

INSTRUCTOR'S MANUAL – MOLECULAR AND ATOMIC SPECTROSCOPY

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The problem sets on spectroscopy can be used in at least two different manners. The primary intent is to use these as in-class, collaborative learning exercises. Groups of 3-4 students work together in discussing and working through the problems. When using the problem sets in this manner, the instructor must actively facilitate and guide students through the material. This manual will guide instructors through each of the problem sets, identifying possible student responses to the questions and the response and activities of the instructor during the progression of the problem.

An alternative to the use of the problems in class is to assign them as out-of-class activities, preferably done as a group activity among students or as a peer-led team-learning activity. The accompanying text provides a detailed discussion of each step of the question, such that students could work back and forth between the problem and text on an iterative basis to gain an understanding of the material.

There is no perfect way to assemble groups for such collaborative learning activities. I gather information on the first day of class (year in college, major, prior chemistry courses) and then use this to set groups of 3-4 students that start on the second day of class. I try to make the groups as heterogeneous as possible and they work together for the entire semester. Another strategy is to assign groups for a shorter period of time that might encompass completion of a specific topic or unit (e.g. fluorescence spectroscopy), and to then create new groups for the next unit. One other possibility is to have different groups every day of class. Since it is important for groups to work well together, having new groups every day may be less successful than allowing groups to work together for more extended periods of time. I would recommend that the instructor assign groups rather than allowing the students to pick their own. This avoids the potential problem of friends who want to be in the same group but who then do not work well together or stay focused on the assigned task. It also avoids the problem of the student who is left without a group at the end of the selection process, something that can be especially problematic if it is a member of a minority group. When using collaborative groups, it is also important for the instructor to monitor the functioning of the groups and to step in to address either dysfunctional groups or the recalcitrant individual within a group. Peer-evaluation processes are often used by instructors who employ group activities as a way of assessing how well groups are working.

I also expect the groups to meet outside of class for any homework assignments, something that is aided because I am at a residential college. An alternative to this is to schedule a room on the evening before a homework assignment is due and encourage them to come to this place and work in any arrangement they wish on the homework. I have run such sessions for several years now and attend them as a facilitator (one result is that it has cut down considerably the individual traffic to my office seeking help on the homework problems) and it has been an excellent way to promote collaboration among the students.

The instructor has an especially important role to fulfill during the group activities. I have observed that the more engaged that I am in the process in helping to guide the students through the material, the more effective the learning that occurs. In many instances, it seems that the students are initially stumped by the question, that they begin to explore things that they do know that might apply to answering the question, and that help from the instructor either by letting them know that they are on the right track or by suggesting another direction in which to take their thinking is necessary. As they begin a question, I roam around the room listening in on conversations and looking over their shoulders at what might be written in their notebook. If I hear something interesting, I indicate that to the group. If I see that someone has written something interesting and relevant in their notebook, I tell other group members that they ought to talk with this individual about what they have written, and that the individual should explain to the other group members why they wrote that down. If I hear a group going entirely in the wrong direction, I probe them on why they are heading in that way and then offer suggestions about things to consider that will set them off in the right direction. When all groups have realized an important point, I call time out and summarize the concept at the board. Then I send them back to continue with the next part of the problem. Most of the problems are handled in such an iterative manner where the students work through some important part of the problem, I summarize it at the board when they have developed the concept, and then they return to the next part of the problem. Occasionally a group will just not see something, whereas every other group has gotten the point, and it may require a direct intervention from the instructor with that group to explain the concept. Similarly, there are times when I call their attention to the board to summarize a point when one of the groups still has not gotten the concept but waiting would slow down the remainder of the class to an unacceptable level.

When using these materials, I want the students to discuss and discover the concepts inherent in the problems, so they do not have the text when working on the problems. After they have completed a particular problem, I then give them access to a copy of that portion of the text. The text thoroughly explains each problem or concept and I encourage the students to read it over that evening to reinforce the concepts developed in class that day. I also give homework problems designed to reinforce the concepts developed in class.

After a very brief introduction to the general concept of spectroscopy (probing chemical species with electromagnetic radiation; that different species and different processes absorb different components of the electromagnetic spectrum; that this can be used for purposes of identification and quantification) I give the students the first set of in-class questions that cover general background information on spectroscopy.

Italicized items throughout this instructor's manual are questions or prompts I often give the students to help them solve the problem.

Electromagnetic Radiation

1. What is the relationship between the energy (E) and frequency (ν) of electromagnetic radiation?

Students usually remember the equation that $E = h\nu$ without any prompting on my part and determine that there is a direct proportionality between the two.

2. What is the relationship between the energy and wavelength (λ) of electromagnetic radiation?

Students usually remember that $c = \lambda\nu$ without any prompting on my part and determine that there the energy and wavelength of radiation are inversely proportional.

3. Write the types of radiation observed in the electromagnetic spectrum going from high to low energy. Also include what types of processes occur in atoms or molecules for each type of radiation.

The students' individual ability to identify all the different types of electromagnetic radiation and rank them in energy usually varies widely. Within a group most are able to generate a complete or close to complete list and rank those that they are most familiar with. One of the most perplexing to most students is where to put microwave radiation in the energy ranking.

Identifying the types of processes that occur in atoms or molecules for each type of radiation presents more difficulties.

What type of process do you already know about in molecules and what radiation produces them?

Within groups they can determine that UV/VIS involves transitions of valence electrons and IR corresponds to molecular vibrations. Many are familiar with the idea of a nuclear spin flip from their organic chemistry course, although they may or may not remember that RF radiation is used to excite nuclear spin flips. Some know that it is possible to rotationally excite molecules, although they often do not know that rotational excitation occurs in the microwave region of the spectrum. It is uncommon for them to know what processes occur with γ -rays and X-rays. Many are not familiar with the idea of an electron spin flip in paramagnetic substances and that it occurs in the microwave region of the spectrum.

At this point, I briefly discuss the difference between absorbance and emission. I also discuss how different spectroscopic methods are of different utility for compound identification and compound quantification. Some techniques (e.g., NMR spectroscopy) are useful for interpretation and identification, whereas others (e.g., IR spectroscopy) are useful for identification but not that amenable to interpretation and instead require use of a computer library to determine the best match.

I then go over the basic design of an absorption spectrophotometer and present them with the following series of questions on Beer's Law.

Beer's Law

4. What factors influence the absorbance that you would measure for a sample? Is each factor directly or inversely proportional to the absorbance?

Students quickly realize that the absorbance relates to the concentration and that it is a direct proportion. They often do not think of path length as a variable, I suspect because they are given specific cuvettes to use in any prior measurement they have performed and then don't think the path length is something they could adjust.

What would be the effect of increasing the path length?

This is usually sufficient for them to see that there ought to be a direct relationship between path length and absorbance. Some students are familiar with the concept of an extinction coefficient from other courses, but rarely do they have an exact understanding of the meaning of the extinction coefficient. I indicate that molar absorptivity is another term for the extinction coefficient and at this point we can write Beer's Law on the board.

How would you measure a spectrum and draw an example of a UV/VIS absorbance spectrum of a chemical species?

Someone in each group usually has enough prior experience and knows that recording a spectrum involves measuring the absorbance as the wavelength is scanned. If so, they can draw a spectrum where the absorbance varies with wavelength so that there are regions of high absorbance and regions of low absorbance. Some may think of an atomic (line) spectrum whereas others think of a molecular absorbance spectrum, and I clarify that they are different but that we can consider the nature of the extinction coefficient using either of them. I also prompt them to consider the concentration and path length when someone records a spectrum, and they realize that both are fixed.

Explain why the absorbance is high in some regions and low in others (or that lines in an atomic emission spectrum have different intensities).

They can usually rationalize that chemical species have the ability to absorb some wavelengths of light and not others, and when pushed on the differences in intensities of lines in an atomic emission spectrum, that some transitions must have a higher likelihood of occurrence than others. They sometimes wonder whether the difference in intensities reflects differences in the detector response, so it is important to point out that it is a fundamental process taking place in the chemical species. At this point, we can now discuss how the extinction coefficient or molar absorptivity is a measure of the probability that a particular wavelength of light can be absorbed. We discuss the aspect of energy transitions and that different transitions within a chemical species have different probabilities of occurrence. I introduce the idea of selection rules and that it is appropriate to talk about the degree to which a transition is allowed. I also introduce the idea that there are some transitions that are not allowed or forbidden.

5. If you wanted to measure the concentration of a particular species in a sample, describe the procedure you would use to do so.

The groups' first response to this is often rather superficial. They tend to think more of putting the sample into a cuvette, measuring the absorbance and somehow equating that with concentration without explicitly stating that you first need to select a wavelength to use and prepare a standard curve.

Referring back to the spectra from the problem above that are still on the board, I point out that the analyst must set a wavelength.

Which wavelength would you choose?

They usually see right away that λ_{\max} is the preferable one and that with the highest molar absorptivity would provide the largest response. I also push them to examine how λ_{\max} would provide the lowest possible detection limits of any of the wavelengths.

Can you imagine a situation where you would not use λ_{\max} for the analysis?

Most groups quickly realize that you would need a different wavelength if the sample had another substance in it that absorbed at λ_{\max} .

Having selected the proper wavelength, how would you relate the absorbance of the sample with an unknown concentration to the actual concentration?

At this point, they realize the need to examine a sample with a known concentration and some students realize that they will need a standard curve with several concentrations whereas others may think only one known concentration is acceptable.

We can then discuss the concept of a blank solution and examine how a standard curve ought to be a linear plot that goes through the origin. We also examine how the slope of the standard curve can be used to determine the molar absorptivity.

6. Suppose a small amount of stray radiation (P_s) always leaked into your instrument and made it to your detector. This stray radiation would add to your measurements of P_o and P . Would this cause any deviations to Beer's law? Explain.

It is helpful to draw a picture on the board that shows a basic design of the spectrophotometer and indicates P_o , P and P_s .

Consider the situation of a sample with a high concentration and another sample with a low concentration of analyte, and think about the relative magnitudes of the different terms at these different conditions.

It can also be useful to indicate on the board the way in which the stray radiation gets incorporated into the expression for the absorbance [$A = \log(P_o + P_s)/(P + P_s)$], and to examine these terms at the extremes of high and low concentrations. At this point, the groups can usually rationalize that the $(P + P_s)$ term will approach P_s or a constant as the concentration of analyte is increased. When asked to draw the standard curve that would be observed, they can draw one that shows a negative deviation at higher concentrations.

7. The derivation of Beer's Law assumes that the molecules absorbing radiation don't interact with each other (remember that these molecules are dissolved in a solvent). If the analyte molecules interact with each other, they can alter their ability to absorb the radiation. Where would this assumption break down? Guess what this does to Beer's law?

Groups usually realize that the molecules are more likely to interact with each other at high concentration.

- 8. Beer's law also assumes purely monochromatic radiation. Describe an instrumental set up that would allow you to shine monochromatic radiation on your sample. Is it possible to get purely monochromatic radiation using your set up? Guess what this does to Beer's law.**

What is meant by "purely monochromatic radiation"?

We have not yet discussed the specific details of a monochromator, but based on earlier discussion related to selecting a λ_{max} value, they already know that some form of wavelength selection device is necessary. They are familiar with the ability of a prism to disperse radiation. I point out that gratings are more commonly used and that we will discuss gratings in more detail later in the course. With a drawing of a prism on the board, and prompted as to how they would direct only one wavelength on a sample, they realize that it will be necessary to use a slit that blocks out the unwanted wavelengths, but that the radiation passing through the device will never be purely monochromatic. At this point, without explaining it further, I indicate that polychromatic light will lead to negative deviations from Beer's Law, especially at higher concentrations.

- 9. Is there a disadvantage to reducing the slit width?**

What varies as one goes from a wide to a narrow slit width?

The groups realize that a wide slit width gives more power (and I point out how we will equate the number of photons with power) and a wider range of wavelengths, whereas a narrow slit width gives fewer photons and a smaller range of wavelengths.

Do you want high or low source power?

Based on our prior discussion of the effect of stray radiation they usually realize that higher power is desirable. This is also a useful time to further introduce the presence of noise and discuss how the signal-to-noise ratio is an important consideration in spectroscopic measurements. They realize that this argues for the use of wide slits.

Is there any situation where you would want to use a small slit width?

The groups can usually figure out that the ability to distinguish two nearby peaks is improved with smaller slit widths. This allows us to discuss what is meant by "resolution" in spectroscopic measurements.

Finally, we can examine Figure 1.5 to look at the effect of polychromatic radiation on the deviation from Beer's law. I also draw Figure 1.6 on the board and ask what wavelength they would use for the analysis and to justify why. They readily appreciate that the broader region is better for use because of the prior discussion about deviations to Beer's Law and because slight changes in the setting of the monochromator will have less significant effects on the measured absorbance.

10. Consider the relative error that would be observed for a sample as a function of the transmittance or absorbance. Is there a preferable region in which to measure the absorbance? What do you think about measuring absorbance values above 1?

Examine separately the extent of error that would occur at low and high concentration.

Groups can usually determine that the error at the extremes of concentration is more pronounced and there must be some mid-range absorbance measurements where the error is minimized.

Determine the percent transmittance that gives an absorbance value of 1 and consider the likelihood that negative deviations to Beer's law occur in this region?

They can figure out that an absorbance of 1 equals only 10% transmittance and realize that negative deviations are likely to occur, enhancing the error of the measurement and reducing the number of significant figures that could be measured. I also discuss with them whether it would ever be acceptable to use a non-linear standard curve.

It is ever acceptable to extrapolate a standard curve to higher concentrations?

They have enough understanding to determine that the possible onset of negative deviations to Beer's Law means that one cannot reliably extrapolate to higher concentrations.

11. What are some examples of matrix effects and what undesirable effect could each have that would compromise the absorbance measurement for a sample with an unknown concentration?

After describing to the class what is meant by a matrix effect, groups are given a few minutes to discuss this question and I have them report out on what they identified. In the aggregate the class is usually to arrive at important variables such as pH, the possibility that other species might absorb at λ_{\max} , and the possibility that another species interacting with the analyte could alter the value of λ_{\max} . Prompting may be required to have them consider scatter from suspended particulate matter and that the solvent may have an effect as well.

Are there any special constraints that must be considered in selecting a buffer?

They can usually identify that the buffer can't absorb at λ_{\max} .

Instrumental Setup of a Spectrophotometer

The following set of questions is given as an **out-of-class exercise**. There are two ways to consider having the students answer them. One is to provide the text that accompanies this unit and have the students read the text and answer the questions. The other is to send them to a resource such as the Analytical Sciences Digital Library or more broadly the internet, to see what they can come up with as answers to the questions. Having worked on the assignment, we then spend a class period developing the different topics covered by the questions in the assignment.

Notes are provided below for questions I ask in class to prompt their consideration and our discussion of the topics.

Sources

- 1. Describe the desirable features of a radiation source for a spectrophotometer.**
- 2. Plot the relative intensity of light emitted from an incandescent light bulb (y-axis) as a function of wavelength (x-axis). This plot is a classic observation known as blackbody radiation. On the same graph, show the output from a radiation source that operated at a hotter temperature.**

I find it desirable to explain something about the origin of blackbody radiation and Planck's explanation of blackbody radiation.

- 3. Examining the plots above, what does this suggest about the power that exists in radiation sources for the infrared portion of the spectrum?**
- 4. Explain the advantages of a dual- versus single-beam spectrophotometer.**

Lasers

- 5. Why is it impossible to create a 2-level laser?**

Whether or not the students have read the textbook or found other sources, the concept of the population of energy states, a saturated transition and a population inversion are usually quite new and foreign to them. I find that it is necessary to take time to explain each of these terms, as well as the process of stimulated emission. Understanding absorption and stimulated emission, the students can then examine and explain why it is impossible to create a 2-level laser.

- 6. Using your understanding of a 2-level system, explain what is meant by a 3-level and 4-level system. 3- and 4-level systems can function as a laser. How is it possible to achieve a population inversion in a 3- and 4-level system?**

It is helpful to discuss the concept of excited state lifetimes and ask the students to consider the relative lifetimes needed to create a 3- and 4-level laser.

- 7. Which of the two (3- or 4-level system) is generally preferred in a laser and why?**

Having considered the 2- and 3-level systems and the corresponding populations, the students can usually explain why a 4-level laser is preferable.

Monochromators

- 8. Explain in general terms the mechanism in a prism and grating that leads to the attainment of monochromatic radiation. Compare the advantages and disadvantages of each type of device. What is meant by second order radiation in a grating? Describe the difference between a grating that would be useful for the infrared region of the spectrum and one that would be useful for the ultraviolet region of the spectrum.**

- 9. Explain the significance of the slit width of a monochromator. What is the advantage(s) of making the slit width smaller? What is the disadvantage(s) of making the slit width smaller?**

This has already been discussed in class.

Detectors

- 10. Explain how a photomultiplier tube works. What are any advantages or disadvantages of a photomultiplier tube?**

- 11. Describe a photodiode array detector. What advantages does it offer over other detection devices?**

Ultraviolet/Visible Absorption Spectroscopy

Given the background we have already developed on spectroscopy, I give them this set of in-class questions without providing any further background on UV/VIS absorption spectroscopy.

General aspects of UV/VIS absorption spectra

- 1. Compare and contrast the absorption of ultraviolet (UV) and visible (VIS) radiation by an atomic substance (something like helium) with that of a molecular substance (something like ethylene).**
- 2. Do you expect different absorption peaks or bands from an atomic or molecular substance to have different intensities? If so, what does this say about the transitions?**

The background for answering these two questions has usually come up earlier in the course when the students were asked to draw a spectrum because some students think of atomic spectra and others think of molecular spectra. Also, the discussion of molar absorptivity introduced the concept of the probability of transitions explaining the difference in intensities.

Why do atomic spectra consist of discrete lines whereas molecular spectra are broadened and continuous in nature? Are there processes that can occur in molecules that cannot occur in atoms?

With these two prompts, the groups can usually figure out that atoms only undergo electronic excitation whereas molecules can also be vibrationally and rotationally excited. They also know that vibrations are excited in the IR and, from our discussion very early in the class, that rotations are excited in the microwave region. In addition they know that the IR and microwave region of the spectrum is lower in energy than the UV/Vis region of the spectrum. This allows us to draw a diagram similar to Figure 2.4 from the accompanying text showing how the molecule will have many more closely spaced transitions than an atom that lead to the continuous nature of the absorbance spectrum.

- 3. Compare a molecular absorption spectrum of a dilute species dissolved in a solvent at room temperature versus the same sample at 10K.**

What would happen to the sample at a temperature of 10K?

The students quickly realize that it will freeze to a solid. It will also help to point out that the freezing of many solvents will produce a transparent glassy material that UV/VIS radiation readily passes through so that it is possible to obtain an absorption spectrum on a frozen sample. I briefly describe the use of molecular beam apparatus as another way to obtain species at ultracold temperatures.

What takes place in a liquid sample that does not occur in a solid sample?

The groups come up with the realization that the molecules in the liquid sample are moving around and colliding with each other.

What happens when molecules collide with each other?

It may help to remind them that molecules consist of nuclei surrounded by electron “clouds”. They can also reason out that the electron clouds become distorted because of the collisions.

What effect would the distortion of the electron clouds have on the energy of the electrons? Do different molecules collide with different degrees of force?

With these prompts, they come to realize that the collisions of molecules leads to a broadening of the spectrum because the energies of a specific transition is slightly different in different molecules. That allows them to understand the rationale for the spectra observed in Figure 2.5.

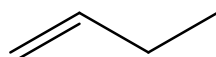
4. Are there any other general processes that contribute to broadening in an absorption spectrum?

They are usually stumped by this question.

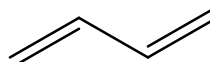
Have you ever heard of the Doppler effect and, if so, what do you know about it?

Some of them have heard of the Doppler Effect in physics or astronomy courses, and we discuss its significance to broadening in spectroscopic measurements.

5. Compare the UV absorption spectrum of 1-butene to 1,3-butadiene.



1-butene



1,3-butadiene

Consider the molecular orbitals involved in 1-butene and to draw an energy level diagram that shows the relative energies of the orbitals.

From organic chemistry, they know that σ - and π -orbitals are involved, and they usually know the relative order in which to put them. This enables a brief discussion of the HOMO and LUMO and the lowest energy transition (π - π^*) for the molecule, which is the important one to consider in answering the question. They also know from organic chemistry that 1,3-butadiene is a conjugated compound. At this point, I direct them to the next question.

6. Using representations of the p-orbitals in which the dark color indicates the positive region of the wave function and a light color indicates the negative region of the wave function, draw all of the possible ways in which the wave functions of the two p-orbitals in 1-butene and four p-orbitals in 1,3-butadiene can overlap with each other.

Rank these from high to low energy.

They have some experience with this from organic chemistry and are able to draw pictures like those in Figures 2.8, 2.12 and 2.13. They also can usually rank them from low to high energy, and determine which ones are filled with electrons and which ones are empty.

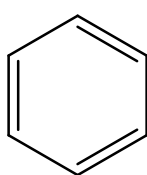
Compare the energy of the HOMO to LUMO.

They can usually see that it will be lower in 1,3-butadiene than in 1-butene (Figures 2.9 versus 2.14). I then show them the spectra in Figures 2.10 and 2.15.

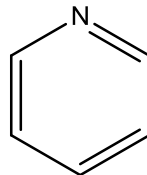
What would happen to the HOMO to LUMO transition in the absorbance spectra for the series of fused ring polycyclic aromatic compounds benzene, naphthalene, anthracene and pentacene?

They reason that the energy of the HOMO to LUMO transition ought to move toward the red as more rings are added to the compound. I then show them the spectra in Figure 2.16.

7. Compare the UV absorption spectrum of benzene and pyridine.



benzene



pyridine

What distinguishes pyridine from benzene?

They quickly realize that the nitrogen atom in pyridine has a lone pair of electrons, and I introduce the idea that from a spectroscopic and energy level standpoint, we think of these as non-bonding electrons.

Draw representative energy level diagrams for benzene and pyridine, show which orbitals are filled, and to compare the energy of the HOMO to LUMO transition for the two compounds. Most are able to reason that the non-bonding electrons ought to go between the π and π^* orbitals and that the lowest energy transition of pyridine ought to be red-shifted relative to that of benzene. I then show them the two spectra in Figures 2.18 and 2.20 to confirm their conclusion.

8. The peaks in the 320-380 nm portion of the UV absorption spectrum of pyridine shifts noticeably toward the blue (high energy) portion of the spectrum on changing the solvent from hexane (C_6H_{14}) to methanol (CH_3OH). Account for this change.

What would occur with pyridine that is different in the two solvents?

Groups have the background to know that methanol will form a hydrogen bond with the nitrogen atom of the pyridine.

What would this do to the energy of the non-bonding electrons?

Usually they are able to determine that it would stabilize them and lower their energy.

Would potential hydrogen bonding by methanol have any effect on electrons in the π or π^ orbitals of the pyridine (pointing out that when a molecule of pyridine absorbs radiation, it promotes an electron to the π^* orbital)?*

They often seem to think that association of the slightly positive hydrogen atom of methanol would have more of a stabilizing effect on the π -electrons rather than the π^* electrons.

Draw the locations of these orbitals in the molecule and which is more exterior and exposed to the solvent?

With this prompt, they realize that an electron in the π^* -orbital extends out further and shows more stabilization than the π -electrons. They also realize that the stabilization of the non-bonding electrons will be much greater than the other orbitals, thereby allowing them to explain the blue shift.

9. The peaks in the UV spectrum of benzene shift slightly toward the red (low energy) portion of the spectrum on changing the solvent from hexane (C₆H₁₄) to methanol (CH₃OH). Account for this change.

Based on the information developed in answering the previous question, it is relatively straightforward for the students to explain the observation in this situation.

UV/VIS spectroscopy as a qualitative and quantitative tool

I first remind them what we mean by a qualitative and quantitative tool before giving them the following question.

1. Is UV/VIS spectroscopy useful as a qualitative tool?

Consider the general features of a UV/VIS absorption spectrum for organic compounds. Is this sufficient to identify an unknown compound?

We also explore whether a match in the UV/VIS spectrum might be used to confirm the identity of an unknown if the person has an idea what its identity might be. We also explore that many transition metal species have more distinct absorption spectra that can be used to confirm the identity of a species.

2. Is UV/VIS spectroscopy useful as a quantitative tool?

Consider things like the power of UV/VIS sources, the sensitivity of detectors, the magnitude of extinction coefficients, and given a certain extinction coefficient (e.g., 5,000) with a certain minimal reading for absorbance (e.g., 0.01), what would be the minimal concentration that could be measured?

With that, they see that UV/VIS spectroscopy is a useful quantitative tool.

3. If you were using UV spectroscopy for quantitative analysis, what criteria would you use in selecting a wavelength for the analysis?

This was covered earlier but serves as a review that λ_{max} is preferable provided there are no interferences in the sample.

4. What variables influence the recording of UV/VIS absorption spectra and need to be accounted for when performing qualitative and quantitative analyses?

Some of these have been covered as well during the discussion of solvent effects. The students can usually think of things like solvent effects and pH as possible variables may alter the value of λ_{max} .

Are there inorganic species that might be in the sample? If so, what effect would they have?

These questions are sufficient to get them to think about the potential impact of metal ions in a sample.

5. Provided the UV/VIS absorption spectra of HA and A⁻ differ from each other, describe a method that you could use to measure the pK_a of the acid.

It will be necessary to set this up by writing the appropriate reaction and discussing the time scale of the reaction relative to the time scale of absorption of a photon. With the understanding that the reaction is slow relative to the process of absorption, students can appreciate that a

species is either in the HA or A^- form during absorption. It also helps to examine the possible resonance forms for a carboxylate ion (RCO_2^-) versus its corresponding carboxylic acid (RCO_2H) to have the students appreciate that the absorption spectra of the two species are likely to be different. At this point, there are usually some students in the class who remember the Henderson-Hasselbalch equation. If not, I ask them:

Do you remember an equation in acid-base chemistry that had an HA and A^- species in it?

With the equation in hand, they sometimes can figure out that they would need to examine a solution that was strongly acidic and another that was strongly basic to determine the extinction coefficients for HA and A^- respectively. If not, I ask them:

How could you prepare a solution with essentially all HA and then one with essentially all A^- ?

By this point they usually recognize that buffered solutions at intermediate pH will give some of both and with the known pH and measured concentrations, they can use the Henderson-Hasselbalch equation to calculate the pKa.

I save a discussion of the relative value of λ_{max} for the HA and A^- form for our unit on fluorescence, but it could be done at this time as well.

Molecular Luminescence

I provide a very brief introduction on the meaning of luminescence and indicate that the process of fluorescence – a subcategory of luminescence – involves emission of radiation from a species that has first been excited by light, the details of which we will develop through a series of questions. I also describe how a fluorescent light works.

Energy level diagrams for organic molecules

- 1. Draw an energy level diagram for a typical organic compound with π and π^* orbitals and indicate which orbitals are filled and which are empty.**

Given our prior discussion of UV/VIS absorption, groups can immediately write the answer to this question.

- 2. Now consider the electron spin possibilities for the ground and excited state. Are there different possible ways to orient the spins (if so, these represent different spin states).**

The groups can usually see that there is only one way to write the ground state. They often see that in the excited state it is possible to have the spins of the electrons paired or parallel. It is worth indicating that for the situation where the excited state has paired spins, it does not matter which one is spin-up and spin-down as these are identical so long as the spins are paired.

- 3. Do you think these different spin states have different energies?**

Many students just make the intuitive guess that they do have different energies, although they really may not yet understand why this is.

- 4. Which one do you expect to be lower in energy?**

I generally find that students get this wrong and think that the excited state with the spins paired would have the lower energy. Even if they think the state with the parallel spins is lower, they rarely if ever provide the proper justification for this answer. I point out that they actually learned something in general chemistry while doing atomic structure that would allow them to answer this question and justify their answer. If this doesn't lead them to the proper answer, I direct them to consider the following:

Think back to atomic structure and remember what happened when two electrons were put into a set of p-orbitals.

They do remember that the electrons go into separate orbitals with parallel spins. We can then discuss why this was the case – it takes energy to pair electrons, therefore parallel spins in degenerate orbitals will be the lower energy of the two possibilities.

Do you think the energy state with parallel spins in non-degenerate π and π^ orbitals will be lower in energy than paired spins?*

At this point they decide that the state with the parallel spins will be lower in energy.

5. If the spin state is defined as $(2S + 1)$ where S represents the total electronic spin for the system, try to come up with names for the ground and possible excited states for the system that are based on their spin state.

They may need to be reminded about the values of electron spin quantum numbers. Recognizing that the ground state and excited state with pair spins have an S of zero and a spin state of one is obvious to them. I point out that they only need to use $+1/2$ for the electron spins for the case where both have parallel spins and they arrive at the number three for the spin state. With those numbers, they usually can come up with the name singlet and triplet or something close to that to distinguish the two states.

6. Draw a diagram of the energy levels for such a molecule. Draw arrows for the possible transitions that could occur for the molecule.

With the knowledge from the previous section of the course on UV-Vis absorption spectroscopy, the students are usually able to draw a reasonable first approximation for the energy level diagram needed to discuss fluorescence. They know about the first and second excited states, and that there are vibrational and rotational levels superimposed on each. They can usually locate the first excited triplet state, and I usually point out that we often write this off to the right side of the first excited singlet state to make the diagram a bit clearer.

As they start to put transitions onto the diagram, they are usually quick to realize there will be absorption into the excited singlet states because that was discussed earlier in the unit on UV-Vis spectroscopy. If not, I may prompt them to show possible absorption transitions on their diagram. They also usually draw an absorption transition to the T_1 state, and I point out to them that absorption transitions that involve a spin flip are forbidden by selection rules (if the idea of selection rules has not been discussed yet in the course, this is a good time to discuss that or remind them how selection rules were important in determining something like the molar absorptivity).

Now that the electron is excited, what are its various options for getting back to the ground state?

They can usually determine that the excited species can either lose the extra energy as heat (I indicate that this is something we can denote on the figure with a squiggly line) or lose it as radiation (I indicate that this is something we can denote on the figure with a solid line). We can then illustrate both transitions for a system in the S_1 state and I indicate that the loss of energy as heat is referred to as radiationless decay and the loss of energy as radiation is referred to as fluorescence. I remind them that fluorescence specifically refers to a system that has been excited by absorbing light (as distinct from being excited by absorbing heat), and that the emission of light must be a transition that goes from one singlet state to another.

What process would promote radiationless decay?

They can usually reason out that collisions of the excited molecule with surrounding compounds in the matrix will promote radiationless decay.

What can happen to an electron excited into the S_2 state (or higher vibrational level within the S_2 state)?

They usually think it is possible to have both radiationless decay and fluorescence, and I indicate that only on a few rare occasions have people discovered molecules that fluoresce from the S_2 state.

At this point, it is useful to mention that it is important to consider the lifetimes of the different states.

Can you guess the lifetime of an electron in a first excited singlet state, second excited singlet state, and vibrational state?

They usually propose that the lifetime of the second excited singlet state is probably less than that of the first excited singlet state. I then have them take guesses and play a game of warmer and colder as we hone in on the values. With the lifetimes now at their disposal, they can appreciate why systems excited to higher energy states than the S_1 state will quickly undergo radiationless decay.

It is now necessary to discuss the process of internal conversion that allows systems in the S_2 state to convert into the S_1 state and to indicate these on the diagram.

Is there only one possible fluorescence transition from S_1 ?

Since they are already familiar with the fact that molecules can be excited into higher vibrational levels of electronic states, they usually reason out that molecules can perhaps undergo fluorescent transitions into higher energy vibrational states of S_0 . We then discuss how fluorescence from a molecule can have a variety of different wavelengths. Also that there will be different probabilities for each of the fluorescent transitions and that the S_1 - S_0 may or may not be the most probable one.

At this point we have Figure 3.4 from the text complete except for a consideration of the T_1 level.

Would it be possible for a molecule to undergo a transition from S_1 to T_1 ?

They remember that we just said transitions that involved spin flips are forbidden, but they usually suspect an S_1 to T_1 transition can happen because we have just spent so much time developing the idea of the triplet state. We then discuss what may account for the intersystem crossing process to occur. We also discuss how the transition can occur into an upper vibrational level of T_1 and then undergoes radiationless decay into the T_1 state.

7. What do you expect for the lifetime of an electron in the T_1 state?

They usually realize that the only way for the electron to get out of the T_1 state is to first undergo a spin-flip, and this will take some time. We play another guessing game of warmer-colder to get the range of lifetimes of systems in the T_1 state.

When prompted they usually think the only possible route to lose the extra energy is through an intersystem crossing back into a higher vibrational level of S_0 followed by radiationless decay. But I also indicate that even though emission of a photon from T_1 to S_0 is “forbidden”, in some

systems it actually happens, and we call this phosphorescence. I point out examples of where they have seen phosphorescence (glow in the dark substances, their TV screen for a few seconds after they turn it off).

8. Why is phosphorescence emission weak in most substances?

They can usually rationalize out that, in most compounds, intersystem crossing is weak to begin with (I use this as an occasion to point out the fact that processes like radiationless decay, fluorescence, and intersystem crossing are all in competition with each other), which is one reason for the weak intensity of phosphorescence. Similarly, they can usually reason out that the long time the system spends in the T1 state means more collisions will occur.

What could you do to a sample to enhance the likelihood that phosphorescence would occur over radiationless decay?

Usually someone in each group can come up with the idea of freezing the sample into a solid to reduce the number of collisions.

9. Which transition (π^* - π or π^* -n) would have a higher fluorescent intensity? Justify your answer.

Think back to our unit on UV-Vis spectroscopy – we discussed at least one important reason that will help answer this question.

Some of the students usually remember that the molar absorptivity for n- π^* transitions is lower than that for π - π^* transitions so that there will be fewer excited molecules and fewer to undergo fluorescence.

I then tell them that the lifetime of the n- π^ excited state is longer than that of the π - π^* excited state, and ask how this will influence fluorescence intensity.*

With that information, they realize that there will be more collisional decay for the molecule in the n- π^* state and therefore lower fluorescence.

Instrumental considerations for luminescence measurements

1. What would constitute the basic instrumental design of a fluorescence spectrophotometer?

The students think of things like a light source, monochromator, sample holder and detector. They rarely seem to be able to think it through to the point of realizing that fluorescence spectrophotometers will need two monochromators, one for the excitation beam and one for the emitted light. I almost always have to remind them of the process – radiation is used to excite the molecule, light is emitted by the molecule – before someone realizes that there are two sources of light to consider and they will need a monochromator for each.

Where would you position the emission monochromator relative to the excitation monochromator?

Some of them realize that the molecules will emit the light in all directions such that the emission monochromator can be placed somewhere else besides at 180° to the excitation monochromator.

Would a 90° placement have any advantage over a 180° placement?

The groups can usually determine that the 180° placement is less favorable since the source light will strike the detector and that at 90° only the fluorescence will be measured.

2. What would be the difference between an excitation and emission spectrum in fluorescence spectroscopy?

They can usually figure out that one involves scanning the excitation and the other the emission monochromator. However, I often need to point out that when scanning the emission monochromator, the excitation monochromator needs to be set to a known excitation wavelength, and when running an excitation spectrum, the emission monochromator needs to be set to a known emitting wavelength.

3. Draw representative examples of the excitation and emission spectrum for a molecule.

The students are usually stumped by this question and I need to provide some prompts to get them to think it through. The first is to redraw the energy level diagram on the board showing the possible absorption and fluorescent transitions. The second is to draw two sets of axes on the board, one on top of the other, where the y-axis is fluorescent intensity and the x-axis is wavelength. I indicate that the wavelength scale on the two axes is identical and ask them to draw this diagram in their notes.

Draw the excitation spectrum on the top.

After all groups have a satisfactory representation of an excitation spectrum, I then instruct them to:

Draw the emission spectrum on the bottom set of axes.

Some of the students finally realize that the two spectra will be mostly offset from each other except for the S_0 - S_1 transition. If not, I may prompt them by asking:

Are there any transitions that have exactly the same energy in the excitation and emission spectrum?

Once both are on the board and understood, I ask them which one most resembles an absorption spectrum and they immediately realize it is the excitation spectrum.

4. Describe a way to measure the phosphorescence spectrum of a species that is not compromised by the presence of any fluorescence emission.

They are usually perplexed by this problem, often remembering back that phosphorescence occurs from solids, but now knowing whether that is useful. Also, they want to think of a way to promote intersystem crossing to get all of the excited-state molecules into the T_1 state so that no fluorescence occurs.

Can they remember any significant differences that exist between the S_1 and T_1 energy states?

Someone usually brings up the difference in lifetimes of the excited states, which leads them to ask whether there is some way to excite the compound, turn off or block the excitation source, and then build a delay into the measurement of the emission. I then discuss the idea of using a pulsed source, and the concepts of having a delay and gate time.

5. If performing quantitative analysis in fluorescence spectroscopy, which wavelengths would you select from the spectra you drew in the problem above?

Because we have discussed wavelength selection in UV-Vis spectroscopy, they usually know to select the λ_{\max} for both the excitation and emission spectrum.

Can they think of any problem with setting both the excitation and emission monochromator to the S_0 - S_1 transition?

Some are able to think of the possibility of scattering taking place. We then discuss how scatter will occur in all directions and be indistinguishable from fluorescence.

6. Which method is more sensitive, absorption or fluorescence spectroscopy?

Before giving them this question, I do a brief lecture on the meaning of a quantum yield. I define the meaning of the term (ratio of the number that fluoresce relative to the number that were excited).

Identify all of all the processes that compete against fluorescence from the S_1 state.

With this decided, we then write the expression for the quantum yield using the rate constants for the different processes. We then examine how the fluorescent quantum yield will range from 0-1 and that it will be rare for a molecule to have a quantum yield of 1. I indicate that molecules with fluorescent quantum yields of 0.01 or higher are useful for analysis by fluorescence spectroscopy.

I then provide them with the question about relative sensitivity of absorption and fluorescence spectroscopy and provide the following additional prompt:

Think about the instrumental setup that is used for absorption and fluorescence measurements and consider exactly what is measured or compared. Also think about each technique when a very low concentration sample is being measured.

At this point, they are able to reason that the values of P_0 and P in absorption spectrophotometry will be quite close in magnitude whereas the fluorescence measurement is just a small signal.

I now ask them to consider an observation with their own eyes where they would examine the difference in intensity between a 99- and 100-Watt light bulb (comparable to absorption spectrophotometry) compared to the difference between a 1-Watt light bulb and darkness.

Which difference would be easier to detect?

They immediately say it would be easier to distinguish the 1-Watt bulb over darkness than the difference between a 99- and 100-Watt bulb. We then discuss how electronic devices can also distinguish this better and fluorescence (or any emission method) has an inherent sensitivity advantage over an absorption method.

Variables that influence fluorescence measurements

1. What variables influence fluorescence measurements? For each variable, describe its relationship to the intensity of fluorescence emission.

I often preface this question by suggesting that the students think back to things we already considered in our unit on UV/Vis absorption spectroscopy. Students come up with the obvious

one of concentration, and usually realize that the path length and molar absorptivity will influence this as well. Some even realize that the source power is important in fluorescence as well. This then allows us to write the equation for fluorescence intensity.

What would the curve look like at high concentration?

Recognizing the negative deviation that occurred in Beer's law, they usually realize that a negative deviation would be expected as well in fluorescence spectroscopy. I then introduce the idea of self-absorption that can occur at high concentrations in emission methods.

What would you do with a sample to insure that it was not at a concentration range where self-absorption was occurring?

They almost immediately recommend diluting the sample.

Are there other variables that influence the magnitude of the quenching?

The importance of collisions and its contribution to radiationless decay has been discussed earlier so some realize that this is likely an issue. Most then realize that temperature is an important variable and can determine that higher temperatures should reduce fluorescent intensity.

Many also suggest that solvent is a variable, and we revisit some of the discussion we had in UV/Vis spectroscopy on the effect of solvent on λ_{max} for π - π^* and n - π^* transitions. Many also suggest that pH is a variable.

I then explain how paramagnetic substances promote intersystem crossing.

Can you think of any important paramagnetic substances that might be present in a sample?

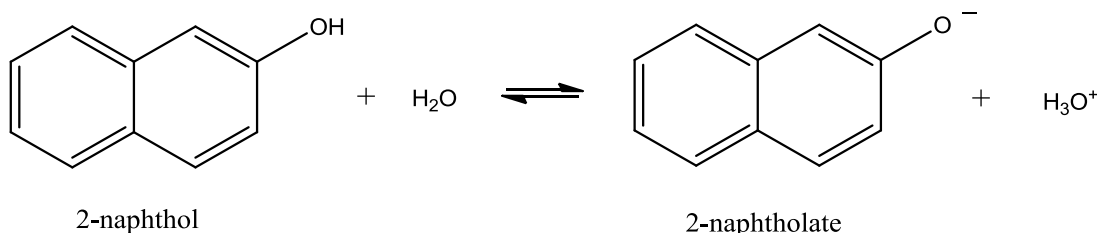
Usually each group has someone who identifies paramagnetic metal ions and dissolved oxygen as possibilities.

Can you think of a way to eliminate dissolved oxygen from a sample?

Some are familiar with using an ultrasonicator to degas a solution and sometimes a student even comes up with the idea of purging the solution with a gas that is not paramagnetic.

We discuss how removing paramagnetic metal ions from a sample is a more difficult problem.

2. Consider the reaction shown below for the dissociation of 2-naphthol. This reaction may be either slow (slow exchange) or fast (fast exchange) on the time scale of fluorescence spectroscopy. Draw the series of spectra that would result for an initial concentration of 2-naphthol of 10^{-6} M if the pH was adjusted to 2, 8.5, 9.5, 10.5, and 13 and slow exchange occurred. Draw the spectra at the same pH when the exchange rate is fast.



This is a complex question with several parts to it, although we did cover some background for this in the unit on UV/Vis spectroscopy. If they have forgotten this, I prompt them to focus on the two extremes and ask them first to describe where the reaction lies at a pH of 2. The groups realize this will be virtually all of the protonated form. I then ask them to describe where the reaction lies at a pH of 13 and they realize it will be virtually all of the deprotonated form.

Do you expect any difference in the emission spectrum of the two species in these two forms, and if so, what might the difference be?

Intuitively, they expect the two forms to have a different emission spectrum – if not, why are we even talking about this problem! After given them a bit of time to talk about it in their groups and hearing some of the things they are thinking about – rarely do they come up with something that is the actual explanation for why the deprotonated form will fluoresce at a longer wavelength than the protonated form

Draw the resonance forms for the two species.

Some are rusty at this but others quickly realize and explain to their group members that the naphtholate ion will have more resonance forms than the naphthol species.

What does the presence of more resonance forms do to the energy of the excited state?

Some propose that it may lower the energy of the excited state and therefore the energy gap such that the transition shifts toward the red.

At this point, we can draw spectra for the two extremes.

Consider the point where the pH equals the pKa, and think about the difference that would be observed between fast and slow exchange.

Usually the groups can reason out what would occur for the two different situations and we can fully draw and discuss the spectra represented in Figure 3.11 of the text.

Which to you think actually happens – fast or slow exchange?

I prompt them to think back about UV/Vis spectroscopy and lifetimes of states as well. Groups arrive at the conclusion that slow exchange is likely to occur on the time scale of fluorescence spectroscopy.

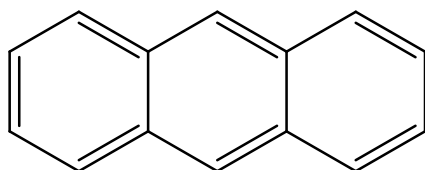
Questions always arise about whether the two species would have the same intensity or not and we have some discussion about that question.

3. Devise a procedure that might allow you to determine the pKa of a weak acid such as 2-naphthol.

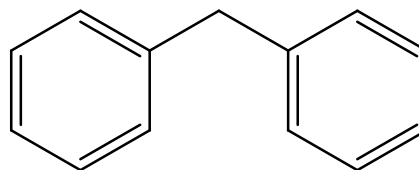
We have examined a similar question in UV/Vis spectroscopy so the students usually hone in on the procedure that would be done.

I then use this as an opportunity to talk about the complication that arises if this experiment is actually performed using fluorescence spectroscopy – namely that the calculated pKa values at each pH will be different because the pKa value of the excited state of the compound is different than the pKa value of the ground state.

4. Which compound will have a higher quantum yield: anthracene or diphenylmethane?



anthracene



diphenylmethane

Students usually want to answer this question by considering the relative extent of conjugation of the system rather than the role of collisional deactivation for the two compounds.

Would collisional deactivation be different for the two molecules?

Not all the students will immediately realize that anthracene will exhibit less collisional deactivation than diphenylmethane (they might propose that since it's bigger, they will collide into each other with more force – if they give this response, it is important to remind them that most of the collisions actually occur with solvent).

Which would come out worse in a collision – a Greyhound bus or a car towing a boat on a trailer?

They usually realize that the collisions with diphenylmethane will lead to more radiationless decay than those with anthracene.

I then discuss how relatively few compounds exhibit intense fluorescence – that fluorescence spectroscopy is far more selective than UV/Vis absorption spectroscopy – and that derivatization of compounds with fluorescent chromophores is sometimes done for the analysis because of the enhanced sensitivity of fluorescence.

Finally, I present to them a brief discussion of topics like chemiluminescence, bioluminescence and triboluminescence. We also talk briefly about the process that takes place in glow sticks.

Infrared Spectroscopy

I do not cover the types of IR spectroscopy included in a typical sophomore-level organic chemistry course, but instead focus on specialized applications and Fourier transform IR spectroscopy.

Background information

1. Can infrared spectra be recorded in air? If so, what does this say about the major constituents of air?

Consider the instrument you used in organic chemistry to record IR spectra – did you try to exclude air from the sample chamber or path of the light beam?

They realize that they did not.

What are the major constituents of air?

They realize they are nitrogen and oxygen gas.

2. Why don't the major constituents of air absorb infrared radiation? It might be worth noting that a molecule such as hydrogen chloride (HCl) does absorb infrared light.

They realize that this must have something to do with the fact that oxygen and nitrogen gas are symmetric molecules and hydrogen chloride is not. I then explain that the selection rule for an infrared-absorbing vibration involves a change in the overall molecular dipole.

3. Describe the vibrations of carbon dioxide (CO₂) and determine which ones absorb infrared radiation.

I go over with them the concept of degrees of freedom and we identify that carbon dioxide has four vibrations. The groups can readily identify the symmetric stretch, asymmetric stretch and bending vibration (I point out how there are two degenerate bending vibrations in two different planes).

Which bond dipole is larger, the one with a shorter C=O bond length or the one with a longer C=O bond length?

If they get this wrong or are not sure, I ask them the following:

What happens if you take this to the limit and actually break the bond, what would happen to any charges or dipoles?

They can usually reason out that they would have neutral atoms with no charge difference, and then realize that the longer the bond, the smaller the bond dipole.

With this, they can determine which ones will involve a change in molecular dipole.

Specialized techniques

- 4. One technique is called non-dispersive infrared (NDIR) spectroscopy. NDIR is usually used to measure a single constituent of an air sample. Think what the name implies and consider how such an instrument might be designed.**

They are quite stumped by this.

What does non-dispersive mean?

The groups can eventually get to the point that it means that the instrument has no monochromator. I also indicate that a common application of NDIR would be in the analysis of carbon monoxide gas in things like car exhaust or a coal mine.

How many active vibrations does CO have?

They can determine that CO only has one stretching vibration and that somehow, without the use of a monochromator, we want to design an instrument that will measure only CO in the presence of other chemicals.

After giving them a few minutes to discuss this, I might have to indicate that the concept of splitting the IR beam into a sample and reference cell as a possibility. Some then suggest filling the reference cell with CO to absorb all of the light that CO can absorb, but then they are still stumped about how to actually compare the intensity of the two beams.

What ultimately happens to the radiant energy absorbed by the CO in a closed chamber?

They can usually reason out that it will eventually get converted to heat.

As this point, I then show them a diagram of an NDIR and explain how it works.

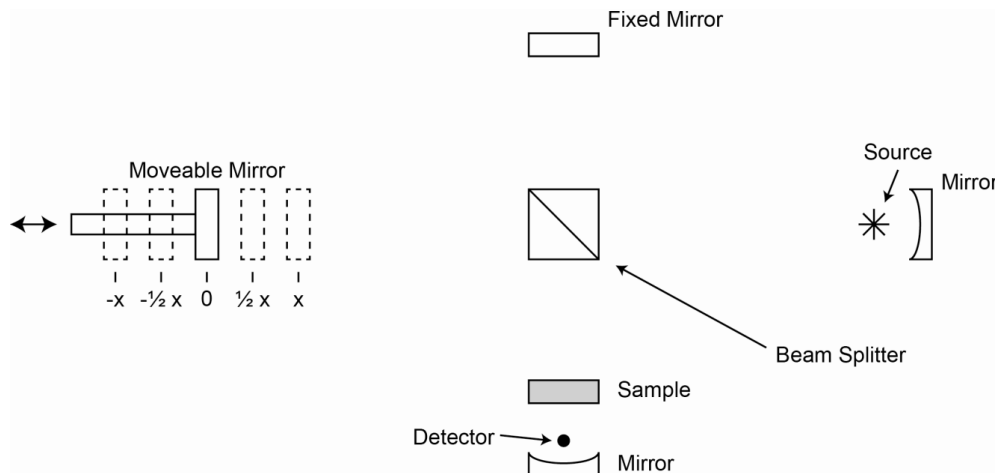
I also show them the procedure of attenuated total reflectance spectroscopy.

What is the purpose of having multiple reflections of the beam of light as it moves through the crystal?

They can usually reason out that it done that way to increase the path length which then increases the magnitude of the absorption.

Fourier-transform Infrared Spectroscopy

5. Consider the light path for a Michelson interferometer and plot the intensity of radiation at the sample versus the position of the moveable mirror for monochromatic radiation of wavelength x , $2x$ or $4x$.



Since this is our first introduction to Fourier transform methods, I first explain the difference between frequency and time domain spectra.

I then explain the design of the instrument and path of the light beam through the Michelson interferometer.

Plot the intensity as a function of wavelength and mirror movement.

When the groups work on the intensity, some students do not realize at first that, when the moveable mirror is displaced by some amount (e.g., $-1/2x$) that the light traveling to it goes an extra distance of x .

With their drawings completed, we can examine how different wavelengths (or frequencies) of light have a different time domain to their behavior and how this can be used to generate a spectrum. We also discuss the importance of knowing exactly where the zero point of the mirror is and of the need for reproducible movement of the mirror.

6. What are the advantages of FT-IR spectrophotometers over conventional IR spectrophotometers that use a monochromator?

What are typical things we ask about an analytical method?

They can identify things like sensitivity, resolution and ease of use. I also ask them to think about specific differences in the instrumental design as they might affect things like sensitivity and resolution. This facilitates discussion of the various advantages of FT-IR over conventional IR spectrophotometers that use a monochromator.

Raman Spectroscopy

I begin this section by indicating that Raman spectroscopy is a way to probe vibrations of molecules. I also describe that, whereas IR spectroscopy could probe vibrations that caused a change in the overall molecular dipole, Raman spectroscopy probes vibrations where a change in the polarizability of the molecule occurs.

What does polarizability mean? How do things like bond strength and bond length affect the polarizability?

From prior experience, the groups can usually determine the correct answers.

Before getting into virtual states and the use of visible light, I give them the next question.

1. Consider the molecular vibrations of carbon dioxide and determine whether or not they are Raman active.

We have already examined carbon dioxide in the unit on IR spectroscopy so they already know the vibrations.

Consider each bond in a particular vibration and determine whether the polarizability of that bond decreases, increases or stays the same for the symmetric and asymmetric stretches.

They can usually reason through the changes in polarizability of the bonds as you lengthen or shorten them in the symmetrical and asymmetrical stretches.

Considering what happens for each bond, are the symmetrical and asymmetrical stretch Raman active?

They can usually reason out that the symmetric stretch will be Raman active but that the effects in the asymmetric stretch cancel each other out such that it is Raman inactive.

Does the polarizability of each bond change in the bending vibration?

They usually realize that it won't change and can rationalize that the bending vibration is Raman inactive.

Compare the activity of the vibrations in the IR and Raman mode.

They reflect back and see that they are completely complementary – those that are IR active are Raman inactive and vice versa.

I then explain that the technique will use a visible light source and explain the idea of a virtual state. I also describe the processes that lead to the origin of Stokes and anti-Stokes lines.

2. Which set of lines, Stokes or anti-Stokes, is weaker?

We have talked often enough earlier in the course about the populations of energy levels so the groups tend to readily appreciate that the anti-Stokes lines will be weaker.

3. What effect would raising the temperature have on the intensity of Stokes and anti-Stokes lines?

They can rationalize out that increasing the temperature raises the population of vibrationally excited molecules such that the intensity of the anti-Stokes lines will increase.

4. What would be the ideal source to use for measuring Raman spectra?

What general criteria have been important in all spectroscopic measurements?

They can usually come up with resolution and sensitivity. I remind them that Raman scatter is a weak process. They realize that a high powered laser will provide better sensitivity than a continuum source.

Is a laser better than a continuum source when trying to measure the frequency of the Raman bands?

They already know that lasers are highly monochromatic and realize that this is another reason to use a laser.

5. The molecule carbon tetrachloride (CCl_4) has three Raman-active absorptions that occur at 218, 314 and 459 cm^{-1} away from the laser line. Draw a representation of the Raman spectrum of CCl_4 that includes both the Stokes and anti-Stokes lines.

I first point out that there will be Rayleigh scatter at the laser line and draw a representation of the Rayleigh line in the spectrum. I also indicate the higher and lower energy side of the spectrum relative to the Rayleigh line.

Draw the placement of the Stokes and anti-Stokes lines of CCl_4 .

I remind them to look back at the energy level diagram as they think through where to place each specific line. Usually they can rationalize out within their group that the placement of the Stokes and anti-Stokes lines from the Rayleigh scatter ought to be mirror images of each other.

6. Why do the anti-Stokes lines of carbon tetrachloride have the following order of intensity: 218 > 314 > 459 cm^{-1} ?

I suggest that they consider the energy level diagram and think about the transitions that correspond to each of these. They can rationalize that the line for the 218 cm^{-1} band originates by forming a virtual state from the most populated vibrational level and the band for 459 cm^{-1} from the least populated vibrational level, which explains the relative intensities.

Atomic Spectroscopy

I use a lecture format to introduce general background information and aspects of flame and furnace atomization that are discussed on pages 79-83 of the text before asking them the following question.

1. What are the relative advantages and disadvantages of using a flame or furnace as an atomization source?

I prompt them by asking them to think back on the types of things we have usually considered with analytical methods to assess their utility. Eventually we generate a list of things like sensitivity, reproducibility, matrix effects and sample size.

It is obvious to them that graphite furnace requires less sample size. They are often at a loss to address the issue of sensitivity. I might ask some leading questions:

Do both methods use all of the sample that has been introduced?

Compare how long the atoms spend in the light path in the two techniques?

Is there a difference between a method that integrates the signal versus one that measures a steady state value?

They are often at a loss to address the question of reproducibility and matrix effects, and we discuss these as a group.

Before examining the next question, I give a brief lecture on the use of the cold vapor method for mercury and the generation of volatile hydrides for elements such as arsenic and selenium.

I then give a lecture on the use of an inductively coupled plasma for atomization (pages 86-89 of the text) as well a very brief coverage of the use of arc and spark devices.

2. If you were to run an analysis using an atomic absorption spectrophotometer, you would note that a separate source lamp called a hollow cathode lamp is needed for each individual element that you wish to measure. For example, a lead lamp emits the specific lines of light that are absorbed by lead. Why is the cathode designed with a hollow configuration?

Before giving them this question, I give a brief overview of the design and operation of a hollow cathode lamp.

Groups can usually suggest the two reasons why it the lamp uses a hollow cathode. If not, I might ask the following:

What problem do you see if you had a flat cathode (Note, I draw a picture on the board)?

What ultimately happens to the gas phase atoms that are sputtered off the surface and what would you prefer happen with them?

They are never able to answer question 3 below without a series of prompting questions that I include in the problem set I provide to them. I introduce question 3 and 4 below at the same time.

- 3. Needing a different lamp for each element is expensive and not as simple as using a continuum source with a monochromator. Why is it apparently not feasible to use a broadband continuum source with a monochromator when performing atomic absorption spectroscopy?**
- 4. One thing you might consider is whether continuum lamps have enough power in the part of the electromagnetic spectrum absorbed by elements. In what part of the electromagnetic spectrum do most atoms absorb (or emit) light?**

The groups usually have no problem determining that this is in the UV/Vis portion of the spectrum.

- 5. Do powerful enough continuum sources exist in this region of the electromagnetic spectrum?**

I remind them of UV/Vis and fluorescence spectroscopy and ask whether those methods used continuum sources and whether we were concerned about their power. They realize that powerful enough continuum sources do exist so that is not the reason for using hollow cathode lamps.

- 6. A more helpful thing to consider is the width of an atomic line. What are the two major contributions to the broadening of atomic lines? (Hint: We went over these earlier in the course).**

They can usually come up with collisional and Doppler broadening, although some have to go back through their notes to find these.

- 7. When these contributions to line broadening are considered, the width of an atomic line is observed to be in the range of 0.002-0.005 nm. Using information about the width of an atomic line, explain why a continuum source will not be suitable for measuring atomic absorption.**

They are initially stumped by this question, so I ask them the following:

How did we select a monochromatic wavelength from a continuum source when recording absorbance with a UV/Vis spectrophotometer?

They can relate this back to the use of a grating and slit.

What was the typical bandpass from such a device?

They usually realize that it was about 1 nm. I then draw the output of a continuum source on the board – y-axis being intensity and x-axis the wavelength showing a width of about 1 nm – and ask them to copy this into their notebook and superimpose on it the atomic line that would be absorbed. This is usually sufficient to get them to realize that the atomic absorbance will only remove a small fraction of the power from such a source, hence the reason for using a hollow cathode lamp.

What is the problem with reducing the slit width of the monochromator to get a narrower line?

From prior material in the course, they realize that the power will now be too low and the noise too high.

8. Why does the hollow cathode lamp have a low pressure instead of a high pressure of argon filler gas?

If they are stumped with this, I ask them the following:

What would happen to gas phase atoms sputtered from the hollow cathode if there was more argon in the lamp?

They can usually determine that more collisions would occur.

Based on prior things we learned in the course with other spectroscopic methods, what will these collisions do to the emission from the sputtered atoms?

They can usually determine that it will broaden the lamp output, and based on the prior discussion, realize that this creates the same problem as a continuum source with a monochromator.

9. Flame noise (either emission from the flame or changes in the flame background as a sample is introduced) presents a significant interference in atomic methods. Can you design a feature that could be incorporated into an atomic absorption spectrophotometer to account for flame noise?

I usually set this up that they work at an instrument company selling AAs. A customer has called and identified this problem and asks if they can provide a solution to it. I am usually pleasantly surprised at how some of the groups can hone in on key things to consider with this problem. Some propose measuring the flame noise before introducing sample, but then I draw on the board a representation of flame noise as some positive signal above zero and indicate that its magnitude may change up or down as a sample different from distilled water is added. Some realize that they need a way to measure the flame signal in the absence of the hollow cathode lamp and someone usually proposes the idea of somehow blocking the source beam. We have talked about the use of pulsed sources in fluorescence spectroscopy so some suggest that we could do this as well. We then discuss the possibility of using a chopper.

10. Particulate matter in a flame will scatter light from the hollow cathode lamp. This is a problem since a detector cannot distinguish the difference between light that is scattered and light that is absorbed.

Molecular species in a flame exhibit broadband absorption of light. Again, a detector cannot distinguish broadband absorption from molecular species from absorption by atomic species.

Can you design to feature that could be incorporated into an atomic absorption spectrophotometer than can be used to account for both scattered light and light absorbed by molecular species?

I usually draw Figure 6.13 on the board showing an atomic absorption line superimposed over a molecular absorption background. The groups can usually realize that they ought to be able to do some sort of background correction by measuring the absorbance near and at the atomic line and then subtracting the two. Some even ask whether it would be possible to have a second line,

and I use this to mention the possibility of using an instrument that exploits the Zeeman Effect but put off a full discussion of that.

Thinking back to our discussion of sources for atomic absorption, can you propose a method that would allow you to measure molecular absorption while not having any significant contribution from atomic absorption?

With this prompt, the groups can usually reflect back on the reason why the use of a continuum lamp was a problem and a hollow cathode lamp was used instead.

Can a continuum source be used to measure molecular absorption?

Based on our unit on UV/Vis spectroscopy, they immediately answer this. We can then discuss the concept of background correction using a deuterium lamp. I remind them of the reason why hollow cathode lamps have a low pressure of Argon gas – which usually prompts them to ask whether it would somehow be possible to pulse the pressure in the lamp – which then serves as a way to introduce the Smith-Hieftje method.

11. Metal complexes with low volatility are often difficult to analyze when performing atomic absorption measurements because the atomization efficiency is reduced to unacceptably low levels. Can you devise a strategy or strategies for eliminating the problem of a non-volatile metal complex?

I indicate that there are three different strategies that they might be able to come up with and let them start discussing the question. If they are completely stumped, I remind them that earlier we had discussed a specialized technique for analyzing arsenic. The groups can usually come up with the ideas of using a protecting agent.

If needed, I might ask whether they can propose a way to eliminate the effect of an undesirable ligand that forms a non-volatile complex.

With this they can come up with the idea of adding a releasing agent. Groups also often suggest raising the temperature of the flame as another possibility.

12. Can you devise a strategy to overcome unwanted ionization of the analyte?

We have talked about how the high amount of argon ions in an ICP helps suppress ionization, so they have that as background. Also, since the discussion on non-volatile complexes promoted the idea of adding things to a sample, members within groups often suggest the idea of adding something that easily ionizes.

13. Devise a general method that can be used to account for the presence of unknown matrix effects.

I remind them of what we mean by a matrix effect, and that matrix effects can either enhance the signal or suppress the signal of the analyte. I also remind them that when we use a standard curve, the standards are usually prepared in distilled water, which might have a substantially different matrix than the sample. Therefore, we somehow need a way to determine whether the matrix is enhancing or suppressing the signal of the analyte.

With this background, usually someone comes up with the idea of adding extra analyte to the sample. When they do, I pose the following question:

How should the amount of additional increment compare to the initial concentration in the sample?

They usually realize that this should be relatively small so that it does not swamp out the matrix.

I then draw a set of axes on the board and show the response for the initial sample and indicate where we will plot the response for samples with additional increments of analyte. I then pose the following:

Draw the curves that would result for two samples with identical concentrations but one has a matrix that enhances the signals and the other a matrix that suppresses the signal.

Groups can usually determine the correct form of the curve and we can then discuss any remaining aspects about standard addition and how one can extrapolate the curve back to get the concentration of the species in the sample.