

Ch3x - Notes

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Chapter 1

Chem 3x lectures

1.1 Photochemistry Fundamentals - January 11

We discuss Beer's Law (Beer's Labert Law). Let there be a cuvette with length l perpendicular to the propagation of some light ray. Let the light before hitting the cuvette be I_0 and the transmitted light be I_t . Transmittance is thus defined as $T = \frac{I_t}{I_0} = 10^{-\epsilon l C}$, where ϵ is the extinction coefficient and C is the molarity/concentration of the solution. We then define absorbance $A = -\log[T] = \epsilon l C$. Because elements absorb differently at different wavelengths, we can construct a plot of $A(\lambda)$ (this is due to resonance frequencies at the subatomic level), which will be our method of analyzing these compounds. We will in our first lab calculate extinction coefficients for various species at various wavelengths. Note that the absorption spectra are actually a sum of Gaussians at the peaks of the spectra; each peak follows a Gaussian.

How do we calculate ϵ ? We know $A = \epsilon l C$, where $l = 1\text{cm}$ because we are using a cuvette. Thus, because ϵ is roughly constant, we vary C and measure A , and the slope of $A(C)$ is ϵ . For us, we will measure absorption spectra at many concentrations and simply measure ratios of absorptions at height of peaks. Note that extinction coefficients will vary with wavelength, as one would expect, and we will calculate extinction coefficients at every peak. Note also that, given a colored solution, we expect the color of the solution to be the opposite of the absorption peaks.

We use AvaSoft for our spectrophotometer measurements. The spectrophotometer comprises two boxes, in the first of which is just the cuvette and a light beam, and in the second there is a series of prisms and sensors to separate and detect the intensities/photon count at various wavelengths. We must begin by "File \llcorner Start New Experiment" and then click "Start", which will begin data collection. We want to amplify the signal as much as possible without saturating the sensors (which occurs at 16,000 count). The way to amplify is to click "stop" and then increase the integration time. Note that any electronics will have some slight leakage (in our case, called dark noise), so to calibrate our sensor we click the black box next to the "Start/Stop" button after setting the spectrophotometer to "TTL." The parameters at the top, "Integration Time" and "Average", refer to the amount of time per trial and the number of trials to average over. If we finish calibrating for dark noise (and calibrating for the presence of a cuvette, of course), then we can click the white box next to the earlier black one, which will save "reference data", or I_0 . Note finally, just to be sure, that spectrophotometers measure transmittance rather than absorbance.

The emission spectrum of the sun peaks rather significantly at blue-green, so our goal is to absorb blue-green light and thus our best chromophore for solar collectors should look red-orange.

When we do the lab, we will use a pipette bulb. Open the valve labelled A, so that can be opened to empty the bulb. If we then open the S valve, which is the one attached to the pipette, then the liquid will be drawn up towards the pipette. If the valve labelled E is then opened, then the pipette will empty. For both pipettes and volumetric flasks, the bottom of the meniscus should be aligned with the etching. The proper procedure to dilute is to draw out some amount into the flask, empty out a small portion via pipetting, and then pipette the same amount back in.

When we put the data into Excel, we will use the command “=linest(ydata, xdata, true, true)” and then hit CTRL+ENTER. The highlighted blocks will then fill with data, but the key is to note that m and b are the first two blocks. The great part is that these calculations are linked to the data! Before we leave lab, we must input data and print both calculations and graph into lab notebook.

1.2 Luminescence - January 18

We discuss energy wells today. Recall that a well (like a parabola) in a potential is a relative minimum. When an excited electron goes back to the ground state, the photon released is a function of the energy gap between the energy state, which is a function of atomic radius. Our upcoming task will be to judge from the released light what the size of the atom is (or at least the radius of the targeted electron orbital).

If we think about having an atom approach another atom like in bonding, there will be a potential well (too far and electron repulsion, too near and nucleic repulsion). The well itself is quantized, like normal modes. We now examine our quintessential favorite compound, $\text{Ru}(\text{bpy})_3\text{Cl}_2$. Recall that bipyrimidine consists of bonded nitrogenated benzene rings (like naphthalene, but with nitrogen substituted in). The lone pair on the nitrogen is the bonding pair of electrons, so there is a positive partial charge on the nitrogens, which ends up balanced by the two chlorine atoms.

We now examine the five d orbitals. d_{z^2} is a big p orbital with a ring, $d_{x^2-y^2}$ is along the x and y axes, and the other three are located in between the axes. Recall then that the ligands, which approach along the axes, produces an interference with the z^2 and x^2-y^2 orbitals, and we no longer have a degenerate sets of 5 but instead those two are higher in energy (recall that this was covered in 1a!). In Ru_2^+ , we have six electrons which must occupy the x^2, y^2, z^2 orbitals because the energy gap is tremendously large. In fact, the gap is so large that no amount of light can make the electron jump this energy gap. There is a lower orbital in energy between the two though, namely the π^* orbital. This, because the π^* orbital is in the ligands, means that shining the correct light can actually make electrons jump from the Ru to the ligands. This is called electron transfer.

Examine now benzene. sp_2 hybridization and leftover π orbitals, which are delocalized to create the ring. These orbitals all have their eigenfunctions, and we can examine the superpositions to evaluate the possible energy states of this delocalized orbital (if all the eigenfunctions are same sign, then we have the lowest energy, if alternating, then highest energy, etc.). The higher energy superpositions are considered antibonding orbitals, the π^* orbital. Remembering that bipyrimidine has benzene rings, this is the π^* orbital we mentioned earlier, the target of the charge transfer. The wavelength of the light to accomplish this charge transfer is 410nm. The electron, upon being excited, will reemit a photon of slightly lower energy due to vibrational losses. This reemission is called fluorescence, a subset of luminescence. Note that this excitation process never changes the spin of the electron. There is actually a neighboring π^* orbital that accepts an electron of opposite spin from the former one (the former is called a singlet orbital while the latter a triplet). For $\text{Ru}(\text{bpy})$, it turns out that this is the transition that we will try to excite. This process of changing spins is called intersystem crossing. But notice that when the electron tries to fall back down, it violates Pauli Exclusion; we must wait for it to flip spins again. The transition from the singlet orbital is on the order of a picosecond, but the waiting for the flip spin takes the time scale up to around a microsecond. The delayed reaction is called phosphorescence rather than fluorescence. We will see that while we shine blue light, the reemitted light is a red-orange light of around 650nm. This shift is called the Stokes shift, or more precisely, a positive Stokes shift for us, because the wavelength shifts up.

The laser we will be using in lab will be a pulse laser; each pulse lasts one microsecond, while the distance between pulses is one millisecond. We will have a synchronized sensor, and it will measure the phosphorescence of the sample. Cool stuff. The sensor will release an increasing waveform over the laser time and a decreasing one once the laser shuts off.

However, since we're in a solar class, we want to capture this energy. So we will add a quencher molecule. The goal of this quencher is to capture the electron from the excited state. One that we will use is methyl pyridine (missed the IUPAC name), which captures perfectly because it's also a pyridine. We will also use $\text{K}_4\text{Fe}(\text{CN})_6$, which captures well because the complex is also six ligands and Fe is similar to Ru. We will

now try to model the phosphorescence process.

We start by trying to find the rate of excitation. Consider a Beer's Law setup. The rate of excitation is the rate of absorption, which is simply $I_0 - I_t = I_0(1 - T)$ where T is transmittance. We then look for the decay rate, which is:

$$\begin{aligned}\Delta Ru^* &= -k[Ru^*]\Delta t \\ \frac{dRu^*}{dt} &= -k[Ru^*]\end{aligned}$$

We then want to combine the two effects, which is done by:

$$\begin{aligned}\frac{dRu^*}{dt} &= I_0(1 - T) - k[Ru^*] \\ \frac{dRu^*}{dt} + k[Ru^*] &= I_0(1 - T)\end{aligned}$$

This is the differential equation of form $\frac{dy}{dt} + \alpha y = C$, which has solution $y = Ae^{\alpha t} + C/\alpha$, which gives us $[Ru^*] = Ae^{-kt} + \frac{I_0(1-T)}{k}$. We can then solve the initial value problem for A , because we know the initial conditions means that initial concentration is 0. The final solution is $[Ru^*] = \frac{I_0(1-T)}{k}(1 - e^{-kt})$. If we recall earlier that the photon absorption increased then decreased during the laser pulse, the $1 - exp$ is the increasing part and the exp is the decreasing part. This is the graph we aim to capture (before we add a quencher). The addition of the quencher produces a term $k_q[Ru^*][Q]$ in the differential equation, where Q is the concentration of the quencher. Note that we can set up $[Q] \gg [Ru^*]$, and thus we can call $[Q]$ a constant. Thus, we have:

$$\begin{aligned}\frac{d[Ru^*]}{dt} &= I_0(1 - T) - k[Ru^*] - k_q[Ru^*][Q] \\ &= I_0(1 - T) - \underbrace{(k + k_q[Q])}_{\text{observed } k}[Ru^*]\end{aligned}$$

This is a problem that we already know how to solve, the same differential equation as earlier. If we plot this, we will find that increasing Q will make the graph smaller. If we then calculate the observed k , we have a linear function in $[Q]$ and thus we can measure our way through to finding k_q by fitting stuff.