood. In the energy range from 4 to 10 eV, O<sub>2</sub> ions are produced by dissociative attachment (DA) via the transient O<sub>2</sub><sup>-</sup>(<sup>1</sup>Δ<sub>g) state. This same DA process has been identified in electron-stimulated desorption (ESD) of O<sub>2</sub> ions from O<sub>2</sub> condensed on thick rare-gas (Ar, Kr, or Xe) films. However, electron-energy-dependence curves of the O<sub>2</sub> yield is quite different from that for gaseous O<sub>2</sub> as shown in Fig. 1. The gas-phase curve rises slowly at the threshold and has a symmetric bell shape, while the condensed-phase curve rises sharply at the threshold and has an asymmetric triangular shape. Furthermore, the threshold energy of the condensed-phase curve depends on the rare-gas substrate, as shown in Table 1. In this note, we offer an explanation for the threshold changes and suggest a trajectory for the O<sub>2</sub> ion desorption via the O<sub>2</sub><sup>-</sup>(<sup>1</sup>Δ<sub>g) intermediate state. We shall explain the different energy dependence elsewhere. (A.R.)</sub></sub>

**2. DISCUSSION**

**2.1 Two possible trajectories**

Figure 2 illustrates two possible O<sup>-</sup> desorption trajectories for an inclined O<sub>2</sub> on a rare-gas substrate. In one trajectory, DA yields an O<sup>-</sup> ion moving away from the surface (we shall call this the direct-path (DP) trajectory), while in the other it yields an O<sup>-</sup> ion moving initially towards the surface requiring it to "bounce" off the surface (we shall call this the indirect-bounce (IB) trajectory). The schematic potential curves which lead to these two trajectories are illustrated in Fig. 3. In the IB case, the O<sub>2</sub><sup>-</sup>(<sup>1</sup>Δ<sub>g) intermediate state dissociates into the O+O/RG limit, which means that the O<sup>-</sup> ion initially ends on the rare-gas (RG) surface, while in the DP case, it dissociates directly into the O+O/RG limit, which indicates that the O<sup>-</sup> ion proceeds directly from the surface. The O+O/RG limit is lower than the O<sup>-</sup>+O/RG limit by the surface-polarization energy (E<sub>p</sub>) of the RG substrate. In the Franck-Condon region, the potential curves for the DP and IB trajectories become the same and are lowered by E<sub>p</sub> with respect to the gas-phase potential curve as shown in Fig. 3.</sub>

Fig. 1 Comparison of the ESD O<sup>-</sup> yields from (a) gaseous O<sub>2</sub> and (b) O<sub>2</sub> (0.03 ML)/Kr (20 ML)/Pt.

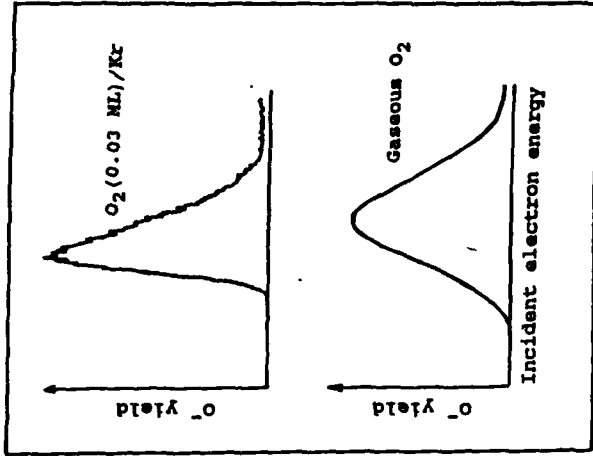


Table 1. Threshold energies (eV) for the O<sup>-</sup> yield from O<sub>2</sub>/RG.

	Ar	Kr	Xe
Experiment	4.3	4.3	4.5
IB trajectory	4.3	4.4	4.5
DP trajectory	3.7	3.7	3.7

**2.2 Threshold energy**

The threshold energies for O<sup>-</sup> desorption via the DP and IB trajectories are given by E<sub>d</sub> and E<sub>d</sub>+E<sub>p</sub> respectively, where E<sub>d</sub> (=3.65 eV) is the dissociation energy (i.e. difference between O<sub>2</sub> and O+O<sup>-</sup>). The threshold energy (E<sub>th</sub>) for the IB trajectory is derived from the equation,

$$E_p = [E_{th} - (E_d - E_p)]/2, \quad (1)$$

which means that the O<sup>-</sup> ion created on the surface must have its kinetic energy larger than the surface-polarization energy E<sub>p</sub> to desorb from the surface. Threshold energies calculated with the E<sub>p</sub>'s obtained by Sanche et al. [5] (i.e., 0.62, 0.72, and 0.89 eV for Ar, Kr, and Xe, respectively) are listed in Table 1. The good agreement between the IB threshold energies



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these intuitive potential curves, one might infer that  $O_2^-$  ( $^2\pi_u$ )/RG should dissociate equally into the  $O+O^-$ /RG and  $O^-+O$ /RG limits and predict that the branching ratios for the DP and IB trajectories should be about equal for high electron energies. Based on theoretical rules, we shall show below that the  $O_2^-$  ( $^2\pi_u$ )/RG state dissociates only into the  $O+O^-$ /RG limit, predicting the predominance of the IB trajectory.

The lowest dissociation limit for  $O_2^-$  is  $O(^3p)+O(^2p)$ . According to the Wigner-Witmer rules, two  $O_2^-$  ( $^2\pi_u$ ) states and two  $O_2^-$  ( $^2\pi_g$ ) states arise from the interaction of the  $O(^3p)$  and  $O(^2p)$  atomic states. The equal number of the  $^2\pi_u$  and  $^2\pi_g$  states is a consequence of the degeneracy of the  $O(^3p)+O(^2p)$  and  $O(^2p)+O(^3p)$  limits. When  $O_2$  is placed on a rare-gas substrate, the two O atoms are no longer identical, e.g.,  $O_F$  and  $O_M$  (farther (F) and nearer (M) from surface). According to Wigner-Witmer rules, two  $O_F O_M^-$  ( $^2\pi$ ) states arise from the  $O_F(^3p)+O_M(^2p)$  atomic states and the other two  $O_F O_M^-$  ( $^2\pi$ ) states, from the  $O_F(^2p)+O_M(^3p)$  limit. According to the non-crossing rule, the lowest two  $O_F O_M^-$  ( $^2\pi$ ) states connect to the  $O_F(^3p)+O_M(^2p)$  limit, which is the lowest limit since  $O_M$  is closer to the surface. The two lowest  $^2\pi$  states are the  $O_2^-$  ground state and the  $O_2^-$  ( $^2\pi_u$ ) state. Therefore, the  $O_2^-$  ( $^2\pi_u$ )/RG state connects to the  $O+O^-$ /RG limit. In other words, the  $O_2^-$  ( $^2\pi_u$ )/RG state dissociates exclusively into the  $O+O^-$ /RG limit.

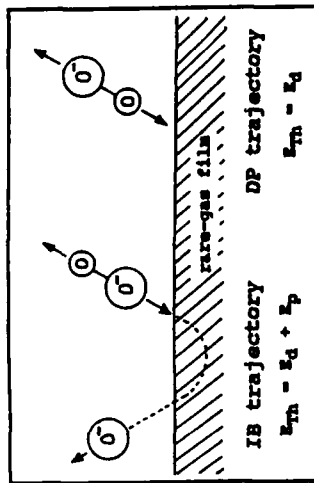
#### 2.4 $Cl^-$ desorption from condensed $Cl_2$

$Cl^-$  desorption from  $Cl_2$  condensed on Pt provides a clear test of the above arguments. For this case, only four  $Cl_2^-$  states, namely, the  $2^2\pi_u$ ,  $^2\pi_g$ ,  $^2\pi_u$ , and  $2^2\pi_g$  states, arise from the lowest dissociation limit,  $Cl(^3s)+Cl(^2p)$ . Analysis similar to that given above predicts that  $Cl^-$  desorption via the  $Cl_2^-$  ( $^2\pi_u$ ) and  $Cl_2^-$  ( $^2\pi_g$ ) intermediate states should follow the IB and DP trajectories, respectively.

The  $Cl^-$  ions in the IB trajectory must bounce off the Pt metal for  $Cl_2$  (1 ML)/Pt or off the  $Cl_2$  film for  $Cl_2$  (4 ML)/Pt where ML=monolayers. Colliding with the Pt metal, the  $Cl^-$  ions are most likely neutralized; colliding with the  $Cl_2$  film, the  $Cl^-$  ions lose most of its kinetic energy so that it cannot overcome the polarization barrier. [The polarization barrier arises from the image charge potential ( $\approx 1.5eV$ ) on the Pt metal substrate or the polarization potential ( $\approx 1eV$ ) for the thicker  $Cl_2$  film.] Therefore, we expect that  $Cl^-$  desorption via the  $Cl_2^-$  ( $^2\pi_u$ ) state, which must follow the IB trajectory, is quenched for both  $Cl_2$  (1 ML)/Pt and  $Cl_2$  (4 ML)/Pt.

The ratio of the  $Cl^-$  yield peaks via the  $Cl_2^-$  ( $^2\pi_g$ ) and  $Cl_2^-$  ( $^2\pi_u$ ) states is about 1/2 for gaseous  $Cl_2$  [6]. For  $Cl_2$  (1 ML)/Pt and  $Cl_2$  (4 ML)/Pt, this ratio nearly vanishes [7], showing that  $Cl^-$  desorption via the  $Cl_2^-$  ( $^2\pi_g$ ) state is indeed quenched. This quenching cannot be attributed to angular discrimination, since the  $Cl_2^-$  ions were collected around  $70^\circ$  in the experiment [7] and the  $^2\pi_g$  peak should disappear only if we collect the  $Cl^-$

Fig. 2 Schematic illustrations of the indirect-path (DP) and direct-path (DP) and indirect-bounce (IB)  $O^-$  desorption trajectories for an inclined  $O_2$  on a rare-gas substrate.



(as opposed to the DP threshold energies) and the observed threshold energies suggests that the  $O^-$  desorption via the  $O_2^-$  ( $^2\pi_u$ ) intermediate state proceeds exclusively along the IB trajectory. We note that the DA mechanism involving the IB trajectory is distinctly different from the Antoniewicz "bounce" mechanism [4].

#### 2.3 Potential curve of $O_2^-$ ( $^2\pi_u$ )/RG

How does the predominance of the IB trajectory follow from the intuitive  $O_2^-$  ( $^2\pi_u$ )/RG potential curves in Fig. 3? Based on

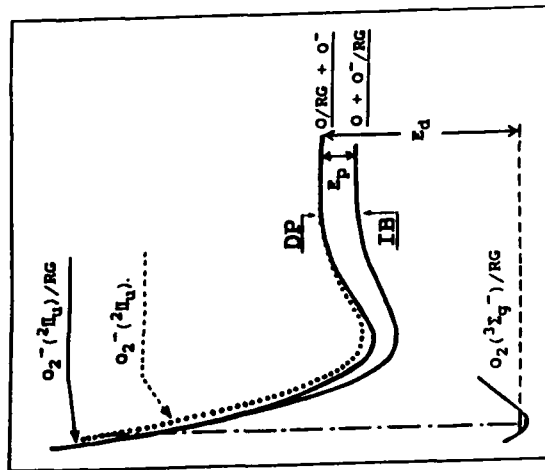


Fig. 3 Schematic  $O_2^-$  ( $^2\pi_u$ )/RG potential curves corresponding to the DP and IB trajectories. Only the IB curve is valid.

ions exclusively at 90° with respect to the incident electron beam [8]. This quenching also cannot be a discrimination due to a high threshold energy, since the expected peak position (=2 eV) of the Cl<sub>2</sub><sup>(2Π<sub>u</sub>)</sup> state is well above the expected threshold energy (=0.0<sup>+</sup> eV).

The Cl<sup>-</sup> desorption through the DP trajectory is expected to be similar to that from gaseous Cl<sub>2</sub>: that is, the Cl<sup>-</sup> ion kinetic energy as a function of the incident electron energy is expected to be a straight line with a slope of 1/2. This has been observed experimentally [7] for the Cl<sup>-</sup> ions from the Cl<sub>2</sub><sup>(2Π<sub>u</sub>)</sup> state, which proceeds through the DP trajectory.

3. CONCLUSIONS

Our study suggests the following generalizations: The ESD of A<sup>-</sup> ions from physisorbed homonuclear diatomic molecules, A<sub>2</sub>, are often produced by DA via a transient A<sub>2</sub><sup>-</sup> state. The trajectory (DP or IB) of the desorbing A<sup>-</sup> ions is uniquely determined by the potential curve of this A<sub>2</sub><sup>-</sup> state. Furthermore, the A<sup>-</sup> desorption via the IB trajectory is often quenched or severely reduced except on rare-gas substrates. In contrast, the A<sup>-</sup> desorption via the DP trajectory proceeds, on most surfaces, similarly to A<sup>-</sup> dissociation from gaseous A<sub>2</sub>.

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 [3] H. Sambe, D.E. Ramaker, L. Parenteau, and L. Sanche, to be published.  
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