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Clark, Melissa L
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Short Range Catalyst-Surface Interactions Revealed by Heterodyne Two Dimensional Sum Frequency Generation Spectroscopy

Jiaxi Wang[1], Melissa L. Clark[1], Yingmin Li[2], Camille L. Kaslan[1], Clifford P. Kubiak[1, 2], Wei Xiong[1, 2]*

[1]Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358 La Jolla, California 92093-0358, United States

[2]Material Science and Engineering Program, University of California, San Diego, 9500 Gilman Drive, MC 0418 La Jolla, California 92093-0418, United States

AUTHOR INFORMATION

Corresponding Author

*w2xiong@ucsd.edu

ABSTRACT In this Letter, Heterodyne Two Dimensional Sum Frequency Generation Spectroscopy is used to study a model CO_2 reduction catalyst, Re(diCN-bpy)(CO)$_3$Cl, as a monolayer on a gold surface. We show that short range interactions with the surface can cause substantial lineshape differences between vibrational bands from the same molecules. We explain this interaction as the result of couplings between CO vibrational modes of the catalyst molecules and the image dipoles on gold surface, which are sensitive to the relative distance between the molecule and the surface. Thus, by analysis of HD 2D SFG lineshape differences and polarization dependences of IR spectra, we can unambiguously determine the ensemble-averaged orientation of the molecules on the surface. The high sensitivity of HD 2D SFG spectra to short range interactions can be applied to many other adsorbate - substrate interactions, and therefore can serve as a unique tool to determine adsorbate orientations on surfaces.

TOC GRAPHICS
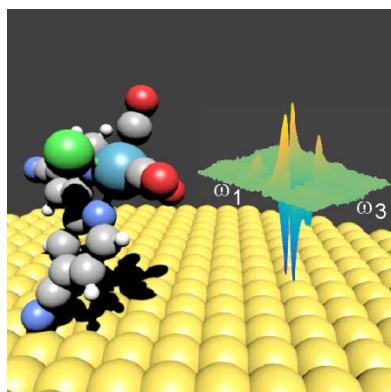
Materials based on a molecular monolayer adsorbed onto a solid surface have drawn significant attention in the field of catalysts,[1] electronics,[2] and biotechnology[3] because of the possibility to precisely control the function of the molecular monolayers. To improve these materials, it is necessary to understand not only the molecular structures, but also the interactions between the molecules and the surface.

In the areas of solar fuels and artificial photosynthesis, the development of catalysts to produce fuels by carbon dioxide reduction reaction (CO_2RR) poses a considerable challenge.[1,4] One important strategy to prepare new catalysts is the attachment of molecular catalysts to surfaces. Surface attached catalysts offer the promise of high selectivity and tunability of homogenous molecular catalysts, and the robustness and the ease of separation of heterogeneous catalysts. However, the subtle interactions between the catalysts and the surface can significantly change the structure and dynamics of the catalyst and will likely impact the performance of the catalyst.[5] Therefore, it is necessary to understand how catalysts attach to the surface and how they interact with the surface. Currently, such information is determined using X-ray or photoelectron spectroscopies,[6–8] which rely on spectral peak position shifts to infer surface interactions, and are typically limited to systems under vacuum. One dimensional sum frequency generation spectroscopy[9–11] is another powerful approach to investigate surfaces under working conditions, but the intrinsic spectral broadening makes extracting surface interactions difficult from either peak positions or lineshapes.[12]

To better reveal the molecular orientation and the interaction with surfaces, we implement surface-sensitive heterodyne 2D sum frequency generation (HD 2D SFG) spectroscopy[13–16] to study a model surface catalyst for CO_2 reduction, which are composed of a monolayer of Re(diCN-bpy)(CO)$_3$Cl (referred as **1**, diCN-bpy = 4,4′-dicyano-2,2′-bipyridine) on a gold

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surface. This complex has been found to be a molecular electrocatalyst for the reduction of two equivalents of CO_2 to CO and carbonate, which will be reported separately. Similar Re-bpy complexes have been extensively studied in homogenous solution phase using 2D IR spectroscopy,[17–19] where charge and solvent dynamics of ground and electronic excited states are investigated. The corresponding monolayers have only been investigated by Lian using time-resolved SFG spectroscopy[20] for vibrational relaxations and by Fayer using 2D IR spectroscopy[21] for spectral diffusion. To the best of our knowledge, there have been no surface spectroscopic studies that focus on the adsorbate-substrate interactions using HD 2D SFG.

HD 2D SFG spectroscopy[13–16] can be viewed as a surface sensitive version 2D IR. It is able to resolve homogeneous and inhomogeneous dynamics, and molecular orientation on molecular submonolayers including air/water interfaces,[14,16] electrode surfaces,[15] and surface bound biomolecules,[13] which makes it an ideal technique to probe molecules on surfaces. The surface sensitivity of HD 2D SFG is because it is a 4th order non-linear optical signal. Similar to 2nd order signals such as second harmonic generation or sum frequency generation, 4th order signals can be only generated from non-centrosymmetric media, such as interfaces. The ability to distinguish dynamics in both fast and slow time scales is because HD 2D SFG measures the same 3rd order vibrational response function as 2D IR does, which tracks the vibration mode evolution as a function of time from femtoseconds to hundreds of picoseconds. In particular, compared to 1D SFG, which determines dynamics from linewidth and peak positions alone, HD 2D SFG provides many additional lineshape parameters — center line slope,[22] nodal line slope,[23] diagonal and antidiagonal linewidth, etc. — making it more sensitive to subtle dynamic changes. Furthermore, heterodyne detection can reveal the phase of the 2D SFG spectra, which is
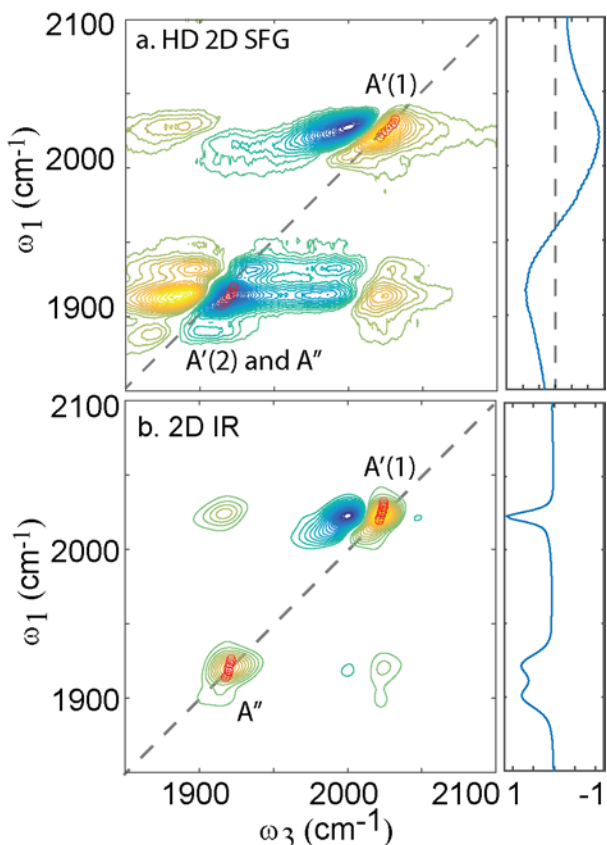
Figure 1. Multidimensional vibrational spectra of **1**. (a) HD 2D SFG spectrum. Right panel of a: HD SFG spectrum of the same sample. The HD SFG spectrum is significantly broadened by inhomogeneous molecular surface distribution. (b) 2D IR spectrum of **1** in DMSO. Right panel of b: FTIR. Please note that FTIR spectrum is taken using a FTIR spectrometer, so it spectral range is not limited by the mid-IR laser spectral bandwidth. Lines of red open circles are the center line slope of the diagonal peaks. Dash gray lines are diagonal. HD 2D SFG has single monolayer sensitivity, whereas 2D IR measures signal from bulk sample.

related to the orientation of surface adsorbate molecules, and also improve its sensitivity to low coverage surfaces[24] thanks to its linear dependence on surface coverage.[12,24,25]

In this Letter, we show that the center-line slope[22] (CLS, red circles in Fig. 1) of HD 2D SFG spectra are uniquely sensitive to the short-range interactions between vibrational modes of

surface molecules and surface substrates. HD 2D SFG peaks of **1** have different CLSs, which can be induced by either different homogenous or inhomogeneous broadening experienced by these vibrational modes. It is often difficult to distinguish which of these mechanisms causes the changes of CLS, however by analyzing the spectral tilts of cross peaks, we unambiguously determine that the origin is homogenous broadening. This approach provides a new and straightforward protocol to disentangle various sources of lineshape broadening, in comparing to the standard but more complicated lineshape fitting methods based on either Kubo or more advanced models. We further attribute this homogenous broadening difference to the distinct amount of interactions between vibrational transition dipoles and the image dipole on the surface.[26,27] Our findings then allow the determination of the ensemble-averaged molecular orientations from HD 2D SFG and Infrared Reflection Absorption Spectroscopy (IRRAS).

To learn the impact of surface attachment, we compare the HD 2D SFG spectrum of the CO vibrational modes of **1** on a gold surface and 2D IR spectrum of the same modes from **1** in solution. In the HD 2D SFG spectrum of **1** on gold (Fig.1a; SI for sketches of the vibration modes), the diagonal peaks at $\omega_1 = 2020$ cm^{-1} correspond to the fundamental transitions of A′(1) carbonyl stretch. The out-of-phase peak that is redshifted from the diagonal peak is the corresponding overtone transition. The peak set between 1950 and 1890 cm^{-1} correspond to the A″ and A′(2) modes of the CO ligands,[17,21] which is also composed of the fundamental and overtone doublet. In the 2D IR spectrum of the same complex in DMSO (Fig.1b), the two sets of peaks at 2020 cm^{-1} and 1919 cm^{-1} originate from the fundamental transition of A′(1) and A″ modes. The A′(2) mode and the overtone of A″ mode are out of the spectral window in the 2D IR spectrum, because both of them manifest large redshifts (see FTIR, right panel of Fig.1b) in solution phase comparing to on the surface.

A careful inspection of the HD 2D SFG spectrum in Fig. 1a reveals that the A′(1) peak and lower frequency peak set of A″ and A′(2) have different lineshapes. Although all diagonal peaks are elongated in HD 2D SFG spectrum, which indicates molecules are inhomogeneously distributed on the surface, the lower frequency peaks are less tilted along the diagonal than the A′(1) peak. This is in sharp contrast to the 2D IR spectra, where both peaks are round and lie along the vertical line, which indicates the molecular vibrational dynamics are dominated by homogenous broadening dynamics, such as solvent interactions. To make a quantitative comparison, we extract the CLS of both the A′(1) peak and the lower frequency peak set in 2D IR and HD 2D SFG spectra (Fig.1; see SI for methods and enlarged figures). While there are several methods to quantify the spectral tilt, we choose CLS because the method is not sensitive to one dimensional apodization,[22] and in our experiment the ω_3 axis was apodized during the SFG upcoversion process. We fit the slope around the center position of the diagonal peak, ±7 cm^{-1}, to avoid the influence caused by multiple peaks from different conformations on the surface or in solution. Clearly, in the 2D IR spectrum of the solution-phase sample, the CLSs of both peaks are similar (A′(1): 0.23 ± 0.07, A′(2) and A″ : 0.25 ± 0.04), which indicate a homogenous environment. This result agrees with previous published results.[21] It indicates both vibrational modes of **1** experience the same microenvironments and solvent dynamics, which leads to the same amount of homogenous broadening. However, in the HD 2D SFG spectrum of the surface sample, the lower frequency peak set has a smaller CLS (A′(2) and A″: 0.72 ± 0.16) than the A′(1) peak (1.03 ± 0.06). This difference is notable and indicates these two sets of normal modes experience different dynamics or environments on the surface.

CLS indicates the balance between the inhomogenous and homogenous broadenings - how much inhomogeneous broadening contributes to the lineshape. As the samples approach fully

inhomogeneous broadening, the spectra are tilted along diagonal line and CLS equals one. On the other hand, when homogenous broadening dominates the lineshape, the spectra are tilted vertically, and CLS equals zero. Therefore, the differences in CLS can be caused by two scenarios: All the modes experience the same amount of homogenous broadening, but the A′(1) mode is more inhomogeneous than the A″ and A′(2) modes (Scenario 1), or that all experience the same inhomogeneous broadening, but the A″ and A′(2) modes are more homogenously broadened than the A′(1) mode (Scenario 2).

Although it is difficult to distinguish between these two scenarios from the diagonal peaks alone, we show here it is straightforward to determine which scenario leads to the CLS difference when we inspect the cross peaks. The cross peaks are due to strong intramolecular coupling. They appear as pairs of out of phase doublets at the corners of both 2D spectra, which are determined by the frequency of two coupled vibrational peaks. To inspect the cross peaks of the HD 2D SFG more clearly, they are plotted in Fig.2a and d, where the red line indicates their CLSs. The upper left cross peak (Fig. 2a) is tilted along the diagonal (dashed gray line) but also broadened along ω_3, whereas in Fig. 2d the lower right cross peaks is less tilted along diagonal but more along the ω_1 axis. This striking contrast in CLS is the key to differentiate the two scenarios.

To show how the cross peak CLS is sensitive to the different contributions of lineshape broadening, we simulated the cross peaks[28] corresponding to the two scenarios mentioned above (SI for details). Under the harmonic oscillator approximation, both fundamental and overtone peaks should have the same lineshape.[29] Therefore, in the simulation we only simulated the lineshape of the fundamental peaks. We note our intention is not to quantitatively fit the experimental spectra and retrieve lineshape broadening parameters but to show how a simple

inspection of the CLSs of cross peaks can reveal whether the vibrational modes experience homogenous or inhomogeneous broadening.
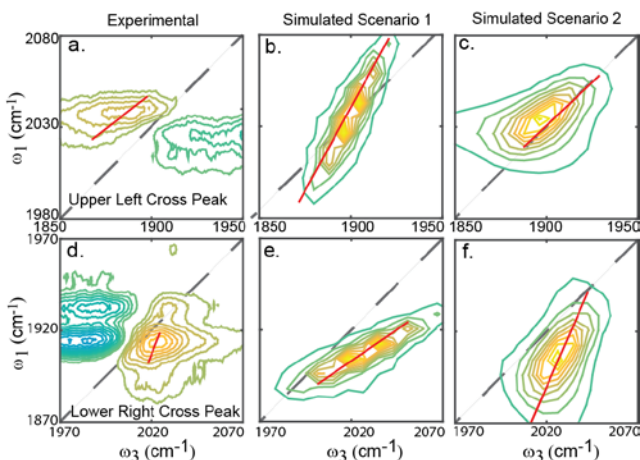

Figure 2. Cross peaks of HD 2D SFG of **1**. Figs a and d: Cross peaks measured in experiment. (same as Fig.1 a, but are zoomed in for clarity). Figs b and e: Simulated cross peaks for Scenario 1. Figs c and f: Simulated cross peaks for Scenario 2. The simulated results clearly suggest that it is Scenario 2 that leads the spectral lineshape in the experiment. Red lines indicate the center line slopes and the dashed gray lines are the diagonal lines.

In Scenario 1, where the A′(1) mode is more inhomogeneous, we found that upper-left peak (Fig. 2b) is stretched along ω_1, and tilted more towards the ω_1 axis, whereas the lower-right peak (Fig. 2e) is tilted towards the ω_3 axis. This is opposite from the cross peaks lineshape in measured spectrum. In Scenario 2 (Fig. 2c and f), where A′(2) and A″ modes are more homogenously broadened than the A′(1) mode, the upper left cross peak is broadened along ω_1 axis and tilted along diagonal, whereas the lower right peak is tilted towards ω_1 axis. This trend from Scenario 2 matches well to the CLSs of measured spectra in Fig. 2a and d. Therefore, we conclude that the A″ and A′(2) modes experience extra interactions that cause more homogenous broadening, but all three modes are similarly inhomogeneously broadened. This also suggests that homogenous broadening is more sensitive to the local environment than inhomogeneous

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broadening, which agrees with previous results. In the 2D IR spectra of a similar Re complex measured by Fayer and co-workers, it was observed that spectral inhomogeneity is not sensitive to the chain length of linker groups between the Re complex and the solid surface.[30] Our results demonstrate that the CLSs of HD 2D spectra is an unambiguous way to reveal subtle interactions or dynamics changes when other parameters such as spectral peak positions or linewidths might not be sensitive to the changes because of spectral convolutions.

Since the gold surface is the only material that is brought close to compound **1**, the difference in homogenous broadening should be caused by short-range interactions between the molecule's vibrational modes and the gold surface, where the interactions strongly depend on the relative direction and distance of the transition dipole moments to the surface. We rule out the possibility of intermolecular interactions, since it has been shown in previous studies that the coupling between molecules in a similar Re-complex monolayer is negligible.[30] Among these short range interactions, contributions to homogenous broadening that require the molecules to be chemisorbed on gold surface can be ruled out as well, because the CO modes do not directly attach to the gold surface through either chemi- or physi-adsorptions. These interactions include the non-adiabatic charge transfer interaction[31] and the coupling to low frequency modes,[32,33] such as hindered rotations and translations.

Therefore, the most likely origin of the adsorbate-surface interaction in play is coupling between vibrational modes and image dipoles.[26,34–42] From early surface IR spectroscopy research[26] it is known that the image dipole interaction is the dominant vibrational decay mechanism on adsorbate-metal interfaces when the vibrational modes do not directly attach to and is <10 nm away from the surface. This interaction depends on both relative orientation and distance of the vibrational modes to the surface. As we reveal below, the ensemble-averaged

angle of the three modes to surface normal are very similar (only directions are different), and we therefore argue that the orientation influence on the image dipole interaction is similar to all three modes. The lifetimes of vibrational modes depend on the relative distance between the vibrational modes and the surface to the 4th power,[26] which means that small changes in distance can cause large difference in vibrational lifetimes. Typically, shorter vibrational lifetime generate broader homogenous linewidth. For the molecules we investigate here, since A′(2) and A″ modes are more homogenously broadened and also have shorter vibrational lifetimes (vibrational life time of A′ (1) is 26 ps and of A′(2) / A″ is 20 ps, see SI for details), this suggests that the A′(2) and A″ modes are closer to the surface.
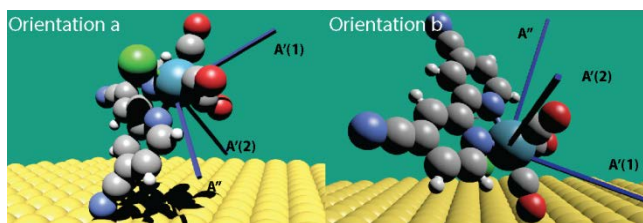

Figure 3. Orientations of **1** on gold surface determined from HD 2D SFG and IRRAS measurements, simulated using DFT. Orientation (a) is preferred. Blue sticks represent the vibrational modes' directions

Combined with sign of HD 2D SFG peaks, our knowledge that the A′(2) and A″ modes are closer to the surface can help to precisely determine the ensemble-averaged molecular orientation. In HD 2D SFG, the sign of the diagonal peak is different between the A′(1) and the other two modes. This difference of signs in HD 2D SFG indicates that A′(1) mode's direction is opposite from A′(2) and A″ modes.[14,15] However, this information is usually not enough to determine the absolute orientations of the molecule, since the phase of the local oscillator, which is the non-resonance signal from gold surface, can be either 0° or 180°.[43] Therefore, it could either be that A′(1) mode is directed upwards and the other two are downwards, or the opposite.

Since we know that the A′(2) and A″ modes are closer to the surface, they must be the modes that point downwards, which makes them closer to the surface, and therefore A′(1) is upwards.

We can further unambiguously determine how the molecules reside on gold surface using the ensemble-averaged orientation determined from the polarization dependence of the IRRAS spectra. IRRAS is a reflection mode IR spectroscopy, which has been used to study thin molecular layers on surfaces. Vibrational modes with various relative angles to the surface normal respond differently to the IR beam with different polarizations. It is established that by measuring the spectral intensity of IRRAS at various IR polarization angles, the ensemble-averaged vibrational modes angle relative to surface normal can be determined.[21] Combining IRRAS and the vibrational modes direction learned from HD 2D SFG, we determine these angles relative to the surface normal in lab frame for A′(1), A′(2) and A″ are 68±11, 118±4, 121±7°, respectively (SI for details). The vibrational mode angles relative to molecular frame are obtained from B3LYP/LanL2DZ DFT calculation. By rotating **1** from molecular frame to lab frame to match these measured angles, we found that **1** resides on the surface with its Re-Cl axis 45° relative to surface normal (SI), where the Cl atom points up and the molecule is anchored through one CN group (orientation **a** in Fig.3). To compare, we also plotted the other "possible" orientation with A′(1) pointing downward (orientation **b** in Fig.3). It is clear that in this configuration neither of the CN groups is close enough to the surface to interact with gold, which suggests that this is an unfavorable orientation. This comparison further confirmed our conclusion that the A″ and A′(2) modes point towards to the gold surface and have stronger interactions with the surface.

In summary, we observed that vibrational peaks from the Re-complex **1** on a gold surface in HD 2D SFG have different center-line slopes, which is caused by the various vibrational modes

experience distinct homogenous broadening but similar inhomogeneous broadening. The drastic difference in homogenous broadening is attributed to the interaction with the image dipole on gold surface, which is highly sensitive to the relative distance of the vibrational modes to the surface. Combining the knowledge of relative distance of vibrational modes to the surface and the polarization dependence of IRRAS spectra, we conclude that the Re-complex should attach on the surface with the Cl atom pointing away from the gold surface. Structure-activity relationships of surface catalysts will be described in our future studies.

Since the adsorbate-metal surface interactions exist in many metal surface based molecular monolayers, we expect HD 2D SFG spectroscopy can be used to determine the ensemble-averaged orientation of the molecules and the strength of the adsorbate-surface interactions on many molecular/metal interfaces. Moreover, since many other interactions exist on liquid/liquid, liquid/solid and gas/liquid interfaces, such as hydrophobic/hydrophilic interactions, or H-bond,[44–46] and they can also influence 2D spectral lineshape, we expect similar approaches that uses HD 2D SFG to determine interfacial interactions can also be extended to these interfaces as well. We acknowledge that at least two vibrational modes need to be measured to determine the ensemble-averaged orientations, which becomes much easily accessible with the current broadband IR generation techniques.[47,48] This capability to determine molecular orientation on surfaces and the sensitivity to local interactions with surfaces are expected to provide important new knowledge about a wide range of materials, including notably the area of surface catalysis.

ASSOCIATED CONTENT

Supporting Information. Supporting information includes additional 2D spectra with center line slope fittings, experimental, simulation and data analysis procedures. This material is

available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interests.

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