Probing Copper and Copper–Gold Alloy Surfaces with Space-Quantized Oxygen Molecular Beam

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ABSTRACT: The orientation and motion of reactants play important roles in reactions. The small rotational excitations involved render the reactants susceptible to dynamical steering, making direct comparison between experiments and theory rather challenging. Using space-quantized molecular beams, we directly probed the (polar and azimuthal) orientation dependence of O$_2$ chemisorption on Cu(110) and Cu$_3$Au(110). We observed polar and azimuthal anisotropies on both surfaces. Chemisorption proceeded rather favorably with the O−O bond axis oriented parallel (vs perpendicular) to the surface and rather favorably with the O−O bond axis oriented along [001] (vs along [1 \bar{1} 0]). The presence of Au hindered the surface from further oxidation, introducing a higher activation barrier to chemisorption and rendering an almost negligible azimuthal anisotropy. The presence of Au also prevented the cartwheel-like rotations of O$_2$.

KEYWORDS: metal surface, oxidation, copper, copper–gold alloy, steric effect

INTRODUCTION

Activation of molecular oxygen (O$_2$) constitutes an important step in oxidative processes, including heterogeneous catalysis, electrocatalysis, and corrosion of metals.$^{1−7}$ The interaction of O$_2$ with various metal surfaces induces changes in its chemical stability and reactivity. It follows that the ability to control such processes bears on the chemical economic world. Alloying of pristine metals provides one of the simplest ways to do so. Understanding the microscopic mechanism behind O$_2$ chemisorption entails unraveling the stereochemistry of the processes involved.$^{8−14}$

O$_2$ dissociative adsorption on Cu(110) provides a model system for understanding the oxidation processes on Cu surfaces.$^{15−32}$ The pristine Cu(110) surface possesses an anisotropic surface structure, on which anisotropic Cu−O chains grow as a precursor to oxide formation.$^{16−32}$ Early molecular beam experiments observed initial sticking probabilities ($S_0$) increasing with translational energy ($E_t$), approaching 0.8 at a high enough $E_t$.$^{24}$

At low $E_t$ two competing mechanisms could account for the observed O$_2$ dissociative adsorption. A precursor-mediated channel (a weakly bound, physisorbed trapping molecular state) dominates at low $E_t$ and low surface temperatures ($T_s$). Activated dissociative chemisorption becomes important as $E_t$ increases, which occurs directly and/or via a short-lived molecularly chemisorbed state. One could also think of a three-well potential$^{33}$ that ascribes transient molecularly chemisorbed states to negatively ionized O$_2^-$, e.g., the peroxo state, as suggested by high-resolution electron energy loss spectroscopy (HREELS) measurements$^{17,18}$ and density functional theory (DFT)-based calculations.$^{19}$ Such negatively charged states could account for the high sticking probability and the well-known efficient catalytic activity of Cu for oxidation.

At high $E_t$, hyperthermal molecular oxygen beam (HOMB) experiments$^{14}$ report effective formation of Cu$_2$O precursor on Cu(110), that exhibits dependence on the azimuthal orientation at which O$_2$ impinges the surface. This demonstrates another important feature that comes from the inherent orientation dependence of reactions. The stereodynamics of reactant molecules (the orientation and the movement of molecules in 3D space) plays an important role in reactions. The small rotational energy excitations involved (ca. less than a few meV) render the reactants susceptible to dynamical steering$^{1,34−36}$ and make direct verification of...
calculated potential energy surfaces (PES) rather challenging.\textsuperscript{11,10\textendash}14,54,39 Helicopter-like rotating O\textsubscript{2} (with dominant rotational angular momentum \(J\) parallel along the surface normal) adsors more effectively than cartwheel-like rotating O\textsubscript{2} (with \(J\) perpendicular to the surface normal).\textsuperscript{19,20,22} As mentioned earlier, a possible candidate for transient molecules chemisorbed state would be an adsorbed O\textsubscript{2} exhibiting peroxy-like character (O\textsubscript{2}−), with azimuthal orientation-dependent stability.\textsuperscript{19,20,22} As expected from previous discussions,\textsuperscript{34\textendash}36 at high \(E\textsubscript{0}\) (ca. 500 meV), the impinging O\textsubscript{2} does not have enough time to reorient (be steered) and the favorable helicopter-like rotating O\textsubscript{2} dominantly account for chemisorption.\textsuperscript{19} On the other hand, at low \(E\textsubscript{0}\) (ca. 50 meV), the impinging O\textsubscript{2} have enough time to reorient (be steered) to more favorable orientations toward reactive sites.\textsuperscript{59}

Ancient people know that alloying with inert gold (Au) protects Cu from further corrosion, and we observe several ancient products enduring in rather pristine condition.\textsuperscript{38} Now, we know that the deeper \(d\)-band center induced by Au alloying prevents the strong bonding–antibonding interaction with the antibonding state of the impinging O\textsubscript{2}, resulting in the inertness of the alloy surface.\textsuperscript{33,39,40} Moreover, the presence of Au changes the electron distribution (electronic corrugation) on the Cu surface. Thus, one would expect different dynamical processes (e.g., translational to rotational energy transfer effects) occurring when O\textsubscript{2} impinges on a Cu–Au alloy surface as compared to a Cu surface.

In this study, we clarify the alignment dependence of O\textsubscript{2} chemisorption on Cu(110) and Cu\textsubscript{3}Au(110). We do this by using a single-quantum-state-selected (space quantized, following the 1922 Stern-Gerlach experiment\textsuperscript{41,42}) O\textsubscript{2} beam developed at NIMS (for which both the molecular alignment and the spin state are well-defined).\textsuperscript{43} On Cu(110), as in previous studies, we observed both polar and azimuthal anisotropies. O\textsubscript{2} chemisorption proceeds rather favorably with the O–O bond axis oriented parallel (vs perpendicular) to the surface and rather favorably with the O–O bond axis oriented along [001] (vs along [1\(\bar{1}\)0]) with respect to Cu(110) (schematically depicted in the lower panel) and corresponding defining magnetic fields \(\vec{H}\). Orienting \(\vec{H}\) perpendicular to the surface, i.e., along [1\(\bar{1}\)0], results in helicopter-like rotating O\textsubscript{2}. Two types of cartwheel-like rotating O\textsubscript{2} can also be realized by orientating \(\vec{H}\) parallel to the surface, i.e., either along [1\(\bar{1}\)0] or [001].

(b) Time evolution of the sticking probability for a space-quantized O\textsubscript{2} impinging on Cu(110) (at a surface temperature of ca. 310 K) with translational energy \(E\textsubscript{0} = 0.10\) eV. Time \(t = 0\) corresponds to the time the beam shutter is opened to allow the molecular beam to impinge on the surface. Following the control signal shown (topmost right panel), the \(\vec{H}\) direction can be modulated to alternately produce helicopter-like (high signal) and cartwheel-like (low signal) rotating O\textsubscript{2} that impinge on Cu(110). Numerical fits to the corresponding sticking probability data points (using exponentially decaying functions extrapolated to \(t = 0\)) also shown to guide the eye. The values at \(t = 0\) correspond to the initial sticking probabilities \(S_0(H), S_0(C)\), and \(S_0(C)\).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(Space quantized) O\textsubscript{2} sticking probabilities on Cu(110). (a) Angular distributions (upper panel) of the molecular axis (O–O bond axis) of an O\textsubscript{2} (in the triplet electronic ground state \(^3\Sigma_g^+\) and spin-rotational state \([J = 2, M = 2]\)) with respect to Cu(110) (schematically depicted in the lower panel) and corresponding defining magnetic fields \(\vec{H}\). Orienting \(\vec{H}\) perpendicular to the surface, i.e., along [1\(\bar{1}\)0], results in helicopter-like rotating O\textsubscript{2}. Two types of cartwheel-like rotating O\textsubscript{2} can also be realized by orientating \(\vec{H}\) parallel to the surface, i.e., either along [1\(\bar{1}\)0] or [001].

(b) Time evolution of the sticking probability for a space-quantized O\textsubscript{2} impinging on Cu(110) (at a surface temperature of ca. 310 K) with translational energy \(E\textsubscript{0} = 0.10\) eV. Time \(t = 0\) corresponds to the time the beam shutter is opened to allow the molecular beam to impinge on the surface. Following the control signal shown (topmost right panel), the \(\vec{H}\) direction can be modulated to alternately produce helicopter-like (high signal) and cartwheel-like (low signal) rotating O\textsubscript{2} that impinge on Cu(110). Numerical fits to the corresponding sticking probability data points (using exponentially decaying functions extrapolated to \(t = 0\)) also shown to guide the eye. The values at \(t = 0\) correspond to the initial sticking probabilities \(S_0(H), S_0(C)\), and \(S_0(C)\).

\end{figure}

\section*{RESULTS AND DISCUSSION}

In Figure 1, we show the measured alignment-dependent O\textsubscript{2} initial sticking probabilities \(S_0\) on Cu(110). O\textsubscript{2} in a spin rotational state \([J, M = (2, 2)]\) exhibit a \(\sin^2 \theta\)-dependent O–O bond axis (angular) distribution, where \(\theta\) gives the polar angle subtended by the O–O bond axis with a predetermined defining magnetic field \(\vec{H}\). Thus, helicopter-like and cartwheel-like rotating O\textsubscript{2} (vide ante) can be generated, achieved by directing \(\vec{H}\) perpendicular or parallel to the surface (Figure 1a). Helicopter-like rotating O\textsubscript{2} have O–O bond axes oriented dominantly parallel to the surface. On the other hand, for cartwheel-like rotating O\textsubscript{2}, the O–O bond axes can assume both parallel and perpendicular configurations. We can further prepare two types of cartwheel-like rotating O\textsubscript{2} depending on their azimuthal orientation, e.g., by aligning \(\vec{H}\) along [1\(\bar{1}\)0] (Cartwheel \((x), C_x\)) or along [001] (Cartwheel \((y), C_y\)) (see Figure 1a).

In Figure 1b, we show the time evolution of the sticking probability for O\textsubscript{2} on Cu(110), measured while modulating \(\vec{H}\) to alternately produce helicopter-like and cartwheel-like O\textsubscript{2} at \(E\textsubscript{0} = 0.10\) eV. We determined the sticking probability curves by fitting the data points corresponding to each geometry to an exponential decay function (see smooth curves), and the values extrapolated to \(t = 0\) (beam shutter removed) correspond to initial sticking probabilities \(S_0(H)\) and \(S_0(C)\), respectively. Because we are discussing the very early stage of oxidation, Cu segregation induced by oxygen adsorption need not be considered in \(S_0\). We see that \(S_0(H) > S_0(C)\) and \(S_0(H) >\)
S_H(C_y) in general, indicating that more reactive parallel-oriented O_2 as compared to perpendicular-oriented O_2. This is consistent with previous XPS studies on Cu(111).^{45} From Figure 1b, we can also see from the time evolution of the sticking probabilities that S_H(C_y) > S_H(C_x), indicating that O_2 with O–O bond axes oriented along [001] are more reactive than those with O–O bond axes oriented [110].

In Figure 2, we show the corresponding results on Cu_3Au(110)-(4×1). Low-energy electron diffraction (LEED) patterns (Figure 2a) indicate Au atom segregation, forming a (4×1) restructured surface^{46} (see Figure 2b). A detailed layer profile of the surface analyses found that 50% of surface Cu atoms on Cu(110) were replaced by Au atoms. This results in a reduction in the O_2 sticking probability to 15% of that on Cu(110). The reduced sticking probability indicates effects from the second-layer Au atoms and/or the nonlocalized contribution of the first-layer Au atoms to the reactive sites. Although we expect the existence of transient molecular states similar to that on Cu(110), the deeper d-states of Au interact weakly with the antibonding states of O_2 without filling them with electrons, rendering it more difficult to form intermediate O_2^- states. Moreover, the expected larger work function of Cu_3Au(110) compared to Cu(110) (ca. 4.48 eV, and ca. 5.37 eV for Au(110))^{47,48} renders negatively charged states unstable. As on Cu(110), we see that S_H(H > S_H(C_y) and S_H(H > S_H(C_x), in general. Again, this indicates more reactive parallel-oriented O_2 as compared to perpendicular-oriented O_2. However, in contrast to the case on Cu(110), we find negligible azimuthal anisotropy on Cu_3Au(110)-(4×1), as now we have S_H(C_y) ~ S_H(C_x).

To determine how the translational/beam energy E_0 affects the steric effect, in Figure 3a, we plot the ratios S_H(H)/S_H(C_y) and S_H(H)/S_H(C_x), determined from S_H(H) and S_H(C_y) obtained simultaneously by a single modulation measurement, as a function of E_0. Theoretically, when O_2 with O–O bond axes oriented parallel the surface adsorb, we have S_H(H)/S_H(C_y) = 2 (or S_H(H)/S_H(C_y) = 2). And when O_2 can adsorb regardless of O–O bond axes orientations, we have S_H(H)/S_H(C_y) = 1 (or S_H(H)/S_H(C_y) = 1). Experimentally, on Cu(110), we find S_H(H)/S_H(C_y) = 1.35 and S_H(H)/S_H(C_x) = 1.5 at E_0 = 0.10 eV, and S_H(H)/S_H(C_y) ~ S_H(H)/S_H(C_x) ~ 1.0 for E_0 ≥ 0.33 eV. This indicates the importance of steric effects at small E_0, becoming negligible for translational/beam energies E_0 ≥ 0.35 eV. On Cu_3Au(110)-(4×1), the E_0-dependence of S_H(H)/S_H(C_y) follows a trend similar to that observed on Pt(111),^{49} i.e., initial increase in S_H(H)/S_H(C_y) and S_H(H)/S_H(C_x) at E_0 ≤ 0.26 eV, and then a gradual decrease from E_0 ≥ 0.26 eV.

To determine how the O–O bond axes orientation with respect to the surface normal affects the sticking probability on Cu(110) and Cu_3Au(110), we plot in Figure 3c the E_0-
dependent orientation-resolved sticking probabilities $S_p[001]$ and $S_p[\overline{1}0\overline{1}]$ for O$_2$ with O–O bond axes oriented parallel to the surface (along [001] and [\overline{1}0\overline{1}], respectively) and $S_p[110]$ for O$_2$ with O–O bond axes oriented perpendicular to the surface (along [110]). (For details on how to determine the orientation resolved sticking probabilities, we refer the readers to the Experimental and Theoretical Methods.)

On Cu(110), $S_p[110]$, $S_p[\overline{1}0\overline{1}]$, and $S_p[001]$ all increase gradually with increasing $E_i$ (see Figure 3c). Again, we observe an orientational dependence favoring O–O bond axes oriented parallel to the surface (see $S_p[110] > S_p[\overline{1}0\overline{1}]$ and $S_p[001] > S_p[110]$ for Cu(110) in Figure 3c). And, as we have observed earlier, we also see that both polar and azimuthal orientational dependence becomes negligible at $E_i > 0.3$ eV.

On Cu$_3$Au(110)-(4 × 1), we also see that $S_p[110]$, $S_p[\overline{1}0\overline{1}]$, and $S_p[001]$ all increase gradually with increasing incident translational (beam) energy (see Figure 3c). Again, we observe an in-plane azimuthal orientation dependence favoring O–O bond axes oriented parallel to the surface along [001] (see $S_p[001] > S_p[110]$ for Cu(110) in Figure 3c). And, as we have observed earlier, we also see that both polar and azimuthal orientational dependence becomes negligible at $E_i > 0.3$ eV.

Thus, it is reasonable to expect that the activation barrier to the O$_2$ state is lower if O$_2$ approaches with its molecular axis parallel to the surface. The potential energy curves (PEC) for O$_2$ on Cu(110) manifest such preference (see Figure 4). Moreover, the preferential orientation of O$_2$ is parallel to the [001] direction.

Therefore, the azimuthal dependence of $S_p$ appears at $E_i \lesssim 0.20$ eV, possibly revealing the azimuthal dependence of O$_2$ stability. Considering bond dissociation, we also plot the potential energy surface (PES) for O$_2$ in Figure 5. Here, the collisions on the on-top site and the bridge site are not considered because the high activation barrier of such sites cannot be overcome at the experimental incident energy. The adsorption energies of O$_2$ on Cu(110), at [001] and [110] bond orientations, are $-1.82$ and $-1.66$ eV, respectively. Moreover, the activation barrier appears in the entrance channel. By tracing the minimum energy path, we found a relatively higher energy barrier for O$_2$ dissociation at the [110] orientation than at the [001] bond orientation on Cu(110). The energy difference between the barriers is about 40 meV.

These comparative results agree well with previous calculations on Cu(110). $S_p$ increasing with increasing $E_i$ can be explained by the widened range of impact parameters at which incident O$_2$ molecules mount the barrier. At $E_i \geq 0.33$ eV, $S_p(H)/S_p(C) \approx 1.0$ and sticking probability saturates at $\approx 0.65$. The high-energy O$_2$ molecules surmount the higher barrier at the bridge and/or on-top sites, but the saturation of $S_p$ is different from such expectation. Moreover, $S_p(H)/S_p(C) \approx 1.0$ at $E_i \geq 0.33$ eV indicates no steric preference in O$_2$ sticking. However, the potential landscape and the corresponding energy dissipation process is expected to be quite different for both geometries. To explain the difference between the results and expectation, we speculate the following. The experimental result of $S_p(H)/S_p(C) \approx 1.0$ at $E_i \geq 0.33$ eV indicates no steric preference in O$_2$ sticking. However, the potential landscape and the corresponding energy dissipation process is expected to be quite different for both geometries.
Au on Cu becomes unstable (ca. > 1 eV) by Au alloying. than on Au.

Figure 5. Potential energy surfaces (PESs) for O$_2$ on Cu(110) and Cu$_3$Au(110)-(4 x 1). Potential energy surfaces (PESs) for O$_2$ and Cu$_3$Au(110)-(4 x 1). PESs shown as functions of the O$_2$ center-of-mass distance Z (Å) (from the 4-fold hollow site (HL) of Cu on Cu(110) (upper panels) and Au on Cu$_3$Au(110)-(4 x 1) (lower panels)) and the O$_2$ bond length r$_{O-O}$ (Å). PESs calculated with the O$_2$ bond axis fixed either parallel to [110] (left panels) or parallel to [001] (right panels). Energies (eV) given with respect to O$_2$ sufficient far (ca. 5.0 Å) from the surface, in increments of ca. 0.04 eV.

The steering effect, which redirects the impinging O$_2$ to the preferred geometry becomes insufficient at high energies, e.g., E$_t$ > 0.26 eV. At higher E$_t$, O$_2$ with O–O bond axes oriented perpendicular to the surface can also overcome the activation barrier. The angular distribution of the O–O bond axes could also smear out the steric effect, with the reaction occurring at a finite range of orientations depending on E$_t$.

In Figure 6, we show the translational energy dependence of the initial sticking probability ratios S$_0$(Cu$_3$Au)/S$_0$(Cu) for S$_0$(Cu) for S$_0$(Cu), S$_0$(Cu)$[^{[001]}]$, S$_0$(Cu)$[^{[110]}]$, and S$_0$(Cu)$[^{[110]}]$. S$_0$(Cu$_3$Au)/S$_0$(Cu) for S$_0$(Cu)$[^{[110]}]$ exhibits the least value compared to the rest and indicates that Au alloying effectively reduces the sticking of O$_2$ with O–O bond axes oriented perpendicular to the surface. Au alloying filters the molecular orientation and permeates only O$_2$ with O–O bond axes oriented horizontal to the surface and supply the O atoms. This filtering effect may lead to the selective surface chemical reactions and selective oxidative catalytic reactions. Reduction in corrosion of Au alloyed Cu may be attributed to the reduction in the presence (if not complete absence) of intermediate short-lived O$_2^{\delta-}$ that increases reactivity but reduces the steric preference in processes at higher E$_t$.

Figure 6. Ratios of (space quantized) O$_2$ initial sticking probabilities on Cu(110) and Cu$_3$Au(110). Initial sticking probability ratios for O$_2$ adsorption on Cu$_3$Au(110)-(4 x 1) and Cu(110), with the O–O bond axis oriented along [110], [001], and [110] (S$_0$(Cu$_3$Au)/S$_0$(Cu)$[^{[110]}]$), S$_0$(Cu$_3$Au)/S$_0$(Cu)$[^{[001]}]$, and S$_0$(Cu$_3$Au)/S$_0$(Cu)$[^{[110]}]$, respectively).
Table 1. Electron Gain (e-Gain) of O₂ Adsorbed on Cu₃Au(110)-(4 × 1) and Cu(110)²⁶

| Surface          | O–O bond axis oriented along | O–O bond length (Å) | e-gain (e) |
|------------------|-----------------------------|---------------------|------------|
| Cu₃Au(110)-(4 × 1) | [001]                       | 1.33                | 0.61       |
| Cu₃Au(110)-(4 × 1) | [110]                       | 1.43                | 0.78       |
| Cu(110)          | [001]                       | 2.13                | 1.58       |
| Cu(110)          | [110]                       | 2.13                | 1.72       |

“e-gain (e)” given with respect to O₂ sufficiently far (ca. 5.0 Å) from the corresponding surfaces.

(approximately) usual two-well potential. Unstable molecular chemisorbed O₂ states on Cu₃Au results in weakened orientation dependence of the O₂ sticking probability. In addition, the large atomic radii of surface Au atoms lessen the anisotropy of the surface charge distribution on Cu₃Au(110) (see Figure 7). Correspondingly, the electron surface corrugation as seen by an impinging O₂ on Cu(110) varies more between [001] and [110] bond orientations, having a relatively smooth electron surface distribution along the [110] direction or the [001] plane. Collectively, these results confirm the azimuthal dependence of O₂ adsorption on Cu(110) and its inertness toward Cu₃Au(110).

Figure 7. Electron distribution on Cu₃Au(110) and Cu(110). 2D cut through the long bridge (LB) and short bridge (SB) sites of the electron distributions as viewed along [110] and [001] on the corresponding surfaces. Note the more pronounced orientation-dependent contour difference observed on Cu(110) than on Cu₃Au(110)-(4 × 1). Electron distributions (e/Å³) given with respect to distances sufficiently far (ca. 5.0 Å) from the surface, in increments of 0.005 e/Å³.

In conclusion, we demonstrate the effect of alloying on the steric effects in O₂ dissociative adsorption. At low beam energies, the dissociative adsorption of O₂ occurs on the adiabatic potential landscape on Cu(110). O₂ with O–O bond axes parallel to the surface exhibit higher reactivity as compared to those oriented normal to the surface. The reactivity also depends on the O–O bond orientations along the surface. At high beam energies, the O₂ in all orientations overcome the activation barrier and steric effects become negligible. Reactions via charge transfer into short-lived O₂⁺ state also smear out the steric effects and reduce initial sticking probability saturations to ca. 0.7. On Cu₃Au(110), the overall initial sticking probabilities reduce to ca. 15% that of on Cu(110). Except for the negligible azimuthal orientation dependence, the reactivity also shows similar dependence on the O–O bond axes orientations with respect to the surface, as on Cu(110). Alloying with Au increases the activation barrier in the entrance channel, increases the work function, and renders the molecularly chemisorbed O₂ (O₂⁺) state unstable.

EXPERIMENTAL AND THEORETICAL METHODS

Sample Preparation

We cleaned the Cu(110) and Cu₃Au(110) samples by 1.0 eV Ar⁺ sputtering and annealing at 773 K. We repeated this procedure until we could no longer detect the impurities by Auger electron spectroscopy (AES).

Space-Quantized, State-Selected O₂(Σₕ₋) Molecular Beam

For details regarding the experimental apparatus, we refer the readers to previous reports.¹⁰,¹¹ Briefly, we generated O₂ molecular beams by the free expansion of seeded gas of O₂/He. We then used hexapole magnets to filter the (J, M) state from the O₂ molecular beam. We could also control the translational energy of the state-selected O₂(J, M) beam by adjusting the number of the hexapole magnets and the O₂/He mixing ratio of the seeded O₂ beam. Note that we use the following notations:

- K: O₂ rotational angular momentum with corresponding quantum number J;
- S: O₂ total electron spin angular momentum with corresponding quantum number S;
- M = Mₑ + Mₛ: projection of J along the external field direction;
- Mₑ and Mₛ: projection of K and S along the external field direction, respectively;
- Thus, we are able to prepare O₂(J = 2, M = 2), which corresponds to O₂(J = 1, Mₑ = 1, S = 1), with rotational energy Eₑ = BK(K + 1) ≈ (0.18 meV)(1)(1 + 1) = 0.36 meV, and translational energy Eₜ. An O₂ in state (K = 1, Eₑ = 100 meV) would have traveled a distance of 15 Å by the time it rotates 90°.

The angular distribution of the O₂(J = 2, M = 2) molecular axis orientation approximately follows a sin²θ distribution, where θ is the polar angle of the O₂ molecular axis relative to the direction of the defining magnetic field Ť. Depending on the orientation of the defining magnetic field Ť, i.e., perpendicular or parallel to the surface, we could have helicopter- or cartwheel-like rotating O₂(J = 2, M = 2). Helicopter-like rotating O₂(J = 2, M = 2) have an O–O bond axis oriented parallel to the surface. Cartwheel-like rotating O₂(J = 2, M = 2) can also have O–O bond axis orientations other than parallel to the surface (i.e., perpendicular and in between). By aligning Ť
parallel to [110] or [001], we can prepare two types of cartwheel-like rotating O₂, which we label as cartwheels C₁ and C₂ respectively. Thus, we can prepare a space-quantized, state-selected O₂(Σ⁻) molecular beam, in which nearly all (ca. 100%) of the molecules are in the spin-rotational state (J = 2, M = 2).

**Initial Sticking Probabilities for Helicopter-like and Cartwheel-like Rotating O₂ (J = 2, M = 2)**

We express the initial sticking probability S₀(H) for helicopter-like rotating O₂(J = 2, M = 2) as

\[
S₀(H) = \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu}(\theta, \phi) \sin^{3} \theta d\theta d\phi
\]

(1)

For the two types of cartwheel-like rotating O₂(J = 2, M = 2), viz., S₀(C₁) and S₀(C₂), we have

\[
S₀(C₁) = \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu}(\theta, \phi)(1 - \sin^{2} \theta \sin^{2} \phi) \sin \theta d\theta d\phi
\]

(2)

and

\[
S₀(C₂) = \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu}(\theta, \phi)(1 - \sin^{2} \theta \cos^{2} \phi) \sin \theta d\theta d\phi
\]

(3)

(θ, φ) give the polar and azimuthal orientation of the O₂ molecular axis with respect to the surface. Rₜ(θ, φ) gives the reaction rate averaged over the surface unit cell. From eqs 1–3, we then determine the initial sticking probability S₀(R) for a random distribution, i.e.,

\[
S₀(R) = \frac{1}{3} S₀(H) + \frac{1}{3} S₀(C₂) + \frac{1}{3} S₀(C₁)
\]

= \frac{1}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu}(\theta, \phi) \sin \theta d\theta d\phi

(4)

For initial sticking probabilities S₀[110], S₀[001], and S₀[011], which correspond to O₂ with molecular axis parallel to [110], [001], and [101], respectively, we have

\[
S₀[110] = - S₀(H) + S₀(C₂) + S₀(C₁)
\]

= \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu} \cos^{2} \theta \sin \theta d\theta d\phi

(5)

\[
S₀[001] = S₀(H) + S₀(C₂) - S₀(C₁)
\]

= \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu} \sin^{3} \theta \sin \phi d\phi

(6)

\[
S₀[011] = S₀(H) - S₀(C₂) + S₀(C₁)
\]

= \frac{3}{4\pi} \oint_{0}^{2\pi} \oint_{0}^{\pi/2} R_{\nu\nu} \cos^{3} \phi d\phi

(7)

**Computational Details**

We performed spin-polarized density functional theory (DFT) based total energy calculations, using the projector augmented wave (PAW) formalism. We employed plane wave basis set with a cutoff energy of 700 eV. We used the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) for the exchange correlation functional. We adopted the Monkhorst and Pack method to perform Brillouin zone integrations, with 10 × 10 × 1 special k-points, and conduct frozen lattice calculations with energy convergence of less than 1 × 10⁻⁵ eV. To model the Cu(110) and Cu₄Au(110), we used a periodic slab, six atomic layers thick with eight atoms per layer, separated by 15 Å of vacuum along [110]. To obtain the optimized geometry after surface cleaving, we relaxed the first 2 atomic layers of the surface slabs until Hellmann–Feynman forces are less than 0.01 eV/Å. We used a (4 × 2) surface unit cell of Cu(110) and Cu₄Au(110) as the supercell for O₂ adsorption. This takes care of the unwanted interaction between periodic images of O₂. In the case of Cu₄Au(111), we adopt the (4 × 1) reconstructed structure for the first two atomic layers. To have a better comparison of the relative strength of adsorption on Au surface atoms of Cu₄Au(110) and on Cu surface atoms of pristine Cu(110), we chose the 4-fold coordinated Au/Cu hollow site as O₂ adsorption site. We determined the adsorption energies from the change in the total energy of the system with respect to the case with O₂ sufficiently far (ca. 5 Å) from the surface. To determine the charge population of O₂ upon adsorption, we used Bader charge analyses. We used the VESTA package to draw the structures and related figures.

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**Notes**

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