Lab 9B • 10/27/11

We're going to use a Pasteur filter pipette. Get just a small piece of cotton. The size of the cotton ball you're really going to have to just learn by experience; what you want is one that is not so large that it prevents the liquid from flowing through, but you also don't want it so loose that any solids might happen to come through – something that will reasonably fit into the bottom of the pipette. Use an empty, clean pipette to push that cotton ball all the way through. You're going to have to kinda learn by experience how forcefully to tamp that down in there – not so tight that liquid can't flow through (at least when you put pressure on it, because even if you do it correctly, the liquid may not flow through by itself, you'll have to use a pipette bulb) – but tight enough that solids don't flow through. Many text recommend to pull the the solution up through the cotton plug and then dispense it into another container. I find two things wrong with that approach – one, that if you're pulling up through the pipette, you're pulling opposite of the way that friction's going to keep that plug in there; also, if you're pulling up your solution, it's very likely that you're going to get solids that come along for the ride, so when you go to squeeze the liquid back out again, the very solids you may try to filter are going to possibly still be present. What I recommend that you do is the following: once you've made your filter pipette, use the empty pipette to pull your entire solution out; even if some of the drying agent goes along for the ride that's perfectly fine. Take that, squeeze it into the top of the filter pipette. That way, when it does come through, the solids will be blocked, and you'll get just the liquid out of it. Pop the pipette off bulb off the clean pipette, put it on to the filter pipette; when you do so, make sure that you've already got a reception flask there, because the act of putting that pipette bulb on is going to put pressure on it and drive some of your product through. Once you do have the bulb on, squeeze and push all of the liquid through the filter pipette. That way, you can do the filtering of your drying agent. Normally, we do chemical reactions with a solvent. The container where the drying agent is is likely going to have some product left stuck to it; we're going to have some unavoidable product loss. Normally, we would, after we pull the entire reaction solution out, we could add some fresh solvent to help pull any compound that might still be stuck on the drying agent out from the drying agent. Today, since we didn't use a solvent, and we don't want to have to go through the hassle of evaporating the solvent, don't worry about the small amount of loss that you are going to have by a little bit of your compound remaining on the drying agent.

[calculate percent yield; measuring mass by tared flasked]
[avoid measuring mass of hot objects due to air currents]

First, you're going to have your round-bottom flask that's going to have your product, and you'll have some drying agent in it. You'll just have a regular pipette that doesn't have a filter in it. In the first step of the process, you're going to pull the liquid into that pipette; if some of the solids happen to come along with the liquid, it's perfectly fine, cause you're going to be filtering it. Once you have the contents in that clean pipette, transfer them into the top of the filter pipette. Lastly, put a pipette bulb on the filter pipette – because your product may be thick enough that it won't just drop through by gravity, but when you do that make sure you've got your tared collection flask ready. [disposal of pipettes]

A brief introduction to spectroscopy

If we're going to begin a discussion of spectroscopy, we're first going to need to review a bit about the electromagnetic spectrum. The electromagnetic spectrum – it's called that because light has two different waves that it's composed of; they're orthogonal waves – one of them is an electric field, the other one is a magnetic field. Put the two of them together and that's why light is known as electromagnetic radiation. There's an equation that holds true for light – and a very similar equation holds true for any propagating wave that has a constant velocity, so any wave that moves forward with a constant velocity, there ends up being a relationship that holds true: that the velocity of that wave is equal to the product of the wavelength and the frequency of that wave. If we're talking about the electromagnetic spectrum, which means we're talking about light, the velocity of that wave is going to be the speed of light, which is generally represented by c. We then have wavelength, which metric unit would be meters, and then frequency, which can be expressed in a number of ways: Hertz, but Hertz itself is inverse seconds (1/s), which, especially in physics texts, we write that as a negative exponent (s^-1). This equation hopefully makes sense, because if you have wavelength in meters, and you have frequency which is per second, put the two units together, you get meters per second, which is velocity. This means for light, the wavelength and frequency are inversely proportional. to each other. There's another important equation that we need when we're talking about spectroscopy, which is the following: h is Planck's constant, which describes the size of energy packets, and it shows up in a number of places; it's also in the spin of electrons, when we learn that spin is $\pm$ 1/2, it's not, it's $\pm$ h/2π, the same h that shows up in this equation: E = hv. What it does is it relates the particle and the wave nature of light. Light acts as both a wave and a particle. When it acts like a particle, it's called a photon. The E in this equation is the energy per photon. And then we have frequency and Planck's constant.

Why do we care about this equation in spectroscopy? Let me walk through the photoelectric effect experiment one last time, because in that experiment you have a metal plate of some sort, and light's shining on it. Under the appropriate conditions, where the light shines, an electric current is generated, which means electrons are being displaced from that metal. If you shine a light beam that has a frequency of light that's too low, it doesn't matter how bright that light source is, that metal plate never responds.

As soon as you pass above a certain minimum threshold frequency, then when it hits the plate, you do generate an electric current, and it turns out that the amount of electrons that are displaced depends directly on the intensity of that light beam. To scientists back in the early 1900s, this was a confusing result, because why should it matter what frequency of light you have; shouldn't just the total amount of energy that you're throwing at this, shouldn't that be what matters? The answer ends up being no; to display an electron – we know that we're talking about valence shells – you're going to have to add energy in order to get that from the outer shell out to being a free electron. There's a specific amount of energy necessary to cause that. It's not the total amount of energy that's coming from light that matters, it's how much energy there is per photon. So, low frequency means low energy per photon. If you use light that has too low of a frequency, each photon hitting that metal surface, no one photon has enough energy for the electrons to be displaced. But get above that threshold frequency, and now because that photon's got enough energy, it can knock an electron out of the way.

The same type of thing goes on in spectroscopy. Think, for example, of your atomic spectra experiment you might have done in 1A, where you zap hydrogen, electrons in hydrogen gain energy. As they fall back down to lower energy levels again, there are only very specific frequencies of light that are released. That's one of the pieces of evidence, in fact, of the wave behavior of electrons, that they have only these very specific energy levels. But the reverse works as well. If you pass light through something, some frequencies of light will be absorbed, and other frequencies won't. The reason that frequencies might be absorbed is that the photons that each have a certain amount of energy that's exactly the right amount of energy to cause some change in that system. Some cases, it might be making a bond vibrate faster, some cases it might be moving an electron from one energy level to another. In another case, it could be that you're flipping the orientation of the nucleus around. In spectroscopy, what we do is zap a range of frequencies through a sample – not just the entire electromagnetic spectrum, though; it's usually some range of that spectrum. You pass these different frequencies through, so there are these different-energy photons that pass through the sample. If they get absorbed, then because of the experience we have with these techniques we can make some sort of relationship between that specific frequency, that specific energy of the photon and some specific structural feature of the molecule. That's spectroscopy in a nutshell.

Let's go back a little bit about spectra. Let me write down what I said about this energy gap. Whether you're talking about electrons or nuclei or bonds vibrating, anything down at the atomic level is quantized in energy, meaning that the energy can only have very specific values. We talk about things having different energy levels. If I write energy as an axis, I could write two arbitrary energy levels here and show that there's some energy difference between those levels. That's going to correspond to a photon that's trying to excite between those levels; that photon's going to have a specific frequency of light associated with it. All other factors aside, in order for this energy gap to be crossed, then, light with the correct frequency – and therefore the appropriate amount of energy per photon – must be used.

I'm going to give you the roughest of outlines of the electromagnetic spectrum, cause we're really only going to care about those ranges we're going to use in here for our spectroscopy. Let's start with visible light right in the middle. If you wanted to overly round, overly simplify the range of wavelengths that visible light shows up at – and I say wavelengths because you're probably more familiar with numbers in wavelength instead of frequency – what would you say is the high-end number, roughly, for wavelengths of visible light? 700 [nm], which would correspond to what color of light, roughly? Red light. For visible light, 700 nm is a very rough cutoff which corresponds to red light, which means lower energy per photon. At the opposite end, violet light, what really rounded number would be close to violet light? About 400 [nm], which would be therefore higher energy per photon. Shorter wavelength – wavelength is inversely proportional to frequency, so shorter wavelength, higher frequency, higher energy per photon. What if we went even shorter wavelength than violet light; what is that kind of light called? If you went just a bit shorter? Ultraviolet, which is abbreviated UV. The UV lamp, for example, that you used in your TLC plate, that had a wavelength of 254 nm, somewhat shorter than violet light. If you went the other direction, if you went past red light to something that was longer wavelength, but just a little bit longer, what range would that be? Infrared, or IR for short. Back to the ultraviolet side: if we kept going higher in energy, then what kind of radiation do we have there? X-rays or gamma rays, neither of which we're going to use in this class. But on the other side of IR wavelengths, we do have something we're going to use. What would be even longer wavelength than IR? Radio waves. As a practical matter, microwaves would be down there as well. Microwaves – the way a microwave over works is that it just happens to excite one of the modes of motion of water molecules; same idea [as] here, except we're not measuring something, we're just bombarding it, but that energy is right in the right energy range to cause a transition in the states of motion, heats the water up, and there you've got a microwave oven.

Let me talk a little bit more about some of these ranges of frequencies and how they're used. They'll be three main forms of spectroscopy that we'll do in this class, and, therefore, three different types of light we'll use. One is abbreviated UV/Vis – ultraviolet/visible – spectroscopy. This is related to electronic energy levels. Think of the different energy levels of an atom. Electrons move back and forth between those; when energy is absorbed, it goes up to a certain energy level, when it fall back it releases that energy as light. Much of that light is in the visible spectrum or the ultraviolet spectrum. The fact that we see colors is because different compounds absorb different frequencies of light in these ranges. Since it causes transitions between different energy levels, it lets us figure out something about the electronic structure of a compound. Second type of spectroscopy that we'll do is infrared. Infrared light falls in the right range to excite the vibrational modes of molecules.

If you think of different kind of bonds, let's say an oxygen-hydrogen, a nitrogen-hydrogen, or a carbon-hydrogen bond; oxygen, nitrogen, carbon, they're different masses of atoms, so take one of those atoms, hook it up to a hydrogen, there's going to be a different kind of vibration that will occur there. To put just a bit of physics terminology there, you could say they have different spring constants. So since different types of bonds have different ways they're going to vibrate, they'll vibrate at different energies, which means we can tell different types of bonds apart from each other. If we could tell different types of bonds apart from each other, that means we also might be able to determine the functional groups that are in a particular molecule. That's exactly how we're going to use IR today: we're going to confirm or try to confirm that your alcohol disappeared and that you made an alkyl halide.

The last form of spectroscopy is NMR, which stands for nuclear magnetic resonance spectroscopy. It uses radio waves. It's vastly more complicated than IR. To give you the brief introduction: nuclei have spin in just the same way that electrons have spin, at least most nuclei do. Particular atoms like hydrogen and carbon, hydrogen-1 (protium) and carbon-13, both of those are nuclei with spin 1/2. Much like electrons can orient with spin ±1/2, nuclei will orient with spin ±1/2 when you put them in a strong magnetic field. What we do is take a sample, put it in a magnetic field, zap it with radiation, and we can cause the nuclei to flip back and forth between these different energy states; that's where the idea of nuclear magnetic resonance comes from. It turns out that what's around an atom, the chemical environment around the nucleus, that has a very profound effect on how much energy it takes to flip a nucleus around. In other words, the nuclear energy involved is very sensitive to the surrounding environment. Over time, we've figured out how to interpret these small differences to be able to determine the full structure of an organic compound. Modern organic synthesis is possible because of this technique, because we can make something and have a reasonable chance of figuring out exactly what we just made. NMR is used to determine full chemical structure. IR is routinely used, but in many cases it's more of a confirmational technique; if by NMR you're proven or demonstrated that there are these different functional groups, IR is so quick to do, you slap it on the IR machine, take a quick spectrum just to get confirmation.

Let's go ahead an focus our discussion on IR. Let me give you a very stylized, cartoon-like picture of how IR works, which is much like how other forms of spectroscopy. You've got some form of light source; that light source can throw out a range of frequencies. You pass that light through some kind of sample; light comes out the other side, and it strikes a detector. If the particular frequency of light, which corresponds to a particular energy of a photon, is just right for some physical aspect of that sample, that light can get absorbed; it won't make it out the other side. There's two different quantities that we can use to express how much actually makes it through or how it gets absorbed. How much light makes it through, that's transmittance, and that's measured in percent. Transmittance is the percentage of light that successfully passes through a sample. Other way of doing it, which is useful for some other calculations such as Beer's law, which can relate this quantity to concentration, it's absorbance, which is the amount of light absorbed by the sample, or the fraction of light absorbed by the sample. There is a conversion, we can go back and forth between absorbance and transmittance, but we're never going to use absorbance in calculations in this class, we're just going to use transmittance, so I'm going to focus on transmittance.

What does a spectrum under IR look like? Looks like this. % transmittance is our y-axis. For historical reasons, there's this unit called inverse centimeters that is used to represent the frequency of radiation. In this unit, typical range of values are from about 4000 to 600. If we're measuring things in percent transmittance, if the light passed through and nothing happened, that means we should have a flat line at the top, 100%. But, depending on what you have on your molecule, you're going to have certain valleys or troughs, you could say. Because spectroscopy is often done in terms of absorbance, instead of calling these valleys, we call them peaks. [comment on spelling of 'peak'] Each peak corresponds to a specific type of energy change, which again corresponds to a particular frequency of light, which again corresponds to a certain energy per photon, which in this case corresponds to a particular bond vibration. There's actually a table of all of these different types of modes in your text. [pointing out tables in lab text] If you look at this, it shows different kind of bonds, different kinds of functional groups, and the frequency range that each of those different kind of functional groups shows up at. For example, on this cartoon graph that I drew, you can see a very broad, droopy kind of peak that generally shows up in the 3200 – 3600 range; that is a characteristic peak of an alcohol, or an –OH group; could be even an –OH group on a carboxylic acid, could be the –OH group in water. This is exactly why we don't want any water in our sample, because the alcohol that's you're starting material (that you're trying to make sure that it isn't there) would have the same kind of peak as water itself. Why is this peak so broad? Because of extensive hydrogen bonding that can occur in solution. If you have an –OH bond that's vibrating, but that bond ends up somehow interacting with yet another atom, it's going to interfere with how it's vibrating. Maybe that atom could cause the vibrations to speed up or slow down; that's why you get this roundedness in the peak. For other functional groups, like things that contain a carbonyl, a ketone or an aldehyde, that carbonyl bond ends up having a very sharp absorbance because it doesn't have the same kind of hydrogen-bonding interactions.

This is a useful piece of information for today's lab since you're trying to see did you successfully transform that alcohol? Did you get rid of the –OH group? When you take a scan of your product, what you're hoping to not see is exactly this kind of broad peak. For todays compound, what are some other important frequency ranges? There's another sharp one that shows up at 2850–2970, somewhere in there. Those are vibrational modes for sp3-hybridized carbons, so alkyl groups. [no memorization of ranges].

Both your product and reactant are going to have this sharp peak that would show up just to the right of where the alcohol peak would disappear. There's one more peak that we care about, which shows up in the 600–800 range. That's for a carbon-chlorine bond.

What we're going to do is the following: we're going to take a spectrum of your product; you have in your textbook the spectrum for your starting material; you can download it as well, though, on the link that's on the class website. There's the alkyl groups I was talking about showing up at about 29-something. What we hope we don't see is a particular peak on the 600–800 range. Something about this side of the spectrum: this range is often called the fingerprint region. There are many, many modes of vibration that can happen in a molecule. Something even like this t-pentyl alcohol: it's got five carbons, twelve hydrogens, and an oxygen – an awful lot of atoms that could be vibrating in different ways. That's why we get all of these different absorbances. These particular absorbances don't really help us analyze the reaction. What we care about is that we can see that there's an alcohol there. When we look at the product spectrum, there's peak in that 600–800 range that's not present in this spectrum; that's what we're looking for – to see if that bond, that vibration that corresponds to a carbon-chlorine bond appears. We look at the starting material, we see that there's an –OH group there; we look at the product and we hope that we don't see that –OH group at all. If you do, then just on the basis of IR you can't prove that that means that there's alcohol present – which means that your reaction did not completely go successfully – or whether you might not have put enough drying agent, and so you have some water present. The other piece of evidence that we're looking for is: is there a new peak that shows up in that 600–800 range of the spectrum, because that is evidence that you have a carbon-chlorine bond, again meaning that your reaction went successfully.

[demonstration of IR]

A background spectrum. What that means is that it's going to take a spectrum just of empty air. But air itself has carbon dioxide, water, other things that can absorb light. If you were to just put your sample in and scan it, without doing this background scan, you'd be collecting both information for the air itself and your sample. To make sure that you don't have any residual signal that comes from the air, you scan the air, subtract that out from the spectrum; the machine can do that for you automatically. When you run a background, you should either have the machine empty, or, you could put in clean sample holders.

[desiccator; keeping closed, indicator, grease]
[salt plates] You can't clean them with water because you'll just dissolve them away. If they are left out in open atmosphere, they're just going to sit there absorbing water and they're going to become fogged up. When it's visibly fogged, that doesn't necessarily mean that it's IR ability to transmit light has been impaired, but the foggier it is, the more like that you're not going to get as good of a signal. [salt plate treatment] How do we clean these since we can't use water? We have acetone, but we have acetone that's got sodium chloride in it; it's saturated to try to prevent much more other ionic compounds that acetone would try to absorb. [cleaning plates] [loading sample into machine] To prepare a sample, you make a sandwich: you place a drop or so of your material on the center of one plate and place your other plate on top of it. How do you know how much sample you should have? There's a could of factors. In general, if you put the two salt plates together and you can't see the liquid layer, there's too little liquid. Your sample will evaporate, because the alkyl halide is volatile, so if you're going to end up standing there 20 minutes in line waiting to use the machine, don't put your sample on until your turn's almost about to come up. If you put the salt plates together and liquid pours out of them, well then clean up the sides a little bit, but that means you have a little too much sample. [demonstrating with sample]

From the spectrum, how do you know that you have too much or too little compound on your plate. What would this look like if you had too much sample? The peaks would all be touching the bottom of the screen, and they'd rounded, all of them; if you get that kind of behavior, too much sample. Notice that the highest transmittance is only about 75%. There is some light be lost as it transits through the machine, or being absorbed by the salt plate itself. But, between the highest absorbance, which is roughly 70, and the lowest, which is roughly 30, that's a pretty good spread. Just a hair more of the compound might have been ok, so we could get more difference between the baseline and the signal. [using instrument]

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1) Pull entire contents of the product flask out using a non-filter pipette
2) Transfer the product to the top of the filter pipette (soilds ok)
3) Place a bulb on the filter pipette and force the product through the filter

Spectroscopy – Electromagnetic spectrum (EM) – light
c (speed of light) = lambda (wavelength, m) • nu (frequency, Hz = 1/s or s–1)
E (energy per photon, particle) = h (Planck's constant) • nu (frequency, wave)

In order for this energy gap to be crossed, light with the correct frequency (and therefore the correct energy per photon) must be used

% transmittance – the % of light that successfully passes through a sample
absorbance – the fraction of light absorbed by the sample
each peak corresponds to a specific change in energy states, which corresponds to a particular frequency of light, which corresponds to a certain energy per photon

UV/Vis – ultraviolet/visible – electronic transitions – electronic structure
IR – Infrared – vibrational transitions – bond types, functional groups
NMR – nuclear magnetic resonance – radio waves – allows for determination of the structure of organic molecules.