CO₂ Reduction Catalysts on Gold Electrode Surfaces Influenced by Large Electric Fields

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Supporting Information

ABSTRACT: Attaching molecular catalysts to metal and semiconductor electrodes is a promising approach to developing new catalytic electrodes with combined advantages of molecular and heterogeneous catalysts. However, the effect of the interfacial electric field on the stability, activity, and selectivity of the catalysts is often poorly understood due to the complexity of interfaces. In this work, we examine the strength of the interfacial field at the binding site of CO₂ reduction catalysts including Re(S-2,2'-bipyridine)(CO)₃Cl and Mn(S-2,2'-bipyridine)(CO)₃Br immobilized on Au electrodes. The vibrational spectra are probed by sum



frequency generation spectroscopy (SFG), showing pronounced potential-dependent frequency shifts of the carbonyl stretching modes. Calculations of SFG spectra and Stark tuning rates based on density functional theory allow for direct interpretation of the configurations of the catalysts bound to the surfaces and the influence of the interfacial electric field. We find that electrocatalysts supported on Au electrodes have tilt angles of about 65-75° relative to the surface normal with one of the carbonyl ligands in direct contact with the surface. Large interfacial electric fields of 10⁸-10⁹ V/m are determined through the analysis of experimental frequency shifts and theoretical Stark tuning rates of the symmetric CO stretching mode. These large electric fields thus significantly influence the CO₂ binding site.

INTRODUCTION

The utilization of anthropogenic carbon dioxide emissions as a reagent to recreate commercially usable energy products would help to decrease both our society's dependence on nonrenewable energy sources as well as greenhouse gas emissions.¹ The difficulty lies in the stability of the CO₂ molecule, leading to high activation barriers for any chemical transformation.^{1,4} The use of organometallic catalysts has been employed to help lower these barriers through proton-assisted processes to produce products such as CO and formate.³⁻⁵ The selectivity, synthetic tunability, and ease of characterization have allowed significant progress to be made in developing molecular CO₂ reduction catalysts.^{6,7}

A promising strategy within molecular CO₂ reduction electrocatalysis is the functionalization of electrodes to incorporate catalysts into heterogeneous systems.^{8,9} Anchoring molecular catalysts onto electrodes would increase catalyst stability and electron transfer while retaining the molecular system's selectivity and activity. One class of catalyst that has received much attention is the Group VII Re(2,2'-bipyridine)- $(CO)_{3}Cl$ (Re-bpy) and Mn(2,2'-bipyridine)(CO)_{3}Br (Mnbpy) family of catalysts, which are some of the most active and selective electrocatalysts for the reduction of CO_2 to CO.^{10–13} Re-bpy and its derivatives have been incorporated into membranes¹⁴ and polymerized onto electrodes,^{15–19} as well as extensively studied when bound to TiO2 surfaces.²⁰⁻²⁴ Mnbpy has also more recently been incorporated into photochemical devices on TiO_2 ,²⁵ Nafion membranes,² multiwalled carbon nanotubes²⁷ and nanowires.²⁸ and

The diverse interest in incorporating Re-bpy into heterogeneous systems calls for fundamental understanding of the effects of the electrochemical interface on molecular catalysts to help guide the design of heterogenized systems. Recently, we studied the structural and electronic effects of the adsorption of cyano-functionalized Re-bpy catalysts on gold electrodes.^{29,30} It was found that the cyano groups deactivated the catalyst; however, the cyano-Au interaction led to a geometry where the would-be catalytically active site was pointing away from the electrode surface. In turn, the CO

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groups facing toward the surface enable electron-hole-induced vibrational relaxation.³⁰ Additional sum frequency generation spectroscopy (SFG) experiments found that the proximity to the surface caused faster vibrational excited state decay.³¹

An important aspect is how the strong electric field at the electrode surface affects the catalytic reaction mechanism.³²⁻³⁶ Electric fields at the electrode/electrolyte interfaces play crucial roles in electrochemistry, catalysis, and solar energy conversion processes.³⁷⁻⁴⁴ In enzyme catalysis, it has been well documented that electrostatic contributions from the protein environment stabilize intermediate and transition state species at the active site of the enzyme. 45,46 In molecular electrocatalysis, through-space Coulombic interactions have been shown to stabilize intermediates in CO₂ reduction, lower the overpotential, and improve catalysis.^{47,48} Similar effects of the electric field on charged molecules have been reported for DNA, peptides, and other redox-active molecules, 49-59 where surface plasmon resonance spectroscopy^{60,61} coupled to electrochemical measurements^{35,62–67} were very helpful to describe the flexibility of surface-attached molecules in loosely packed films. Yet, an important and less well-understood effect is how the strong electric field at the electrochemical double layer affects the efficiency and selectivity of catalytic reactions. A well-known spectroscopic probe to study the local electric strength of many molecular systems, particularly adsorbates at the electrochemical interfaces, is the vibrational Stark effect.^{45,68-70} Previous electrochemical vibrational Stark effect studies mostly focused on small molecules or ions⁷¹⁻⁷⁵ or selfassembled monolayers (SAMs) with electric field reporters.⁷⁶⁻⁸¹ Recently, we combined in situ electrochemical vibrational SFG spectroscopy, density functional theory (DFT) calculations, and molecular dynamics simulations (MD) to investigate the electric field and interfacial structure at Au/diisocyanide/aqueous electrolyte interfaces.⁷⁹ We demonstrated that SFG can be used as a direct probe of the Stark effect at the adsorbate/electrode interface in the presence of electrolyte, where the electric field strength is calculated to be ca. $10^8 - 10^9$ V/m.

To build upon the knowledge gained from this previous work, here we investigate Re-bpy and Mn-bpy catalysts substituted with thiols both as molecular catalysts and as heterogenized complexes covalently bound to an Au surface (Chart 1) by in situ electrochemical SFG spectroscopy, polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS), and DFT calculations. Thiols form strong S-Au bonds, which will both give insights on how the strength of the attachment affects orientation of the catalyst on the surface as well as allow observation of the vibrational spectra of these catalysts at potentials more negative than previously considered. Our computational modeling reveals that the electrochemical vibrational Stark tuning of the $C \equiv O$ modes mostly originates from molecular-gold interactions, rather than from the metal center of the catalyst. In combination with computational modeling, we evaluate the local electric field strength at the active site of these CO₂ reduction catalysts.

RESULTS AND DISCUSSION

Synthesis and Characterization. Complexes fac-Re(4-mercaptomethyl-2,2'-bipyridine)(CO)₃Cl (1) and fac-Mn(4-mercaptomethyl-2,2'-bipyridine)(CO)₃Br (2) were synthesized following well-established protocols^{11,82} and were obtained in good yields (>68%). Mercaptomethyl substituents

Chart 1. Complexes 1-4 Studied in This Work



were chosen to preclude any thiol reactivity during molecular catalysis. For surface attachment, disulfide complexes 3 and 4 were chosen because of their stability and ease of handling, as thiols are known to easily oxidize and polymerize.⁸³ Additionally, disulfides are well known to cleave at the S-S bond on Au.⁸⁴ Synthesis started with formation of 4-thione-2,2'bipyridine (bpy=S) by coupling 4-bromo-2,2'-bipyridine with sodium hydrogen sulfide under basic conditions,⁸³ which was then immediately oxidized to the disulfide (bpySSbpy) using hydrogen peroxide (as shown in Scheme 1 in the Supporting Information).⁸⁶ Dimers 3 and 4 were obtained by refluxing bpySSbpy with the appropriate metal salt to yield orange solids, which are only soluble in DMF and DMSO. The manganese complexes 2 and 4 are light sensitive, and thus, manipulations were done with as little light exposure as possible.

Crystal structures of 1, 2, bpy=S, and bpySSbpy were obtained (Tables S3-S5 and Figures S19-S20). Complexes 1 and 2 show octahedral coordination geometries around the metal center, with bond lengths similar to analogous complexes.⁸⁷ Both have a facial arrangement of the three carbonyl ligands, which is also evidenced by characteristic $\nu(CO)$ stretching modes in FT-IR spectroscopy. The bond distance between the 4-carbon of the bipyridine ring and the sulfur atom is 1.732 Å for 1 and 1.760 Å for 2, which is typical for a C-S partial double bond.⁸⁸ In contrast, the C-S bond in **bpy=S** is shorter and has even more double bond in character at 1.697 Å. Thione-thiol tautomerism of 4-mercaptopyridines has previously been observed in solution, where the thione form is favored in polar solvents.⁸⁹ Crystals of bpy=S were grown from ethanol; thus, the thione version was expected. Once oxidized, this bond elongates back to a single bond at 1.774 Å as observed in the structure of bpySSbpy, which has C_2 symmetry with a typical S–S bond distance of 2.029 Å.⁹⁰

Homogeneous Electrochemistry. Complexes 1 and 2 were synthesized as homogeneous analogues to characterize catalysis without interference from possible thiol-electrode interactions. Under inert atmosphere (Ar) using a glassy



Figure 1. Cyclic voltammograms of 1 (Re, a) and 2 (Mn, b) under the same conditions: 1 mM complex, 5 mL of 0.1 M TBAPF₆ in CH₃CN; glassy carbon working, platinum counter, and Ag/AgCl reference electrodes; scan rate 0.1 V/s.



Figure 2. Comparison between ν (CO) frequencies in FT-IR solution phase spectra (DMF, black) and PM-IRRAS on Au spectra (red) for complexes 3m (a) and 4m (b).

carbon working electrode and dry acetonitrile (MeCN), complex 1 shows two reductions at -1.76 and -2.04 V vs $Fc^{+/0}$ (Figure 1). The first reduction is reversible when scanning is stopped before the second reduction. This behavior is consistent with previous studies and is therefore attributed to the reduction of the bipyridine ligand.⁹¹ The second reduction is irreversible and corresponds to reduction of the metal center to Re⁰, coupled with the loss of Cl^{-,91} These features remain steady at increasing scan rates, showing that the complexes freely diffuse from the surface as defined by the Randles-Sevcik equation (Figures S21 and S22).92 A small oxidation peak can be seen at -0.5 V at slower scan rates, corresponding to breakage of a Re-Re dimer that is known to be a deactivation pathway for Re-bpy complexes that do not have bulky bpy substituents.⁹³ Consistent with previous studies, the oxidation disappears at faster scan rates, indicating that the kinetics of dimerization is slow.¹¹ These reduction potentials are slightly more positive than $Re(bpy)(CO)_3Cl$ by 20 and 80 mV for the first and second reductions, respectively.¹¹

Manganese complex 2 also exhibits an electrochemical response like other substituted Mn-bpy complexes.^{82,94} Under Ar on a glassy carbon working electrode, two irreversible reductions are seen at -1.62 and -1.86 V vs Fc^{+/0}, which are 140 and 180 mV more positive than the reductions of 1 (Figure 1). On the basis of previous studies,⁸² the first reduction can be assigned as the reduction of the metal center, followed by the loss of Br⁻ and rapid dimerization. This Mn-Mn dimer is then reduced to form the catalytically active [Mn(bpy-SMe)(CO)₃]⁻ anion. Oxidative cleavage of the dimer can be seen at -0.65 V. Complex 2 is also freely diffusing. The difference in behavior between Mn and Re

bipyridine complexes has been studied by Riplinger et al.⁹⁵ and can be attributed to the relative energies of the d_{z^2} orbital of the metal center to the π^* orbital of the bpy.

Under an atmosphere of CO2, only 1 exhibits catalytic current at the second reduction. This corresponds to an i_{cat}/i_{p} of 16 (scan rate = 0.1 V/s), and by increasing the scan rate to achieve a plateau current, a maximum turnover frequency (TOF_{max}) of 368 s⁻¹ (scan rate = 10 V/s) was determined (see Supporting Information for details). Bulk electrolysis experiments showed 99% \pm 2% Faradaic efficiency for the formation of CO with less than 0.1% Faradaic efficiency for hydrogen formation. 2,2,2-Trifluoroethanol (TFE, $pK_a(CH_3CN) =$ $(35.4)^{96}$ was then added as a proton source until maximum current was achieved. At 0.5 M TFE, the peak current shifted more positive by 470 mV to -2.04 V (from -2.51 V vs Fc^{+/0}), corresponding to a TOF_{max} of 2740 $\rm s^{-1}$ (25 V/s). These TOF_{max} values are very similar to $Re(bpy)(CO)_3Cl$, which has a TOF_{max} of 155 and 3965 s⁻¹ under CO_2 and CO_2 with 1 M phenol, respectively.⁹⁷ Therefore, the sulfur group moves the potential slightly more positive but makes the TOF_{max} slightly worse.

Complex 2 was catalytically active only after addition of a proton source,⁹⁴ and with 0.5 M TFE there was a 12-fold increase in current and a TOF_{max} of 460 s⁻¹ (25 V/s). Bulk electrolysis experiments with 0.5 M TFE showed 100% \pm 5% efficiency for CO and <0.4% for H₂ over three runs. The activity of complex 2 is very similar to that of Mn(4,4'-di-*tert*-butyl-2,2'-bipyridine)(CO)₃Br, which has a TOF_{max} of 340 s^{-1.82} Therefore, the sulfur group provides marginal improvements to the potential and TOF_{max} of this catalyst family.



Figure 3. DFT-optimized geometry of the Re monomer **3m** (a and b) and Mn monomer **4m** (c and d) on an Au cluster. Halogen is facing away from the surface in a and c and toward the surface in b and d. Color code for atoms: yellow = Au, orange = S, white = H, gray = C, red = O, blue = N, azure = Re, purple = Mn, brown = Br, green = Cl.

Since these complexes are meant to be analogues to those covalently attached to Au electrodes, electrochemistry was also done using a gold working electrode. Scans of 1 and 2 under Ar were almost identical compared to those taken on glassy carbon, with an exception of more dimer oxidation (-0.5 V) observed for 1 at higher scan rates (Figures S23 and S24). Both complexes were freely diffusing. Under an atmosphere of CO_{2} , 1 showed an increase in current corresponding to an i_{cat}/i_p of 15.3. This slight increase in activity compared to using a glassy carbon working electrode has also been observed for $Mo(bpy)(CO)_4$, contributing to the affinity of Au for CO, helping product dissociation during catalysis.⁹⁸ Again, no increase in current was seen under CO_2 for 2, and TFE was not added as a proton source due to its small electrochemical window for gold electrodes.

Surface Attachment and PM-IRRAS/SFG Measurements. Self-assembled monolayers (SAMs) of the monomers of complexes 3 or 4 (3m and 4m) were made by soaking a freshly cleaned gold-coated slide in a 1 mM solution of the complex in DMF for 24 h. The slide was rinsed copiously with organic solvents and dried under a stream of nitrogen before taking any measurements. Polarization modulation infrared reflection-absorption spectroscopy (PM-IRRAS) was performed as an initial means of characterizing the SAMs in air. The PM-IRRAS shows all three ν (CO) stretching frequencies for both 3m and 4m (Figure 2a and 2b). Compared to their solution FT-IR spectra, the carbonyl modes are shifted to higher energy by ca. 12 cm⁻¹. The broadening of the peaks is most likely due to surface roughness of the Au slide.^{24,99} **3m** and **4m** on gold electrodes; however, the complexes dissociate around -0.9 V vs Ag/AgCl, which is before catalytic potentials are reached (vide infra). However, since complexes **3** and **4** are electronically analogous to complexes **1** and **2**, we expect that the electrochemistry of the former complexes **3** and **4** should be similar to the electrochemistry of complexes **1** and **2**, respectively.^{95,97}

SFG measurements were performed in the CO stretching region (methods discussed in the Supporting Information). Figure S1 shows the ppp-polarized SFG spectra of dried 3m and 4m monolayers adsorbed on Au thin film surfaces. The SFG spectra are characterized by a band at higher frequencies than can be ascribed to the a'(1) symmetric CO stretch and a broad feature at lower frequencies that correspond to the asymmetric modes. In contrast to the IR spectra of the molecules in solution, once attached to the surface is it not possible to resolve the low frequency peaks. Moreover, it is noted that the in-phase symmetric CO stretching mode a'(1)of 4m shows a dip around 2030 cm⁻¹, which could correspond to the shoulder observed in the PM-IRRAS spectrum (Figure 2b). Such dual a'(1) modes were not observed in the SFG spectrum of **3m**. In previous works, the multiple a'(1) peaks have been assigned to the formation of dimer or trimer on the surface.¹⁰⁰ To determine the binding geometry of 3m and 4m on Au film surface, we also performed heterodyne-detected SFG (HD-SFG) measurements (Figure 4), vide infra.

DFT Geometry Optimization, SFG Simulation, and Orientation Assignment. To examine the binding configuration of the Re and Mn complex adsorbed on gold, we performed DFT optimizations of the **3m** and **4m** complex on a gold model. Following our previous study,⁸⁷ the surface was modeled as a cluster composed of 32 gold atoms, arranged in two layers of 27 and 5 atoms, respectively (see Figure 3). To characterize the orientation of the complex on the surface, we make use of the Euler angles relating the molecular frame to the laboratory frame fixed on the surface according to the tilt (θ), twist (ψ), and azimuthal (φ) angles (see Figure S17). Here, θ is the tilt angle of the bipyridine plane relative to the surface normal, φ the rotation of the molecule relative to the normal to the gold surface, and ψ the rotation of the complex along the *c* axis (see Figure S17). Additional computational details can be found in the Supporting Information.

Minimum energy structures were found for both **3m** and **4m** on gold (Figure 3). These structures are characterized by a tilted ($\theta \approx 65-75^{\circ}$) bipyridine ring with respect to the surface normal, with either the CO motif or the halogen atom facing the surface. Table 1 summarizes the relevant properties for

Table 1. Geometrical and Energetical Parameters of theOptimized Structures Shown in Figure 3

structure	group facing surface	$\begin{array}{c} {\rm tilt}\\ {\rm angle}^a\\ (\theta) \end{array}$	twist angle ^a (ψ)	relative energy (kcal/mol)	S-Au ^b (Å)
3m	СО	67°	265°	0	2.33
	Cl	74°	95°	-8.2	2.35
4m	СО	66°	265°	0	2.32
	Br	73°	9 7°	-13.5	2.31
				1	

^{*a*}For the definition of the tilt and twist angles see text. ^{*b*}Distance between the sulfur atom and the gold plane.

these structures, including geometrical and energetics parameters. Interestingly, both **3m** and **4m** present the same orientation despite the different transition metal. We found that the distance of the S atom to the gold surface is practically unchanged between the different orientations and metal centers, with the sulfur atom binding across two gold atoms in a bridging mode. Whether the bridging or tripod mode is most favorable is not yet clear in the literature.¹⁰¹

To determine which orientation most likely exists on the surface, we computed the homodyne and heterodyne SFG spectra for each of the above structures and compared them to the experimental SFG data. The procedure to compute DFT-derived SFG spectra is based on previous studies^{20,22,23,79,87,102} and is presented in full detail in the Supporting Information. Briefly, the calculation involves the computation of the second-order hyperpolarizability tensor $\beta_{ijk}^{(2)}$ at the DFT level in the molecular frame and the subsequent rotation to the laboratory frame (using Euler angles) to obtain the second-order susceptibility $\chi_{IJK}^{(2)}$. The final spectrum is related to the absolute value (for homodyne) or imaginary part (for heterodyne) of the effective susceptibility that is a linear combination of different elements of the $\chi_{IJK}^{(2)}$ response and depends on both the Fresnel factors of the interface and the beam incident angles.

In Figures S8–S15 we present typical computed SFG spectra obtained for orientations close to the ones determined in the DFT optimizations. The spectra are characterized by a broad band at low frequencies that corresponds to the overlapping a'(2) and a'' stretching modes and a higher frequency peak due to the symmetric a'(1) stretching mode. We found that small variations in the orientation of the molecule produce huge changes in the spectra, since both the

intensity and the sign of the peaks are very sensitive to the tilt and twist angles. In particular, the low-frequency peak inverts its sign from positive to negative when ψ or θ changes in 5– 10° from the optimized structure of the complex with the CO facing the surface (Figures S8, S10, S12, and S14). For the geometry with the halogen atom facing the surface, the changes are not so dramatic, although the relative intensity between the asymmetric a'(2) and the symmetric a'(1) stretching modes is dependent on small variations of the angles (see Figures. S9, S11, S13, and S15).

On the basis of these results, to determine which orientation gives the best agreement with the experimental SFG spectra, we performed a scan on the tilt (θ) and twist (ψ) angles for orientations close to the configurations found in the DFT optimization and compared the computed SFG spectra with the experimental one. Following previous studies,^{79,87,102} frequencies and damping constants for each vibrational mode were allowed to relax within ±20 and ±10 cm⁻¹, respectively, to obtain a more accurate spectral fit (see Supporting Information for additional details). Figure 4 represents the



Figure 4. Best-matched DFT-based calculated SFG spectra (blue line) and experimental results (open circles) for the heterodyne SFG spectra of Re monomer 3m (top) and Mn monomer 4m (bottom) on Au.

best-matched calculated spectra along with the experimental result for the heterodyne spectra of both complexes on gold. The agreement between theory and experiments is reasonably good, with a correct description of peak positions and lineshapes of the spectra. The fitting of the homodyne spectra is presented in Figure S19, where the agreement between theory and experiment is slightly deteriorated, likely due to the distortion of the peaks and line shape in the SFG due to the nonresonant background. Note that the *same* orientation

0.3

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Figure 5. Potential-dependent SFG spectra of (a) 3m and (b) 4m SAMs in 10 mM KOH aqueous solution measured in the potential range from 0.3 to -1.3 V (vs Ag/AgCl). Scan rate is 2 mV/s. Arrows indicate the direction of potential scanning. Dashed lines are used as guides for the eyes for a'(1) modes.



Figure 6. Stark tuning for the cathodic and anodic sweeps of symmetric CO band of (a) 3m and (b) 4m SAMs. Large error bars in b are due to lower S/N ratios of SFG spectra at potentials of -0.4 and -0.5 V. Solid lines are linear fits for the potential range between 0 and -1.0 V. Potentialdependent nonresonant signal amplitudes for (c) 3m and (d) 4m SAMs.

provides an independent reasonably good agreement for both the homodyne and the heterodyne spectra, providing strong evidence of the correct assignment of the absolute orientation of the complex on the surface. Interestingly, the configurations giving rise to these spectra correspond to an orientation with θ = $75/80^{\circ}$ and $\psi = 255^{\circ}$, close (within 10°) to the structures with the CO facing the surface found in the DFT optimization, although the structures with the halogen facing the surface were found to be lower in energy (Table 1). Note that a configuration with the CO facing the surface will expose the halogen atom to the solution, providing a favorable orientation for redox state transitions and catalysis. This orientation is in agreement with previous results of similar complexes on gold surfaces.⁸⁷ The reported agreement between theory and experiment presented in Figure 4 supports the value of DFT calculations for rigorous interpretation of SFG spectra and highlights the importance of HD-SFG for the determination of the absolute orientation of molecules on interfaces.

We remark in passing that although the SFG spectra presented in Figures 4 and S8-S15 neglect the influence of thermal fluctuations since they are based on a unique optimized structure, it should be possible to include thermal averages in the calculation of the SFG spectra by using configurations gathered from a MD trajectory¹⁰³ as long as reliable force field parameters become available for the simulation of metal complexes in solution. Nevertheless, the reasonable agreement between experiment and theory (Figure 4) supports the assignment of the SFG signal to a predominant orientation of the complex on the surface.

Potential-Dependent SFG Measurement. To evaluate the electric field strength at the catalytically active site of 3m and 4m at the electrode/electrolyte interface, bias-dependent SFG measurements were performed for 3m and 4m SAMs in 10 mM KOH aqueous solutions (see ref 79 and Supporting Information for details of electrochemical SFG measurements). An aqueous solution was chosen because the SAMs are not

stable in commonly used organic solvents (e.g., acetonitrile) under bias. Figure S2a shows the cyclic voltammogram (first scan) of 3m SAMs. During the cathodic sweep, there is a reductive current peak at -0.85 V, which is assigned to reductive desorption of molecules from the gold surface (Au- $SR + e^- \rightarrow Au + RS^-$).¹⁰⁴⁻¹⁰⁷ The significant current increase at a potential lower than -1.00 V is attributed to hydrogen evolution.¹⁰⁵ In the anodic sweep, the current peak at -0.82 V is assigned to oxidative readsorption of **3m** to the gold surface $(RS^- + Au \rightarrow Au-SR + e^-)$.^{104–107} It was noted that the CV is reversible for additional scans, which is consistent with the strong oxidative readsorption peak. For 4m SAM, two reductive peaks around -0.35 and -0.90 V are possibly due to reduction and desorption processes, respectively (Figure S2b). In the anodic sweep, an oxidative readsorption peak around -0.85 V is also observed. The CV curves of 3m and 4m SAMs measured without adding CaF₂ window on the electrode surface (Figure S5) and the quantitative analysis of the reductive desorption can be found in the Supporting Information.

Potential-dependent SFG spectra of 3m in 10 mM KOH solution which are synchronized with the CV measurement are presented in Figure 5a. Frequency and amplitude of C=O stretches and nonresonant signal are strongly dependent on the applied potential. At a potential of -1.3 V, where the SAM is believed to desorb from the gold surface, the SFG signals from 3m molecules are still clearly observed, indicating that the desorbed 3m molecules are near the gold surface with an ordered structure. For the anodic sweep, the spectral shape and intensity recover when the potential is scanned from -1.30 to 0.3 V, as shown in the symmetric contour plot of Figure 5a. This observation is consistent with the CV results, which shows that most of the 3m molecules can be readsorbed to the gold electrode surface. Figure 5b shows the potentialdependent SFG spectra for 4m SAM. The C≡O stretches of 4m show a similar trend of frequency shift as SAM 3m during the cathodic sweep. This change is also reversible after the anodic sweep.

To further analyze the Stark tuning of the C \equiv O band, the spectra in Figure 5 were fitted according to the expression of SFG intensity (see Supporting Information).⁷⁹ Due to the peak overlap between a'(2) and a'' modes in the low-frequency region, we will focus on the a'(1) mode. Figure 6a and 6b shows the potential dependence of the a'(1) mode frequencies for 3m and 4m SAMs, respectively. The linear fitting for the potential region between 0 and -1.0 V gives Stark tuning slopes $d\omega/d\phi$ of 21.0 ± 2.0 and 10.0 ± 2.0 cm⁻¹/V for 3m and 4m, respectively. It is also noted that the change of $C \equiv O$ frequency is less significant at potential < -1.0 V, which is similar to the phenomenon observed for the 4-mercaptobenzonitrile SAM under current-carrying condition as reported by Patrow et al.⁷⁸ It should be noted that the SFG spectra of 4m exhibit two a'(1) modes like the spectra measured in air. However, the peak position of the a'(1) with a higher frequency is difficult to extract from the spectra due to the lower intensity and complicated interference with the adjacent mode. On the basis of the SFG spectra as shown in Figure S2, we estimate that the Stark tuning rates of both a'(1) modes for 4m should be similar.

Furthermore, it is noted that the magnitude of nonresonant signals for both 3m and 4m have a minimum around from -0.2 to -0.1 V and from -0.5 to -0.4 V, respectively (Figure 6c and 6d). Such minima can be also clearly seen in the

contour plots, as the two blue regions around -0.2 V in Figure 5a. Since there is no molecular resonance around 2100 cm^{-1} , the SFG intensity is dominated by the nonresonant response from the gold electrode, i.e., $I_{SFG} \propto |A_{NR}|^2$. Figures S3 and S4 show the averaged SFG intensity for the region of 2100-2110 cm^{-1} , which show the same trend as revealed by the fitted nonresonant signals. In previous electrochemical second harmonic generation (SHG) studies, the SHG intensity is suggested to be related with potential of zero charge (PZC).¹⁰⁸⁻¹¹⁰ The minimum of nonresonant SFG signal has been also observed for other systems by electrochemical SFG spectroscopy and is attributed to the influence of PZC.¹¹¹⁻¹¹⁵ As discussed in these previous studies, the contribution of the $\chi^{(3)}$ term to the SHG or SHG intensity is minimized due to cancellation of the electrostatic field at the interface. To further clarify the origin of the observed minimum of nonresonant response in our systems, we performed capacitance measurements of the 3m and 4m SAMs (Figure S6). The potentialdependent capacitance of the 3m and 4m SAMs shows minima between -0.3 and -0.1 V and -0.4 and -0.2 V, respectively. Such minima could be attributed to the PZC of the SAM systems.¹¹⁶ These capacitance results are roughly consistent with the SFG measurements and support that the minima of nonresonant SFG response is related to the PZC. In addition, the PZC of alkanethiols with varied length on polycrystalline Au and Au (111) have been reported to locate in the potential region from -0.10 to -0.55 V (vs Ag/AgCl), which is close to the present catalyst SAMs.^{117–119}Another feature observed in Figure 6c and 6d is that the nonresonant SFG signal gradually decreases as the potential shifts more negative than -1.0 V. This phenomenon can be explained by the change of gold electronic structure after the desorption of the molecules around -1.0 V (Figure S2).

DFT Stark Tuning Rates and Evaluation of Local Electric Fields. To determine the electric field strength at the catalytically active site of 3m and 4m at the electrode/ electrolyte interface, it is necessary to relate the experimental Stark tuning slope to the electric field experienced by a molecular probe at the interface. To linear order in the field, the change in vibrational frequency as a function of electric field is given by^{70,120}

$$\omega(\phi) = \omega_0 - \Delta \mu \bullet F(\phi) \tag{1}$$

where $\overline{F}(\phi)$ is the bias-dependent interfacial electric field, ω_0 is the frequency in the absence of field, and $\Delta \overline{\mu}$ is the difference in the dipole moment between the ground and the excited vibrational states, also known as the Stark tuning rate. For convenience, in what follows we will treat eq 1 in its scalar form, in which $\Delta \mu$ is the projection of $\Delta \overline{\mu}$ along the electric field.

The Stark tuning rate $\Delta \mu$ was determined theoretically by computing the change in frequency for the symmetric stretching mode a'(1) after applying a uniform electric field perpendicular to the gold cluster, as described in detail in the Supporting Information. Briefly, the geometry of the complexes **3m** and **4m** with both the CO motif and the halogen atom facing the surface was optimized in the presence of a uniform field. A subsequent harmonic frequency calculation, also in the presence of the electric field, provides the field dependence of the vibrational frequency of the a'(1) mode. The top panels of Figures S6 and S7 show the results of the vibrational frequency as a function of the electric field for **3m** and **4m**, respectively. In the presence of a uniform electric field the harmonic frequency of the symmetric mode increases for both the CO and the halogen facing down conformations, although at different rates. Note that the strong fields applied in the calculation (of the order of ~1 V/nm) may modify the orientation of the molecule on the surface. We found that the orientation of the molecule is only slightly affected by the field, as can be appreciated by the small dependence of the tilt and twist angles on the field (Figures S6 and S7 for **3m** and **4m**, respectively). Since the geometry of the molecules does not change with the applied field, the Stark tuning rates $\Delta \mu$ were determined from linear fits of the field dependence of the vibrational frequency (eq 1) and are shown in Table 2.

Table 2. DFT-Computed Stark Tuning Rate $\Delta \mu$ for the a'(1) Mode

structure	group facing surface	Stark slope for $a'(1) (cm^{-1}/V/nm)$
3m (on Au)	СО	-7.5 ± 0.2
	Cl	-4.0 ± 0.2
3m (gas phase)	СО	-2.8 ± 0.2
	Cl	-3.1 ± 0.1
4m (on Au)	СО	-7.7 ± 0.2
	Br	-3.7 ± 0.5
4m (gas phase)	CO	-2.1 ± 0.4
	Br	-3.6 ± 0.1

Several interesting trends are worth mentioning for the data presented in Table 2. First, the values computed for the Stark tuning rate for a given conformation are statistically identical for both complexes, regardless of the different metal center involved. Note, however, that for conformations with the CO facing the surface, which is found to be the orientation that most likely exists on the surface, $\Delta \mu$ is consistently twice as big as the one found for the conformation with the halogen facing the surface, although the tilt angle for these orientations is almost identical. The differences of the Stark rates in these conformations can be traced back to the close proximity of the axial CO motifs to the gold surface in the former orientation (~2.8 Å) in comparison to the latter (~7.4 Å). In fact, the Stark tuning rate computed for a complex in the same orientation as before but without the gold surface (labeled "gas phase" in Table 2) shows that little effect is observed for the molecule with the halogen facing the surface (compare, i.e., rows 6 and 8), whereas the presence of the gold substrate has an appreciable effect on the Stark slope when the CO is facing down the surface (row 5 versus 7). This surface effect on the susceptibility of the frequency shift is akin to the one found in a previous study of diisocyanides molecules bound to gold surfaces⁷⁹ and is also related to the electron-hole-pair-induced fast vibrational energy relaxation of Re catalyst found on gold surfaces,³⁰ demonstrating the importance of moleculesubstrate interactions in modulating the properties of anchored catalysts on surfaces.

Having determined the values of the Stark tuning rate $\Delta \mu$, namely, -7.5 cm⁻¹/V/nm for **3m** and -7.7 cm⁻¹/V/nm for **4m**, it is possible to calculate the electric field strength at the catalytic active site. In our previous paper,⁷⁹ we assumed a double-layer model to estimate the strength of the electric field along the electrode/SAM/electrolyte interface. However, eq 1 provides a clear mapping between electric field and voltage independent of the assumption of any model provided that one knows the potential of zero charge of the system, namely, the

voltage at which the electric field is zero. From the minimum of the magnitude of nonresonant signals (vide supra), the PZC was determined to be -0.2 V for **3m** and -0.4 V for **4m**. Using the average of experimental cathodic and anodic frequencies ω (Figure 6a and 6b) measured at the potential ϕ of interest as well as the frequency at the PZC ω_0 , the electric field at the active site of the catalyst-solid–liquid interface is found to be 10^8-10^9 V/m for both Re and Mn catalysts, and it is plotted as a function of applied voltage in Figure 7. Note that within



Figure 7. Electric field strength at different applied potentials for the Re monomer 3m (black circles) and Mn monomer 4m (red circles) in close contact with the gold surfaces. Dashed lines are linear fittings to the data.

statistical uncertainties both Re and Mn complexes sense a similar electric field at the interface. We remark that the order of magnitude of the strength of the electric field is consistent with the magnitude previously reported for nitrile- and isocyano-terminated SAM on Au and Ag electrodes.^{76–79}

Determination of the magnitude of the electric field at the interface with a direct spectroscopic probe that provides spatial resolution has two major implications. First, the results presented in Figure 7 establish a direct relation between the applied voltage, an experimentally controllable parameter, and the interfacial electric field, a macroscopic property of the electrochemistry, catalysis, and solar energy conversion processes.^{37–44} Thus, with these maps it is possible to tune the interfacial properties with simple controllable bulk parameters.

Second, by invoking a particular electrochemical doublelayer model it is possible to obtain molecular information on the adsorbates on the interface. We emphasize that the determination of the electric field strength presented in Figure 7 is model free and does not rely on any approximation (besides the neglect of higher terms in the electric field dependence of the vibrational frequency in eq 1) and that the use of an electrochemical model is just to provide additional information on the interface. A commonly used model to understand the electric field at the electrode/SAM/electrolyte interface assumes a Helmholtz layer of length *d* in contact with an electrode and a diffuse layer of electrolytes described by Gouy–Chapman theory.^{77–79,121–124} In a previous paper,⁷⁹ we show that at large applied potentials the field strength becomes linearly dependent on the applied potential with a slope related to the effective thickness of the monolayer *d*, namely, $dF/d\phi \approx$ d^{-1} . Hence, the slope of the data presented in Figure 7 provides an estimation of the length of the monolayer formed by both complexes. From the linear fits (dashed lines in Figure 7), the effective thickness of the SAM is determined to be 3.7 \pm 0.2 Å for 3m and 7.6 \pm 0.2 Å for 4m. These values are in reasonable agreement with the metal-gold distance determined from DFT calculations (~5 Å). Note that a simplified double-layer model that neglects the formation of SAM, such as Gouy-Chapman theory, would predict a change of electric field with applied potential related to the inverse Debye length $\kappa = \sqrt{2z^2 e^2 n/\varepsilon \varepsilon_0 k_{\rm B} T}$, namely, $dF/d\phi \approx \kappa$, where z is the absolute charge of the ion, e is the elementary charge, n is the electrolyte concentration, ε is the dielectric constant of the aqueous solution, ε_0 is the absolute permittivity, $k_{\rm B}$ is the Boltzmann constant, and T is the absolute temperature. For a 0.01 M KOH solution, $\kappa^{-1} = 30$ Å, a value that is not consistent with the experimental results. These findings highlight the importance that SAM monolayers can have on the interfacial electric field78 and underline the significant information that the interfacial electric field strength can provide for the development of electrochemical double-layer models.

The importance of the electric field in the context of catalysis cannot be stressed enough. The order of magnitude of the electric field strength determined in this work $(10^8 - 10^9 \text{ V})$ m) is akin to those determined inside catalytically active sites in protein environments.^{45,46,69} In these enzymatic systems, the specific electrostatics interactions to their bound substrate are crucial for the stabilization of intermediates and transition states, thus facilitating the reaction and enhancing the reactions rates. Hence, one should expect that similar modulations of the stabilization of intermediates states may occur for catalysts undergoing chemical reactions in the electrochemical electrode/electrolyte interface. However, understanding the effect of interfacial electric fields on the reactivity and efficiency of catalysts in operando conditions is challenging.³² In this context, the implementation of robust SFG response over a range of potentials as the one obtained in this work is promising for future work on observing surface-immobilized catalysis intermediates via SFG.

CONCLUSIONS

Molecular catalysts 1 and 2 have been synthesized and characterized for the selective electrochemical reduction of CO_2 . Both Re and Mn complexes show reactivity similar to that of the unsubstituted Re– and Mn–bpy complexes, with TOF_{max} values with 0.5 M TFE of 2740 and 461 s⁻¹ for Re (1) and Mn (2), respectively. Disulfide complexes 3 and 4 were synthesized and covalently attached onto Au surfaces. PM-IRRAS characterization of the monolayers shows a broadening of the carbonyl stretching frequencies, suggesting inhomogeneous molecular packing of the complexes on the surface. Monolayers 3m and 4m dissociated from the Au surface at a potential of roughly –0.9 V vs Ag/AgCl in 10 mM KOH.

Using static/electrochemical SFG and theory we assigned the orientation of the catalysts on the surface and observed the Stark tuning rate of carbonyls not covalently attached to the gold surface. DFT calculations of the Stark tuning rate for the molecules in the absence and presence of the gold surface assign the origin of the Stark tuning rate to the interactions with the gold substrate rather than within the molecule. The electric field strength at the catalytically active site of Re and Mn complexes at electrode/electrolyte interfaces is found to be of the order of $10^8 - 10^9$ V/m. Characterization of the interfacial field is supported by the calculated Stark tuning rate, with the Stark tuning slope measured by electrochemical SFG and the experimentally determined PZC of the gold surface. The direct relation between the strength of the electric field and the applied potential provides a practical map between an experimentally controllable parameter (voltage) and the electrode/electrolyte interface electric field, crucial in electrochemistry and catalysis. The robust SFG response over a range of potentials as well as the with high spatial and temporal spectroscopic resolution provides a significant step toward understanding in situ electrochemical catalysis of heterogenized catalysts under operando conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b09852.

Details of synthesis procedure, X-ray crystallography, sample preparation, homogeneous electrochemistry, PM-IRRAS measurement, SFG measurement, electrochemical SFG setup, quantitative reductive desorption analysis, capacitance measurement, DFT methodology, and additional references (PDF)

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Notes

The authors declare no competing financial interest.

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