# Unlocking the Facet-Dependent Ligand Exchange on Rutile $\mathrm{TiO}_{2}$ of a Rhenium Bipyridyl Catalyst for $\mathrm{CO}_{2}$ Reduction 

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#### Abstract

Covalent attachment of molecular catalysts to electrode surfaces is an attractive approach to develop robust catalytic materials. Selectivity and tunability of the resulting catalytic surface can be achieved by ligand design, making surfaceattached $\mathrm{CO}_{2}$ catalysts of immense interest for zero carbon technologies. Unfortunately, the functionality of heterogenized catalysts strongly depends on the nature of the electrode surface and the specific binding mode of the catalyst on the electrode surface. Here, we perform experimental and theoretical vibrational sum-frequency generation spectroscopy (VSFG) to investigate the binding configuration of a popular molecular $\mathrm{CO}_{2}$ reduction catalyst, the $\operatorname{Re}(\mathrm{dcbpy})(\mathrm{CO}){ }_{3} \mathrm{Cl}$ (dcbpy $=4,4^{\prime}$-dicarboxy-2,2'-  bipyridine) complex ( ReCOA ), heterogenized on a $0.5 \%$ niobium $(\mathrm{Nb})$-doped rutile $\mathrm{TiO}_{2}(100)$ crystal. We find evidence of ligand exchange induced upon binding to the (100) $\mathrm{TiO}_{2}$ facet that was not observed on other $\mathrm{TiO}_{2}$ facets. The structural changes are induced by the sawtooth morphology of the $\mathrm{TiO}_{2}$ (100) facet, establishing interactions that lead to chloride $\left(\mathrm{Cl}^{-}\right)$ligand exchange with hydroxide $\left(\mathrm{OH}^{-}\right)$and formation of the $\mathrm{Re}($ dcbpy $)(\mathrm{CO})_{3} \mathrm{OH}(\mathrm{ReOH})$ adsorbate. DFT calculations show bidentate binding of ReOH through its carboxylate $\left(\mathrm{COO}^{-}\right)$ groups in a flat-lying orientation stabilized by hydrogen-bonding of the $\mathrm{OH}^{-}$proton to the $\mathrm{TiO}_{2}$ surface. The OH -substituted site interacts strongly with the (100) $\mathrm{TiO}_{2}$ surface in a configuration unfavorable for the $\mathrm{CO}_{2}$ exchange that is necessary for catalytic functionality. These findings provide evidence of facet-dependent changes of the heterogenized molecular catalyst, underscoring the critical role of the surface facet while designing electrocatalytic materials.


## I. INTRODUCTION

Conversion of carbon dioxide $\left(\mathrm{CO}_{2}\right)$ to carbon-based fuels is a promising approach to zero carbon renewable energy production. Both homogeneous and heterogeneous electrocatalysts are of great interest, so the pros and cons of both approaches have been discussed. ${ }^{1-5}$ Covalent attachment of molecular catalysts to electrode surfaces can combine the selectivity and tunability of homogeneous catalysts with the stability and easy product separation of heterogeneous catalysts. ${ }^{6-8}$ However, the efficiency and functionality of surface-attached catalysts depend on several factors, including the specific binding motif determined by the crystallographic facet of the electrode surface, the orientation of the catalyst relative to the surface, and the nature and extent of the catalyst-substrate interaction. ${ }^{9-13}$ Therefore, the characterization of the binding motif and orientation of heterogenized molecular catalysts on electrode surfaces remains a subject of great research interest.

The family of rhenium (Re) tricarbonyl complexes $\operatorname{Re}(\mathrm{L})$ $(\mathrm{CO})_{3} \mathrm{X}$ (where L is a bidentate-substituted pyridyl ligand and X is an anionic ligand) is one of the most extensively studied sets of transition metal-based $\mathrm{CO}_{2}$ reduction catalysts. ${ }^{14-17}$ These complexes can be readily analyzed by probing the CO stretching modes with various vibrational spectroscopic techniques, including infrared (IR). For example, transient IR spectroscopy ${ }^{18-20}$ and two-dimensional (2D) IR spectroscopy ${ }^{21-24}$ have been used to study the vibrational dynamics, adsorption structure and electron transfer dynamics of this class of Re complexes on $\mathrm{TiO}_{2}$ substrates. Furthermore, vibrational sum-frequency generation (VSFG) spectroscopy,

[^0]
an interface-specific spectroscopic technique, has been applied in combination with DFT calculations to interrogate the geometry and binding orientation of monolayers of several analogues of this $\mathrm{CO}_{2}$ reduction catalyst on various semiconductor (nanostructure or single crystalline) and metal surfaces. ${ }^{25-29}$ Ultrafast vibrational dynamics of surface-bound Re catalysts has also been investigated using time-resolved SFG and two-dimensional SFG spectroscopic studies. ${ }^{9,30-34}$ Some of these catalysts exhibit impressive photo- or electrocatalytic activity toward $\mathrm{CO}_{2}$ reduction to CO , which is a synthetic precursor to many liquid fuels. ${ }^{35-41}$ They were also shown to exhibit increased catalytic activity when attached to $\mathrm{TiO}_{2}$ substrates. ${ }^{42,43}$

The combination of experimental VSFG spectroscopy and ab initio DFT calculations of VSFG has demonstrated great power for interrogating the orientation of heterogenized systems, providing a clear picture of the binding motif at the molecular level. ${ }^{44}$ Our studies have previously investigated the binding configuration and orientation of $\operatorname{Re}(\mathrm{L})(\mathrm{CO})_{3} \mathrm{Cl}$ type complexes tethered to metal $(\mathrm{Au})$ and semiconductor $\left(\mathrm{TiO}_{2}\right)$ substrates. ${ }^{25-28,45-48}$ Those experiments have explored binding of the Re catalyst to a rutile $\mathrm{TiO}_{2}$ substrate, with emphasis on surface facets with a high degree of planarity to simplify the corresponding analysis, including the (001) facet with $C_{4}$ symmetry, or the 2 -fold symmetric (110) facet. ${ }^{25,27}$ Here, we focus on the rutile $\mathrm{TiO}_{2}(100)$ facet that has a sawtooth surface morphology ${ }^{49}$ establishing rather distinct interactions with the surface adsorbate. The resulting interactions are expected to strongly affect the binding geometry of the catalyst. In addition, the (100) facet of rutile $\mathrm{TiO}_{2}$ crystal is commercially available as a $0.5 \%$ niobium ( Nb )-doped semiconductive substrate and can be implemented in electrochemistry experiments with ease. ${ }^{13,44-47,50-53}$

In this paper, we focus on determining the binding configuration of the $\mathrm{CO}_{2}$ reduction catalyst Re (dcbpy)$(\mathrm{CO})_{3} \mathrm{Cl}$ (dcbpy $=4,4^{\prime}$-dicarboxy-2,2'-bipyridine) $(\mathrm{ReCOA})$ bound to the surface of a $0.5 \% \mathrm{Nb}$-doped rutile $\mathrm{TiO}_{2}$ (100) semiconductor electrode. The result is surprising: the ReC0A molecule binds to the $\mathrm{TiO}_{2}$ (100) substrate by exchanging its $\mathrm{Cl}^{-}$ligand by $\mathrm{OH}^{-}$, producing a hydroxyl-substituted complex that binds to the surface and adopts a flat configuration on the $\mathrm{TiO}_{2}$ surface. Such a binding motif has not been observed on the rutile $\mathrm{TiO}_{2}$ (001) and (110) facets, underscoring the importance of carefully considering the specific surface morphology when designing heterogeneous catalytic materials. Our findings also demonstrate the capabilities of a combined experimental and computational methodology, including an interface-sensitive spectroscopy technique like VSFG combined with ab initio DFT calculations, as applied to the characterization of molecular orientation and binding motifs that critically affect the functionality of molecular electrocatalysts on various substrates.

## II. EXPERIMENTAL METHODS

Niobium ( Nb )-doped rutile $\mathrm{TiO}_{2}$ (100) crystals were purchased from MTI corporation. The crystals were cleaned and soaked in a solution of ReCOA according to previous reports. ${ }^{27,48}$ Before performing SFG experiments, the sensitized $\mathrm{TiO}_{2}$ crystal was rinsed with acetonitrile to remove any unbound ReCOA complex from the surface and dried with air. The morphology of the crystal was confirmed using X-ray diffraction (XRD) (Figure 1) with a diffractometer Rigaku XtaLAB Synergy-S with HyPix-600HE (hybrid photon


Figure 1. Rutile single crystal of $\mathrm{TiO}_{2}$ (100). (A) Model of the crystal structure showing layers of $\mathrm{Ti}^{4+}$ (blue) and $\mathrm{O}^{2-}$ (red) atoms with view from the side ( $c$ axis) of the crystal. Both the $a$ and $b$ axes are orthogonal to the $c$ axis from this view and perpendicular to each other. The sawtooth structure is shown as a dotted line. (B) Model of the crystal structure with view from the top along the $a$ axis. (C) Model of the crystal structure with view along the $b$ axis.
counting detector). The crystal face was indexed and the axes were determined to be $a(100), b$ (010), and $c(001)$, where the (100) axis is out of the plane of the $\mathrm{TiO}_{2}$ surface.

Vibrational sum-frequency generation (VSFG) is a secondorder nonlinear optical spectroscopic technique which is forbidden in centrosymmetric media but allowed at the surface of a material, or at the interface between two materials, where bulk centrosymmetry is broken, thus providing a noninvasive tool to investigate interfacial characteristics. ${ }^{9,26,47,54-59}$ A typical broadband VSFG experiment requires two laser beams: a femtosecond IR pulse with a bandwidth of $\sim 200-$ $300 \mathrm{~cm}^{-1}$ and a picosecond narrowband ( $\sim 10-15 \mathrm{~cm}^{-1}$ ) visible (Vis) pulse which are overlapped on the sample spatially and temporally. The VSFG frequency is the sum of the frequencies of the two input beams ( $\omega_{\mathrm{SFG}}=\omega_{\mathrm{IR}}+\omega_{\mathrm{VIS}}$ ) and is emitted in the phase matching direction. For this experiment, the angles of incidence for the IR (1800-2100 $\mathrm{cm}^{-1}$ ) and the visible ( 800 nm ) beams are $50^{\circ}$ and $65^{\circ}$, respectively, with respect to the surface normal, and the VSFG spectra are collected using a PPP polarization combination (polarizations of the VSFG, Vis and IR beams are written from left to right). The power of the IR and the visible beams are 4.5 and $4 \mu \mathrm{~J} /$ pulse, respectively, at the sample stage with a repetition rate of 1 KHz . To determine rotational anisotropy of the surface bound catalyst, the $\mathrm{TiO}_{2}$ (100) crystal is kept on a rotational stage parallel to the laser table and the VSFG spectra are measured for every $20^{\circ}$ in-plane rotation of the sample with respect to the surface normal. The details of the laser system and experimental setup for the VSFG measurements have been described in our previous publications and included in the Supporting Information Sections S1-S3. 9 ,26,27,47,48

## III. COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were performed with Vienna Ab Initio Simulation Package (VASP) 4.1 to generate a rutile $\mathrm{TiO}_{2}$ (100) surface model slab with periodic boundary conditions. The resulting slab minimum energy configuration was then used to create a cluster model for
subsequent calculations (see Supporting Information Section S4). The open valences of internal 2- and 3-fold oxides were capped with hydrogen atoms to ensure neutrality, and surface facing protons were manually directed away from binding sites to avoid unphysical effects (Figure S3). Doubly deprotonated ReC0A monomers were allowed to relax on the $\mathrm{TiO}_{2}$ (100) surface from a variety of monodentate, bidentate, and tridentate starting geometries to explore the complete space of binding orientations on $\mathrm{TiO}_{2}$ (100) (Figures S8S11). ${ }^{48,60-64}$ In addition, four dimeric species, shown in Figure S12, were optimized on $\mathrm{TiO}_{2}(100)$ to analyze the possibility of dimerization of the adsorbed complex as previously suggested in studies of ReCOA binding to $\mathrm{TiO}_{2}$ (110). ${ }^{60}$ These and subsequent calculations were performed at the DFT level using the $\omega$ b97XD hybrid functional, ${ }^{65}$ the LANL2DZ basis set for metal atoms, ${ }^{66}$ and the $6-31 \mathrm{G}(\mathrm{d})$ basis set ${ }^{67,68}$ for all other atoms, as in previous studies. ${ }^{60}$ The $\omega$ b97XD functional incorporates the modeling of dispersion effects, ${ }^{69}$ which were critical for describing noncovalent interactions of the molecule with the surface particularly for configurations of the bipyridine ring lying flat to the $\mathrm{TiO}_{2}$ surface or interacting closely with other ReC0A molecules in the dimers. Minimum energy configurations were obtained with Gaussian 16 Revision C. 01 with its default optimization criteria and integration grid. ${ }^{70}$
Sum-frequency spectra in the PPP polarization combination were calculated for the adsorbed ReCOA monomers and dimers using DFT. VSFG spectra were calculated for the free ReCOA molecule in the orientation determined by the surfaceattached optimization since the SFG signal is only dependent on the orientation of the vibrational probes (see Supporting Information Section S5). VSFG spectra were calculated from ab initio derivatives of the polarizability and dipole moment with respect to normal mode coordinates. ${ }^{60-64}$ In particular, the VSFG intensity is proportional to the second-order electric dipole susceptibility, $\chi^{(2)}$, estimated as the sum of nonresonant and resonant contributions, as shown in eq $1 .^{71}$

$$
\begin{align*}
I_{\mathrm{SFG}} & \propto\left|\chi_{\mathrm{NR}, \mathrm{eff}}^{(2)}+\chi_{\mathrm{R}, \mathrm{fff}}^{(2)}\right|^{2} \\
& =\left|A_{\mathrm{NR}, \mathrm{eff}} \mathrm{e}^{\mathrm{i} \delta}+\sum_{q} \frac{A_{q, \mathrm{eff}}}{\omega_{\mathrm{IR}}-\omega_{\mathrm{q}}+\mathrm{i} \Gamma_{q}}\right|^{2} \tag{1}
\end{align*}
$$

The resonant susceptibility can be approximated as the sum of Lorentzian functions, where $A_{q, \text { eff }} \omega_{q}$, and $\Gamma_{q}$ are the effective amplitude, frequency, and damping constant, respectively, of the $q^{\text {th }}$ SFG active vibrational mode and $\omega_{\text {IR }}$ is the frequency of the incident tunable IR beam. $A_{\mathrm{NR}, \text { eff }}$ is the nonresonant amplitude and $\delta$ is the relative phase between nonresonant and resonant signals (details included in Supporting Information Sections S6-S8). Additional theoretical details have been extensively covered in previous literature. ${ }^{57,60,62}$

## IV. RESULTS AND DISCUSSION

Experimental Results. Figure 2 shows the solution-phase FTIR spectrum of ReC0A in acetonitrile, including three CO stretching modes at 2025, 1921 and $1905 \mathrm{~cm}^{-1}$ corresponding to the in-phase symmetric stretching mode, $A^{\prime}(1)$, the antisymmetric stretching mode, $\mathrm{A}^{\prime \prime}$, and the out-of-phase symmetric stretching mode, $\mathrm{A}^{\prime}(2)$, respectively. Comparison of this solution IR spectrum with that of ReCOA adsorbed on


Figure 2. Solution infrared (IR) spectra of ReCOA in acetonitrile solvent. $\mathrm{A}^{\prime}(1)$ and $\mathrm{A}^{\prime}(2)$ are in-phase and out-of-phase symmetric stretching modes of the carbonyl groups; $\mathrm{A}^{\prime \prime}$ represents the asymmetric stretching mode. The displacement vectors of the carbonyl groups are also shown for all three normal modes.
nanoporous $\mathrm{TiO}_{2}$ thin films suggests, upon binding, all carbonyl stretching modes are blue-shifted by about 5-15 $\mathrm{cm}^{-1}$ and inhomogeneously broadened, resulting in the closely spaced lower frequency peaks merging together. ${ }^{27}$

Figure 3 compares the PPP VSFG spectrum of ReC0A adsorbed on a single crystal of $0.5 \% \mathrm{Nb}$-doped $\mathrm{TiO}_{2}$ (100) to the corresponding spectra of the complex bound to the (110) and (001) surfaces. Remarkably, the two lower frequency peaks of the complex on the (100) facet overlap quite significantly, with the peak at $\sim 1940 \mathrm{~cm}^{-1}$ appearing as a shoulder in the spectrum. Equation 1 enables fitting of the VSFG spectrum. Each normal mode of ReCOA is modeled using a Lorentzian with $A_{q, \text { eff }}, \omega_{q}$ and $\Gamma_{q}$ being the amplitude, frequency, and line width of the Lorentzian, respectively. $A_{\mathrm{NR}, \text { eff }}$ represents the amplitude of the nonresonant response from the $\mathrm{TiO}_{2}(100)$ surface and $\delta$ is the phase associated with it. The imaginary part of the three Lorentzians is plotted beneath the VSFG spectrum, showing that the amplitudes of the modes at 2012 and $1910 \mathrm{~cm}^{-1}$ have the same sign, while that of the 1935 $\mathrm{cm}^{-1}$ mode is opposite. The resonant signals from these three modes interfere with each other and with the nonresonant signal, giving rise to the observed VSFG spectrum. The fitting parameters are tabulated in Table S1 of the Supporting Information.

To contrast our results with those previously published, we have digitized the VSFG spectra of ReCOA attached to rutile $\mathrm{TiO}_{2}$ (001) and (110) surfaces, as shown in Figure 3a,b, respectively. ${ }^{25,27}$ We note that these results are surprisingly different. The spectrum of ReCOA bound to the (001) surface (Figure 3a) shows no signal corresponding to the lower frequency modes in the PPP VSFG spectrum while the sole peak at $\sim 2035 \mathrm{~cm}^{-1}$ corresponds to the in-phase symmetric stretching, $\mathrm{A}^{\prime}(1)$, mode. In contrast, the corresponding spectrum of ReCOA on $\mathrm{TiO}_{2}$ (110) (Figure 3b) includes the $\mathrm{A}^{\prime}(1)$ peak at $\sim 2040 \mathrm{~cm}^{-1}$ as well as the lower frequency modes with lower intensity than the band of the $\mathrm{A}^{\prime}(1)$ mode. Notably, the intensities of the low-frequency modes are


Figure 3. Normalized PPP VSFG spectra of ReC0A bound on rutile $\mathrm{TiO}_{2}$ (a) (001), (b) (110), and (c) (100) surfaces (this study). The VSFG spectra of ReC0A attached to $\mathrm{TiO}_{2}$ (001) and (110) surfaces have been digitized from ref 27 . All spectra are measured under similar experimental conditions.
dramatically higher (Figure 3c) for ReC0A bound to the (100) facet (this work), resulting in a reversal of relative intensities between the higher and lower frequency vibrations. This implies that a substantial change in the binding orientation of ReC0A must have been induced upon interaction with the (100) surface.

We note that the frequencies of the carbonyl vibrations of ReC0A bound to the (100) facet are significantly red-shifted when compared to those of $\operatorname{ReCOA}$ bound to the (001) and (110) facets. The red shift is more pronounced for the $\mathrm{A}^{\prime}(1)$ mode, by about $25-30 \mathrm{~cm}^{-1}$, and smaller for the lowfrequency vibrations $\left(\sim 10 \mathrm{~cm}^{-1}\right)$. Such an unprecedented difference in the experimental VSFG spectra due to merely changing the semiconductor crystal facet reinforces how important it is to control each parameter during substratecatalyst integration for optimal functionality of heterogenized catalysts.

Figure 4 shows the analysis of an azimuthal anisotropy experiment to understand the orientation of the ReC0A complex on the $\mathrm{TiO}_{2}$ (100) surface. The angle-dependent intensities enable us to perform comparisons with DFT calculations of the corresponding spectra to estimate the molecular Euler angles, as determined by the tilt of the bipyridine plane of the catalyst with respect to the surface normal $(\theta)$, the azimuthal angle describing the rotation of the catalyst relative to the normal to the $\mathrm{TiO}_{2}$ surface $(\varphi)$, and the twist angle ( $\psi$ ) of the catalyst. ${ }^{48}$

The VSFG spectra of ReCOA bound to $\mathrm{TiO}_{2}$ (100) were collected for rotational anisotropy measurements in $20^{\circ}$ increments for in-plane rotation of the sample (between $0^{\circ}$ to $360^{\circ}$ ) with respect to the surface normal, as shown in Figure 4a for five representative angles. The crystal axes in the plane of the $\mathrm{TiO}_{2}$ surface, $[\overline{0} 01]$ and $[\overline{0} 10]$, are also shown in the same figure. The peak intensities change significantly as a function of crystal rotation. We have performed a global fitting of all eighteen spectra using eq 1 , keeping the frequency $\left(\omega_{q}\right)$ and the line width $\left(\Gamma_{q}\right)$ of each mode constant while the resonant amplitude ( $A_{q, \text { eff }}$ ), nonresonant amplitude ( $A_{\mathrm{NR}, \text { eff }}$ ), and phase ( $\delta$ ) were allowed to vary with in-plane rotational angle.

Polar plots of the azimuthal dependence of the amplitude for each vibrational mode were generated by plotting $A_{\text {q eff }}$ as a function of rotational angle (Figure 4). All three modes show a 2-fold rotational anisotropy, as shown in Figure 4b-d for 2015, 1935 and $1910 \mathrm{~cm}^{-1}$ modes, respectively. Interestingly, the amplitudes for the modes $\sim 2015 \mathrm{~cm}^{-1}$ (red) and $\sim 1910 \mathrm{~cm}^{-1}$


Figure 4. (a) Five representative PPP VSFG spectra for consecutive $20^{\circ}$ in-plane rotations of the $\mathrm{TiO}_{2}$ crystal. The crystal axes [ $\overline{0} 01$ ] and [ $\overline{0} 10$ ] in the plane of the $\mathrm{TiO}_{2}$ surface are also indicated in the same figure. Polar plot of the azimuthal dependence of the amplitudes of (b) $2030 \mathrm{~cm}^{-1}$ (red), (c) $1935 \mathrm{~cm}^{-1}$ (blue) and (d) $1910 \mathrm{~cm}^{-1}$ (green) modes as a function of rotational angle. Note that the radius (which signifies the amplitude) of the polar plot in Figure 4 b is different from that of Figure 4c,d. (e) Azimuthal dependence of the nonresonant amplitude.
(green) (in-phase, $\mathrm{A}^{\prime}(1)$, and out-of-phase symmetric stretching, $\mathrm{A}^{\prime}(2)$, modes respectively) are maximum along the [ $\overline{0} 10]$ axis of the crystal surface, whereas the maximum amplitude for the $\sim 1935 \mathrm{~cm}^{-1}$ (blue) mode (asymmetric stretching, $\mathrm{A}^{\prime \prime}$ ) is observed along the [ $\overline{0} 01$ ] axis, being offset by $90^{\circ}$ as compared to that of the $\mathrm{A}^{\prime}(1)$ and $\mathrm{A}^{\prime}(2)$ modes. Moreover, the nonresonant response ( $A_{\mathrm{NR}, \text { eff }}$ ) from the crystal surface also shows a 2 -fold anisotropy (Figure 4e) with maximum amplitude along the [ $\overline{0} 10$ ] axis. This has been further verified by measuring the nonresonant signal from the bare $\mathrm{TiO}_{2}$ (100) surface (i.e., with no adsorbed ReCOA molecules), as shown in Figure S2. It should be noted that the nonresonant signal originates from the collective response of electrons at the surface in the presence of intense laser fields and gives information about the electronic distribution on the $\mathrm{TiO}_{2}$ surface. Equipped with these experimental data, we have calculated the spectra corresponding to the DFT binding geometry of ReCOA on $\mathrm{TiO}_{2}$ (100) allowing for comparisons to the corresponding binding configuration on the (001) and (110) surfaces.

Computational Results. The VSFG spectrum of ReC0A bound to the (100) facet of rutile $\mathrm{TiO}_{2}$ is quite different from the spectra of ReCOA on the (001) and (110) facets. The high PPP intensity of the low-frequency modes on the (100) facet indicates that those transition dipole vectors assume a drastically different orientation. The PPP signal contains contributions from the ZZZ, XXZ, XZX, and ZXX components of the second-order nonlinear susceptibility tensor, which complicates interpretation of the reversed intensity ratios between the low- and high-frequency modes. However, we can contrast against the previously determined orientations. The VSFG spectra from both previous studies were shown to correspond to upright orientations of the ReC0A catalyst with the bipyridine ring perpendicular to the surface. On the contrary, we suggest that binding to the (100) facet involves orientation of the bipyridine ring parallel to the surface with the axial Re (I) ligands pointing toward the $\mathrm{TiO}_{2}$ surface, nearly perpendicular to the previously elucidated binding motifs of ReCOA on the (001) and (110) surfaces. That orientation, however, would lead to repulsion of the axial Cl or CO ligand with protruding oxides of the sawtooth (100) surface, and no ReC0A binding mode could be optimized with the spectroscopically implied flat-lying binding orientation. In fact, none of the optimized ReC 0 A on $\mathrm{TiO}_{2}$ structures generated VSFG spectra or rotational anisotropy with even qualitative agreement with experiments (see Supporting Information Section 9).
The experimental observation of a $\sim 25 \mathrm{~cm}^{-1}$ red shift of the totally symmetric $\mathrm{A}^{\prime}(1)$ mode of ReCOA on $\mathrm{TiO}_{2}$ (100) compared to the (001) or (110) facets was the key to unlocking our conclusion of facet-dependent ligand exchange of $\mathrm{Cl}^{-}$for $\mathrm{OH}^{-}$. The red shift magnitude suggests a substantial change in the carbonyl bond character. Two plausible explanations for this observation are (1) the carbonyl bond is weakened due to interaction with the Lewis acidic titanium ( $\mathrm{Ti}^{4+}$ ) atoms on the surface or (2) ligand exchange of $\mathrm{Cl}^{-}$at the $\operatorname{Re}(\mathrm{I})$ center increases $\mathrm{Re}-\mathrm{CO} \pi$-back-bonding interaction, resulting in the observed red shift. We have explored both possibilities by optimizing configurations with those structural characteristics, computing their Raman spectra, and comparing the obtained frequency shifts to the experimental spectrum.
The ligand exchange hypothesis yielded a spectrum with good agreement with the experiment (Figure 5) while the


Figure 5. DFT based Raman spectra of $\operatorname{Re}($ dcbpy $)(\mathrm{CO})_{3} \mathrm{X}$ catalysts with $\mathrm{X}=\mathrm{H}_{2} \mathrm{O}, \mathrm{OH}^{-}, \mathrm{Cl}^{-}$, and an empty coordination site ("bare") attached to $\mathrm{TiO}_{2}$ (100) for analogous bidentate binding orientations. The red shift for $\mathrm{X}=\mathrm{OH}^{-}$as compared to $\mathrm{X}=\mathrm{Cl}^{-}, 20 \mathrm{~cm}^{-1}$, corresponds well to that measured on $\mathrm{TiO}_{2}$ (100), $\sim 25 \mathrm{~cm}^{-1}$. Raman intensities are reported in arbitrary units.
carbonyl- $\mathrm{Ti}^{4+}$ interaction hypothesis was ruled out due to poor agreement of the calculated peak positions as compared to experiment (Figure S18). Three possibilities for ligand exchange were explored, including $\mathrm{Cl}^{-}$exchange by $\mathrm{H}_{2} \mathrm{O} / \mathrm{OH}^{-}$ or simply $\mathrm{Cl}^{-}$detachment leaving an empty coordination site ("bare"). The source of $\mathrm{H}_{2} \mathrm{O} / \mathrm{OH}^{-}$is assumed to be the adventitious water in the solvent. Although we used fresh acetonitrile (containing ReCOA ) under an inert atmosphere to perform the 24 h soaking of the crystal, it is nigh impossible to get rid of the trace adventitious water from the solvent. Therefore, we believe that the ligand exchange takes places during the time of this long soaking. As we will see later in the manuscript, the alignment between experiment and computation supports full $\mathrm{OH}^{-}$exchange during the soak, with $\mathrm{Cl}^{-}$ions being left behind in solution and not present for VSFG measurements. Figure 5 shows the calculated Raman spectra of $\operatorname{Re}($ dcbpy $)(\mathrm{CO})_{3} \mathrm{X}$ catalyst attached to $\mathrm{TiO}_{2}$ (100) with $\mathrm{X}=$ $\mathrm{H}_{2} \mathrm{O}, \mathrm{OH}^{-}$or $\mathrm{Cl}^{-}$or an empty coordination site ("bare"), as obtained at the DFT level of theory (structures shown in Supporting Information Section S10). For analogous binding orientations, the experimental red shift of $\sim 25 \mathrm{~cm}^{-1}$ can only be reproduced for the OH -substituted Re complex (as compared to that of Cl -substituted complex), whereas the other substitutions ( $\mathrm{H}_{2} \mathrm{O}$ or "bare") lead to a blue shift. Therefore, we have optimized the geometry of the $\operatorname{Re}(d c b p y)-$ (CO) ${ }_{3} \mathrm{OH}$ complex, henceforth referred to as ReOH , on $\mathrm{TiO}_{2}$ (100) surface, as shown in Figure 6.

Figure 6 shows four binding modes of the ReOH complex on the rutile $\mathrm{TiO}_{2}$ (100) surface. A complete report of local binding minima can be found in Supporting Information Section S9. Notably, the anticipated parallel orientation of the bipyridine group to the surface (i.e., flat-lying binding orientation) is natural for these structures since the axial hydroxyl $\left(\mathrm{OH}^{-}\right)$proton establishes hydrogen bonds with the surface oxides.

The most plausible binding orientation at the $\mathrm{TiO}_{2}$ interface was assessed by comparing the DFT-computed SFG spectra for the optimized binding modes with that of the experiment (see Section 9 of Supporting Information for complete VSFG spectra). Binding configuration 5 was the only one that produced a VSFG line shape and anisotropy in good agreement with experiment. Three peaks corresponding to


Figure 6. Schematic representation of several configurations of the ReOH complex on the $\mathrm{TiO}_{2}$ (100) surface. Dotted lines indicate an interaction of ReOH and the $\mathrm{TiO}_{2}$ cluster through covalent (thick) or hydrogen bonds (thin). The $\mathrm{TiO}_{2}$ (100) crystal has been stylized as a cartoon to improve readability, as shown on the right.
the $A^{\prime}(2), A^{\prime \prime}$, and $A^{\prime}(1)$ carbonyl stretching modes were located at 1895, 1909, and $2004 \mathrm{~cm}^{-1}$ respectively in the DFTbased spectra of 5 , with relative intensities that showed good agreement with the experimental profile (Figure 7). Rotational anisotropy was calculated by scanning the azimuthal angle, $\psi$,


Figure 7. (a) PPP VSFG signal (experiment, blue; calculation, red). Intensity units are arbitrary for the calculated spectrum and were scaled by a factor of 2.5 to align with the experimental intensities. (b) Azimuthal anisotropy for configuration 5. Calculated anisotropy for the $A^{\prime}(1)$ (green), $A^{\prime \prime}$ (blue), and $A^{\prime}(1)$ (red) modes shows 2-fold alignment with the appropriate crystal axes. Experimental and DFT anisotropy intensities were normalized to the largest intensity of their respective $A^{\prime}(1)$ line (green), and the relative intensities from DFT are congruent with experiments.
in the Euler rotation matrix applied to $\chi_{\text {eff }}$ and calculating the resonant amplitude, $A_{q, \text { eff }}$. These calculations showed correspondence to the experimental anisotropy, correctly predicting the relative intensities of the normal modes as $A^{\prime}(2)>A^{\prime \prime}>$ $A^{\prime}(1)$. The peak intensity order showed the opposite trend for previously studied rutile $\mathrm{TiO}_{2}$ facets; however, the flat-lying orientation of ReOH on the surface of $\mathrm{TiO}_{2}(100)$ results in a negligible contribution of the $\mathrm{A}^{\prime}(1)$, totally symmetric transition dipole toward the laboratory $z$-axis, giving rise to less intense PPP-VSFG signal for the mode.

The shape of the calculated rotational anisotropy for ReOH 5 qualitatively matches the experiment (Figure 7b,c). The amplitude corresponding to the $\mathrm{A}^{\prime}(1)$ (red) mode was correctly predicted to be maximum along the [010] axis. The amplitude of the $\mathrm{A}^{\prime}(2)$ (green) mode is predicted to be nearly isotropic as observed in experiments, with the same slight intensity maximum along the [010] direction. Furthermore, the experimental amplitude ratio of the $\mathrm{A}^{\prime}(2)$ to $A^{\prime}(1)$ mode along the $[010]$ axis (9.7) is adequately matched by theory (6.7). The anisotropy of the $A^{\prime \prime}$ mode (blue) was offset by $90^{\circ}$ with its maximum along the [001] axis as observed in experiments, and the experimental amplitude ratio of the $A^{\prime}(1)$ to $A^{\prime \prime}$ modes along the [010] axis (2.1) is reproduced by the DFT calculation (2.1). The calculated anisotropy of the $A^{\prime \prime}$ mode along the [001] axis (Figure 7b, blue) is weaker than in experiments, but this peak is obscured by the larger $\mathrm{A}^{\prime}(2)$ mode in the spectrum, making it difficult to resolve and insufficient to make conclusions about the molecular orientation. The overall synergy between experimental and theoretical results show a unique degree of correspondence strongly supporting the conclusion that the flat-lying ReOH mode 5 is formed on rutile $\mathrm{TiO}_{2}$ (100) through ligand exchange of $\mathrm{Cl}^{-}$for $\mathrm{OH}^{-}$.

ReOH 5 binds in a bidentate fashion through its carboxylate groups, with linkages positioned along the crystal [001] axis (Figure 6). The axial OH ligand contributes an additional interaction with the $\mathrm{TiO}_{2}$ surface through a hydrogen bond between the hydroxyl proton and a protruding oxide ( $2.14 \AA$ ). The tilt angle of the plane of the bipyridine rings was determined to be $91.6^{\circ}$ from the surface normal as obtained
from the optimized geometry using the methodology of previous reports. ${ }^{27}$ This is the most dramatic tilt angle observed in studies of ReCOA binding to $\mathrm{TiO}_{2}$ surfaces, with the (001) facet ( $\sim 11.7^{\circ}$ ) and (110) facet ( $\sim 18-26^{\circ}$ ) displaying upright binding configurations. ${ }^{60,62}$ Such a significant change in orientation stems from the facet-dependent ligand exchange of the ReCOA catalyst on the $\mathrm{TiO}_{2}$ (100) substrate.

The $\mathrm{OH}^{-}$substitution modulates ReCOA to an entirely different catalyst, $\operatorname{Re}($ dcbpy $)(\mathrm{CO})_{3} \mathrm{OH}$, with new orientational possibilities afforded by hydrogen-bonding interaction between the hydroxide proton and the protruding surface oxides of the $\mathrm{TiO}_{2}$ (100) surface. The favorable H -bonding interaction results in a binding geometry with the labile axial group interacting with the surface and oriented away from bulk solution while the bipyridine ring is oriented parallel to the surface. Such a geometry is expected to be suboptimal for electrocatalytic activity that requires exchange of a labile axial group for small molecule substrates. Therefore, heterogenized Rebpy catalysts are expected to be less active toward $\mathrm{CO}_{2}$ reduction when bound to the (100) facet of $\mathrm{TiO}_{2}$.

Proposed Explanation of Facet Dependence. What remains to be explained is why the (100) facet of $\mathrm{TiO}_{2}$ selectively enables ligand exchange. A simple thermodynamic argument can be made based on the feasibility of establishing hydrogen-bonding interactions between the axial $\mathrm{OH}^{-}$ligand and the surface oxides. Rutile $\mathrm{TiO}_{2}$ is composed of octahedral $\mathrm{Ti}^{4+}$ centers having one or two open coordination sites at the interface that can interact with anionic ligands such as $\mathrm{OH}^{-}$. Axial ligand exchange from $\mathrm{Cl}^{-}$to $\mathrm{OH}^{-}$is therefore thermodynamically favorable when the axial $\mathrm{OH}^{-}$can hydrogen bond to the surface oxides without disrupting the ReCOA carboxylate binding. On the contrary, ligand exchange would not produce a thermodynamically favored molecular species if the crystal facet impedes $\mathrm{OH}^{-}$hydrogen-bonding.

The $\mathrm{TiO}_{2}$ (100) facet uniquely enables axial $\mathrm{OH}^{-}$hydrogenbonding without disrupting carboxylate attachment due to the geometric characteristics of its surface. For each crystal facet, the open coordination site points in a different direction with respect to the surface normal, engendering a difference in the natural "binding vector" for ligands on each facet. For example, the $\mathrm{Ti}^{4+}$ framework of $\mathrm{TiO}_{2}$ (110) has open axial coordination sites parallel to the surface normal so ligands encounter least hindrance by binding in the vertical direction (Figure 8a).

The binding geometries of ReCOA on rutile $\mathrm{TiO}_{2}$ (110), (001) and (100) surfaces are compared in Figure 8a-c, respectively. The former two geometries are adopted from


Figure 8. Optimized binding orientations of the $\operatorname{Re}($ dcbpy $)(\mathrm{CO})_{3}$ complexes studied on the (a) (110), (b) (001), and (c) (100) facets of rutile $\mathrm{TiO}_{2}$. The natural binding vectors enforced by the octahedral $\mathrm{Ti}^{4+}$ geometry differ depending on the crystal facet, leading to distal positioning of the Re center on the (110) and (001) facets, and more proximal positioning on the (100) facet. The angle between the surface normal and the open coordination site, $\theta$, is $43^{\circ}$.
previously determined binding structures. ${ }^{25,27}$ For ReCOA on $\mathrm{TiO}_{2}$ (110), the Re center is positioned far above the electrode surface with no opportunity for establishing hydrogen bonds between an axial $\mathrm{OH}^{-}$ligand and the surface oxides. The (001) facet encounters a similar constraint due to the natural binding vectors of its two equatorial coordination sites. The tridentate binding motif shown in Figure 8b stands vertically on the surface to achieve the most favorable overlap of carboxylate orbitals and equatorial $\mathrm{Ti}^{4+}$ sites, leaving the Re center distal to the plane of the surface. In contrast, the sawtooth morphology of $\mathrm{TiO}_{2}$ (100) results in a more flatlying orientation of the bound molecule while satisfying the coordination constraints. The open axial coordination site on (100) is at an angle with respect to the surface normal $(\theta=$ $43^{\circ}$ ), so the Re center naturally adopts a more proximal position to the electrode surface without distortion to ReC0A binding (Figure 8c). In addition, the surface oxides protrude above the $\mathrm{Ti}^{4+}$ coordination sites, bringing the plane of the surface even closer to the Re center and its axial ligands. The result is facet-dependent ligand exchange of a repulsive $\mathrm{Cl}^{-}-$ $\mathrm{O}^{2-}$ contact for a favorable $\mathrm{OH}^{-}-\mathrm{O}^{2-}$ hydrogen-bonding interaction.

## v. CONCLUSION

We have characterized the binding orientation of the $\mathrm{CO}_{2}$ reduction catalyst ReCOA on the rutile $\mathrm{TiO}_{2}(100)$ surface. We found evidence of a distinct binding mode on the (100) facet of $\mathrm{TiO}_{2}$ induced by ligand exchange of the heterogenized molecular catalyst. Measurement of the PPP VSFG spectra showed two higher intensity peaks at $\sim 1900$ and $\sim 1920 \mathrm{~cm}^{-1}$ in addition to a lower intensity peak near $2010 \mathrm{~cm}^{-1}$. The relative intensities of the low- and high-frequency peaks were reversed and the $2010 \mathrm{~cm}^{-1}$ peak red-shifted by $\sim 25 \mathrm{~cm}^{-1}$ compared to analogous studies on the (001) and (110) facets of $\mathrm{TiO}_{2}$. We found that the sawtooth morphology of the (100) facet favors $\mathrm{Cl}^{-}$ligand exchange by $\mathrm{OH}^{-}$to form the $\mathrm{Re}($ dcbpy $)(\mathrm{CO})_{3} \mathrm{OH}$ complex, enabling a hydrogen-bonding interaction between the incorporated axial $\mathrm{OH}^{-}$ligand and the surface. The binding configuration best supported by computational results is 5 (Figure 6a), which reproduced the experimental PPP VSFG line shape, peak intensity ratios, and in-plane rotational anisotropy (Figure 7). This ReOH binding mode positions the plane of the bipyridyl ring flat on the surface at a tilt angle of $91.6^{\circ}$ from the surface normal, distinctly different from the binding modes of the complex on the (001) and (110) surfaces. We found that the interaction of the $\mathrm{OH}^{-}$ligand with the electrode surface through favorable hydrogen-bonding leaves no labile site exposed to solution for redox chemistry, likely hindering the functionality of the catalyst as applied to electrocatalytic $\mathrm{CO}_{2}$ reduction. These findings are particularly relevant to the design and development of catalytic materials since they demonstrate the influence that the specific facet of the host substrate can assert on the binding orientation, spectroscopy, and even the identity of a heterogenized molecular catalyst.

## ASSOCIATED CONTENT

## (s) Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00491.

Detailed experimental and theoretical procedures, table of fitted amplitudes, PPP VSFG response and polar plot,
periodic calculations of $\mathrm{TiO}_{2}$ (100) and small cluster optimization, molecular models, free molecule approach to computing VSFG spectrum of binding configurations, validation of the free molecule approach to computing VSFG intensities, refractive indices, parameters for theoretical calculation of VSFG spectra, theoretical simulation of VSFG rotational anisotropy, relationship between laboratory and molecular coordinates, geometry visualizations for several binding orientations, VSFG spectra and anisotropy plots, and coordinates of optimized structures (PDF)

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## Notes

The authors declare no competing financial interest.

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