



Case Study: Surface Catalyst Structure and Dynamics Revealed by Multi-Dimensional SFG Spectroscopy

The combination of high pulse energy and long term stability from a Coherent Astrella ultrafast amplifier enables precise characterization of how molecules are bound to surfaces, with implications from green energy catalysts to electronics and biological membranes.

Summary

At Professor Wei Xiong's laboratory at the University of California, San Diego, researchers are using a Coherent Astrella ultrafast amplifier in a novel setup to perform Heterodyne Two Dimensional Sum Frequency Generation Spectroscopy (HD 2D SFG) studies of a CO₂ reduction catalyst, Re(diCN-bpy)(CO)₃Cl, as a monolayer on a gold surface. These experiments reveal unique information about the structure, surface alignment and dynamics of the immobilized molecules. Each data set may require as long as 48 hours measurement time so the long-term stability of the ultrafast laser amplifier is quintessential to obtain repeatable data with an excellent signal-to-noise ratio.

The Goal – Probing Molecules on Surfaces

Professor Xiong explains¹, “In the areas of solar fuels and artificial photosynthesis, the development of catalysts to produce fuels by carbon dioxide reduction reaction (CO₂RR) poses a considerable challenge. 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 flexibility 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 its performance. For instance, coupling and interstate coherence between vibrational modes can be altered, which influence the channels for energy transfer quickly sampling all of the vibrational modes, in order to break chemical bonds and release products. Therefore it is necessary to understand how the vibrational coupling and coherence dynamics of these catalysts are affected by surface attachment.”

Re(diCN-bpy)(CO)₃Cl is in itself an important research subject², but the techniques described here could be used to provide fundamental insights into the structure and dynamics of many other surface-bound molecules, in fields such as electronics and biotechnology.



Two Dimensional Spectroscopy

Infrared absorption spectra have long been used by chemists and physicists, typically obtained using a FTIR instrument. Here, data is presented and analyzed as a plot of absorption versus wavelength; each peak corresponds to a different molecular vibration (fundamental or overtone).

In recent years, researchers have begun to take advantage of the high brightness of the laser in order to obtain two dimensional spectra. As shown in figure 1, the signal (e.g., infrared absorption) is measured as a function of two independent source wavelengths.³ If the two source wavelengths are the same (the diagonal line in this plot), then the peaks along this line are just the usual FTIR spectrum. But now consider if wavelength 1 is fixed at absorption peak B of the sample. This will excite a vibration just as in FTIR *and* will also perturb (change) the absorption of wavelength 2 (peak C), if wavelength 2 *is simultaneously exciting a vibration that couples to the first vibration*.

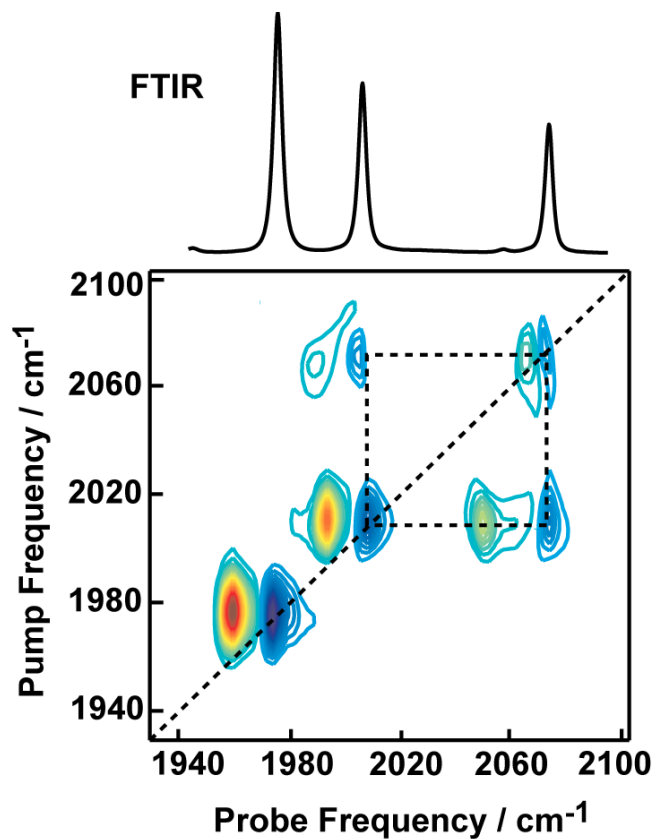


Figure 1. Experimentally measured (top) FTIR and (bottom) 2D IR spectra for a mixture of compounds. From the FTIR spectrum, one cannot determine how many types of molecules are contained in the mixture. The 2D IR spectrum exhibits a pair of diagonal peaks for each of the peaks in the FTIR spectrum. The cross peaks in the 2D IR spectrum reveal that the two higher frequency peaks are coupled to each other, indicating their belonging to the same molecule. In fact, these spectra were collected for a mixture of two compounds.



Referring to figure 1, any pair of vibrations linked by common atoms in this way are called coupled vibrations, and will give rise to so-called cross peaks, displaced from the diagonal (one-dimensional) spectral line. So at the very least, 2D spectroscopy can tell us which vibrations are coupled. (As shown in figure 1, the peaks are usually plotted as intensity contours and two contrasting colors, e.g., blue and red, are used to indicate the relative sign of the peaks.)

Although this is an important capability, in theory this information could be obtained by other analytical means, such as isotopic substitution. However, the vibrational interstate coherences observed by 2D absorption spectroscopy can provide a wealth of both structural and dynamic (e.g., intramolecular energy flow) information beyond this. Just as in FTIR, additional information is obtained from a detailed analysis of absorption linewidths and line shapes. The nature of two-dimensional spectroscopy makes it more sensitive to subtle dynamic changes, including providing clear distinction between homogeneous and inhomogeneous broadening. And as with FTIR, the use of polarized light sources for the two wavelengths can provide further stereochemical insights.

Time-Domain Using Ultrafast Broadband Pulses

When 2D spectroscopy was first developed, spectra such as figure 1 were sometimes recorded using two, narrow bandwidth, tunable light sources. (Because of the non-linear nature of this essentially two-photon effect, the sources have to be pulsed lasers in order to have high peak power.) Today however, the majority of 2D spectra are obtained in the time domain using ultrafast laser pulses. Here the two narrow band pulses (wavelengths 1 and 2) implied in figure 1 are each replaced with pairs of femtosecond pulses whose bandwidth covers all the vibrational modes at once. Data is collected as a function of the time-delays within each pair. Frequency domain data is then obtained by taking a Fourier transform.

Working in the time domain also provides yet another mechanism to interrogate the sample. Specifically, by varying the time delay between laser 1 and laser 2, the data reveal the time evolution of the molecular vibrations, including dephasing rates, i.e., the timescale of energy flow. Moreover, because the lasers cause coherent excitation of coupled vibrations, the use of heterodyne detection enables the changing phase of the cross peaks to be observed in real time.

Two Dimensional SFG Spectroscopy

A key focus of Professor Xiong's group at UCSD is to use multidimensional spectroscopy to study molecules attached to surfaces, such as a monolayer arrangement of the CO₂ reduction catalyst Re(diCN-bpy)(CO)₃Cl on gold.¹ (From here on, we refer to this Rhenium compound as "the catalyst" for simplicity). In this study, a challenge is to separate the spectroscopic signals from the surface bound molecules from the large potential background signals due to bulk (unbound) material in the solvent.



What is needed is a spectroscopic technique that *only* produces resonant vibrational signals at the surface or phase interface and surface Sum Frequency Generation (SFG) spectroscopy (first demonstrated in 1987) is just such a technique⁶. Here, two intense laser beams (a visible and an infrared one) are focused on the interface. If the target is non-centrosymmetric, a weak visible wavelength beam at the sum of the two laser frequencies is generated. When the infrared laser wavelength is resonant with a vibration mode of the molecules at the interface, the probability of SFG shoots up by several orders. Tuning the infrared laser, thus gives a method of generating a vibrational spectrum of surface bound molecules only. In practice, the blue shifted visible beam is then detected in reflection for opaque surfaces like gold, or in transmission for transparent interfaces such as lipid membranes.

While working in the research group of Professor Martin Zanni (University of Wisconsin, Madison), Xiong and others showed that SFG could be combined into a 2D spectroscopy setup, publishing their first data in 2011⁷. Moreover, they showed that this set-up delivered all the subtleties and multi-leveled information for surface samples that 2D IR had already demonstrated for bulk samples. Xiong summarizes, “2D SFG with heterodyne detection is able to resolve homogeneous and inhomogeneous dynamics, and molecular orientation on molecular sub-monolayers, including air/water interfaces, electrode surfaces, and surface bound biomolecules, which makes it an ideal technique to probe molecules on surfaces.”

Experimental Details

Figure 2 schematically shows the main elements of the setup currently used by Professor Xiong’s team to perform heterodyne 2D and 3D SFG spectroscopy. The laser engine of the entire system is the Coherent Astrella ultrafast amplifier. This is a one-box amplifier capable of producing over 7 mJ per pulse at a pulse width < 35 fs, a wavelength of 800 nm and a repetition rate of 1 kHz. The 800 nm output is actually used as the “visible” wavelength while the mid IR wavelength is generated by using a two-stage tunable optical parametric amplifier (OPA) – the Topas Prime Plus from Light Conversion Inc. In the work discussed here, the center of the OPA output is set to a wavelength of 5.06 μm (i.e., 1975 cm^{-1}). The spectral bandwidth of the 35 fs pulses then covers the entire 1850 to 2100 cm^{-1} spectral region, where resonant vibrations associated with carbonyl (CO) ligands of the catalyst are located.

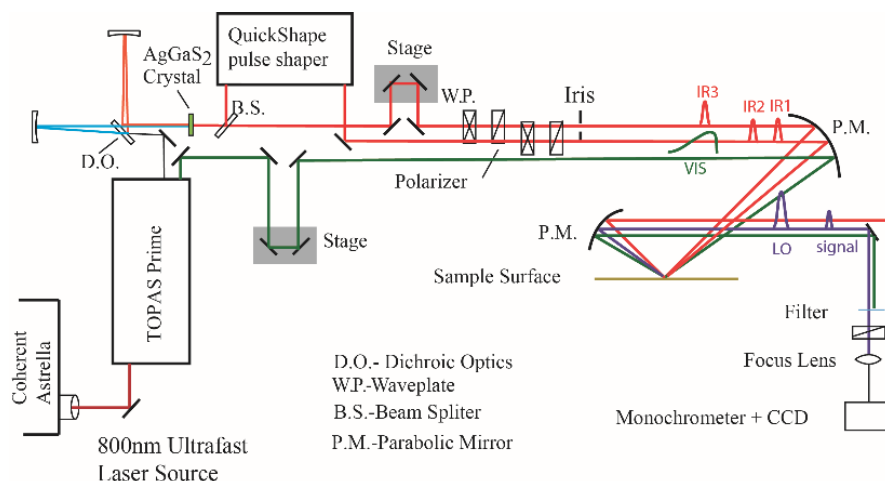


Figure 2. The Xiong group experimental setup is configured to support both 2D SFG and 2D IR.

The special pulse shaping and pulse delay adjustments are performed in a 2DQuickShape pulse shaper supplied by PhaseTech Spectroscopy, Inc., which utilizes patented pulse shaping technology from the Zanni Research Group^{8,9}. The Xiong group’s spectrometer also includes a low noise CCD camera to simultaneously record dispersed SFG spectra at 1024 wavelength channels centered around 690 nm. Prior to reaching the detector array, the SFG signal is boosted by a local oscillator and combined with a SFG signal from an uncoated gold substrate to enable heterodyne detection.

Results from $\text{Re}(\text{diCN-bpy})(\text{CO})_3\text{Cl}$ on Gold

The Xiong group configured their experimental setup to perform both 2D IR and 2D SFG, which is a significant accomplishment in itself. They then used both techniques to study **the catalyst** on gold. A full and detailed discussion of this comprehensive scientific study is beyond the scope of this document so we now discuss some of the more interesting data and implications. In the first part of these studies, the researchers compared the Heterodyne(HD) 2D SFG spectrum of the CO vibrational modes of **the catalyst** on a gold surface with the 2D IR spectrum of the same modes from **the catalyst** in solution (in DMSO) in order to obtain and analyze the spectral differences due to surface attachment. Typical data from these experiments are shown in Figure 3.

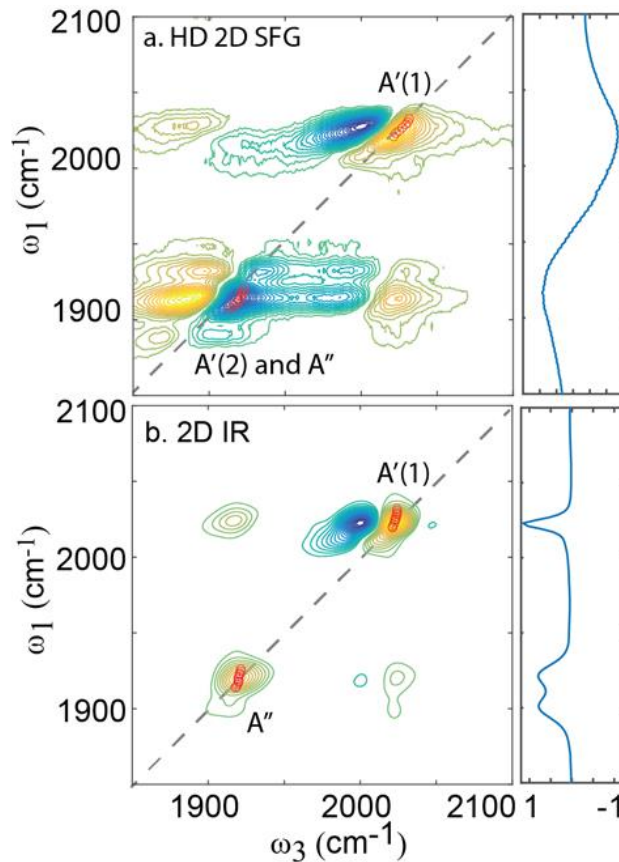


Figure 3. The upper plot is a HD 2D SFG spectrum of **1** on gold; the right hand panel is a one-dimensional (diagonal) HD SFG spectrum of the same sample. The lower plot shows a 2D IR absorption spectrum of **1** in solution (in DMSO). Again the right hand panel is one dimensional spectrum, this time from a conventional FTIR instrument. Lines of red open circles are the center line slope (CLS) of the diagonal peaks. Dash gray lines are the true diagonal. The sign of the HD 2D SFG diagonal peaks indicate the directions of vibrational modes.

In the HD 2D SFG spectrum of **the catalyst** on gold (Fig. 3a), the diagonal peaks at $\omega_1 = 2020 \text{ cm}^{-1}$ 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 sets between 1950 and 1890 cm^{-1} , correspond to the A'' and A'(2) modes of the CO ligands, which are also composed of the fundamental and overtone doublet. Since only organized monolayers can generate large HD 2D SFG signals, the strong spectral intensity indicates that the catalysts form an ordered monolayer on the surface. In the 2D IR spectrum of the same complex in DMSO (Fig. 3b), 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 of the large redshift (see FTIR, right panel of Fig.3b).

A careful inspection of the HD 2D SFG spectrum in Fig. 3a, reveals that the A'(1) peak and lower frequency peak sets of A'' and A'(2) have different line shapes. The team then accurately measured the line shapes and particularly the CLS of the cross peaks. These data provide



unique information on homogeneous vs. inhomogeneous broadening. In particular, it is well known that image dipole interaction is the main vibrational decay mechanism for adsorbates on metal surfaces. And the strength of this mechanism depends on distance from the surface. Since $A'(2)$ and A'' modes are more homogeneously broadened, this suggests that the $A'(2)$ and A'' modes are closer to the surface.

Combined with the sign of HD 2D SFG peaks, the knowledge that the $A'(2)$ and A'' modes are closer to the surface enabled the Xiong lab to determine two possible molecular orientations – see figure 4. The polarization dependence of reflection mode (one dimensional) infrared absorption indicates that there are the two possible orientations (shown in figure 4). Combined with the HD 2D SFG results, the Xiong lab reported orientation “a” is the preferred arrangement.

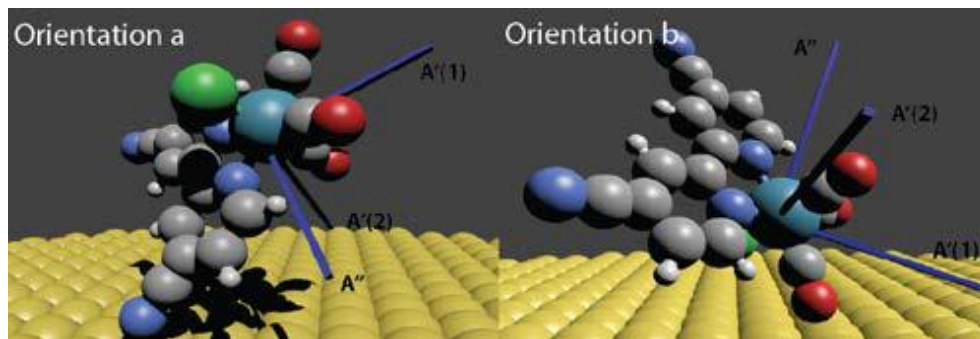


Figure 4. Orientations of the catalyst on gold surface determined from HD 2D SFG data and data from reflection mode IR spectroscopy, simulated using Density Functional Theory (DFT). Orientation “a” is preferred. Blue sticks represent the vibrational modes direction.

While structural information is important for a monolayer catalyst, the ultimate goal of a surface catalyst is to combine the advantages of heterogeneous and homogeneous catalysts. A major influence on catalytic activity is the effect of surface adhesion on molecular energy flow between different vibrations. For this reason, the Xiong team followed up their structural analysis by performing 3D studies, where the 2D data is collected as a function of the delay between the infrared and visible pulses – the so-called t_2 time delay. This enabled the team to observe how molecular vibrations evolve over time and how the coupling proceeds with time. For example they studied the time dependent behavior of the cross peaks from coupling of the $A'(1)$ mode at 2020 cm^{-1} and the A'' mode at 1919 cm^{-1} . As with the structural studies the team compared 3D SFG data from surface bound catalyst to 3D IR spectra from catalyst in DMSO solvent. Figure 5 shows some typical data from these experiments. As the t_2 interval is scanned from 80 to 320 fs, the intensity of the cross peaks oscillates. A Fourier transform confirms that the oscillation interval matches the energy difference between the two vibrational states: 103 and 96 cm^{-1} for the solution and surface samples, respectively. Importantly, further linewidth



analysis indicates that the dephasing or coupling time is shorter for the surface bound molecules and enabled the team to separate homogenous and inhomogeneous contributions to the linewidth. This analysis showed that surface attachment induces both homogenous and inhomogeneous dephasing dynamic of the vibrational modes, but the coherence is preserved upon surface attachment.

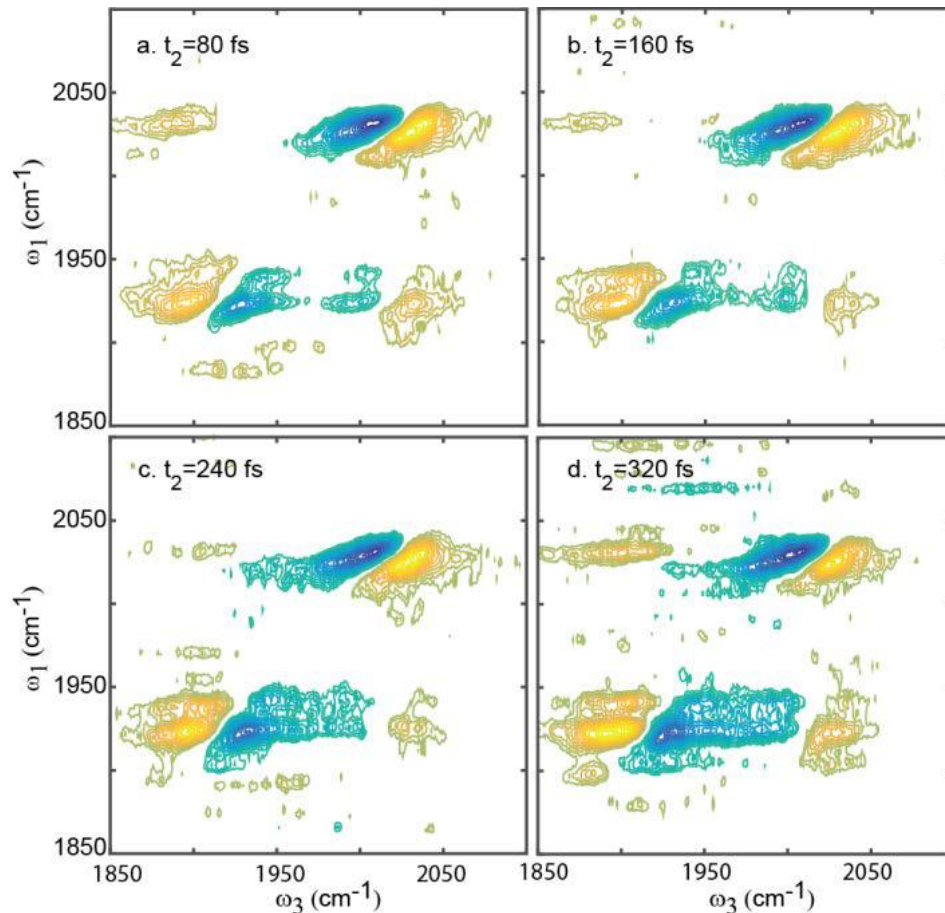


Figure 5. t_2 dependent HD 2D SFG spectra. As t_2 is increased from 80 to 320 fs (a-d) the cross peak intensity oscillates back and forth. All spectra are normalized to the absolute peak intensity of the A(1) mode.

Why Astrella?

In 2D SFG and 2D IR spectroscopies as in many other time-resolved applications requiring energetic ultrafast laser pulses, the ultrafast amplifier represents the single largest capital investment in the entire experimental setup. The choice of ultrafast amplifier is thus always critical, but especially so for a new professor like Wei Xiong, where a startup grant typically



provides a single laser system that is the engine of the publishable research of the next several years.

According to Professor Xiong, "Our experimental setup is necessarily complex; it's an optomechanical alignment challenge and the experimental signals are very low with incredibly long data acquisition times. As a result, key considerations are high pulse energy, ease of use, stability and reliability. For example, we can obtain a plot like figure 4(a) in maybe 20 minutes. But to obtain a full series of these plots at different delay times (e.g., figure 5) we sometimes have to average data for 48 hours, which puts extreme demands on laser stability. During this period it is critical that the amplifier output be stable and without drifts in beam pointing, beam quality, pulse energy, etc. The stability of Astrella means we can do these long data runs while remotely controlling the laser from an office near the laboratory.

"Pulse energy and output power are also important for 2D SFG experiments. First, the non-linear processes need to generate tunable mid-IR from a 800 nm fixed wavelength amplifier are inefficient, with a highly non-linear dependence on the peak power of the amplifier. And second, the 2D SFG process is a fourth order optical effect, which adds more than an order of magnitude to the non-linear power dependence of the data. Finally, we are studying monolayers where any signal will be much weaker than from a bulk sample."

"Together with the phase stability gained from using the 2DQuickShape pulse shaper, having a highly stable ultrafast amplifier also means that we can turn off the entire system at the end of an experiment and the next day we can get the signal back in one hour or less. Anyone familiar with 2D spectroscopy will know that this is a massive advance over just a few years ago and greatly increases the data throughput of our group; it allows my students to concentrate on the science rather than the hardware."

Summary

2D spectroscopies in general, have rapidly transitioned from laboratory novelties to powerful research tools for real science, thanks to advances in lasers and related technologies, and 2D SFG is one of the most recent and challenging variations of these techniques. In the laboratory of Professor Wei Xiong, 2D SFG is being used to obtain important information on surface bound molecules that could not be derived by any other method. This important information can impact fields as diverse as green energy catalysis, electronics and membrane science.



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