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Single Nanoparticle Absorption Spectroscopy: Chemical Dynamics using Optical Microresonators

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Can you see a single molecule?

Levi Hogan

What's the smallest object you can see?

Would you believe that you can see *a single molecule*? Not only would that be **really**

cool...studying single molecules would also

be very useful for scientists, especially

chemists. Traditional chemical measurements

look at many molecules, often billions of

billions, at the same time. While this is good

for some experiments, it can cause you to miss

out on a lot of information. This is because different copies of the same molecule can behave differently! An analogy is shown to the right. Up above, you see a confusing jumble of an image.

Below, you see six images of artwork by my favorite painter, Vincent van Gogh. They're so

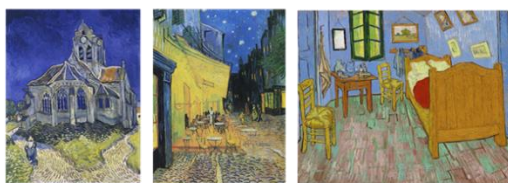
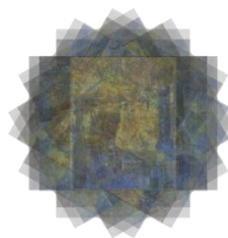
beautiful! The above image is actually an overlaid composite I made of many copies of the bottom

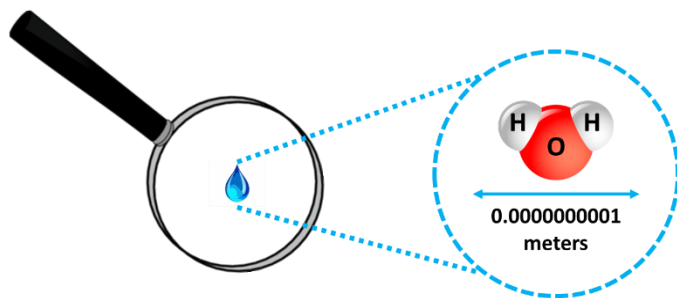
images. It's hard to understand what's happening in the composite image on top! Similarly, it can

be hard to know what's going on in chemistry if you look at a billion billion molecules at once,

all doing their own thing at their own speed. Therein lies the reason why we want to look at single molecules.

Now that you're excited about looking at single molecules...how should we go about seeing them? Do you have any ideas? A water molecule, for example, is about 0.1 *nanometers*





across (that's one ten-billionth of a meter!). Just how small is that? Well, if we consider a drop of water, it will have about 1.6×10^{21} molecules within it (that's a billion trillion molecules!). If I had that

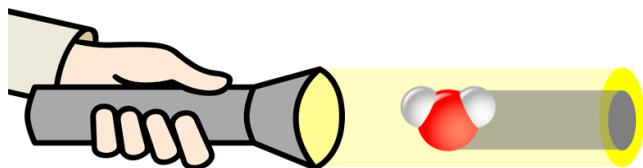
many US pennies, and gave you \$1 million in pennies **every second**, it would take well over **500,000 years** to give you all of my money! It turns out that molecules are just too small for your eyes to pick up on. So how in the world are we going to see single molecules? We'll explore two different ways to do just that in this chapter, both of which I've employed during my thesis work.

The first way to see single molecules is using a process called *fluorescence*, where we make molecules emit **light** which we then measure. While your eyes can't see something as small as a single molecule, they happen to be **very**



sensitive to light, and laboratory cameras can be made even more sensitive. I like to think about a fluorescence experiment like standing in a dark American football stadium, perhaps during halftime show at a Super Bowl game (where of course Kansas City is winning the game). Perhaps I'm at the game with my grandma (an aggressive Kansas City football fan), and am trying to see where she is in the crowd in the stands. This is impossible in the dark! However, if she takes out her cell phone, and takes a picture with the flash on, I'll easily be able to see the light from that camera flash, telling me where she is located. Similarly, if molecules emit light, we can use a microscope to easily see where those molecules are, and study that light to learn about molecular properties. In chapter 6 of my thesis, I describe my fluorescence experiments looking at a special

type of *nanoparticle* called “Carbon Dots”. I studied these dots to better learn how their chemical components give rise to their light-emitting properties, which have a variety of applications in medicine and other technologies such as television displays.



Fluorescence sounds great! Can we

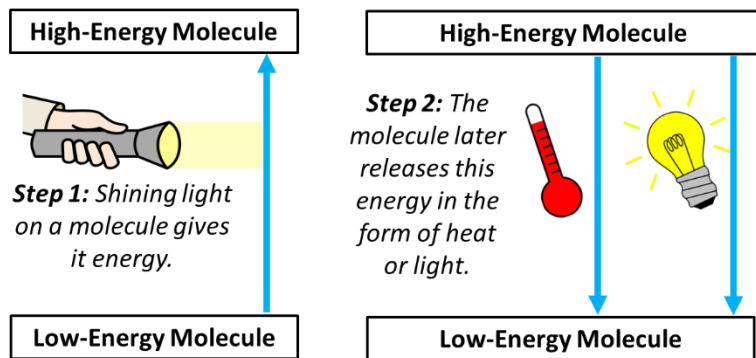
just use it for every single-molecule study that we want to do? Unfortunately not,

because not everything fluoresces. So what do we do in the scenario where our molecule won't emit light for us? What if instead, we shine a light on a molecule, and look for the shadow that the molecule casts? This is actually a common technique when looking at a collection of many molecules, but **is it possible to see the shadow of a single molecule?** Let's return to the stadium analogy...

Imagine you're back in the people-filled stadium, but this time, the stadium is lit brightly. Your job is to count the number of the people in the lit-up stadium over and over again, so that you know when a single person has left. If the stadium starts with 80,000 people, that means you have to be able to quickly tell the



difference between 80,000 people and 79,999 people. That sounds pretty hard! This example is like doing the single-molecule shadow experiment described above...shining light at a molecule and trying to measure the teensy, tiny part of the light missing on the other side.



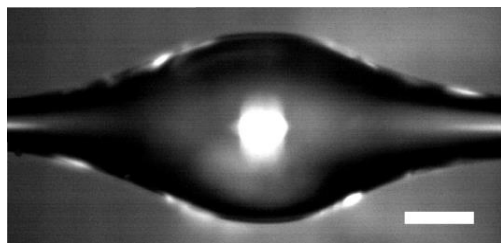
So, measuring the missing light from a single molecule's absorption might be harder than we want to deal with! What else could we measure? If we shine light on a molecule, let's think for a bit about

where the absorbed energy goes. If it doesn't get released as light (fluorescence), then the only other way for it to be released is as **heat!** And when heat is released from an object, that changes the temperature of the object's surroundings. Can we measure that temperature change using a thermometer? The heat output from a single molecule is going to be quite small...so we'll need a **very** sensitive thermometer to detect the temperature change from a single molecule after it absorbs light! Experiments that measure temperature changes from the absorption of light are called *photothermal* experiments.

In many of my experiments, I use a tool called an *optical microresonator* to make such photothermal measurements! "Optical" means light, and "micro" means small (a micrometer is 1 millionth of a meter, or about 1/100th the width of a human hair). "Resonator" means that



certain wavelengths, or **colors** of light "resonate" within the structure. You're probably already familiar with a similar kind of resonance, an *acoustic* resonance. Have you ever heard a trombone played? When a trombonist plays, the instrument emits a specific note based on the length of the instrument. By changing the trombone slide length, the note that resonates also changes! This is because for a specific trombone length, only certain *wavelengths* (notes) of sound will build up



in volume (get louder). For our photothermal experiments, we study *optical* resonances, meaning that rather than the volume of sound building up, the brightness of light builds up! My resonator is a hollow

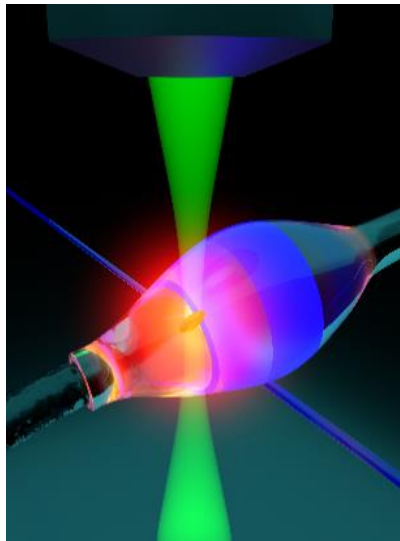
glass bubble around 50 micrometers across. I trap light in the resonator's walls, similar to how light travels through a fiber optic cable. Light can then circulate around the resonator many times, but only very specific wavelengths (colors) of light will resonate.

Now we know how resonators work...but how do we use them to measure temperature changes? It turns out when a material changes temperature, that also changes how fast light travels through it! You're likely already familiar with this fact. Have you ever



noticed that the asphalt of a road, and the air above it, looks strange on a hot day? That's because the heat from the asphalt is changing the air's density above it, and thus the speed of light through the air. That hot air then bends sunlight differently, making pavement look shiny, and the air above it blurry. In the case of my microresonators, temperature increase changes the resonance wavelength! Because the light travels around our resonator many, many times, we can measure the change in the light's properties due to even a very tiny temperature change in the resonator.

In my experiments, I measure an optical resonance using a laser going through a fiber optic (the blue line crossing the picture below to the left). I also shine a second laser onto the resonator (the vertical green part of the image). When the second laser hits a molecule (shown as the gold oval), that molecule releases heat (shown by the red plume). By monitoring the resonance while heating up the molecule, I learn information about how the molecule absorbs light! For



example, I have employed this technology to study the chemical reactions of single gold nanorods (see Chapter 4 of this thesis for more!). This technique has also been used by my research group to study the physics of electrically conductive plastics, with applications in solar cell technology.

In conclusion, single molecule studies can be quite challenging, but they are worth all the effort! In my research, I have studied a variety of interesting nanoparticles and molecules by examining the energy that they release, either by looking for light they emit or by making very sensitive temperature measurements. **Thank you** for joining me in this fascinating journey to see single molecules, and please feel free to peruse the other chapters of my thesis if you wish!

The reason that I wrote this chapter is twofold:.

- (1) I believe that science literacy and appreciation is crucial in our society, and wanted to communicate my research (largely paid for by taxpayer dollars!) to the public at large. More specifically, I think that optics and nanophotonics have the potential for revolutionary impacts in computers, healthcare, climate monitoring, and other critical research areas in the coming years. Plus, lasers are cool. Who doesn't like lasers?!?*
- (2) I believe that it is important for scientists to practice communicating their work to the public, and to keep in mind how their research will impact society at large. Thus, this chapter was both a challenge to myself, and a suggestion to my colleagues to pursue similar challenges.*

I thank Elizabeth Reynolds for her editing and suggestions for this chapter. I thank Cayce Osborne for all of her support in my public engagement pursuits these past few years. And I deeply thank my friend and mentor Bassam Shakhshiri for instilling in me a deep sense of responsibility as a scientist-citizen.

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