Electron Stimulated O⁺ Desorption from O₂ Condensed on a Rare-Gas Film: Evidence for an Indirect "Bounce" Trajectory

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**Supplementary Notation**

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**Abstract (Continued on reverse if necessary and identify by block number)**

Rare gas solids, Oxygen, Chlorine, Dissociative attachment, ion trajectories

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Electron-Stimulated O⁻ Desorption from O₂ Condensed on a Rare-Gas Film: Evidence for an Indirect "Bounce" Trajectory.

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1. INTRODUCTION

The electron-stimulated O₂ dissociation of O₂ gas is well understood. In the energy range from 4 to 10 eV, O₂ ions are produced by dissociative attachment (DA) via the transient O₂⁻(H⁺) state. This same DA process has been identified in electron-stimulated desorption (ESD) of O₂⁻ ions from O₂ condensed on thick rare-gas (Ar, Kr, or Xe) films [2]. However, electron-energy-dependence curve of the O⁻ yield is quite different from that for gas-phase O₂ 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⁻ ion desorption via the O₂⁻(H⁺) intermediate state. We shall explain the different energy dependence elsewhere [2].

2. DISCUSSION

2.1 Two possible trajectories

Figure 2 illustrates two possible O⁻ desorption trajectories for an inclined O₂ on a rare-gas substrate. In one trajectory, DA yields an O⁻ ion moving away from the surface (we shall call this the direct-path (DP) trajectory), while in the other it yields an O⁻ 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. 2 in the IB case, the O₂⁻(H⁺) intermediate state dissociates into the O⁺/RG limit, which means that the O⁻ ion initially is on the rare-gas (RG) surface; while in the DP case it dissociates into the O⁺/RG limit, which indicates that the O⁻ ion proceeds directly from the surface. The O⁺/RG limit is lower than the O⁻/RG limit by the surface-polarization energy (E₁) 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 E₂ with respect to the gas-phase potential curve as shown in Fig. 3.

![Fig. 1. Comparison of the ESD O⁻ yields from (a) gas-phase O₂ and (b) O₂(0.03 ML)/Kr(20 ML)/Pt.](image)

Table 1. Threshold energies (eV) for the O⁻ yield from O₂/RG.

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<th>RG</th>
<th>Ar</th>
<th>Kr</th>
<th>Xe</th>
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<tr>
<td>IB</td>
<td>4.3</td>
<td>4.4</td>
<td>4.5</td>
</tr>
<tr>
<td>DP</td>
<td>3.7</td>
<td>3.7</td>
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2.2 Threshold energy

The threshold energies for O⁻ desorption via the DP and IB trajectories are given by E₁ and E₂, respectively, where E₂ (≈0.65 eV) is the dissociation energy (i.e., difference between O⁺ and O⁻). The threshold energy (E₁) for the IB trajectory is derived from the equation,

\[ E₁ = \left( E₂ - (E₁ - E₂) \right) / 2, \]

which means that the O⁻ ion created on the surface must have its kinetic energy larger than the surface-polarization energy E₁ to desorb from the surface. Threshold energies calculated with the E₁,s obtained by Sánchez 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...
these intuitive potential curves, one might infer that O$_2$\(^{(2\Pi_u)}/\text{RG}$ should dissociate equally into the O$^+$/RG and O$^+$/O/RG limits and predict that the branching ratio 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)}/\text{RG}$ state dissociates only into the O$^+$/RG limit, predicting the predominance of the IB trajectory.

The lowest dissociation limit for O$_2$ is O\(^{(2\Pi)}$/O^-$\(^{(2\Pi)}$). According to the Wigner-Wittmer rules, two O$_2$\(^{(2\Pi_u)}$ states and two O$_2$\(^{(2\Pi_g)}$ states arise from the interaction of the O\(^{(2\Pi)}$) and O\(^{(2\Pi)}$) atomic states. The equal number of the \(\Pi_u\) and \(\Pi_g\) states is a consequence of the degeneracy of the O\(^{(2\Pi)}$) + O\(^{(2\Pi)}$) and O\(^{(2\Pi)}$) + O\(^+(\Pi)$) limits. When O$_2$ is placed on a rare-gas substrate, the two O atoms are no longer identical, e.g., O$_2$\(_N\), and O$_2$\(_F\) (farther (F) and nearer (N) from surface). According to Wigner-Wittmer rules, two O$_2$\(_N\)\(^{(2\Pi_u)}$ states arise from the O\(_N\)^{(2\Pi)}$/O^+(\Pi)$ atomic state, and the other two O$_2$\(_F\)\(^{(2\Pi_u)}$ states, from the O\(_F\)^{(2\Pi)}$/O^+(\Pi)$ limit. According to the non-crossing rule, the lowest O$_2$\(_N\)\(^{(2\Pi_u)}$ states connect to the O\(_N\)^{(2\Pi)}$/O^+(\Pi)$ limit, which is the lowest limit since O$_N$ is closer to the surface. The two lowest \(\Pi_u\) states are the O$_2$\(_N\)\(^{(2\Pi_u)}$ ground state and the O$_2$\(_F\)\(^{(2\Pi_u)}$ state. Therefore, the O$_2$\(^{(2\Pi_u)}/\text{RG}$ state connects to the O$^+$/RG limit. In other words, the O$_2$\(^{(2\Pi_u)}/\text{RG}$ state dissociates exclusively into the 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 $^2\Sigma_u^+$, $^2\Sigma_g^+$, $^2\Pi_u$, and $^2\Pi_g$ states, arise from the lowest dissociation limit, Cl$^-$\(^{(2\Pi_u)}$/Cl$^+(\Pi)$). Analysis similar to that given above predicts that Cl$^-$ 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$_2$(4 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 ($\approx 3.5$ eV) on the Pt metal substrate or the polarization potential (1 eV) 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_u)}$) and Cl$_2$\(^{(2\Pi_g)}$) states is about 1/2 for gaseous Cl$_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)}$) state is indeed quenched. This quenching cannot be attributed to angular discrimination, since the Cl$^-$ ions were collected around 70° in the experiment [7] and the Cl$^-$ peak should disappear only if we collect th Cl$^-$ (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)}/\text{RG}$

How does the predominance of the IB trajectory follow from the intuitive O$_2$\(^{(2\Pi_u)}/\text{RG}$ potential curves in Fig. 3? Based on

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**Fig. 2** Schematic illustrations of the direct-path (DP) and indirect-bounce (IB) O$^-$ desorption trajectories for an inclined O$_2$ on a rare-gas substrate.

**Fig. 3** Schematic O$_2$\(^{(2\Pi_u)}/\text{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 (\(\pm 2\) eV) of the Cl\(^+\) (" state is well above the expected threshold energy (\(>0.0\) eV).

The Cl\(^+\) desorption through the DP trajectory is expected to be similar to that from gaseous Cl\(_2\) that is, the Cl\(^+\) 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\(^+\) ions from the Cl\(_2\) (" state, which proceeds through the DP trajectory.

3. CONCLUSIONS

Our study suggests the following generalizations: The ESD of A\(^-\) ions from physisorbed homonuclear diatomic molecules, A\(_2\), are often produced by DA via a transient A\(_2\)^{•} state. The trajectory (DP or IB) of the desorbing A\(^+\) ions is uniquely determined from the potential curve of this A\(_2\)^{•} state. Furthermore, the A\(^+\) desorption via the IB trajectory is often quenched or severely reduced except on rare-gas substrates. In contrast, the A\(^+\) desorption via the DP trajectory proceeds, on most surfaces, similarly to A\(^-\) dissociation from gaseous A\(_2\).

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research.

REFERENCES

[4] P.E. Antoniewicz, Phys. Rev. B 21 (1980) 3811. In the Antoniewicz "bounces", an ion A\(^+\) created on a metal surface moves towards the surface due to the image-charge attraction; and the neutralization of the A\(^+\) leads to desorption of the neutral A because of the repulsion between the A and the metal surface.