Chapter 14 Applications of UV/Vis Molecular Spectroscopy
Problems: pick 5 - I don't have any favorites they are very practical, I am more interested in theory from this chapter

14A Magnitudes of Molar Absorptivities

0 to $10^5$ in Vis/UV range

$\varepsilon = 8.7 \times 10^{19}$ P A

$P$ is the transition probability (varies between 0 and 1)

'Allowed' transitions $0.1$ to $1$

'Forbidden' transitions $<0.01$

$A$ is the cross sectional target area (in cm$^2$)

$A$ is estimated to be about $10^{-15}$ cm$^2$ for typical organic molecules based on Xray and electron diffraction

Combine factors together

'Strong' bands $\varepsilon = 10^4$-$10^5$

Low or weak bands $\varepsilon < 10^3$

14B Absorbing species

can consider a two step process

$M + h\nu \rightarrow M^*$

$M^*$ = electronically excited species

lifetime of $M^*$ brief $10^{-8}$ - $10^{-9}$ sec

Then relaxation

$M^* \rightarrow M + ?$

$? = $heat, internal conversion

= light phosphorescence or fluorescence

$M^*$ disappears so fast its concentration is negligible

thermal heating derived from $M^*$ state is minimal

Thus absorption creates minimal disturbance to solution

except is photochemical decomposition

UV/Vis absorption usually due to changes in bonding electron orbitals

can correlate band to bonds in molecule

can be used to identify functional groups in molecule

But more often used for quantitation

Will recognize transitions involving 3 types of electrons

1. $n, \pi,$ and $\sigma$

2. $d$ and $f$ electrons

3. Charge transfer electrons
14B-1 Absorbing species containing $n$, $\pi$, and $\sigma$ electrons

14B-1 Absorbing species containing $\pi$, $\sigma$, or $n$ electrons
Organic molecules and ions
Many inorganic ions

Because all valence electrons can absorb radiation, and all organic molecules contain valence electrons, all organics can absorb light

E need to excite electrons in single bond is high, usually around $<$185 nm so in vacuum UV
Building spectrometer and using it in this range is difficult so not often done

Most spectroscopy $>$185 nm
in this range looking at functional groups or chromophores of lower E

While bands look broad and simple
actually very complex with superposition of vibrations on top of electronic transitions
Also complex to model so detailed theoretical analysis difficult
Will be making semiqualitative statements

Type of Absorbing electrons
1. Electrons that participate in bonds, so are shared between t atoms]
2. Nonbonding outer electrons associated with a given atoms
   a. Usually O, Halogens, S or N

Molecular Orbitals - orbitals where electrons move about 2 atomic centers
ans serve to hold these centers together
   Low E bonding orbitals
   High E antibonding orbitals
Figure 14-1

$\sigma$ bonds along line connecting two atoms, bond is rotationally symmetric about this axis
$\pi$ bonds - formed by parallel overlap of p orbitals
   - on either side of line connecting atoms
   - in fact has a nodal plane along this line (i.e. no intensity)

$n$ electrons - nonbonding electrons
   - not shared between atoms
   - typical of formaldehyde (figure 14-2)
Energy levels vary

Usually as in figure 14-3

\( \sigma \) lowest, then \( \pi \) then \( n \) then \( \pi^* \) then \( \sigma^* \)

Observe 4 major types of transitions in organics

- \( \sigma \rightarrow \sigma^* \) Highest E
- \( n \rightarrow \sigma^* \) 2nd highest E
- \( n \rightarrow \pi^* \) Lowest E
- \( \pi \rightarrow \pi^* \) Also fairly low

**\( \sigma \rightarrow \sigma^* \) Transitions**

Said earlier that single bond transitions were High E.

A \( \sigma \rightarrow \sigma^* \) is such a transition.

High E so usually in vacuum UV range

C-H bond in methane absorbs at 125 nm

Ethane has additional absorption at 135 nm, so guess is C-C bond

CH bond E is \( > \) than C-C bond E

So fits that CH bond absorbs at shorter wavelength

\( \sigma \rightarrow \sigma^* \) bands never seen in normal UV so won’t discuss further

**\( n \rightarrow \sigma^* \) Transitions**

Found in saturated compounds with non-bonding electrons

Lower E than \( \sigma \rightarrow \sigma^* \)

Generally 150-250 nm

Most <200 nm

**Typical examples Table 14-1**

E (wavelength) seems to depend on kind of bond

Absorptivities are low to medium

Because these electrons are used in polar interactions

If look at compound in polar solvent, absorbance will shift to shorter wavelength (higher E) (Will explain in next section)

Not many \( n \rightarrow \sigma^* \) transition in normal UV spectrum

**\( n \rightarrow \pi^* \) & \( \pi \rightarrow \pi^* \) Transitions**

Most UV absorption of organics due to these two transitions

200-700 nm

Both arise only in molecules with double bonds for \( \pi \) electrons

**Characteristics**

- \( n \rightarrow \pi^* \)

  - Low absorptivities (10-100 L cm\(^{-1}\) mol\(^{-1}\))
  - Shift to higher E (shorter \( \lambda \)) in more polar solvents

- called a hypsochromic or blue shift
$n$ electrons are solvated so are at lower $E$ in polar solvent
Shift can be as much as 30 nm in water where have H bonding
$E$ of shift seems to be about the same as the $E$ of the H bond
Upper end of transition unaffected by solvent

\[ \pi - \pi^* \]
high absorptivities (1000-10,000)
Often (but not always) shift to lower $E$ (larger $\lambda$) in polar solvents
- called a bathochromic or red shift
Much smaller than hypsochromics shift, only 5 nm
Both $\pi$ and $\pi^*$ electrons slightly solvated and favored $\pi^*$ is slightly more strongly favored so overall transition $E$ decreased as polarity increases

**Organic Chromophores**
Table 14-2 most common and wavelengths
use as a rough guide
  - Can be changed by solvent
  - Can be changed by structural interactions with the molecules

**Effect of Conjugation**
When conjugated (resonance structures) electrons delocalized over more than 2 atoms
Lowers $E$ of $\pi^*$ electons
Maxima shift to longer wavelengths

When chromophore are **Not** conjugated
  - Must be separated by $>1$ single bond
  - Can treat chromophores independently
  - Spectrum looks like some of parts

When Chromophores conjugated see strong shifts
  **Table 14-3**
  Compare and contrast position of double bonds

Also see conjugation in C=O and C=C systems (again look at table 14-3)

**Absorption by Aromatic Systems**
Three sets of bands in aromatics derive from $\pi - \pi^*$ transitions
Benzene

? Band 184, 60,000
(This far into the UV don’t study too much)
E2 204 nm 7900
B band 256nm 200

Typical very sharp in vapor phase with lots of vibrational structure
Broadened out or completely removed in solution
(Figure 14-5
Band strongly affected by ring substitutions (table 14-4

New Term - Auxochrome functional group that doesn’t absorb in the UV, but shifts chromophore peak to longer λ and increases their intensity
Both -OH and -NH₂ are auxochromic on benzene
Have at least 1 pair of n electrons that can interact with aromatic π’s
Apparenty stabilized the π* state, - lowers E of transition-bathochromic shift

Note indirect pH shifts as well
High pH phenol to phenolate anion
Extra pair of electrons, stranger effect
Low pH Aniline to anilinium cation - loses lone pair,
auxochromic effect disappears

Absorption by Inorganic Anions
A number of inorganic anions have n-π*
NO₃⁻(313nm), CO₃²⁻(217nm), NO₂⁻(360&280nm), CN⁻(230nm), and trithiocarbonate(500nm)

14B-2 Absorption Involving d and f electrons
Transition metals absorb in UV or vis
3rd row 3d transitions
4th row 4d transitions
Lanthanide 4f transitions
Actinide 5f electrons

Absorptions by Lanthanides and Actinides
Also Vis and UV
vary narrow, well defined and characteristic Figure 14-6
(Tis is not the was of most inorganic and organic absorbers)
Little affected by ligands on atom
Electrons thought to be well shielded by electrons with lower quantum number?
Absorption by 3rd and 4th row transition metals
(1st and 2nd transition metal series)
Tend to absorb UV radiation in att oxidation state
Bands are broad, strongly influenced by ligands
Transition involves moving electron between d orbitals
Two theories used to rationalize observed colors
  - Crystal-Field theory - Simpler, discussed here - OK for basic understanding
  - Molecular Orbital Theory - More complex, but better numbers - not covered
Theory
  5 d orbitals
  In absence of external magnetic or electric field are degenerate
    (All the same E)
    Then electrons can move freely between orbitals
In a complex (or in solution)
Ligands molecules have electrons, hence there is an external magnetic field
With external field, now some d’s have different E
  Now can absorb E as electrons move

5 D orbitals shown in figure 14-8
  Note d_{xy}, d_{xz} and d_{yz} similar shape, and oriented between axes
  Dx^2-y^2 and dz^2 oriented along the axes

Most common complex octahedral,
  One ligand along each axis
  This will place electrons and electric field at axes
    Will have minimal, equal, effect on d_{xy}, d_{xz} and d_{yz}
    Will raise E of Dx^2-y^2 and dz^2
  Shown in figure 14-9
Change in E makes a difference in E of Δ

Do same kind of stuff with tetrahedral ans square planar ligand fields

Magnitude of Δ depends on several factors
  Charge of metal
  Position of atom in periodic table
  Ligand field strength (property of ligand)
    High ligand field strength - large Δ - shorter λ
  Ligand Field strengths
I<Br<Cl<F<OH<\text{C}_2\text{O}_4^{2-}<\text{H}_2<\text{SCN}<\text{NH}_3<\text{ethylenediamine}<\text{o-phenanthroline}<\text{NO}_2<\text{CN}

See table 14-5

14B-3 Charge Transfer Absorption

Very strong absorptions, so sensitive means to detect and quantitate
Many inorganic complexes exhibit charge transfer absorption
Hence called charge transfer complexes
Examples
- Fe$^{3+}$ SCN$^-$ complex
- Fe$^{3+}$ Phenol complexes
- Fe$^{2+}$ 0-phenanthroline
- I$_3^-$ (complex of I$^-$ and I$_2$)

One group must be strong electron donor (Lewis base)
Other must be strong electron acceptor (Lewis acid)
Transition involves moving electron from donor to acceptor
Can think of as internal redox reaction

Note: Other transition have studied, moved electron between molecular orbitals, did not move from one atom to another

Fe$^{3+}$ SCN$^-$ $\rightarrow$ Fe$^{2+}$SCN$^0$

Usually electron returns to original state quickly
If complex dissociates before this happens, have a photochemical redox reaction

Most of the time the metal is the electron acceptor (but not always)

Some organic molecules can make charge transfer complexes

14C Applications of Absorption to Qualitative Analysis

Characterizing qualities of compounds (not quantitative-amounts)

14C-1 Methods of plotting

Figure 14-11
several different ways of plotting

14C-2 Solvents

Solvent must be transparent in \( \lambda \)'s being studied
also may interact with chromophores

Polar solvents water, alcohols esters and ketones tend to obliterate fine structure
If use nonpolar solvents like hydrocarbons, spectra look more like vapor phase
Table 14-6
Common solvents, and cutoff

14C-3 Detection of Functional groups
Unlike IR, hard to use UV to distinguish functional groups, but some trends
   Carbonyl groups
   Weak absorption 280-290 - moves toward shorter $\lambda$ with more polar solvents

   Aromatic rings
   Weak absorption near 260 with some fine structure
   Can look for further pH effects for phenols and anilines

14D Quantitative Analysis
Widely applicable to both organics and inorganics
Sensitive in $10^{-4}$ to $10^{-5}$ range
   Can be extended down to $10^{-7}$ in some cases
Moderate to high selectivity
Good accuracy (1-3%) with care <1%
Easy to do

14D-1 Scope - All sorts of UV procedure out there
   Just saw all sorts of chromophores could apply this to measure
   Can also apply to non-absorbing species is use a chemical reaction
   Often will do chemical reaction on chromophoric species just to
   make analysis more convenient or more sensitive

14D-2 Procedural details
i. Use $c_{\text{max}}$
   Give greatest sensitivity
   Beer’s law should be obeys because $c$ constant for all $\lambda$ in
   bandwidth
   Also least error if slightly off on $\lambda$
ii. Watch out for things that can change absorbance
   (1) Different solvents
   (2) Change in pH
   (3) T of solution
   (4) Ionic Strength
   Should know how these will affect assay
iii. Cleaning and Handling of Cells
   (1) Good quality matched cells
   (2) Frequently check cells against each other to detect problems
   (3) Clean outside with MeOH and Lens paper before use
(Better than dry paper alone)

(4) Make sure inside is clean !!

4. Determining relationship between A and []

Don’t assume Beer’s law
Check it for yourself
Don’t use literature

Make calibration standards match sample in all respects
Watch out for possible matrix effect with sulfates and phosphates

May need to use method of standard addition here as well

Analysis of mixtures covered in last semester
If use computers can actually look at more than 2 components
    (But need more than 2 absorption Max for good results)

14D-3 Derivative and Dual Wavelength Spectrophotometry
  Haven’t used much
  not for quantitate work as much as qualitative
take 1sr or even second derivative of spectrum
  Figure 14-17
  Picks up and magnifies small spectral details
   (Also magnifies any noise!)

14E Photometric Titrations
  Can use absorbance to follow a titration as well
  typical curves shown in figure 14-18
  Note, endpoint is NOT sharp like a pH
  Need to extrapolate from linear regions to find E.P.
  Skip 14E-2 and 14E-3

14F Photoacoustic Spectroscopy
  Can’t do here, a very specialized technique so won’t cover in depth, just want to
get a feel for it

Used on opaque sample! - Solids, semi-solids, turbid liquids
Developed in early 70’s First noted by Edison in 1880’s!

Setup shown figure 14-20
  Shine light as substance
  Substance absorbs a slight amount of E
  pressure of gas over and around substance changes slightly

Ordinarily this effect is too small to detect
Flash light on and off at acoustic frequency (a frequency you can hear) use sensitive microphone to pick up the changes in pressure as sound at that same frequency!

Very indirect, but sensitive method

See Figure 14-22 for use to read a TLC plate