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Inverse Design, Development and Characterization of Catalytic Adsorbates at Semiconductor/Liquid Interfaces

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| <b>14. ABSTRACT</b><br>The collaborative team of Batista (Yale University), Kubiak (University of California, San Diego) and Lian (Emory University), have made significant progress in the understanding of the operation of catalysts for CO2 reduction on surfaces, including Re(I) bipyridyl complexes, Ni (cyclam) complexes, and pyridine-based molecules as well as development of in situ spectroscopic techniques for studying catalytic reactions during the last grant period. Each project involves an intimate combination of synthetic, electrochemical, computational, and spectroscopic techniques, especially as related to sum frequency generation spectroscopy (SFG) and in situ electrochemical SFG.                                                                                                                                |             |                                       |                                                                  |             |                                                                      |   |   |   |                                                                                             |  |                                                                                       |  |
| <b>15. SUBJECT TERMS</b><br>Theoretical mechanistic studies of CO2 reduction, sum frequency generation (SFG) spectroscopy of catalysts at electrode surfaces, Re(I) bipyridyl complexes, Ni(cyclam) catalyst, pyridine-based electrocatalyst,                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |             |                                       |                                                                  |             |                                                                      |   |   |   |                                                                                             |  |                                                                                       |  |
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# 2016 AFOSR Final Report

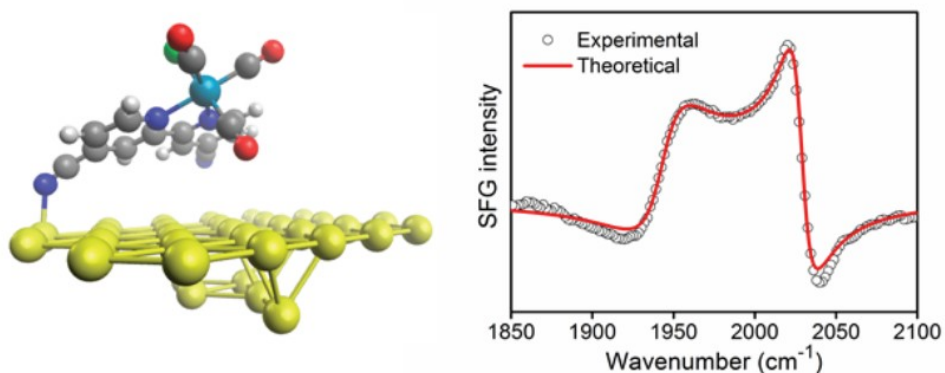
Victor S. Batista, Clifford P. Kubiak and Tianquan Lian

## Research progress.

We, the collaborative team of Batista (Yale University), Kubiak (University of California, San Diego) and Lian (Emory University), have made significant progress in the understanding of the operation of catalysts for CO<sub>2</sub> reduction on surfaces, including Re(I) bipyridyl complexes, Ni(cyclam) complexes, and pyridine-based molecules as well as development of *in situ* spectroscopic techniques for studying catalytic reactions during the last grant period. Each project involves an intimate combination of synthetic, electrochemical, computational, and spectroscopic techniques, especially as related to sum frequency generation spectroscopy (SFG) and *in situ* electrochemical SFG.

### 1. Coupled experimental and theoretical determination of orientation of Re(I) bipyridyl complexes for CO<sub>2</sub> reduction on Au and on TiO<sub>2</sub>.

We have recently determined the binding orientations of Re(I) bipyridyl complexes with different anchoring groups on two different surfaces. First, we used sum frequency generation spectroscopy and calculations of SFG spectra, based on density functional theory, to investigate Re(R-2,2'-bipyridine)(CO)<sub>3</sub>Cl (R = 4-cyano or 4,4'-dicyano) electrocatalysts binding to gold electrodes. Understanding the orientation of these complexes is critical for redox state transitions and catalytic turnover.



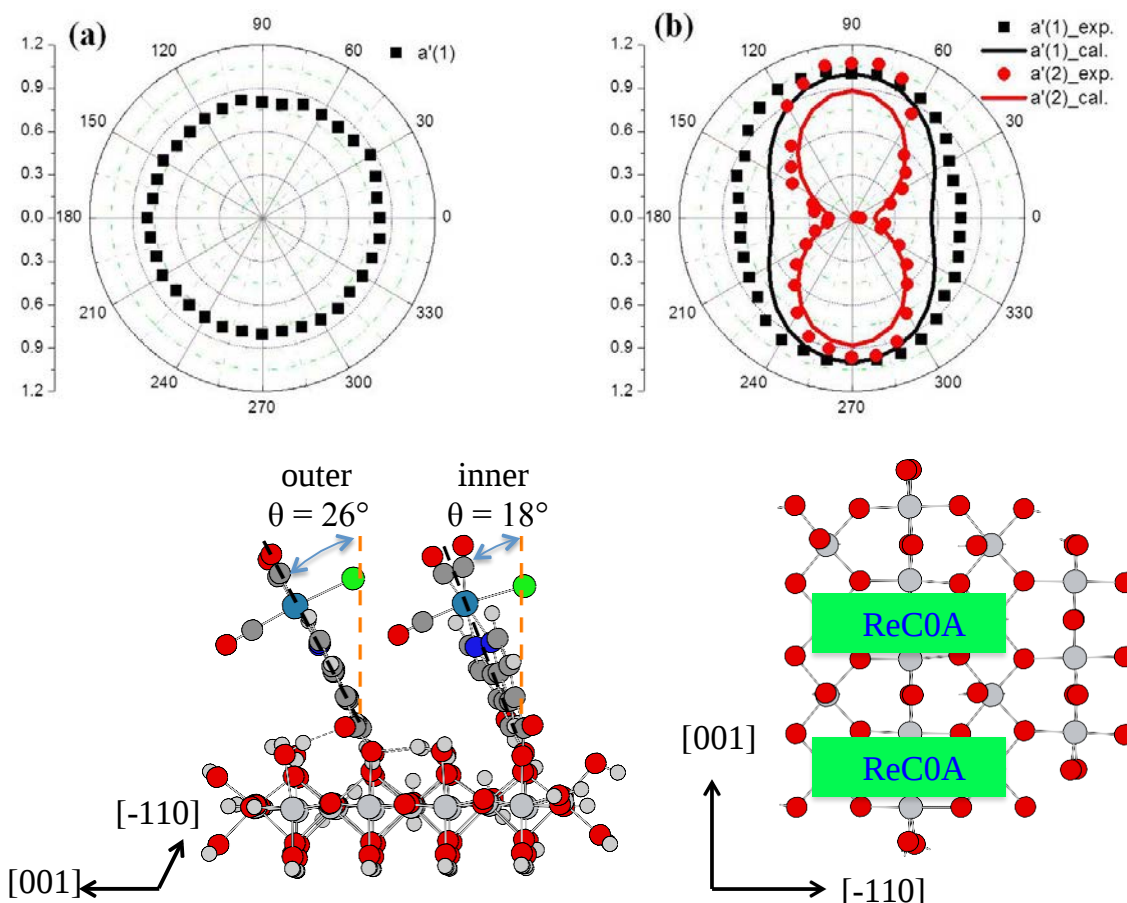
**Figure 1.** *Left.* DFT optimized monodentate geometry for the dicyano Re complex with its axial CO facing the surface with a tilt angle of 63° relative to the surface normal. *Right.* Representative PPP-polarized SFG spectra of monolayers of the dicyano Re

complex adsorbed onto gold thin films (black circles) with DFT simulations of the SFG spectra using the geometry on the left (red).

We found that the electrocatalysts lean on the Au surface and orient the plane of the bipyridine ligand at  $63^\circ$  relative to the surface normal by computing several binding geometries in DFT and determine which gives orientations and thus SFG spectra that best match the experimentally measured spectra. These findings, recently published in the Journal of Physical Chemistry C (Clark 2016), demonstrate the capabilities of the approach including rigorous spectroscopic and theoretical methods for revealing the conformation and orientation of CO<sub>2</sub> reduction catalysts bound to electrode surfaces. This information has consequences for catalytic turnover, as the labile chloride ligand and therefore reactive site of the metal is oriented away from the surface, thus no crowding will occur. Current efforts are focused on exploring alternative anchoring groups including thiol, phosphonate, and isocyanide as well as other substrate surfaces including Si.

Our other effort, recently published in the Journal of Physical Chemistry C (Ge 2016), was focused on surface-induced anisotropic binding of the same catalyst, but with carboxyl anchoring groups (ReC0A) on rutile single-crystalline TiO<sub>2</sub> (110) surfaces relative to (001) surfaces using vibrational sum frequency generation (SFG) spectroscopy. The SFG signal shows an isotropic distribution with the rotation of the TiO<sub>2</sub> (001) surface relative to the incident plane, but an anisotropic distribution with the rotation of the TiO<sub>2</sub> (110) surface (Figure 2, top). By combining these results with *ab initio* SFG simulations and with modeling of ReC0A-TiO<sub>2</sub> cluster binding structures at the density functional theory level, we revealed that the origin of the optical anisotropy for ReC0A on the TiO<sub>2</sub> (110) surface is associated with the binding preference of ReC0A along the [-110] axis. Along this direction, the binding structure is energetically favorable due to the formation of proper hydrogen bonding between the carboxylate group and passivating water molecules on the TiO<sub>2</sub> (110) surface (Figure 2, bottom). The tilt angle, defined by the bipyridyl ring angle relative to the surface normal, of the catalyst is found to be a combination of  $26^\circ$  and  $18^\circ$ , which corresponds to an aggregate at high surface coverage with minimal steric interactions. Since molecular orientation in these systems can significantly influence their catalytic performance, the ability to control the molecular ordering through careful selection of the surface structure and symmetry would be

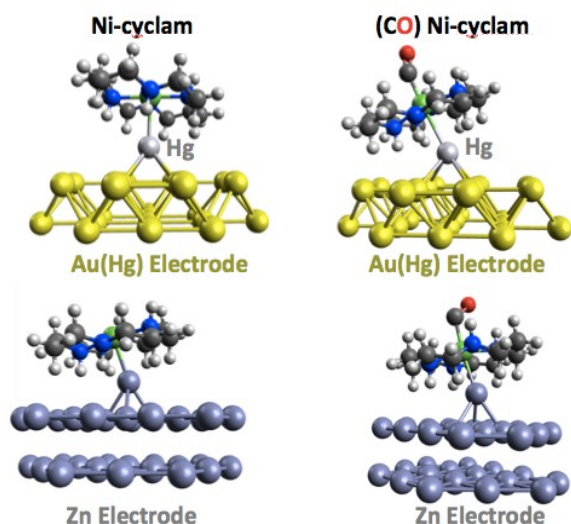
extremely beneficial. This investigation of catalytic molecules on surfaces with different symmetries helps to elucidate how the degree of molecular ordering depends on surface structure and therefore is of great practical interest, which will inform our selection of substrates in future work.



**Figure 2.** *Top.* Polar plots of the azimuthal dependence of the amplitude for (a) the  $a'(1)$  mode of ReC0A on  $\text{TiO}_2$  (001) and (b)  $a'(1)$  and  $a'(2)$  modes of ReC0A on  $\text{TiO}_2$  (110). Black squares ( $a'(1)$ ) and red circles ( $a'(2)$ ) are experimental results; Solid lines are theoretical results. The amplitude of the  $a'(1)$  mode at  $\phi = 90^\circ$  for ReC0A/ $\text{TiO}_2$  (110) system is normalized to one with all other data points for each mode scaled accordingly. *Bottom.* Binding structures of two ReC0A complexes as a dimer on the  $\text{TiO}_2$  (110) surface along the  $[-110]$  axis from the side (left) and from above, with the ReC0A complexes represented by green rectangles indicating the binding sites (right). Hydrogen bonding to the ReC0A complexes is depicted using dashed bonds. The atoms are colored as follows: with green = Cl, silver = Ti, cerulean = Re, white = H, red = O, gray = C, and blue = N. The tilt angles of each catalyst are indicated by the angle formed by the bpy ring (black dotted line) and the surface normal (orange dotted line). The black arrows indicate the crystal directions on the surface for each panel.

## 2. The surface as a ligand: the electronic origins of catalytic enhancement of Ni(cyclam) activity by amalgated gold electrodes (Au/Hg).

Ni(cyclam) has been the focus of many investigations as a CO<sub>2</sub> reduction catalyst, but it suffers from poisoning from CO. However, a dramatic enhancement of electrochemical CO<sub>2</sub> conversion to CO, catalyzed by [Ni(cyclam)](PF<sub>6</sub>)<sub>2</sub>, is observed on Au/Hg electrodes when compared to other metallic electrodes such as Zn. Thus, our recent efforts, in an article being prepared for submission, have focused on understanding the underlying reaction mechanism responsible for the increase in turnover frequency using DFT calculations on cluster models with or without CO bound. The computed *trans*-III conformer structures on the Au/Hg and Zn electrodes are given in Figure 3 where similar effects are found between conformers. We found that that Hg provides favorable interactions for enhanced reaction kinetics by stabilizing the CO unbound form of the catalyst, predominantly with the *trans*-III conformation, due to reduced Ni-CO reverse dative interactions when compared to the complex in solution, or bound to other metallic surfaces. The higher CO stretching frequency, shorter CO bond, longer Ni-C(O) bond, more linear Ni-C-O angle, and spin-density closer to the formal oxidation number of Ni(I) correlate with lower CO desorption free energies. These findings are particularly relevant to the design of electrode surfaces for activation of electrocatalytic transition metal complexes with common surface interactions that could improve catalyst performance under cell operating conditions.

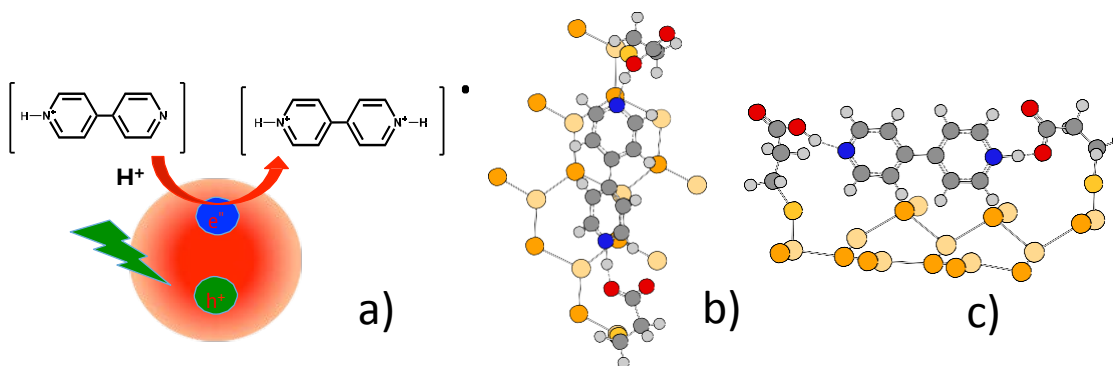


**Figure 3.** DFT optimized configurations of  $[\text{Ni}(\text{cyclam})]^+$  on Au/Hg (top) and Zn (bottom), without CO (left) and CO bound (right). Color key: yellow: Au, silver: Hg, blue: N, white: H, green: Ni, red: O, dark gray: carbon, purple: Zn.

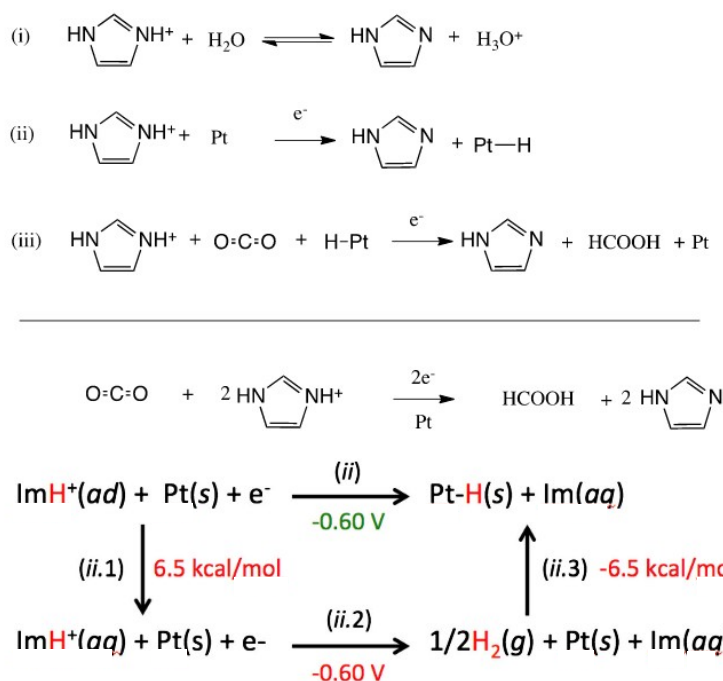
### 3. Proton-coupled electron transfer (PCET) in the reduction of 4,4'-bipyridine with CdSe quantum dots and in the reduction of pyridinium on platinum for the conversion of $\text{CO}_2$ to methanol.

Our efforts into the understanding of PCET in pyridine-based molecules are based on two fronts: reduction of bipyridine by CdSe quantum dots and of pyridinium by Pt electrodes. In the first case, recently published in the Journal of the American Chemical Society (Chen 2016), we studied the photo-reduction of 4,4'-bipyridinium (bPYD) using CdSe quantum dots (QDs) as a model system for interfacial PCET. We observed ultrafast photo-induced PCET from CdSe QDs to form doubly protonated  $[\text{bPYDH}_2]^{++}$  radical cations at low pH (4-6). Through studies of the dependence of PCET rates on isotope substitution, pH and bPYD concentration, the radical formation mechanism was identified to be a sequential interfacial electron and proton transfer (ET/PT) process (Figure 4a) with a rate limiting pH independent electron transfer rate constant,  $k_{\text{int}}$ , of  $1.05 \pm 0.13 \times 10^{10} \text{ s}^{-1}$  between a QD and an adsorbed singly protonated  $[\text{bPYDH}]^+$ . In the presence of sacrificial electron donors, this system was shown to be capable of generating  $[\text{bPYDH}_2]^{++}$  radical cations under continuous illumination at 405 nm with a steady-state photoreduction quantum yield of  $1.1 \pm 0.1\%$  at pH 4. DFT geometry optimizations of

4,4'-bipyridine on a model CdSe cluster were carried out in the presence of bound 3-mercaptopropionic acid (MPA) and were compared to equivalent calculations of methylviologen. The binding geometry is given in Figures 4b and 4c. The optimized structure for bPYD shows asymmetrical hydrogen bonding so that only one  $\text{H}^+$  is bonded to the bPYD (1.22 Å) while the other  $\text{H}^+$  is merely hydrogen bonding to it (1.59 Å), corroborating the role of  $[\text{bPYDH}]^+$  in electron injection. The hydrogen bonding interaction with the MPA prevents bPYD from getting close to the surface, as opposed to methylviologen with its permanent positive charge, suggesting that the faster injection into methylviologen is due to its ability to bind closer to the surface. Theoretical studies of the adsorption of  $[\text{bPYDH}]^+$  and methylviologen on QD surfaces revealed important effects of hydrogen bonding with the capping ligand (3-mercaptopropionic acid) on binding geometry and interfacial PCET. The mechanism of bPYD photo-reduction reported in this work may provide useful insights into the catalytic roles of pyridine and pyridine derivatives in the electrochemical and photoelectrochemical reduction of  $\text{CO}_2$ . This work established that QDs can be used as a model system for studying interfacial PCET mechanisms.



**Figure 4.** Interfacial proton-coupled electron transfer from QDs. a) Scheme of proton-coupled electron transfer from QDs to bipyridine. b) and c) Structure of bPYD on the CdSe {100} cluster model from above (panel b) and from the side (panel c). The color code is as follows: white = H, red = O, gray = C, yellow = S, blue = N, brown = Se, and tan = Cd.



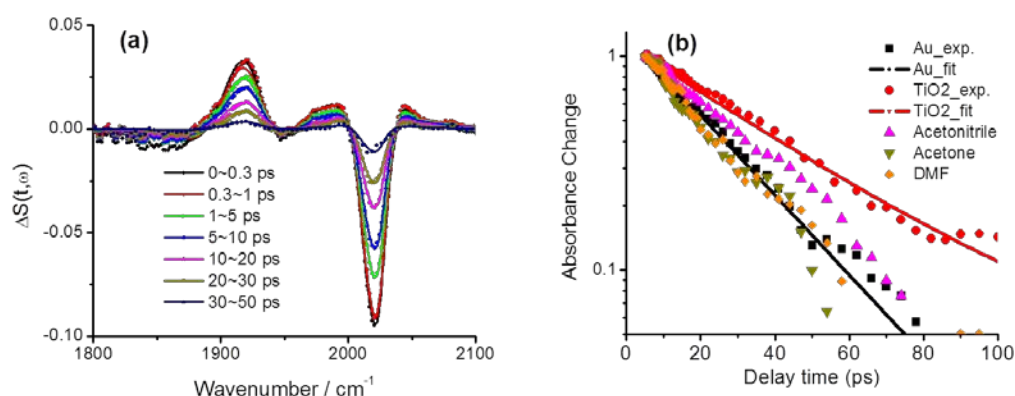
**Figure 5.** *Top:* proposed mechanism of electrochemical reduction of CO<sub>2</sub> on Pt (111) in an aqueous imidazole solution (pH = 5.2). *Bottom:* Thermodynamic cycle (ii.1)–(ii.3) used to obtain the free energy change due to reduction of imidazolium adsorbed to the Pt surface to form Pt-hydride on the surface.

In the second case, as published recently in collaboration with Bocarsly and co-workers in Topics in Catalysis (Liao 2015), we have computationally found that the mechanism of CO<sub>2</sub> reduction by imidazolium is similar to the reduction by pyridinium, as given in Figure 5, top. It was found to form H adsorbates on the electrode surface through a one-electron PCET reaction (-0.68 V vs. SCE as computed by Figure 5, bottom) rather than a one-electron reduction to the imidazolium radical. The cycle includes surface desorption of imidazolium to dihydrogen and imidazole in the aqueous solution (ii.2), and dissociative desorption of H to the Pt surface (ii.3). The reduction potential of imidazolium to H and imidazole (ii.2) was predicted to be -0.60 V, in good agreement with the reduction potential observed by CV experiments, while the free energy changes for reactions (ii.1) and (ii.3) approximately cancel each other. These results are particularly valuable since they suggest that H adsorbates, as recently corroborated through our other recent collaborative work with isotope effects on electrochemistry, published in the Journal of the Electrochemistry Society (Zeitler 2015), could be

generated at low overpotentials by either of the two electrocatalysts. The H adsorbates might react as Pt-hydrides and reduce CO<sub>2</sub> through a proton coupled hydride transfer (PCHT) mechanism, as recently proposed for the electrocatalytic reduction of CO<sub>2</sub> to formic acid in the presence of pyridinium where the electrophilic attack of CO<sub>2</sub> onto the surface hydride is activated by the Brønsted acid in solution.

#### **4. Vibrational relaxation dynamics of Re(R-2,2'-bipyridine)(CO)<sub>3</sub>Cl (R = 4,4'-dicyano) electrocatalyst.**

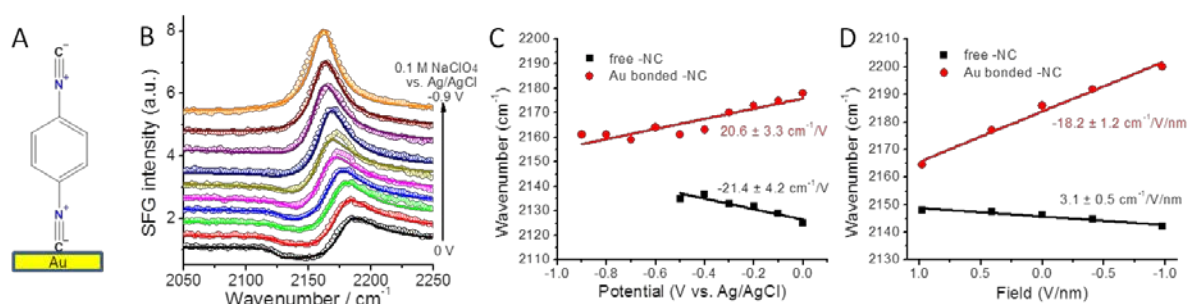
We have started to investigate how metal electrodes and interfacial solvent environment affect vibrational energy relaxation dynamics of catalysts, a process that is intimately coupled to chemical reactions. We have studied vibrational relaxation dynamics of Re(R-2,2'-bipyridine)(CO)<sub>3</sub>Cl (R = 4,4'-dicyano) electrocatalyst on gold and TiO<sub>2</sub> surfaces and in different solvents. Vibrational dynamics of Re complex monolayer bound to the gold surface was probed by IR pump/SFG probe spectroscopy (Figure 6a). Vibrational relaxation dynamics of Re complexes adsorbed on nanoporous TiO<sub>2</sub> thin film and in solution were measured by IR pump/IR probe transient absorption spectroscopy. Our initial results showed that the both metal electrodes and solvent facilitates the vibrational relaxation of CO stretching modes in the Re complex (Figure 6b). Ongoing theoretical calculations are aimed at revealing the mechanisms by which the substrate and solvent affect the vibrational relaxation of Re(I) electrocatalysts using anharmonic coupling constants as yielded by electronic structure calculations.



**Figure 6.** a) Normalized time resolved-SFG difference spectra of three CO stretching modes of Re(I) electrocatalyst on Au at indicated averaged delay times. Solid circles represent experimental data; solid lines represent fits. b) Kinetics of the GSB of in-phase symmetric stretch mode for Re(I) electrocatalyst on Au, TiO<sub>2</sub>, and in different solvents. Symbols represent experimental data; lines represent fits.

### 5. *In situ* electrochemical SFG: electric field effects at the electrode.

Our latest effort involves investigating the electrochemical Stark effect via SFG spectroscopy in order to correlate dependence of vibrational frequencies of chemisorbates on the electrode potential to useful information about the double-layer structure at the electrode/solution interface. We are investigating the Stark effect from the nitrile/isocyanide-terminated self-assembled monolayers (SAMs) on the gold electrode surface. A series of molecules with different terminal groups, symmetry, or length was chosen to systematically study the local electrical fields near the electrode surface. To further understand the Stark effect on the SAMs systems, theoretical calculations were performed to simulate the vibrational frequency shift of nitrile or isocyanide groups in response to local electrical fields. For example, Fig. 7a shows a scheme of 1,4-phenylene diisocyanide (PDI) adsorbed on the electrode surface. Fig. 7b shows the potential-dependent SFG signals of isocyanide groups. At 0 V vs. Ag/AgCl, two peaks around 2120 (free -NC) and 2170 cm<sup>-1</sup> (Au bonded -NC) were observed. At more negative potentials, a blue shift of the free N=C mode and a red shift of the Au bonded N=C mode were observed (Fig. 7c). Such a difference could be explained by the different responses to the electric fields for these two groups, which have opposite dipoles (Fig. 7d).



**Figure 7.** (a) Scheme of PDI adsorbed on gold electrode surface. (b) Potential-dependent SFG spectra of the PDI SAM. Circles represent experimental data, solid lines represent fitting results. (c) Experimental peak positions of free -NC and Au bonded -NC under different potentials. (d) Calculated peak positions of free -NC and Au bonded -NC under different electric fields.

#### Publications with Acknowledgments to the AFOSR:

1. Vibrational Relaxation Dynamics of Catalysts on TiO<sub>2</sub> Rutile (110) Single Crystal Surfaces and Anatase Nanoporous Thin Films. Allen M. Ricks, Chantelle L. Anfuso, William Rodríguez-Córdoba, and Tianquan Lian. *Chem. Phys.* **422**: 264-271 (2013).
2. Functional Role of Pyridinium During Aqueous Electrochemical Reduction of CO<sub>2</sub> on Pt(111), Mehmed Z. Ertem, Steven J. Konezny, C. Moyses Araujo, and Victor S. Batista. *J. Phys. Chem. Lett.* **4**: 745-748 (2013)
3. Electrochemical Reduction of Aqueous Imidazolium on Pt (111) by Proton Coupled Electron Transfer. Kuo Liao, Mikhail Askerka, Elizabeth L. Zeitler, Andrew B. Bocarsly, and Victor S. Batista. *Top. Catal.* **58**: 23-29 (2015).
4. Isotopic Probe Illuminates the Role of the Electrode Surface in Proton Coupled Electron Transfer Electrochemical Reduction of Pyridinium on Pt(111). Elizabeth L. Zeitler, Mehmed Z. Ertem, James Pander, Yong Yan, Victor S. Batista, and Andrew B. Bocarsly. *J. Electrochem. Soc.* **162**: H938-H944 (2015)

5. Short-Range Catalyst–Surface Interactions Revealed by Heterodyne Two-Dimensional Sum Frequency Generation Spectroscopy. Jiayi Wang, Melissa L. Clark, Yingmin Li, Camille L. Kaslan, Clifford P. Kubiak, and Wei Xiong. *J. Phys. Chem. Lett.* **6**: 4204-4209 (2015)
  
6. Orientation of Cyano-Substituted Bipyridine Re(I) *fac*-Tricarbonyl Electrocatalysts Bound to Au Electrodes, Melissa L. Clark, Benjamin Rudshiteyn, Aimin Ge, Steven A. Chabolla, Charles W. Machan, Brian T. Psciuk, Jia Song, Gabriele Canzi, Tianquan Lian, Victor S. Batista, and Clifford P. Kubiak. *J. Phys. Chem. C* **120**: 1657-1665 (2016).
  
7. Surface-Induced Anisotropic Binding of a Rhenium CO<sub>2</sub>-Reduction Catalyst on Rutile TiO<sub>2</sub> (110), Aimin Ge, Benjamin Rudshiteyn, Brian T. Psciuk, Dequan Xiao, Jia Song, Chantelle L. Anfuso, Allen M. Ricks, Victor S. Batista, and Tianquan Lian. *J. Phys. Chem. C*. In Press (2016).
  
8. Ultrafast Photo-Induced Interfacial Proton Coupled Electron Transfer from CdSe Quantum Dots to 4,4'-Bipyridine. Jinqian Chen, Kaifeng Wu, Benjamin Rudshiteyn, Yanyan Jia, Wendu Ding, Zhao-Xiong Xie, Victor S. Batista, and Tianquan Lian. *J. Am. Chem. Soc.* **116**: 26377-26384 (2016).
  
9. Characterizing Interstate Vibrational Coherent Dynamics of Surface Adsorbed Catalysts by Fourth-Order 3D SFG Spectroscopy, Yingmin Li, Jiayi Wang, Melissa L. Clark, Clifford P. Kubiak and Wei Xiong. *Chem. Phys. Lett.* **650**: 1-6 (2016).
  
10. Yanyan Jia, Jinqian Chen, Kaifeng Wu, Alex Kaledin, Djamaladdin G. Musaev, Zhao-Xiong Xie, and Tianquan Lian. Enhancing Photo-Reduction Quantum Efficiency Using Quasi-Type II Core/Shell Quantum Dots. *Chem. Sci.* **7**, 4125-4133 (2016).

11. Mikhail Askerka, Reinhard J. Maurer, Victor S. Batista, and John C. Tully. Role of Tensorial Electronic Friction in Energy Transfer at Metal Surfaces. *Phys. Rev. Lett.* **116**, 217601 (2016).
12. Benjamin Rudshiteyn, Hunter B. Vibbert, Richard May, Eric Wasserman, Ingolf Warnke, Michael D. Hopkins, and Victor S. Batista. Regulation of the Redox Properties of Tungsten-Alkylidyne Complexes by Ligand Design. *Inorg. Chem.* Submitted. (2016).
13. Prasad S. Lakkaraju, Mikhail Askerka, Heidie Beyer, Charles T. Ryan, Tabbetha Dobbins, Christopher Bennett, Jerry J. Kaczur, and Victor S. Batista. Formate to Oxalate: A Crucial Step for Conversion of CO<sub>2</sub> into Multi-Carbon Compounds. *ChemCatChem*. Under Revision. (2016).
14. Benjamin Rudshiteyn, Yueshen Wu, Jesse D. Froehlich, Almagul Zhanaidarova, Wendu Ding, Clifford P. Kubiak, and Victor S. Batista. Diminished Reverse Dative Effect Induced by Electrode Surface Enhances Catalytic Activity of the Ni(cyclam) Complex During Electrochemical CO<sub>2</sub> Reduction. *Manuscript in preparation*. (2016).
15. Aimin Ge, Jingyi Zhu, Benjamin Rudshiteyn, Melissa L. Clark, Mikhail Askerka, Kenneth Jung, Clifford P. Kubiak, Victor S. Batista, and Tianquan Lian. Vibrational Relaxation Dynamics of Rhenium Bipyridyl CO<sub>2</sub>-Reduction Catalyst Monolayer on Gold. *Manuscript in preparation*. (2016).
16. Aimin Ge, Benjamin Rudshiteyn, Gwendolynne L. Merlen, Melissa L. Clark, Jia Song, Clifford P. Kubiak, Victor S. Batista, and Tianquan Lian. Probing Electric Fields at the Nitrile/Isocyanide-Terminated SAMs/Electrode/Liquid Interface by Vibrational SFG Spectroscopy. *Manuscript in preparation*. (2016).

17. Pranammaya Dey, Benjamin Rudshteyn, Mikhail Askerka, Wendu Ding, Victor S. Batista. The Electronic Structure of an Intermediate in a Carbon Dioxide Reduction Reaction as Determined by Computational SFG Spectroscopy. *Manuscript in preparation*. (2016).

**1.****1. Report Type**

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FA9550-13-1-0020

**Principal Investigator Name**

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Victor S. Batista

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The AFOSR Program Manager currently assigned to the award

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**Reporting Period Start Date**

01/01/2013

**Reporting Period End Date**

06/30/2016

**Abstract**

The collaborative team of Batista (Yale University), Kubiak (University of California, San Diego) and Lian (Emory University), have made significant progress in the understanding of the operation of catalysts for CO<sub>2</sub> reduction on surfaces, including Re(I) bipyridyl complexes, Ni(cyclam) complexes, and pyridine-based molecules as well as development of in situ spectroscopic techniques for studying catalytic reactions during the last grant period. Each project involves an intimate combination of synthetic, electrochemical, computational, and spectroscopic techniques, especially as related to sum frequency generation spectroscopy (SFG) and in situ electrochemical SFG.

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11. Mikhail Askerka, Reinhard J. Maurer, Victor S. Batista, and John C. Tully. Role of Tensorial Electronic Friction in Energy Transfer at Metal Surfaces. Phys. Rev. Lett. 116, 217601 (2016).

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