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Physics 531: Quantum Mechanics Fall 2012

Project #1: The Absorption Spectrum of a Carbocyanine Dye

To set the stage for this project, please make sure you’ve watched and worked through the powerpoint lecture on Blueline (in the modules section under Project #1) titled Spectroscopy and the Atom.

One of the first mysteries of quantum mechanics was the quantization of energy, which manifested itself as discrete absorption and emission lines from molecules and atoms. Although we have not yet tackled the hydrogen atom, we saw (or you will see) how energy quantization arises in the infinite and finite wells: boundary conditions force particles to behave as “standing waves” leading to fixed modes and quantized energies. Your project is to model a more complex and realistic system, a Carbocyanine Dye. Carbocyanine dyes are a set of compounds that strongly absorb light in the visible region of the EM spectrum and have myriad uses. To cite one example in biology, carbocyanine dyes have been used to identify living neutrons in long-term cultures.

**Project in a Nutshell**: For the 1,1’-diethyl-2,2’-cyanine iodide and 1,1’-diethyl-2,2’-carbocyanine iodide dyes, use 1D quantum mechanics to determine why these dyes absorb light in the visible spectrum, why this absorption is peaked around a single wavelength or frequency, and what is that peak wavelength or frequency.

General Background:

I. Carbocyanine Dyes

 The carbocyanine dyes are homologous set of aromatic compounds:

 

 **Fig. 1.** The general carbocyanine dye molecule.

The counter–anion is usually chloride or iodide, but that choice does not affect our discussion here.

 The name of the dye depends on the value of the integer *m*:

 *m* = 0: 1,1’-diethyl-2,2’-cyanine chloride

 *m* = 1: 1,1’-diethyl-2,2’-carbocyanine iodide

 *m* = 2: 1,1’-diethyl-2,2’-dicarbocyanine chloride

 *m* = 3: 1,1’-diethyl-2,2’-tricarbocyanine iodide, etc...

the integer *m* is called the *homology number*.

 As most effective dyes do, this compound absorbs light in the visible region of the spectrum, and this absorption physically occurs in the region of the molecule’s *π*-electron system. For the *m* = 1 homolog, we have the following resonance structures:



Having two resonance structures really means that the approximate wave function for this molecule has equal contributions from the two electronic states (electron configurations). Therefore, all the bonds along the chain are roughly equivalent, with a bond order of 1.5. (The bond order of a pure single bond is 1; the bond order of a pure double bond is 2, etc.)

**Stage 1**

We’ll be tackling our projects in stages. Each stage will suggest questions to consider or strategies to employ that need to be completed before moving on to the next stage. Some of this is scaffolding and will be reduced in future projects, and some of it is very much a quality control issue. Since you are not sitting through lectures, I very much need to determine that you’ve thought through and worked through the material at the appropriate level.

Questions to consider and answer for this stage:

1. Since we’re physicists, familiarize yourselves with covalent chemical bonding, particularly π-bonding. How is π-bonding different from other forms of covalent bonds such as σ-bonding? Are these bonds weaker or stronger than other covalent bonds?
2. Are the electrons involved in π-bonding localized or un-localized in the dye? How does the existence of two resonance structures affect your answer?
3. How many π-electrons are there in this molecule? How does this depend on the homology number m?
4. At this stage, what are your thoughts about how to model this system? What kind of potential would be suitable? How can we apply/modify the potentials we have seen before? This project should guide your work on your H.E.L.L. packets – what items are crucial for you to learn so that you can make progress here?

**Stage 2**

Now that you’ve thought about π-bonding, a potential model for our system, and other issues, we’ll work on refining our model. As a first step we’ll consider replacing the π-electron system in the dye with a number of free electrons that can effectively roam the length of the molecule.

1. If electrons are confined to the length of the molecule in which there is a constant (or zero) potential energy, and this potential rises sharply at the ends of the molecule (to effectively confine the “free” electrons), what kind of a particle in a potential well model is most appropriate here?
2. Given a homology number m, how many “free” electrons do we need to take into account given a molecular length of a (shown below)?
3. How does Pauli’s Exclusion Principle impact how these electrons occupy allowed states (energy levels) within our potential? What is the lowest unoccupied state?



Next we need to determine the length of our molecule. The relevant part of the dye is the region a in the diagram above.

What is the length of the box, *a*? A glance back to the figure above and simple geometry will give us an answer:

 

Geometry of a chain of *sp*2 hybridized carbons in the

trans configuration.

1. Assuming a trans configuration for all of the π-bonds, what are α and l? How long is the relevant length of the molecule?

**Stage 3**

By now we’ve determined that our organic dye can be best modeled as a collection of free electrons inside of an infinite potential well (particle in a box). In this stage we want to compute the primary absorption wavelength of the dye and begin to grapple with concepts such as selection rules and absorption strength.

1. Calculate the energy of a photon which will be absorbed by the dye molecule (given a homology number m) using our particle in a box model.
2. What is the wavelength of this photon?

Next we need to deal with two real world issues:

1. Although molecules and atoms absorb EM energy through the jumping of electrons between energy levels, are all transitions allowed or are there selection rules which determine which transitions can occur?
2. Even if a transition is allowed, what is the intensity of the absorption?
3. After researching selection rules, establish how we can determine if a particular transition is allow or forbidden.
4. How can we calculate absorption intensities theoretically? How are they measured experimentally?

**Stage 4**

Finally let’s determine whether or not our chosen transition is allowed or forbidden. As you found in your research, to do that, we must calculate the *transition dipole moment* for this transition: The transition dipole moment is defined as:

 

where *ψn’* is the wave function of the lower state (i.e. the state in which the electron begins), and *ψm’* is the wave function of the upper state (i.e. the state in which the electron ends up in).  is the quantum dipole moment operator of the molecule. (, where *e* is the charge on the electron involved in the transition.) If there is no transition dipole moment for a particular excitation (i.e. ), then the transition will not occur.

1. Evaluate the transition dipole moment and determine if it is indeed non-zero for the transition in question.

**Stage 5**

The final stage of this project is to compare our theoretical predictions to spectra obtained experimentally for m=0 and m=1 conjugated dyes.

On Blueline in the project folder you’ll find an excel data file which contains experimental data for the absorbance spectra for both m=0 (red) and m=1 (blue) conjugated dyes. Plot the absorbance vs. wavelength (in nm) for each dye.

From the data you’ll see that the dye molecules do not absorb light at a single wavelength or frequency; instead, one observes absorption bands. Most bands have an approximately Gaussian shape, so we can model the frequency dependence of absorption by

 

where *νm* is the frequency of the maximum absorbance, *Am*, and *σ* is the *half*-width at half-height of the absorption band.

Use the experimental data to determine (for each dye):

1. The experimental frequency and wavelength of maximum absorbance, νm and λm respectively
2. The amplitude of maximum absorbance, Am
3. σ, the half-width at half-height of the maximum absorbance
4. λ’ and ν’, the wavelength and frequency respectively at half of the maximum absorbance
5. Using the above parameters plot A(ν) (using the form given above) superimposed over the experimental data. Does a Gaussian absorption band fit the data?

Now we finally get to compare our theoretical calculations to experimental data. In Stage 3 you computed the wavelength and frequency of the photon that will be absorbed by the dye molecule.

1. How do the values you calculated from our model compare with the wavelength and frequency of maximum absorbance from the experimental data for each dye?
2. One large source of uncertainty is the length of the infinite well we used as our model. By how much do you need to adjust the length of the infinite well in order to better fit the experimental data? More specifically, if the length of the infinite well is given by



you can adjust the length of the well by changing 2m+8 to 2m+y. What value of y gives the best fit to the experimental data FOR BOTH the m=0 and m=1 dyes?

1. The experimental value for the oscillator strength can be found with:



where C is the concentration of the dye and L is the path length of the sample. Use L= 1 cm and C=9.997x10-6 M for the red dye and C = 9.991x10-7 M for the blue dye. How good is the theoretical value for the oscillator strength that we derived?