Part A. Electronic Energy Levels and UV/Vis Spectroscopy

1. Molecules that absorb energy in the UV/Vis range tend to have broad absorbance bands, rather than discrete peaks, due to the possibility of different vibrational energy states associated with each electronic transition. Add arrows in Figure 4 to show at least three different energy transitions corresponding to promotion of an electron from E_0 to E_1.
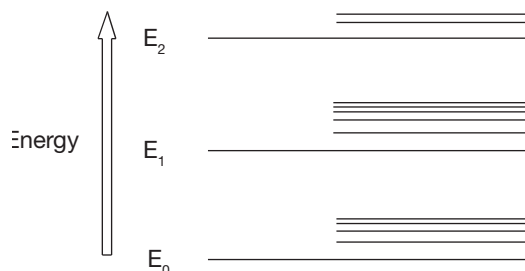

Figure 4. Electronic and vibrational transitions.

2. UV spectra are typically measured from 200 to 400 nm. The ultraviolet spectrum of the amino acid tyrosine is shown below in Figure 5. What are the wavelengths of maximum absorbance for the two major peaks in the UV spectrum of tyrosine?
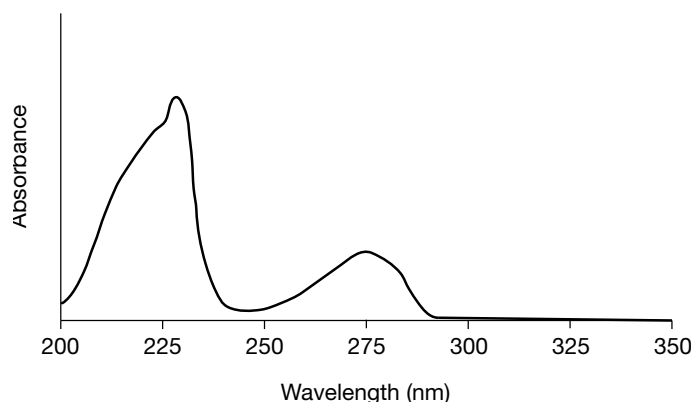

Figure 5. Ultraviolet spectrum of tyrosine.

3. Using Equation 1 and Planck's law (see the *Background* section), calculate the energy for the lower energy transition in the UV spectrum of tyrosine (Figure 5). The speed of light $c = 3.0 \times 10^8$ m/sec.

4. The UV spectra of organic molecules involve electrons in pi-molecular orbitals (double and triple bonds) or nonbonding orbitals (atoms with unshared pairs of electrons). Absorption of UV light results in promotion of these electrons to anti-bonding molecular orbitals. How will the wavelength of light absorbed by an organic molecule change as the energy gap between bonding and antibonding molecular orbitals decreases?

5. Indicators and other organic dyes contain a series of double bonds separated by single bonds. This pattern of bonding, called conjugation, reduces the separation between the ground state and the excited state of the pi-electrons. Use this fact to explain why organic dyes are highly colored.

6. Transition metal ions have filled or partially filled d-orbitals. The presence of water molecules or other ligands surrounding a transition metal ion leads to energy differences among the d-orbitals. Depending on the metal ion involved, the energy difference may correspond to different wavelengths and energies of visible light. This property of transition metal ions gives many their characteristic—and beautiful—colors. Why are most zinc salts colorless?

7. What does the transmitted color of a solution tell you about the color of light it absorbs?

8. Chromium(III) ions appear purple or violet in aqueous solution. Which wavelengths of light would you expect to be most strongly absorbed by Cr^{3+} ions?
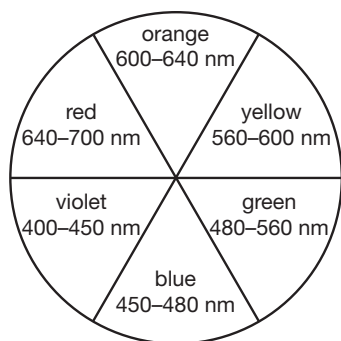
Part B. Vibrational Energy Levels and Infrared Spectroscopy

1. Bond formation is due to a decrease in potential energy when two atoms approach each other, as shown below for HBr (Figure 6). Label the point on the *x*-axis corresponding to the equilibrium H–Br bond length.
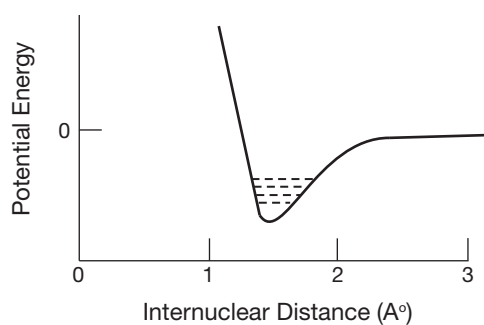

Figure 6. Potential energy diagram for HBr.

2. Vibrational energy levels are shown by means of dashed lines in Figure 6. Explain how the dashed lines illustrate the relationship between the absorption of infrared radiation and bond stretching.

3. IR spectra are typically plotted as shown below (Figure 7), with percent transmittance on the *y*-axis versus wavenumber on the *x*-axis.
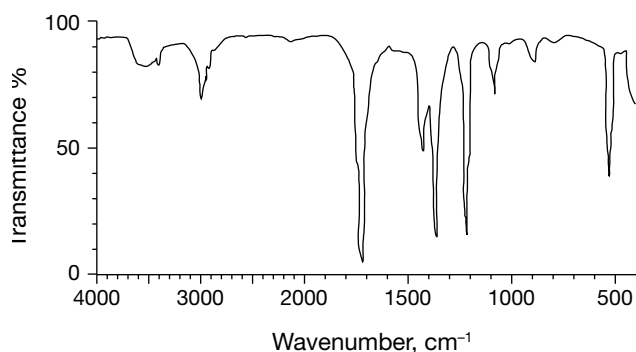

Figure 7. IR spectrum of acetone.

(a) What are the units of wavenumber? Describe the expected relationship between wavenumber and frequency.

(b) Is wavenumber directly or inversely proportional to energy? Label Figure 7 to show the direction of increasing vibrational energy along the *x*-axis.

4. Estimate the wavenumber for maximum absorbance observed between 1500 and 2000 cm^{-1} in the IR spectrum of acetone.

5. Predict the general relationship between bond strength, the energy required to stretch a bond, and the stretching frequency observed for the bond in the IR spectrum.

6. The stretching frequency for a carbon–carbon bond occurs at approximately 1600 cm^{-1} for a C=C double bond and at 2100–2200 cm^{-1} for a C≡C triple bond. Explain the relative frequencies based on bond strength.

7. The intensity of a band in the IR spectrum depends on the change in dipole moment that accompanies a vibrational transition in a molecule. Predict the relative intensity of IR bands due to C=C versus C=O stretching vibrations.

Table 1 summarizes general infrared absorption frequencies for common structural units (functional groups) in organic molecules.

Table 1.

Bond	Functional Group Class	Stretching Frequency v (cm–1)
O–H	Alcohols ROH	3400–3600
	Carboxylic acids RCO₂H	2500–3000
C–H	Alkynes RC≡C–H	3300
	Alkenes R₂C=C–H	3100
	Aromatic compounds	3000
	Alkanes	2900
C=O	Carboxylic acids	1750
	Aldehydes and ketones	1720
C≡C	Alkynes	2100
C=C	Alkenes	1650

8. The IR spectrum of aspirin (acetylsalicylic acid) is shown below, along with its structure. Use the information in Table 1 to identify the peaks in the IR spectrum corresponding to stretching vibrations of the following bonds:

   (a) O–H group

   (b) C=O groups (there are two)

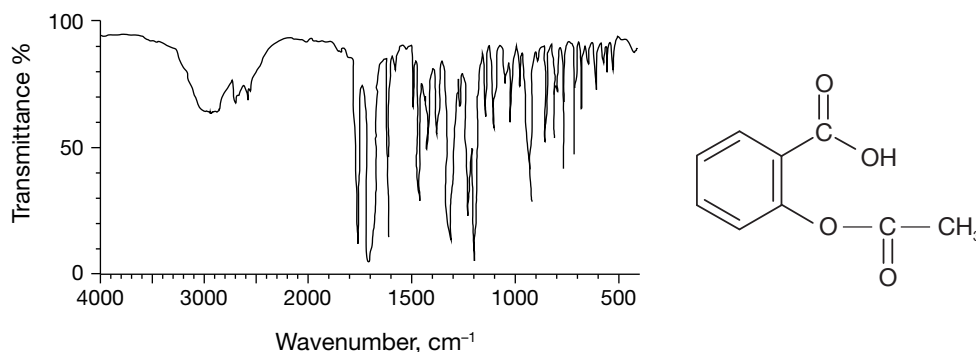   (c) C=C bonds in the benzene ring

Figure 8. IR spectrum and structure of aspirin.

9. A portion of the IR spectrum of ethyl alcohol, CH_3CH_2OH, is shown below. Note the broad band associated with the O–H group, as opposed to the sharp peak for the C–H stretching vibration. The width of the O–H band is usually attributed to hydrogen bonding. Why would hydrogen bonding lead to a broad band for the O–H stretching vibration?
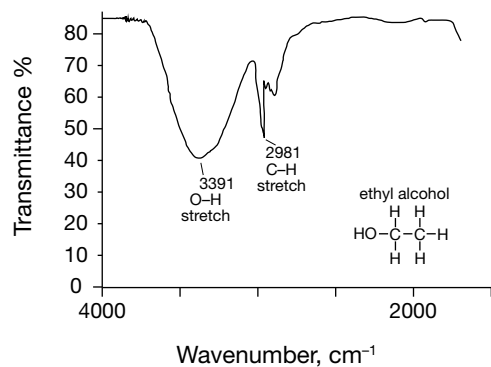
Part C. Beer's Law and Quantitative Analysis

Figure 9 shows a typical visible spectrum. The wavelength range for visible spectroscopy is 350–700 nm. In general, *absorbance* is proportional to concentration for each wavelength. The higher the concentration of a substance in solution, the more intense its color will be, and the greater its absorbance. The linear relationship between absorbance *(A)* and concentration *(c)* is expressed in Beer's law, Equation 3, where b is the path length, in cm, of solution the light passes through, and a is a proportionality constant. If c is given in units of molarity (M = moles/L), then a is known as the molar absorptivity coefficient, with units M^{-1} cm^{-1},

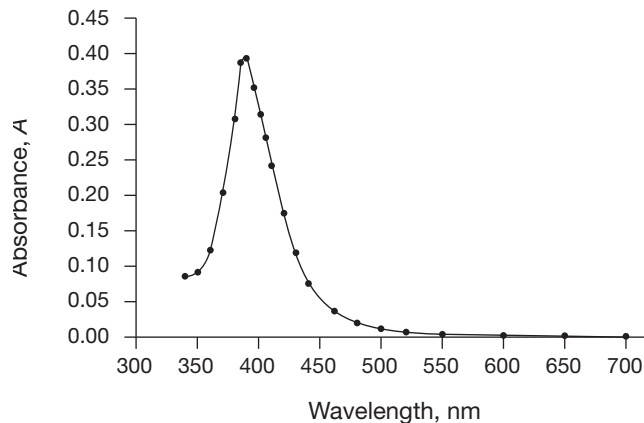$$A = abc \qquad \qquad \qquad \text{\textit{Equation 3}}$$

Figure 9. Visible spectrum of nickel nitrate.

1. The graph is for a 0.08 M solution of Ni^{2+} ions. At what wavelength is the value of molar absorptivity the highest?

2. If the path length, b, is 1 cm, calculate the molar absorptivity *(a)* of the Ni^{2+} ion at this wavelength.

3. Predict the absorbance value for a 0.03 M $Ni(NO_3)_2$ solution if measured at this wavelength.

4. What concentration of Ni^{2+} ions would be expected to have an absorbance of 0.25 at this wavelength?

A digital spectrophotometer measures both the percent transmittance of light and the absorbance. When light is absorbed, the radiant power (*P*) of the light beam decreases. Transmittance (*T*) is the fraction of incident light (P/P_o) that passes through the sample. The relationships between transmittance and percent transmittance (*%T*) and between transmittance and absorbance (*A*) are given in Equations 4 and 5, respectively.

$$\%T = T \times 100 = P/P_o \times 100\% \qquad \qquad \text{\textit{Equation 4}}$$

$$A = \text{absorbance} = -\log_{10} T \qquad \qquad \text{\textit{Equation 5}}$$

5. What is the percent transmittance, *%T*, when *A* equals zero? When *A* equals 1.0?

6. For most substances, Beer's law is linear for absorbance values below 1.000 and above 0.025. Based on the mathematical relationship between absorbance and transmittance in Question 5, explain why Beer's law graphs of absorbance versus concentration may deviate from a straight line when $A < 0.1$ and when $A > 1$.

7. The Beer's law graph shown below was generated by measuring absorbance values at 630 nm for a series of standard solutions containing known concentrations of Cu^{2+} ions. A sample of steel was treated with acid to dissolve the copper content, and the absorbance of the resulting solution at 630 nm was found to be 1.345, outside of the range of the Beer's law plot. Which step (*a*, *b* or *c*) would you recommend for determining an accurate concentration of copper in this sample? Explain.

(*a*) Extrapolate the curve to include 1.345 *A*.
(*b*) Run the calibration curve using higher concentrations of copper.
(*c*) Dilute the sample to bring its absorbance between 0.200 *A* and 0.800 *A*.

Beer's Law Graph for Copper (630 nm)

y = 2.35x
R² = 0.999

Absorbance, A

Concentration of Cu²⁺ Ions, M
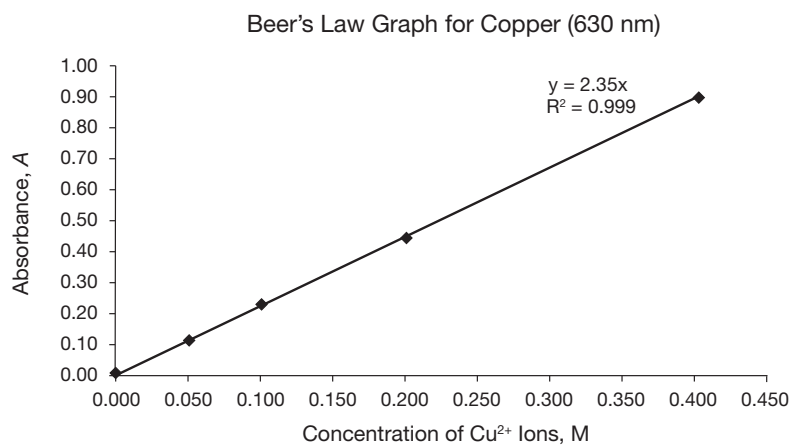
Stainless steel is an alloy of iron with other metals that are added to increase its corrosion resistance. One specific alloy of stainless steel contains 21% chromium. Quality control groups routinely test batches of this alloy by spectroscopy to determine the element content, including % chromium. The absorption spectra for both Fe^{3+} ions and Cr^{3+} ions are shown in Figure 10.
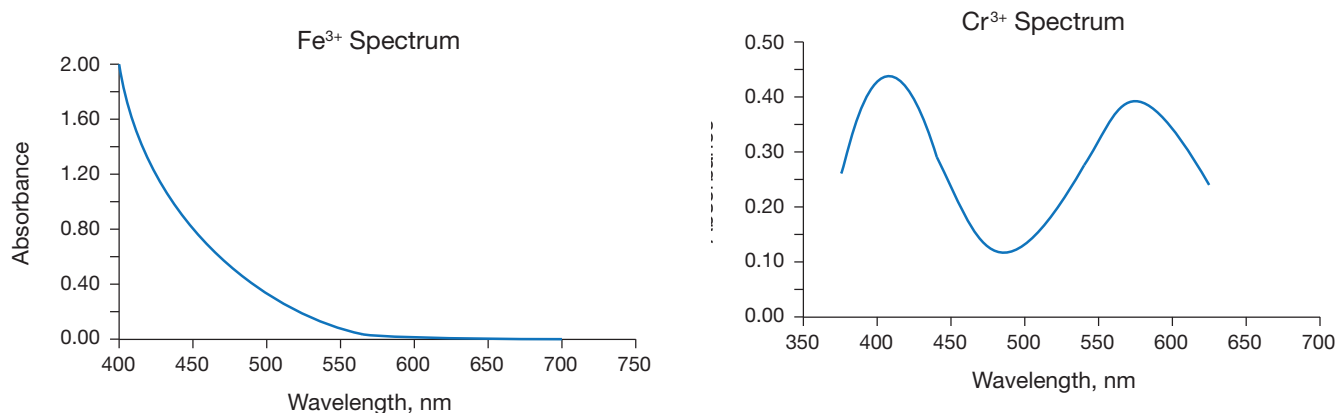

Figure 10. Visible spectra of Fe^{3+} and Cr^{3+} solutions.

8. A calibration curve (Beer's law plot) was created using the wavelength of 405 nm. A series of $Cr(NO_3)_3$ standard solutions were tested to generate this calibration curve. The absorbance of the steel sample at 405 nm was determined. When the % Cr in the sample was calculated, the answer was a whopping 79%! What is the likely source of this very large error?

9. A second calibration curve was generated for Cr^{3+} ions, this time using the absorbance at 575 nm (Figure 11). When a 1.215-gram steel sample was dissolved in acid and diluted to 50.0 mL, the absorbance of the resulting solution at 575 nm was 0.520 A. Calculate the % Cr in the steel sample.
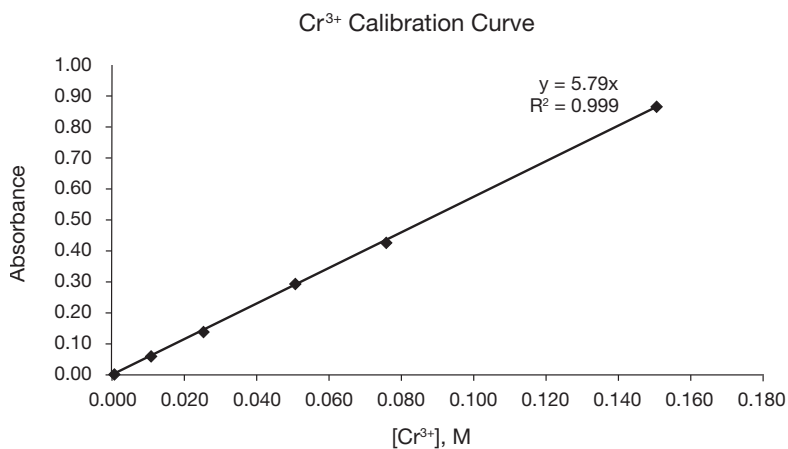

Figure 11. Calibration curve for Cr^{3+} ions at 575 nm.