Practice Problem Set 7
Applications of UV-Vis Absorption Spectroscopy

1. $\pi-\pi^*$ Transition is the most convenient and useful transition in UV-Vis Spectroscopy. Why?

**In $\sigma-\sigma^*$ transitions**
- The high energy required can cause rupture of the $\sigma$ bonds and breakdown of the molecule
- Air components absorb in vacuum UV which limits the application of the method
- Working in vacuum UV requires special training and precautions which limit wide application of the method.
- Special sources and detectors, other than those described earlier, must be used
- All solvents contain $\sigma$ bonds

**In n-$\sigma^*$ transitions we have:**
The absorption wavelength for a n-$\sigma^*$ transition occurs at about 185 nm where, unfortunately, most solvents absorb. For example, the most important solvent is, undoubtedly, water which has two pairs of nonbonding electrons that will strongly absorb as a result of the n-$\sigma^*$ transitions; which precludes the use of this transition for studies in aqueous and other solvents with nonbonding electrons. In addition, in polar solvents the energy required for the n-$\sigma^*$ increases and thus the probability for the transition decreases.

In n-$\pi^*$ transitions we have:
The $n-\pi^*$ transition requires very little energy, However, unfortunately, the absorptivity of this transition is very small which precludes its use for sensitive quantitative analysis. In addition, using polar solvents increases the energy required for this transition, thus decreasing its probability.

In $\pi-\pi^*$ transitions we have:
The most frequently used transition is the $\pi-\pi^*$ transition for the following reasons:
1. The molar absorptivity for the $\pi-\pi^*$ transition is high allowing sensitive determinations.
2. The energy required is moderate, far less than dissociation energy.
3. In presence of the most convenient solvent (water), the energy required for a $\pi-\pi^*$ transition is usually smaller.

2. What are the effects of conjugation and aromaticity on UV-Vis absorption spectroscopy?
Conjugation of double bonds decreases the energy required for the $\pi-\pi^*$ and thus increases its absorptivity. In addition, the absorption wavelength is shifted to longer $\lambda$'s (a bathochromic shift). Aromaticity results in a similar effect like conjugation but to a much larger extent.

3. Why do many transition and inner transition metals absorb in the UV-Vis, although they lack $\pi$ bonds?
This is due to d-d transitions in transition metals and f-f transitions in inner transition metals. The energy splitting of the d and f orbitals results from the field of the ligands or solvent.
4. What are the criteria for selecting a wavelength for a specific analysis in UV-Vis absorption spectroscopy?

1. If more than an absorption maximum is available in the absorption spectrum, the wavelength far from the instrument extremes should be preferred
2. A wavelength at the maximum of a broad peak should be preferred to another of a sharp peak
3. The peak with a maximum peak height is preferred
4. If interferences are present, the wavelength that is far away from interferences should be selected
5. Working in the visible region should be preferred

5. Sometimes, the method of standard addition is used for the analysis of an analyte. Describe the method and comment on its merits.

The method involves addition of the same sample volume to a set of tubes or containers. Variable volumes of a standard are added to the tube set followed by completion to a specific volume. Now, all tubes contain the same amount of sample but different concentrations of analyte. A plot is then made for the volume of standard and absorbance. This plot will have an intercept (b) with the y axis and a slope equals m. The concentration of the analyte can be determined by the relation:

\[ C_x = \frac{bC_s}{mV_x} \]

Where, \( C_x \) and \( V_x \) are concentration and volume of analyte and \( C_s \) is the concentration of standard.

The use of this method provides better correlations between absorbances of standards and sample which corrects for the matrix effects.

6. What are the advantages of derivative UV-Vis spectroscopy?

1. Better qualitative analysis and identification of the number of absorbing species in a sample
2. Accurate determination of \( \lambda_{max} \)
3. Obtaining spectra in solutions with high scattering was possible using dual wavelength instruments
4. Spectral resolution of multi component systems by measurement at two wavelengths; where the interferent has identical molar absorptivity while the analyte does not, can result in good exclusion of interferences.

7. What are the advantages of photometric titrations?

1. Usually, photometric titrations are more accurate than visual titrations.
2. Photometric titrations are faster than visual titrations as only few points at the beginning and end of the titration is necessary. Extrapolation of the straight lines will intersect at the end point.
3. Titration reactions that are slow at the end point can not be performed by visual titrations but are well suited for photometric titrations. Only few points at the beginning and end of the titration, well away from the equivalence point where the reaction is slow, are necessary. Extrapolation of the straight lines will intersect at the end point. Therefore, dilute solutions or weak asids and bases can be also titrated photometrically.
4. Mixtures can be easily titrated using photometric titrations if absorbance is measured at the absorption wavelength of one of the two analytes. In addition, if both
analytes give colored products but with different molar absorptivities, they can be determined photometrically.

8. Predict the photometric titration curves for the reaction of colored analyte with a colored reagent that results in a colorless product.

9. What is UV-Vis photoacoustic spectroscopy? What is it used for?

The technique of photoacoustic spectroscopy involves subjecting the sample in a photoacoustic cell (containing a gas) to a chopped beam of radiation. If the sample absorbs the incident wavelength, as the chopper rotates, the sample emits the absorbed energy as heat. Periodic absorption and reemission causes periodic fluctuations in the gas temperature and thus pressure. If the chopper rotates in a rate that occurs in the acoustical range, the fluctuations in pressure can be detected by a sensitive microphone.

Using UV-Vis photoacoustic spectroscopy enables collection of UV-Vis spectra of solid, semisolid, and turbid samples.

10. UV-Vis absorption spectra are broad band spectra. Why is that?

In molecules, vibrational and rotational energy levels are superimposed on the electronic energy levels. Because many transitions with different energies can occur, the bands are broadened. The broadening is even greater in solutions owing to solvent-solute interactions.
11. How is derivative spectra mathematically collected?
If a spectrum is expressed as absorbance (A) as a function of wavelength (λ), the derivative spectra are:

Zero order: \[ A = f(\lambda) \]

First order: \[ \frac{dA}{d\lambda} = f'(\lambda) \]

Second order: \[ \frac{d^2A}{d\lambda^2} = f''(\lambda) \]

The first derivative is the rate of change of absorbance against wavelength. It starts and finishes at zero, passing through zero at the same wavelength as \( \lambda_{\text{max}} \) of the absorbance band. This derivative has a positive and a negative band with maximum and minimum at the same wavelengths as the inflection points in the absorbance band. This bipolar function is characteristic of all odd-order derivatives.

The most distinctive feature of the second-order derivative is a negative band with minimum at the same wavelength as the maximum on the zero-order band. This derivative also shows two positive satellite bands on either side of the main band. The fourth derivative shows a positive band with a maximum at the same wavelength as the maximum on the zero-order band.
12. What is a chromophore?
A chromophore is a molecular group usually containing a π bond. When inserted into a saturated hydrocarbon (which exhibits no UV-visible absorbance spectrum), it produces a compound with absorption between 185 and 1000 nm.
Absorption bands are particularly evident for conjugated π-bond systems. Most single bond transitions are inaccessible, being derived from higher energy σ-orbitals, with wavelengths below 185 nm, i.e. in the ‘vacuum ultraviolet’. Many isolated triple bonds also absorb below 185 nm. The $\text{C–C}$ (~185) and $\text{C–N}$ (~190) double bonds exhibit strong π–π* interactions but unless there is very good control of stray light, measurement is still unreliable in this region. At longer wavelengths there are rather weak n–π* interactions, such as $\text{N–O}$ and keto $\text{C–O}$ in the range 280–300 nm. Simple benzene compounds show medium intensity multiplets around 254 nm for non-conjugated derivatives, and shifted to longer wavelengths when substituents are conjugated to the aromatic system. In the table at the end of this section there are examples of commonly encountered chromophores, including conjugated alkene, carbonyl and aromatic systems which exhibit bathochromic (longer wavelength) and hyperchromic (enhanced absorptivity) changes.
### Selected chromophores and their absorbance maxima

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Formula</th>
<th>Compound</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxyl</td>
<td>RCOOH</td>
<td>Acetic acid</td>
<td>204</td>
</tr>
<tr>
<td>Amide</td>
<td>RCONH₂</td>
<td>Acetamide</td>
<td>208</td>
</tr>
<tr>
<td>Ethylene</td>
<td>RCH=CHR</td>
<td>Ethylene</td>
<td>193</td>
</tr>
<tr>
<td>Acetylene</td>
<td>RC=CR</td>
<td>Acetylene</td>
<td>173</td>
</tr>
<tr>
<td>Nitrile</td>
<td>RC=N</td>
<td>Acetonitrile</td>
<td>&lt;160</td>
</tr>
<tr>
<td>Nitro</td>
<td>RNO₂</td>
<td>Nitromethane</td>
<td>271</td>
</tr>
</tbody>
</table>

13. What are the main components of a UV-Vis absorption instrument? A spectrophotometer is an instrument for measuring the transmittance or absorbance of a sample as a function of the wavelength of electromagnetic radiation. The key components of a spectrophotometer are:

- a source that generates a broad band of electromagnetic radiation
- a dispersion device that selects from the broadband radiation of the source a particular wavelength (or, more correctly, a waveband)
- a sample area
- one or more detectors to measure the intensity of radiation

14. What sources are used in UV-Vis spectroscopy? Describe their performance characteristics.

The ideal light source would yield a constant intensity over all wavelengths with low noise and long-term stability. Unfortunately, however, such a source does not exist. Two sources are commonly used in UV-visible spectrophotometers. The first source, the deuterium arc lamp, yields a good intensity continuum in the UV region and provides useful intensity in the visible region. Although modern deuterium arc lamps have low noise, noise from the lamp is often the limiting factor in overall instrument noise performance. Over time, the intensity of light from a deuterium arc lamp decreases steadily. Such a lamp typically has a half-life (the time required for the intensity to fall to half of its initial value) of approximately 1,000 h.

The second source, the tungsten-halogen lamp, yields good intensity over part of the UV spectrum and over the entire visible range. This type of lamp has very low noise and low drift and typically has a useful life of 10,000 h. Most spectrophotometers used to measure the UV-visible range contain both types of lamps. In such instruments, either a source selector is used to switch between the lamps as appropriate, or the light from the two sources is mixed to yield a single broadband source.