Lab 9A • 10/26/11

We're going to use a Pasteur filter pipette. Take a very small piece of cotton. How small? I can't really tell you – it's one of those things you're going to have to discover through practical experience by actually making them. You want a piece of cotton large enough that it will block the flow of solids coming through the pipette, but you don't want it so large that you prevent liquid from passing through. So, some medium-sized ball of cotton. Put it into one of your pipettes; take another clean pipette and gently tap that piece of cotton into place. Don't tap it in so tightly that liquid won't flow, but make sure it's not too loose either, because that's how we're going to filter the solids out. Once you've assembled this, take the empty, clean pipette, put a pipette bulb on it, squeeze the bulb, stick it in your product, pull all of your product out, including, if it happens to come with it, some of your drying agent. It's fine, because you're just about to filter your drying agent. Take that pipette, squeeze the contents into the top of your filter pipette. {commentary on how this is backwards from the technique often shown} Coming up through the cotton plug doesn't make sense to me because you're going to have solids that get trapped below that may very well come right back out after you try to dispense, and, if friction is holding the piece of cotton in, then if you're pulling liquids this direction, then it means the piece of cotton may pop out. After you've pulled all of your compound up into the filterless pipette, squeeze the entire contents of that into the top of your filter pipette, pop off the pipette bulb, put it on the filter pipette. When you do, make sure that you've got some form of collection flask ready to receive your compound, because when you put that bulb on, you may start forcing some of your product through. Once you do have the bulb on, squeeze it and force that product through. Your drying agent will be left behind on the backside of that filter, and you'll have your filtered product that comes out. Normally, when we're doing chemical reactions, we would have some kind of solvent that the product would have still been residing in. Normally, after transferring everything out of your product flask, you would have added some clean solvent to help dissolve up any compound that might have been stuck, might have been some residual product left on that drying agent. But, we did this reaction neat, so you don't want to wash your glassware with anything; just transfer out as much as you can get and then filter that through. That will means some product loss.

{measuring by tared flask}

Spectroscopy

I'm going to give you a general overview of spectroscopy – what spectroscopy is, what the physical set-up of a spectrometer is, then I'm going to focus our discussion on infrared spectroscopy. We first need to talk about the electromagnetic spectrum. Light is superposition of two different oscillating waves: one of them, a magnetic field, one of them an electric field. Those fields are 90° to each other. That's why light is called electromagnetic radiation. Since light's a wave, there is a certain relationship that holds true for light. Actually, this relationship holds true for any wave that has a fixed forward velocity to it. For the case of the light, the equation is this: that the speed of light (c), is the product of the wavelength (lambda), which is expressed as meters, and frequency (nu), which is expressed as Hertz, which is the same thing as inverse seconds. If you're using the unit of measure of meters for wavelength and if you have per seconds as a unit, put the two together you get meters per second, which is velocity. Since speed of light is constant, that means there's a constant inverse relationship between wavelength and frequency. So, higher frequency, shorter wavelength; longer wavelength, lower frequency. There's another important equation, though. h in this equation stands for Planck's constant, which is the bridge between viewing matter as a wave and viewing it as a particle, matter or light.

Best way to explain this is to go back to the photoelectric effect. In that experiment, you have a metal plate that light is being shined on. If you use light that is of a too-low frequency, then you don't get any kind of response from this metal plate, no matter how much light that you shine on it. But if you use light of a certain minimum frequency, then the plate will respond by a current flow; in other words, electrons are being displaced. The amount of response that you get in that case now depends on how much light is being shined on the plate. This is rather curious behavior, but what Einstein ended up determining is that there is some kind of process that involves a fixed amount of energy – the processes to cause an electron to be released requires a certain amount of energy. The way it happens, you can't add all of the energy of the light beam, because the light actually consists of these different particles called photons. In order to bridge that energy gap, you have to have a photon that has at least that minimum energy to it. That's related to this equation. The lefthand side refers to energy per photon, so looking at light as a particle. The righthand side has frequency, which means you're treating it as a wave. So it's one of the mathematical correspondences between the wave behavior of light and the particle behavior of light.

More generally, if you have two different energy states – these might be electronic states, like the different energy levels in an atom; they could be different bonding orbitals, like a pi bond and pi* orbital; they might be vibrational energy states. It turns out that not just spin and orbital angular momentum and some of these atomic properties are quantities; other things like bond vibrating, those different vibrations can only happen at very specific energy levels. If you have this energy difference that corresponds to a particular energy per photon that therefore corresponds to a particular frequency of light, you have to have the right frequency of light for that energy gap to be excited.

In IR spectroscopy, we are worried about bond vibrations. Different bond vibrations have different effective energy contents. Imagine that two atoms connected by a bond we pretend is acting like a spring. Some springs are tougher than others, so some springs require more energy to get them to be pulled, to get them to displace. In a similar way, different bonds end up having different amounts of energy associated with them. Imagine if you had an oxygen-hydrogen bond versus a nitrogen-hydrogen or carbon-hydrogen bond. Those atoms, the oxygen, nitrogen, and carbon, they're different sizes, different masses, so that's going to cause a different vibration. Each one of those different vibrations would could excite using the right frequency of light. Kinda related, that's how microwave ovens work. You're excited certain energy states of water, so you pour this energy in, the water absorbs it, stuff heats up; same kind of thing here.

What we do then is take a range of frequencies. That range of frequencies is called a spectrum. So, the electromagnetic spectrum refers to taking all of the possible frequencies of light. We don't use the whole spectrum, generally, at once, we use portions of it. Within that portion, we vary the frequency and we see what kind of excitations occur. When does light get absorbed; when does the molecule respond to that light? In different case, it tells you different physical properties, structural properties of the molecule that you're trying to characterize.

Let me write up a rough picture of the electromagnetic spectrum, and let's say we put visible light right in the middle. What would be the high-end cutoff, in terms of wavelength, a very rounded number, what would be a good cut-off value for the longest wavelength of visible light? About 700 nanometers. Red light shows up at about 700 nanometers. Red light is less energetic light in terms of energy per photon. If you're heard the expression "red hot"; there is this expression "blue hot", like we have with our bunsen burners. Blue indicates something that's hotter, more energetic. Red light, less energy per photon. What about the opposite end? What would be a rounded number for the low end of wavelengths of visible light? About 400. 3-something, really. This would be violet light, which is higher energy per photon. If we have the region of the spectrum that's just a little bit longer wavelength that red light, what do we call that? Infrared. What about the opposite side? A little bit short wavelength than violet light? Ultraviolet. If we went way to the right and I went to really long wavelength radiation, what kind of radiation would that be? Microwaves. What else woud be down there? Radio waves. If you have 101.5 MHz, that translates into a very long wavelength, something like a meter or so. What if we went to the extreme other end? X-rays, gamma rays, things like that.

There are three regions of the spectrum that in organic chemistry we tend to use the most in spectroscopy – ultraviolet/visible light; infrared; and radio waves.

Let me show you a very cartoonish picture of what a spectrometer would look like. Many forms of spectroscopy work this way: you have some source of radiation, and that radiation is shown through some sort of sample. A certain amount of that light may make it through the sample; some of it might end up being absorbed by the sample. We monitor how much light does make it through. There are two different unit of measurement that we can use to express the light and whether it makes it through or not. One way is to focus on how much made it through; that is transmittance. Another way to view it, though, would be how much light ends up getting absorbed by the sample; we call that absorbance. There is a conversion between the two units. For IR, we'll be using transmittance as our unit.

Here's what we'll be looking for. We're going to be looking for a certain number of peaks. {Commentary about pronunciation of peak; pin, pan, pen} Peak refers to the fact that if you're looking at the spectrum in terms of absorbance that you'll see a shark increase in the amount of absorbance when you get to some portion of the spectrum where the sample actually interacts with the light. That sudden upshoot then the drop looks like a little mountain; that's where the term peak comes from. We're actually going to be doing transmittance, though, so our peaks are going to be reversed; they're actually going to be [stalagmite/tite?].... These are going to be the ones that are pointed down, so our spectrum is going to look something like this. % transmittance is the x-axis. If I'm talking about IR, then there's this unit inverse centimeters; that's the way that frequency is expressed. Since frequency is inversely related to wavelength, it's indirectly related to frequency. You have a range of frequencies that you're looking at. You might end up with a pattern that looks kinda like this. Each peak – or this case, trough – 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 – this is where electronic transitions occur. In the atomic spectra you observed in Chem 1A, you did the reverse. You zapped some sample with electricity, causing light to be generated. Because that light was generated by electrons going back and forth between very specific energy levels, you only got very specific colors of light out. The reverse is true of substances as well: that if you shine light on a substance, certain substances will absorb more at certain frequencies better than others. That's why, for example, things have color. Some of the things that we're wearing, the dyes, absorb particular frequencies of light. These particular frequencies in the visible and ultraviolet range correspond to electrons moving between energy levels; that's what I mean by electron transitions. That means it tells us something about the electronic structure of the molecule. We can use this to see what is that gap between a pi bond and its antibond; does that tell us anything about the structure of the molecule.

Second form of radiation – IR, infrared – this corresponds to different vibrational transitions. Think of the standing wave problem, where only specific waves can exist. Long story short, same thing happens when molecules vibrate; there only certain vibrations that can exist. Each of those has a different energy level, so if you suddenly make something vibrate faster, that requires a certain energy input, which corresponds to a specific frequency of light. In the case of IR, what that means is that we see the different bond types, and that potentially means we can identify different functional groups.

The important technique we're going to learn is NMR – nuclear magnetic resonance spectroscopy; it uses radio waves. What happens in this technique is we take a sample and put it in a very strong magnetic field. Just like electrons have spin, nuclei have spin. In the magnetic field, those nuclei can align one way with the field or the opposite way, against that field. Those two different orientations have two different energies associated with them. With the right amount of energy, you can flip the orientation of that nucleus. That's where this idea of nuclear resonance comes from, that you're flipping nuclei back and forth. The energy needed to do that is very low frequency, down in the radio wave region of the spectrum. It's related in MRI – magnetic resonance imaging. Why is this so important? Because the exact frequencies of transition that occur for these nuclei are very very sensitive to what's around them. A little small change in structure – a methyl versus an ethyl, a chloro verus an iodo, three carbons versus four. That can change the chemical environment around the nuclei enough to cause the frequencies to change. We'll learn how to use these subtle differences to establish the full structure of organic molecules. We can know what the structure is, that's why modern synthesis is possible – we can make something and figure out what we made. [story about taking quantum mechanics]

These are the type of radiation. Let me bring this back to IR. [note about spectroscopy info in text] In the text is a series of tables where it lists a whole bunch of different functional groups or different kinds of bonds. It gives the different frequencies that those bonds absorb at. For example, if you had a starting material that was an alcohol, I could look up on this table and it says, alcohols have an absorbance frequency 3200-3600, and it talks about it being a broad peak. What does that mean? Broad means you get this rounded type of formation, exactly what I have in the drawing. That's very characteristic of an alcohol because alcohols undergo extensive hydrogen bonding in solution. Imagine that you have the O–H bond itself that's doing its thing, but it ends up interacting with another oxygen because of hydrogen bonding. That's going to interfere with how it's wiggling. Maybe sometimes, by hydrogen bonding, it'll wiggle faster, it'll wiggle slower. Out of all of the molecules in solution, some of them are at slightly different vibrational frequencies than the others, which is why we end up with this rounded curve. The point of this story is: if we walk into the instrument room and take a spectrum of your compound and we see this big peak at 3200-3600, it means we have an –OH group. That means we have a problem: is it the original alcohol that has this –OH group that is showing up? If you made your product and you see that alcohol, you know, oh, maybe the reaction didn't go completely successfully. Maybe it's water, because water's got an –OH group in it as well, just like an alcohol does. Water, will in fact, show up in the same way in the same place on the spectrum. But this is how we use IR. We can scan and say: is this kind of bond present? What you hope to see in your starting material is you do have an alcohol.

Further in the table, we'll see that a carbon-chlorine bond has a frequency range of 600-900, on the righthand side, by convention, in the IR spectrum. In the 600-900 range, we would expect to see some kind of absorbance if we did have a chlorine present. Here's what we're going to do with IR today. [note on ability to download reactant spectrum] In the reactant spectrum, you can see this huge drop-off at 3400, a very noticeable, broad peak, very characteristic of an alcohol. We hope to see this, since this is the starting material. This sharp peak at 2900-3000, that's where alkyl groups in general; sp3 hybridized carbons tend to show up at that region of the spectrum. There's a whole bunch of other peaks which correspond to different complicated types of motion, but we're not going to worry about that region of the spectrum. Let's see how this compares to the product. If you're worried about whether you really did obtain the product, you could always compare it to the spectrum in the text. Notice that the region where the alcohol was present, that peak is gone, which you hope so, because if the peak is gone, if the alcohol is gone, it's not going to show up. Right here, between 600-800, there's a strong absorbance that you'll find is not present in the starting material. This peak is at roughly 760; that would correspond to the fact that you did successfully make that carbon-chlorine bond.

Here's what we're going to do. In the product, when you are scanning, you are looking to confirm: is there no alcohol peak there. If you don't see anything there, that means the reaction was probably successful, you got rid of the alcohol, and you did a good job drying your product because there's no water showing up either. You also, in your product, will hopefully see the same kind of peak here at about the 750-800 range; that would be some positive confirmation that you got the carbon-chlorine bond and no longer have the alcohol. We're going to use this as a way of proving the reaction was successful. [demonstration of IR]

Let me talk about sample preparation. You all have liquid products, which are much easier to deal with. We're going to make a thin film using salt plates. When I say salt plate, that literally does mean yes, it's made out of salt, potassium bromide. For the most part, they're transparent when new, but as you can see, they've been dropped or nicked over time, and you can see that they're slightly foggy. That's because if they're left sitting out, as they unfortunately are sometimes, they'll just sit there and absorbe water from the atmosphere, so over the long run, you'll have a little puddle of salt water, if you don't put these away or treat them properly. [admonition that no new plates will be given out if the plates are not treated well]

About cleaning these plates. Because they are salt, you can't use water; you're just going to dissolve the plate way. So, we generally use acetone, but since acetone has some water automatically in it – water's very soluble in acetone – we have a bottle that's saturated with sodium chloride, to help prevent it leeching off any salt from the salt plates. [use of chemwipes] I'll go ahead and clean off the plate, to make sure we don't have anything to contaminate it to begin with. [storage in desiccator; properly handling greased lid] [launching acquisition program] There's an option here called background. If you are the first person to use the machine that day, it will come up and ask if you want to collect a new background. A background is this: even if we don't put a compound in the IR machine, when we pass light through here, it's going to be absorbed, because there water, carbon dioxide, other things in the atmosphere that will partially absorb that light, and this machine is sensitive enough that it will detect that. If you then put in your sample to be scanned, the light will absorbed by the sample, but it will still be partially absorbed by the atmosphere around the same. If you want to neglect, ignore, cancel out the effects of the atmosphere, we collect a background first, where you look at the atmosphere. Then, on number on a number basis, you subtract [the background] out when you scan your compound. That way, the difference between the two, any absorbance that occurs is only due to your compound. Backgrounds need to be run periodically throughout the day, because it's possible that water levels, carbon dioxide levels change in the room as the day progresses. Make sure that you really are using clean plates, or don't use plates at all, when acquiring your background. [demonstrating machine] [preparing plate]

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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 pipette and force the product through the filter

Spectroscopy – Electromagnetic spectrum (EM)
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

UV/Vis – ultraviolet/visible – electronic transitions between energy levels – electronic structure
IR – Infrared – vibrational transitions – bond types, functional groups
NMR – nuclear magnetic resonance – radio waves – used to determine full chemical structure

% transmittance – the % of light that successfully passes through a sample
absorbance – the fraction of light absorbed by the sample
each peak corresponds to a particular mode of bond vibration