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Over 20 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of \$250 for UW-Madison chemistry Ph.D. candidates.



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**UW-Madison Department of Chemistry
1101 University Avenue
Madison, WI 53706-1396
Contact: Prof. Bassam Z. Shakhashiri
bassam@chem.wisc.edu
www.scifun.org**

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Advances in 2D IR Spectroscopy and Applications to Sensitized Thin Films

by Tracey A. Oudenhoven

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This dissertation is approved by the following members of the Final Oral Committee:

Martin T. Zanni, Professor, Chemistry
Jordan R. Schmidt, Associate Professor, Chemistry
Etienne Garand, Assistant Professor, Chemistry
F. Fleming Crim, Professor, Chemistry
Padma Gopalan, Professor, Materials Science and Engineering

Abstract

Two-dimensional infrared (2D IR) spectroscopy has been used to study molecular interactions and dynamics within complex systems for years. However, limitations in experimental design and sample concentration have limited its scientific breadth. In this thesis work, new technical advancements have been added to a 2D IR optical table to both increase the throughput of mid-IR to the sample cell as well as simplify the alignment when changing laser pulse wavelengths. By incorporating more reflective optics into a standard 2D IR pulse shaper, initial alignment and realignment due to a change in wavelengths are greatly simplified. Additionally, studies on dye-sensitized thin films have revealed the presence of dye aggregate domains at the interface. Vibrational coupling and energy transfer between aggregate domains could influence both the electron transfer mechanism and kinetics between the dye and semiconductor interface. With these new technological advances and thin film characterizations, preliminary work studying a monolayer of dyes on a glass window are presented. Using 2D IR to study monolayers gives interface specificity without the need of more complicated experimental designs like 2D sum frequency generation (SFG) spectroscopy. These technological advances will surely prove to expand the range of systems and problems that 2D IR spectroscopy can characterize and solve.

Appendix 1

Summary for the General Public

In my thesis work at the University of Wisconsin, I have used ultrafast lasers (not the same lasers as those used by the Navy to blow up ships – but still cool) to study systems that are similar to that of solar panels. Many people think from high school chemistry that a molecule is just a static structure, but nothing could be further from the truth. Molecules are always moving, and how they move individually and collectively affects the function of a device or the kinetics of a molecular reaction. Lasers shed light (literally) on these movements and help us disentangle some very convoluted molecular dances.

A1.1 Why do we need ultrafast lasers?

As I have already mentioned, ultrafast lasers enable us to look at very quick movements of a molecule's motion.¹⁻⁴ Imagine you are dancing at a disco and there is a strobe light. Depending on how often the strobe light fires and how long the light is on, you can either see a person's every motion or very little of their motion. Doing "the sprinkler" would look pretty weird if the strobe light only fired off for a millisecond every two seconds.

This is a lot like how lasers work, with very quick pulses of light. For us, the lasers generate pulses usually at 1 kHz (1000 pulses every second) and about 100 femtoseconds (fs, 1×10^{-13} seconds) in duration, from when the pulse first hits a

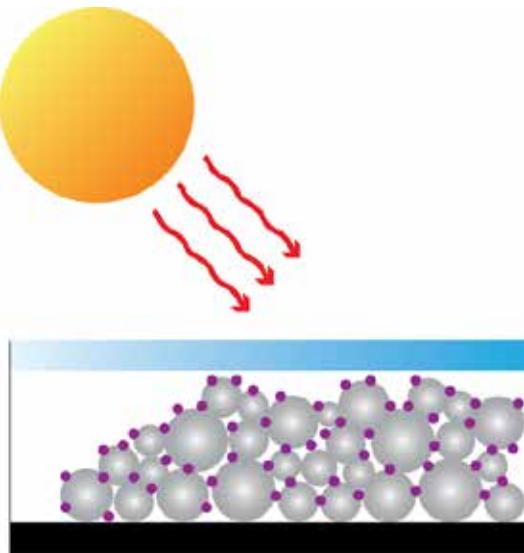


Figure A1.1: Cartoon of a dye-sensitized solar cell. Sunlight hits a dye (purple dot) that is adsorbed onto a semiconductor substrate (gray circle). The dye generates an electron that is transferred to the semiconductor. The blue and black rectangles are electrodes used for the operation of a DSSC.

molecule to when it leaves the molecule. The shorter the pulse is, the more motion we can see.

In my thesis work, I have used lasers that can excite and probe molecular motions at the vibrational level - vibrational spectroscopy.⁵⁻⁶ When two atoms are bonded together (like hydrogen and oxygen in water), there is a characteristic energy between the atoms that dictates the bond's springiness. If you had another pair of atoms, like carbon and oxygen in carbon dioxide, there would be a different characteristic energy between those atoms. We can use these characteristic energies not only to identify which atoms we are looking at, but how those atoms are oriented in their environment.

A1.2 Why are interfaces important?

Solar cells are a thriving area of study in renewable energy.⁷⁻⁹ But perhaps even more important than the solar cell itself is understanding the fundamental principles of how the device works to enable new developments and better solar cells in the future.¹⁰⁻¹⁸ Figure A1.1 shows a cartoon of a dye-sensitized solar cell, where a particular dye (purple dots) is adsorbed (or attached) onto a semiconductor substrate, or a surface for the dyes to attach to (gray circles). When sunlight hits the dye molecule, the dye produces an electron that is transferred to the semiconductor substrate. This is the first step in a series that produces renewable electricity.

The kinetics of how this electron transfers from the molecule to the substrate is extremely important. If there are alternate pathways that could hinder the

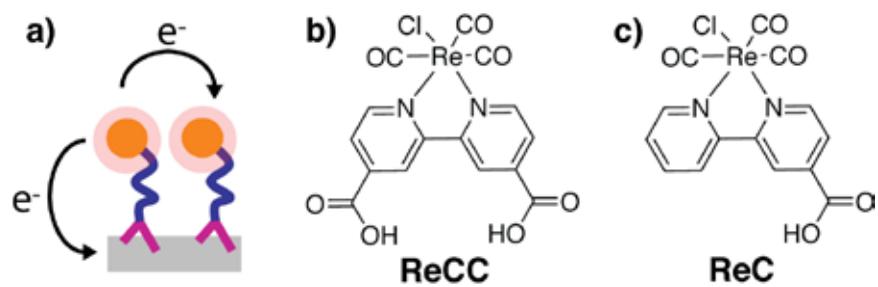


Figure A1.2: a) Cartoon of an electron transferring between molecules rather than to the substrate and dye molecules studied in this thesis, b) ReCC and c) ReC.

electron from reaching the substrate, the efficiency of the electricity produced decreases.¹⁹⁻²⁴ One alternative for the electron is to hop between dye molecules rather than to the substrate, as shown in Figure A1.2a. If the dye molecules are in close proximity, the probability for the electron transferring between molecules increases.

In order to study these molecular interactions, I use vibrational spectroscopy to look at the characteristic vibrational markers of individual dye molecules (Fig. A1.2a and b) as well as the differences that arise when the molecules are interacting with each other. The specific spectroscopy I use is called two-dimensional infrared (2D IR) spectroscopy. 2D gives us more information than 1D, and infrared refers to the wavelength of light we use to study molecular vibrations.²⁵⁻²⁷ For example, blue light is around 400 nanometers (nm, 1×10^{-9} m), red light around 800 nm, and the infrared light I use is about 5000 nm. 5000 nm is not visible to the human eye, so in many ways, I am literally working in the dark.

A1.3 How do I make sense of all the 2D IR peaks?

2D IR uses multiple laser pulses to get a specific signal or response from a molecule. As I mentioned before with the strobe lights, we still get laser pulses 1000 times a second, but each of those laser pulses is split into three, all of which can hit the sample at the exact same time or at 3000 fs apart. We like to put space between the divided laser pulses so we can follow what the molecule is doing. The first two laser pulses “tag” a molecule, or tell us what the molecule is doing at time zero, and the third laser pulse tells us what the same molecule is doing some time later. In this

way, we can follow what motions the molecule is going through as well as how it is interacting with its neighboring molecules.^{6, 28-31}

As I said before, molecules have a characteristic frequency that they absorb at. You can think of these energies like a ladder – each time you get that amount of energy you go up a rung on the ladder. Figure A1.3a has this “ladder” or energy level diagram for 2D IR. A series of laser pulses (red arrow) give the molecule the energy it needs to go up one rung on the ladder, which we call the 1st vibrational state. These laser pulses also “tag” the molecules so we know which molecule is which. Then, another laser pulse comes in and does one of two things – it either helps the molecule absorb more energy, raising it to the 2nd vibrational state. Or, it causes the molecule to lose energy, bringing it back to the 0th vibrational state, or the ground state.

I mentioned that 2D gives us more information than 1D. Let’s say we have two molecules, A and B (Fig. A1.3b). Molecule A absorbs energy E_a , and B absorbs energy E_b . If we give the molecules a little bit of time to move around, there is a chance that molecule A will transfer its energy to molecule B. When that happens, the energy of what we are looking at will no longer be E_a , but E_b . 2D IR tells us if the energy in the system stays where it started or moves somewhere else.

A 2D IR spectrum (fancy word for ‘plot’) can be a little intimidating to look at the first (or the one hundredth) time. Figure A1.3b is a cartoon of a 2D IR spectrum. First, notice there are always pairs of peaks – one is red, the other is blue. Both of the peaks are from the same molecular vibration – the blue from energy lost, and the

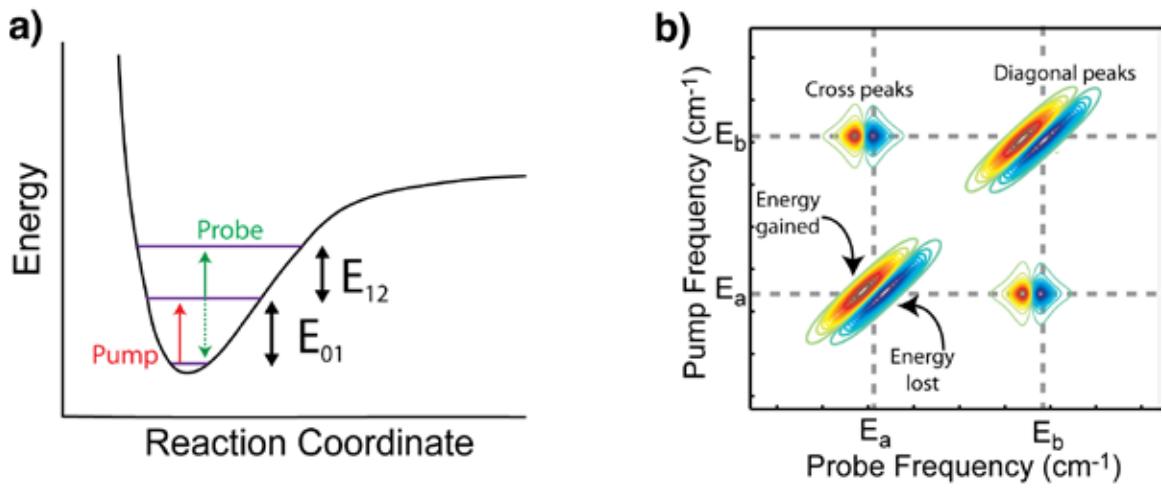


Figure A1.3: a) Energy level diagram in 2D IR, b) Cartoon of a 2D IR spectrum.

red from energy gained. The peaks along the diagonal are when the energy does not move from where it started. The peaks in the upper left and lower right corners are when the energy has changed from where it started, perhaps energy transfer between molecules A and B. We call these off-diagonal peaks “cross peaks”.

A1.4 What can 2D IR tell us about interfaces?

Now that we have learned more about 2D IR and how to interpret a spectrum, we can look at some real data I acquired for my thesis.⁵⁻⁶ Figure A1.4 has four 2D IR spectra. Fig. A1.4a has the molecule, ReC, in what we call amorphous deposits, which are really just clumps of dye sitting on glass. These dyes are randomly oriented with respect to one another and are not like the ideal cartoon of upright molecules right next to each other like in Fig. A1.2. Fig. A1.4b is this same sample, but after letting the energy at the first vibrational state evolve for 3.5 picoseconds (ps, or 3500 fs). This gives the molecules a chance to transfer energy if they are going to. Fig. A1.4c is the same dye, only this time adsorbed onto TiO₂ nanoparticles, like in a dye-sensitized solar cell. These molecules are more like the ideal cartoon we saw in Fig. A1.2. Fig A1.4d has the spectrum after waiting 3.5 ps.

So what should you really be looking for among all of the pretty colors? Notice that in both the top and bottom rows, we have two peaks along the diagonal. These are from dye aggregation, or when two dye molecules come together and form a group.

Now, look at the second column compared to the first where the waiting time is now 3.5 ps. In the top row, there are cross peaks that form (emphasized with

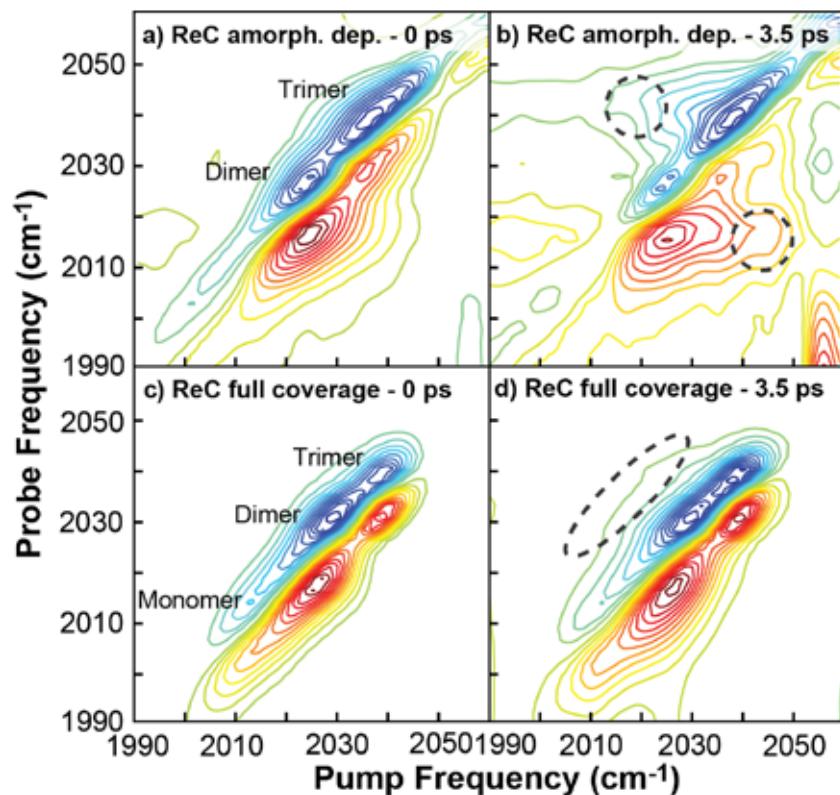


Fig. A1.4: 2D IR spectra of ReC in amorphous deposits (top) and on TiO₂ nanoparticles (bottom). The left spectra are taken at a waiting time of zero and the right spectra are at a waiting time of 3.5 ps.

black dashed circles), where energy has transferred between the different aggregates. They do not form the ideal peaks like we saw in Fig. A1.3, but trust me, that spectrum is showing us that there is energy transfer. The bottom row, on the other hand, shows very little cross peak formation. In fact, it is really only a bulge in the contour rather than an additional peak. This implies that the energy transfer is very weak compared to that of the amorphous deposits.

But what is the bottom line of these results? When the dyes can randomly orient themselves in the amorphous deposits (or clumps), they form many aggregates. These aggregates can also transfer energy between themselves. Neither of these findings is too surprising considering the molecules are able to orient themselves without restrictions. The situation changes when the dyes are adsorbed onto TiO_2 nanoparticles. Now, the crystal lattice dictates the spacing between molecules. Although these dyes also form aggregates, they do not form aggregates that are able to readily transfer energy between themselves.

So, why are finding these aggregates and the energy transfer between them important? Renewable energy is greatly needed as an energy source in the future and increasing the efficiency of charge transfer across interfaces like the system I have studied is extremely important. Although not all solar cells use the dye I have studied, many solar cell dyes have similar structures that can cause aggregation like the ones I studied. The energy transfer between aggregates strongly suggests that electrons could also be transferred between aggregates.³²⁻³³ Ideally, electrons would transfer to the substrate directly for the most efficient energy harvesting.

A1.5 Is graduate school really worth it?

The most common question I am asked by non-scientist friends and family is if graduate school is really worth it. Is it worth my time, my adviser's time, and most commonly, the taxpayer's dime? I am among the majority of graduate students in chemistry who came directly after my undergraduate studies. I saw it as a stepping stone to careers that interested me, especially teaching at the college level. This process has taught me that graduate school is worth so much more than simply preparing for one career.

Academia is the perfect place to do fundamental research. Fundamental research is the basis of everything we know and use today – from the light bulb to the iPhone, all of what we see and use takes years and years of research. Academia is filled with people whose minds are malleable and ready for creativity and innovation. We learn the fundamentals of science and we stand on the shoulders of giants to discover new concepts and convert innovative ideas into reality. There is really no other structure that quite has the flexibility to study the range of what we do, as well as attain the collaborations to tackle complex problems that require multiple disciplines to solve.

Graduate school is also the boot camp for scientific thinking. It does not matter what field you are in – engineering, physics, math, etc – we learn to think. We come in knowing how to learn from books and we leave applying what we know to learn from our experiences. To study a system that is just an idea takes an enormous amount of ingenuity as well as practicality. We take what seems like an overwhelmingly impossible problem and successfully study it until we are the world

expert in what we are studying. This self-confidence of being able to learn and solve problems does not just apply to our scientific discipline, but to how we approach problems in our future careers and in society.

So, when people ask me if graduate school has been worth it, I say without hesitation that it has definitely been one of the best experiences of my life. It has formed me into a better person and scientist and I have acquired skills that I will carry with me for the rest of my life. Graduate school was not what I expected, but I would do it again in a heartbeat.

A1.6 Summary

In my thesis work, I have used 2D IR spectroscopy to study dye aggregation and its implications on electron transfer kinetics. I have identified and characterized dye aggregates in a variety of situations and quantified the amount of electron transfer that occurs in different environments. This has been one aspect of my thesis work; the other major aspect has been technology development for increased sensitivity in 2D IR.

Beyond the results that I have described, I have also acquired and honed a variety of different skills and talents. Even though I may not do ultrafast laser spectroscopy forever, I will take these skills with me wherever I end up. After eight years of intense coursework and research, I will always be a scientist.

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