

Chem 434 Instrumental Analysis Test 2

1. Describe the different sources that can be used to generate UV light for a UV/Vis spectrophotometer.

H₂ or D₂ lamps - run a low voltage (~40V) through a low pressure of D₂ or H₂
Output between 160-375nm D₂ somewhat bigger and brighter than H₂ also a better shelf life because doesn't diffuse out as quickly

Tungsten Filament- Vis/near IR- bulb runs about 2870K, need a very stable power supply

Tungsten Halogen - Similar to above, but add a touch of I₂ inside bulb. This allows W to redeposit back on filament, so bulb lasts longer. As a result can operate at higher T (3500K). With higher T lamp has output in UV, so if use quartz bulb can do near UV region

Xenon Arc - Xe gas under high pressure, have continuum between 200 and 1000 nm

2. In Chapter 14 you found that various metal ions can absorb UV/visible light. Some metals absorb light in very narrow bands and the wavelength of these bands are not affected by the ligands coordinated to the metal, while other metals have much broader absorbances, and the wavelength of the absorbance maxima shift quite a bit as when different ligands are bound to the central metal.

A. What types of metals have the narrow absorbances that are not influenced by ligands?

This is typical of Lanthanide and Actinide metals with electrons in the f orbitals

B. What types of metal have broad absorbances that are influenced by ligands?

This is typical of the transition metals with electrons in the d orbitals

C. In this last class of metals, how are the absorbances influenced by the structure of the coordination complex between the metal and the ligand?

The various ligand geometries interact 5 d orbitals (d_{xy}, d_{xz}, d_{yz}, d_{z2} and d_{x2-y2}) in different ways. The Octahedral geometry increases the energy of the d_{z2} and d_{x2-y2} orbitals relative to the d_{xy}, d_{xz}, d_{yz} orbitals, a tetrahedral geometry increases the energy of the d_{xy}, d_{xz}, d_{yz} orbitals relative to the d_{z2} and d_{x2-y2} orbitals while the square planar geometry give the d_{x2-y2} orbital the highest E, the d_{xy} the next higher e, the d_{z2} the third highest E and the d_{xz} and the d_{yz} the lowest E, so the shape of the complex influences which orbitals are involved in light absorbing transitions. The ligand involved in the complex also influences the absorption. Ligands with a high 'ligand field' like NO₂⁻ or CN⁻ absorbances to higher energy (shorter wavelengths) while ligands with lower

ligand fields like I^- , Br^- or Cl^- shift absorbances to lower energy (longer wavelengths)

3. When looking at either the strength or wavelength of UV/ visible light absorbance, what differences are observed between isolated double bonds, double bonds in conjugated systems, and double bonds in aromatic systems.

Double bonds can be involved in either $n \rightarrow \pi^*$ transitions or $\pi \rightarrow \pi^*$ transitions observed in the UV end of the spectrum. Conjugation lowers the energy of the π^* state and resonance lowers the energy even more. Thus you will observe a shift to longer and longer wavelengths with conjugation and resonance. For instance a typical isolated C=C bond has a $\pi \rightarrow \pi^*$ transition at ~ 180 nm. When it is conjugated to another double bond the wavelength drops to ~ 215 nm and if it is conjugated with two double bonds the wavelength shifts to about 250 nm. C=C in a resonance system like benzene absorb light at even longer wavelengths, ~ 260 nm.

4. After a molecule is excited into either an S_1 or a T_1 excited state, there are a variety of ways for it to lose its energy to return to the S_0 state. Name and give a brief description of each of these processes.

Vibrational relaxation - molecules relax almost instantly to their lowest vibrational state.

Internal Conversion - Molecule goes to a lower electronic state without emitting radiation.

External Conversion - Energy is lost by a transfer to a solvent molecule.

Intersystem Crossing - Spin of excited electron is reversed so have $S \rightarrow T$ or $T \rightarrow S$ conversions.

Predissociation - S_1 converted to such a high E S_0 state that the molecules dissociates.

Dissociation - Energy is used to directly dissociate the molecule.

Fluorescence - Energy lost by emitting light in an $S_1 \rightarrow S_0$ transition.

Phosphorescence - Energy lost by emitting light in a $T_1 \rightarrow S_0$ transition.

5. Fluorescence varies with both the internal molecular structure and with the environment around the molecule. Discuss several ways the structure of a molecule can increase or decrease its fluorescence, and several ways in which the environment around a molecule can increase or decrease the molecule's fluorescence.

Molecular structure

Best fluorescence is found in unsubstituted aromatic ring systems, and this fluorescence can be increased if multiple aromatic rings are linked together in a rigid system.

Substitutions like halogens tend to increase phosphorescence and decrease fluorescence. Iodo groups or nitro groups tend to undergo predissociation. Carbonyls and carboxylic acids both inhibit fluorescence.

Heterocyclic ring systems do not fluoresce, but rings with N fused into ring can fluoresce nicely.

Solvent/Environment

Fluorescence increases as the T decreases

Fluorescence increases as the viscosity of the solvent increases

Fluorescence decreases if the solvent contains dissolved O₂ or heavy atoms with lots of electrons

6. Describe the different sources used to create IR radiation.

Nernst Glower - Cylinder of rare earth oxide, pass current through until warms to 1200-2200K. Takes special electronic control because as gets warmer resistance to electrical current decreases so even more current flows

Globar - silicon carbide rod, heat with electrical current, but here resistance increases with T, so don't need special current limiting power supply.

Incandescent wire. Simple pass current through a nichrome wire. Low intensity but cheap and long life

Tungsten filament - ordinary light bulb, good from 4000-12,800 cm⁻¹

Mercury Arc - Pass current through Hg gas. Best for far IR

CO₂ laser - lots of lines between 900 and 1100 cm⁻¹ very bright source and can be tuned to a single line.

Take home questions

1. If the force constant of a double bond is $\sim 1 \times 10^3$ N/m, estimate the approximate wave number of the fundamental absorption due to the stretching frequency of S=O bond.

$$\text{Mass of sulfur atom in kg} = 32 \times 10^{-3} \text{ kg} / 6.023 \times 10^{23} = 5.31 \times 10^{-26} \text{ kg}$$

$$\text{Mass of oxygen in kg} = 16 \times 10^{-3} / 6.023 \times 10^{23} = 2.7 \times 10^{-26} \text{ kg}$$

$$\begin{aligned} \text{reduced mass } (\mu) &= (m_1 \times m_2) / (m_1 + m_2) \\ &= (5.31 \times 10^{-26} \times 2.7 \times 10^{-26}) / ((5.31 \times 10^{-26} + 2.7 \times 10^{-26})) \\ &= 14.34 \times 10^{-52} / 8.01 \times 10^{-26} \\ &= 1.79 \times 10^{-26} \text{ kg} \end{aligned}$$

$$\begin{aligned} v &= 5.3 \times 10^{-12} \text{ sqrt}(1 \times 10^3 / 1.79 \times 10^{-26}) \\ &= 5.3 \times 10^{-12} \times \text{sqrt}(5.59 \times 10^{22}) \\ &= 5.3 \times 10^{-12} \times 2.36 \times 10^{11} \\ &= 1.25 \text{ this looks bad} \end{aligned}$$

Checking over the problem I see that K should be 1×10^3

Trying again

$$\begin{aligned} v &= 5.3 \times 10^{-12} \text{ sqrt}(1 \times 10^3 / 1.79 \times 10^{-26}) \\ &= 5.3 \times 10^{-12} \times \text{sqrt}(5.59 \times 10^{28}) \\ &= 5.3 \times 10^{-12} \times 2.36 \times 10^{14} \\ &= 1253 \text{ cm}^{-1} \text{ this looks much more reasonable} \end{aligned}$$

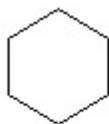
2. I have a 25μ cell (0.025 mm). When I use IR interference fringes to find the exact pathlength of the cell, how many interference fringes should I observe between 2000 and 3000 cm^{-1} ?

$$.025 \text{ mm} = .0025 \text{ cm}$$

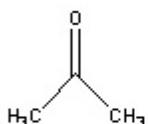
$$.0025 \text{ cm} = X/2(3000-2000)$$

$$.000025(2000) = 5$$

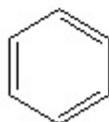
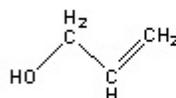
3. The following compounds have the same empirical formulas. What specific differences would you look for in their IR spectra to differentiate between these compounds?



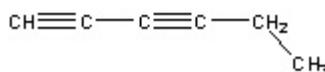
and



and



and



All compounds have C-H bonds. So all will show a strong CH stretch at ~ 2900 and a strong CH bend at ~ 1400

In addition.

In the first one you have a saturated hydrocarbon vs a hydrocarbon with a double bond

The compound with the double bond will have an additional band at 700-800 for the C=C-H group and a weaker band at 3050, it will also have a band 1610-1680 for the C=C vibration

In the case of acetone vs 3 hydroxypropene

The acetone will have band due to the C=O at ~ 1700

The propene will have bands at 700-800, 3050, and 1610-1680 for the C=C group and a broad band at ~ 3600 for the alcohol OH band at ~ 1200 for the C-O.

In benzene vs the di-alkyne

The aromatic benzene ring will have a medium band ~ 3050 and a strong band at ~ 700 -800

The alkyne will have a strong band at 3300 and a variable intensity band ~ 2100

Depending on which tables you used, and if you took all peaks or just the strong peaks, there was quite a bit of variability in the answers I accepted for this problem.