At this semester we will learn

Ultraviolet /Visible Spectroscopy

Infra-Red Spectroscopy

NMR and mass Spectroscopy

Theory and applications

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With my best wishes

INSTRUMENTAL METHODS OF STRUCTURE DETERMINATION

1. Ultraviolet spectroscopy (UV)– Raise of electrons to higher energy levels through irradiation of the molecule with ultraviolet light. Provides mostly information about the presence of conjugated π systems and the presence of double and triple bonds

2. Infrared Spectroscopy (IR)– Relating to
molecular vibrations through irradiation with infrared light. Provides mostly information about the presence or absence of certain functional groups.

3. Nuclear Magnetic Resonance (NMR)– Excitation of the nucleus of atoms through radio frequency irradiation. Provides extensive information about molecular structure and atom connectivity.

4. Mass spectrometry– Bombardment of the sample with electrons and detection of resulting molecular fragments. Provides information about molecular mass and atom connectivity.

IF we have more time, we will talk on another subjects

Electromagnetic Radiation

The electromagnetic radiation can be divided into different regions from very short wavelength to the longer one as in order: gamma rays, X-rays, UV, Visible, IR, microwaves and the radio waves.

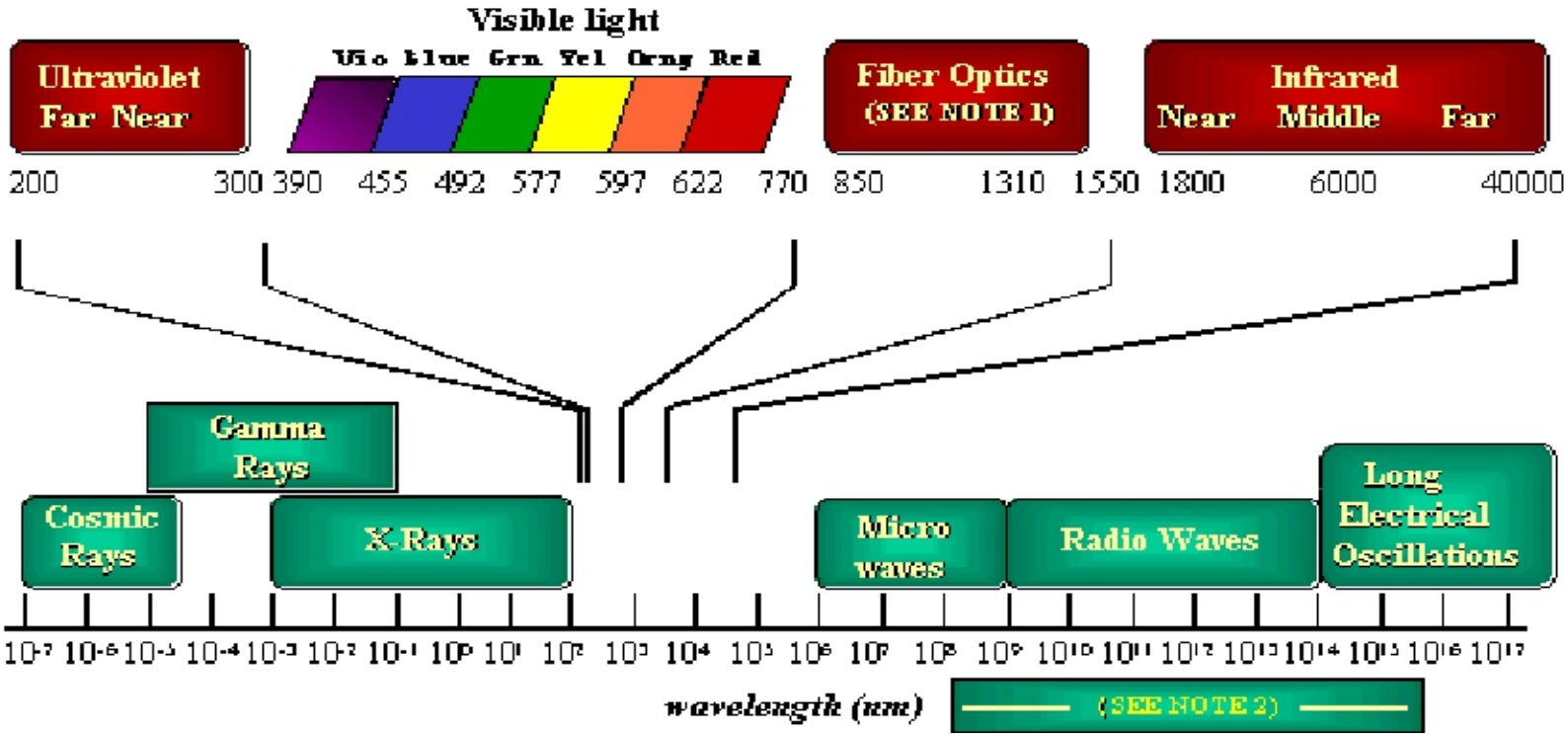
In each of these regions there are specific transitions such as Electronic for UV and Visible, Vibrational for IR (infra-red), Rotational for Radio and microwave and Photoelectron for X-Ray and Far UV.

In the vacuum all electromagnetic radiations travels at the same speed which is the **speed of light (C)** and may be characterized by its **wavelength (λ).**

$$\lambda = C / \nu = 1 / \bar{\upsilon}$$

Electromagnetic Spectrum

There are various kind of radiation which can be classified in electromagnetic radiation (EM) and particle radiation (p). The X-rays and γ-rays are part of the electromagnetic spectrum; both have a wavelength range between 10^{-4} and 10^{1} nm, they differ only in their origin.



The distinction between Gamma Ray and X-ray is related to the radiation source rather than the radiation wavelength.

Electronic transitions

The absorption of UV or visible radiation corresponds to the **excitation of outer electrons**. There are three types of electronic transition which can be considered;

1. Transitions involving **s , p, and *n*** electrons
2. Transitions involving **charge-transfer electrons** (What does it mean)
3. Transitions involving ***d* and *f*** electrons for transition metals.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state.

In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have separate energy levels.

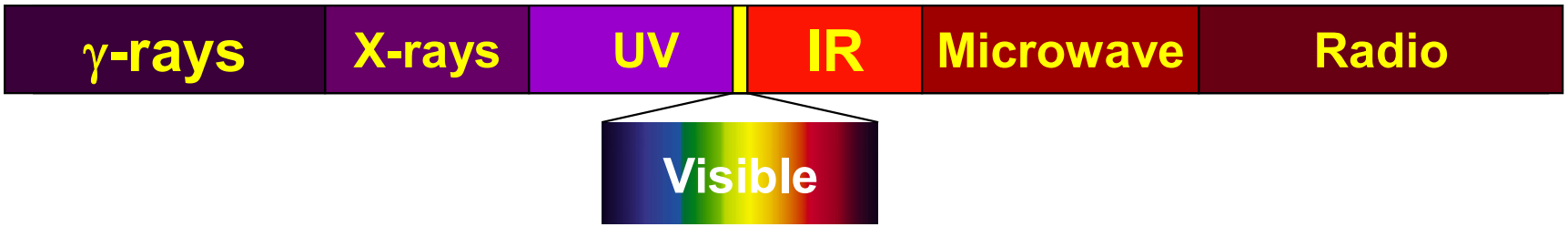
I. Introduction

UV radiation and Electronic Excitations

1. The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole

2. This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum

3. For comparison, recall the EM spectrum:



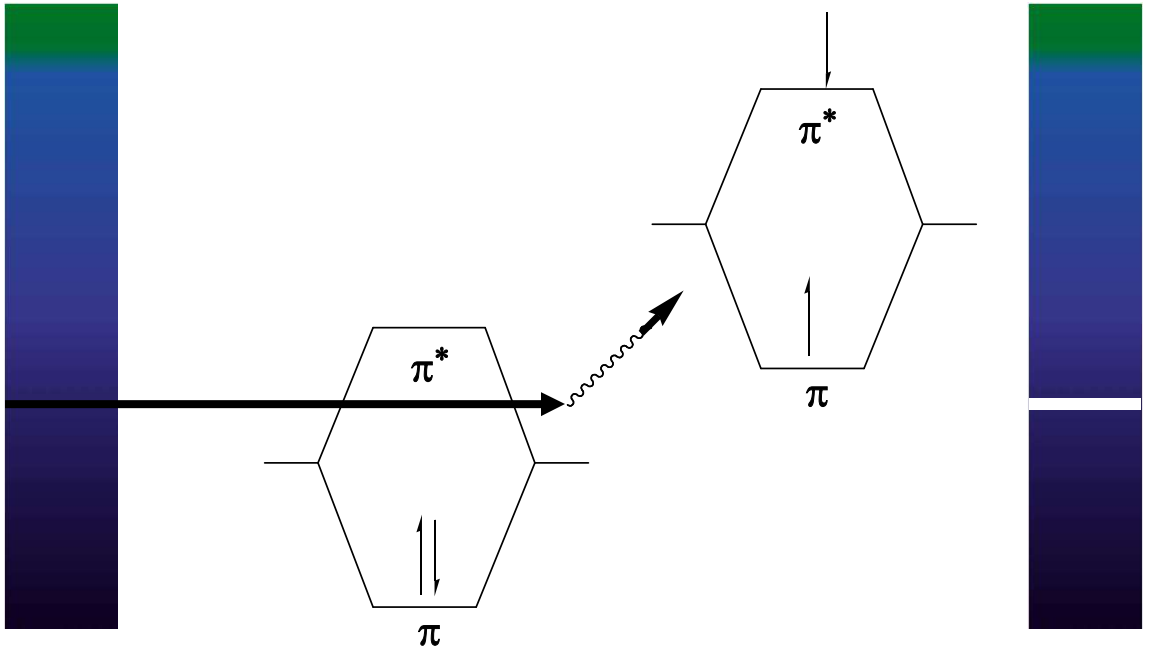
4. Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm

5. For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV

I. Introduction

The Spectroscopic Process

1. In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation
2. If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed
3. The remaining UV light passes through the sample and is observed
4. From this residual radiation a spectrum is obtained



I. Introduction

Observed electronic transitions

1.The lowest energy transition is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO)

2.For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every bonding orbital "created" from this mixing (σ, π), there is a corresponding anti-bonding orbital of symmetrically higher energy (σ^*, π^*)

3.The lowest energy occupied orbitals are typically the σ; likewise, the corresponding anti-bonding σ^* orbital is of the highest energy

4.π-orbitals are of somewhat higher energy than σ, and their complementary anti-bonding orbital somewhat lower in energy than σ^*.

5.Unshared pairs lie at the energy of the original atomic orbital, most often this energy is higher than π or σ.

Molecular orbital:

- is the nonlocalized fields between atoms that are occupied by bonding electrons. (when two atom orbitals combine, either a low-energy bonding molecular orbital or a high energy antibonding molecular orbital results.)
- **Sigma (σ) orbital**

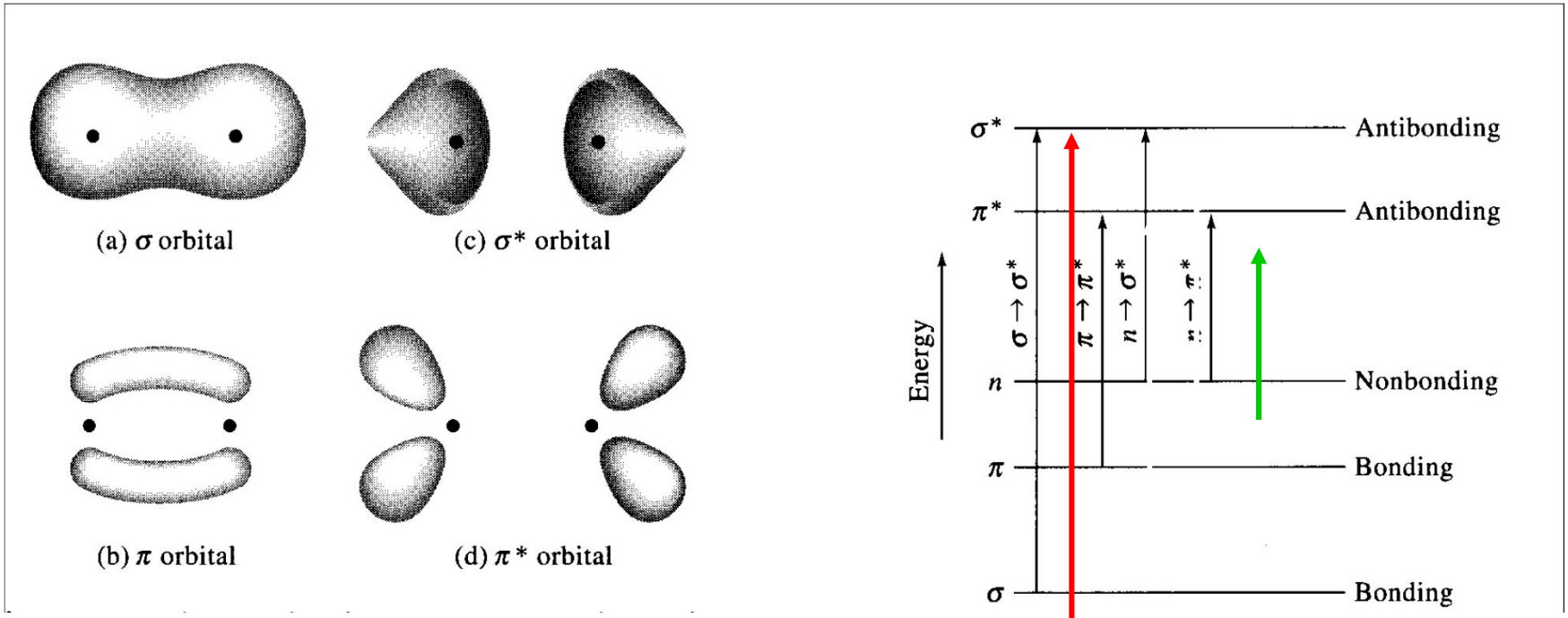
  The molecular orbital associated with single bonds in organic compounds
- **Pi (π) orbital**

  The molecular orbital associated with parallel overlap of atomic P orbital.
- **n electrons**

  No bonding electrons

Molecular Transitions for UV-Visible Absorptions

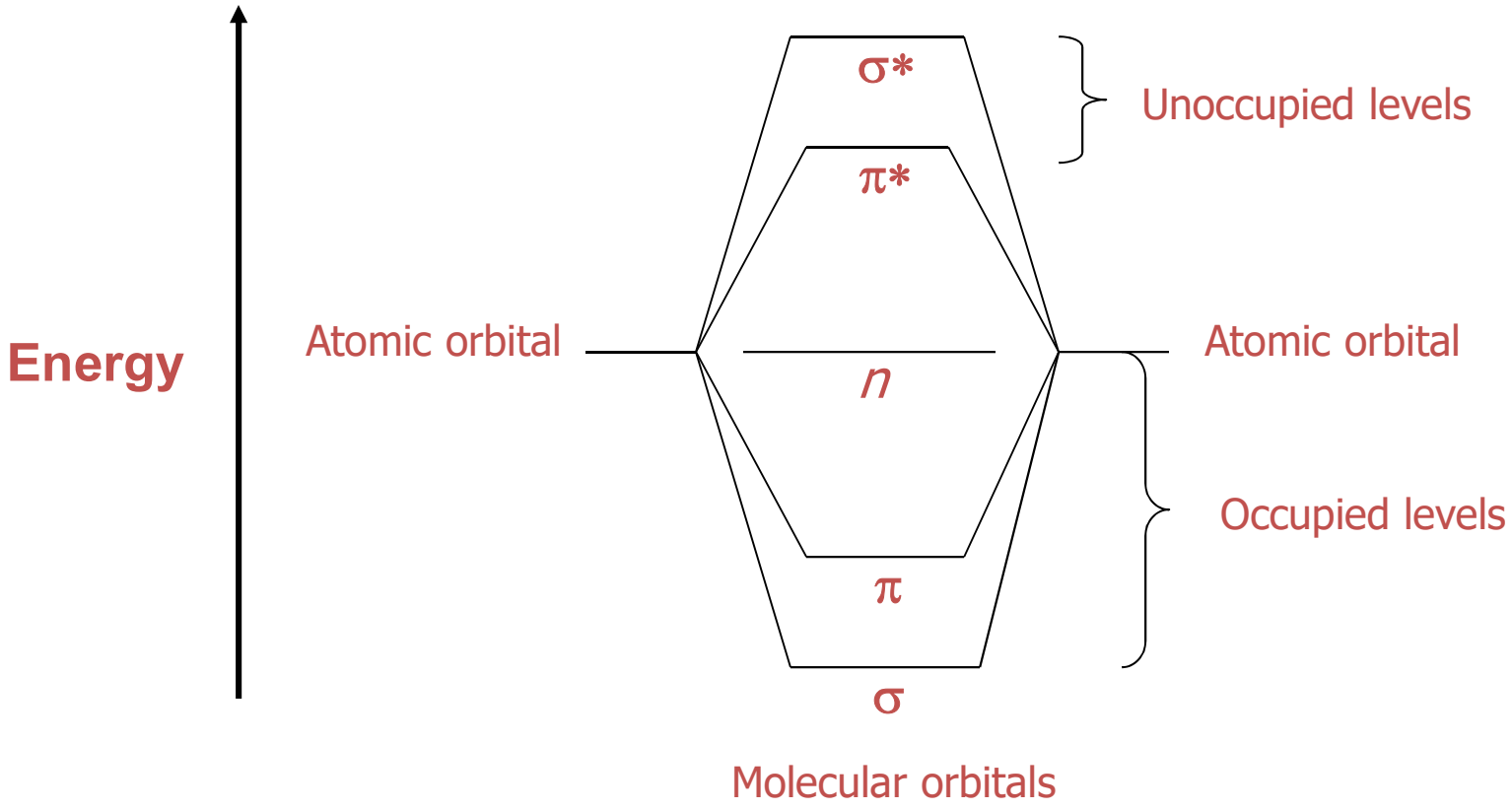
What electrons can we use for these transitions?



I.Introduction

Observed electronic transitions

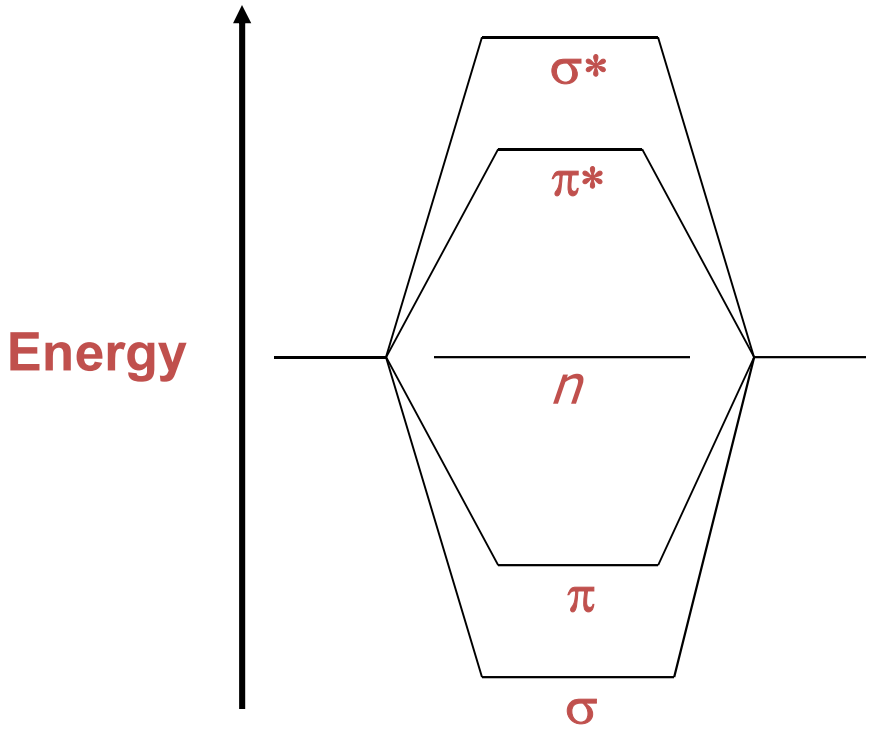
6.Here is a graphical representation



I.Introduction

Observed electronic transitions

7.From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:



$\sigma \rightarrow \sigma^*$ alkanes

$\sigma \rightarrow \pi^*$ carbonyls

$\pi \rightarrow \pi^*$ unsaturated cmpds.

$n \rightarrow \sigma^*$ O, N, S, halogens

$n \rightarrow \pi^*$ carbonyls

The origin of the absorptions

Valence electrons can generally be found in one of three types of electron orbital:

1- single, or σ, bonding orbitals;

2- double or triple bonds (π bonding orbitals);

3- non-bonding orbitals (lone pair electrons).

Sigma bonding orbitals tend to be lower in energy than π bonding orbitals, which in turn are lower in energy than non-bonding orbitals.

When electromagnetic radiation of the correct frequency is absorbed, a transition occurs from one of these orbitals to an empty orbital, usually an antibonding orbital, σ*or π*

I.Introduction

Observed electronic transitions

8. Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm

9. Special equipment to study *vacuum* or *far UV* is required

10. Routine organic UV spectra are typically collected from 200-700 nm

11. This limits the transitions that can be observed:

$\sigma \rightarrow \sigma^*$	alkanes	150 nm	
$\sigma \rightarrow \pi^*$	carbonyls	170 nm	
$\pi \rightarrow \pi^*$	unsaturated cmpds.	**√ - if conjugated!** 180 nm	
$n \rightarrow \sigma^*$	O, N, S, halogens	190 nm	
$n \rightarrow \pi^*$	carbonyls	300 nm	√

Type of Transitions

- $\sigma \rightarrow \sigma^*$

  High energy required, vacuum UV range

  CH_4: λ = 125 nm

- $n \rightarrow \sigma^*$

  Saturated compounds, CH_3OH etc (λ = 150 - 250 nm)

- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$

  Mostly used! λ = 200 - 700 nm

Type of transitions

s to s* and *n* to s*

1. s to s* Transitions

An electron in a bonding s orbital is excited to the corresponding antibonding orbital. The energy required is large. For example, **methane (which has only C-H bonds, and can only undergo s to s* transitions)** shows an absorbance maximum at 125 nm. Absorption maxima due to s to s* transitions are not seen in typical UV-Vis. spectra (200 - 700 nm)

2. n to s* Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of *n* to s* transitions. These transitions usually need less energy than s to s * transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm.

n to p* and p to p* Transitions:

Most absorption spectroscopy of organic compounds is based on transitions of *n* or p electrons to the p* excited state. This is because the absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200 - 700 nm). **These transitions need an unsaturated group in the molecule to provide the p electrons.**

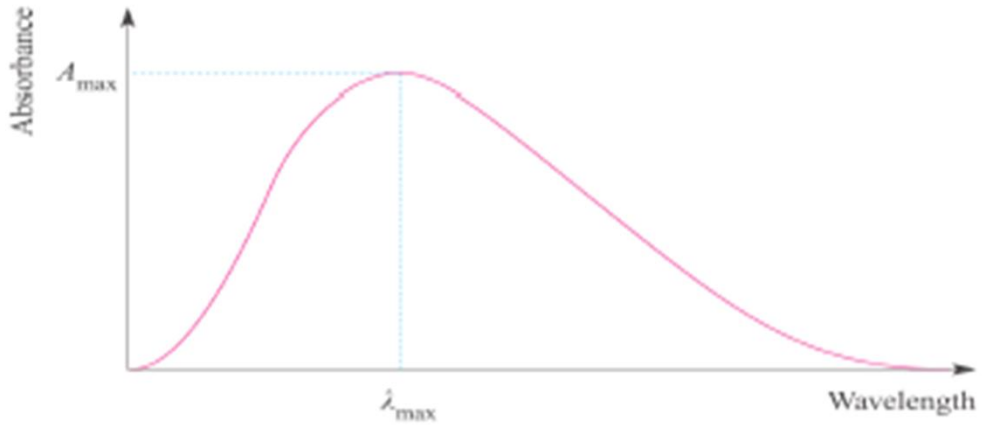
Molar absorptivity's from *n* to p* transitions are relatively low, and range from 10 to 100 L mol^{-1} cm^{-1} . p to p* transitions normally give molar absorptivity's between 1000 and 10,000 L mol^{-1} cm^{-1}

Often, during electronic spectroscopy, the electron is excited first from an initial low energy state to a higher state by absorbing photon energy from the spectrophotometer. If the wavelength of the incident beam has enough energy to promote an electron to a higher level, then we can detect this in the absorbance spectrum.

Once in the excited state, the electron has higher potential energy and will relax back to a lower state by emitting photon energy. This is called fluorescence and can be detected in the spectrum as well.

- 400 nm corresponds to 25000 cm^{-1}
- Absorption bands in electronic spectra are usually broad
- Absorption of a photon of light occurs in ≅ 10^{-18} s and molecular vibrations and rotations occur more slowly.

20.18



I.Introduction

Band Structure

1.Unlike IR (or later NMR), where there may be upwards of 5 or more resolvable peaks from which to elucidate structural information, UV tends to give wide, overlapping bands

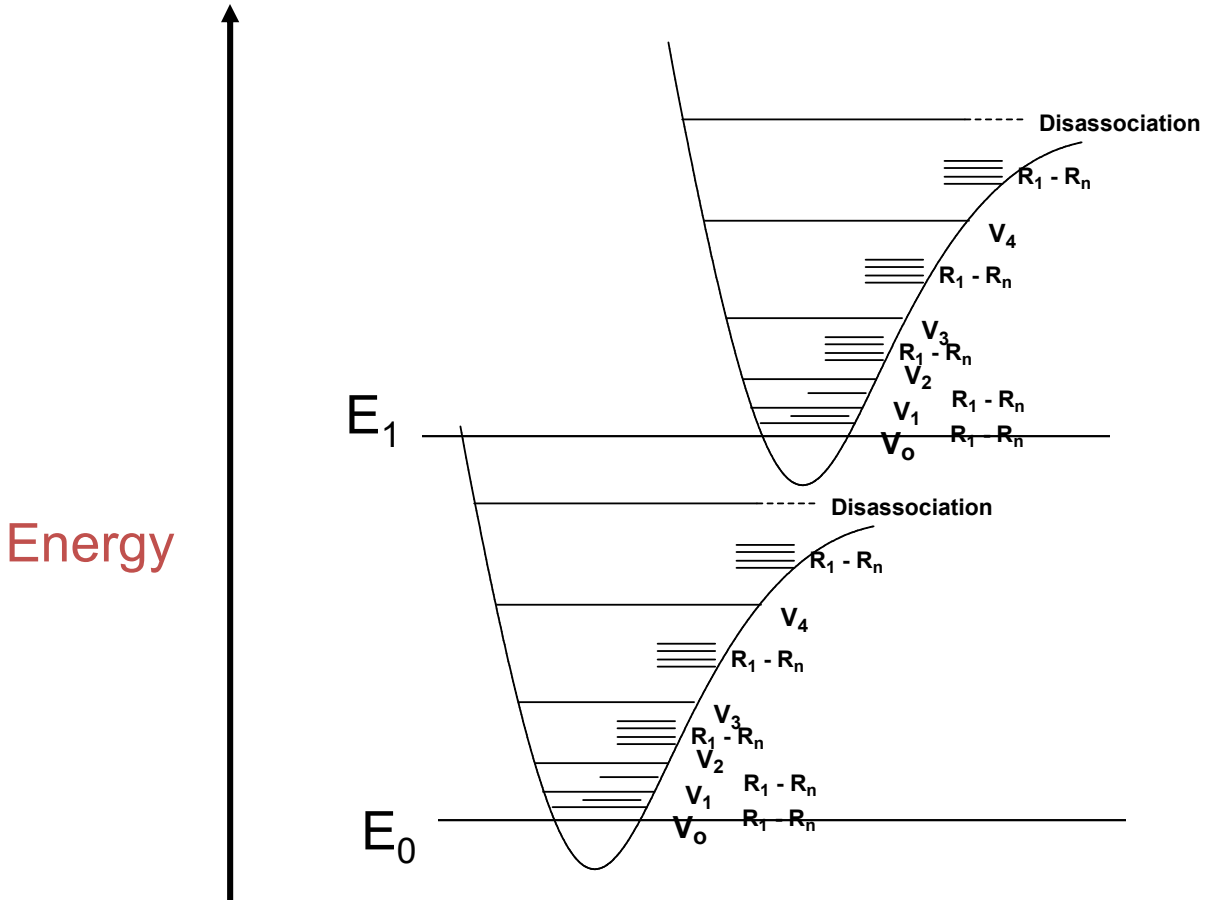
2.It would seem that since the electronic energy levels of a pure sample of molecules would be quantized, fine, discrete bands would be observed – for atomic spectra.

3.In molecules, when a bulk sample of molecules is observed, not all bonds (read – pairs of electrons) are in the same vibrational or rotational energy states

4.This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels in neat samples

I.Introduction
E.Band Structure

5.When these energy levels are superimposed, the effect can be readily explained – any transition has the possibility of being observed



Components of instrumentation:

- Sources
- Sample Containers
- Monochromators
- Detectors

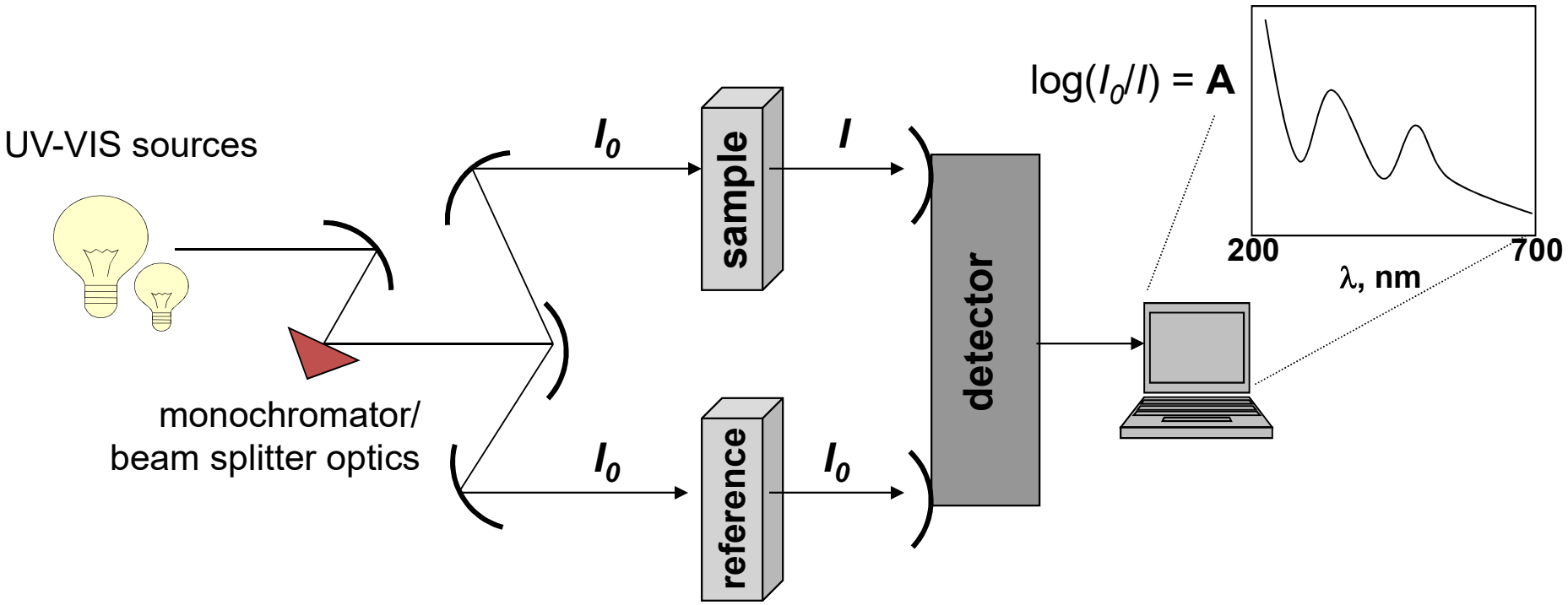
- Sources: Argon, Xenon, Deuterium, or Tungsten lamps
- Sample Containers: Quartz, Borosilicate, Plastic
- Monochromators: Quartz prisms and all gratings
- Detectors: Photomultipliers

II. Instrumentation and Spectra

Instrumentation

1. The construction of a traditional UV-VIS spectrometer is very similar to an IR, as similar functions – sample handling, irradiation, detection and output are required

2. Here is a simple schematic that covers most modern UV spectrometers:



II. Instrumentation and Spectra

Instrumentation

3. Two sources are required to scan the entire UV-VIS band:
   - Deuterium lamp – covers the UV – 200-330
   - Tungsten lamp – covers 330-700

4. As with the dispersive IR, the lamps illuminate the entire band of UV or visible light; the monochromator (grating or prism) gradually changes the small bands of radiation sent to the beam splitter

5. The beam splitter sends a separate band to a cell containing the sample solution and a reference solution

6. The detector measures the difference between the transmitted light through the sample (I) vs. the incident light (I_0) and sends this information to the recorder

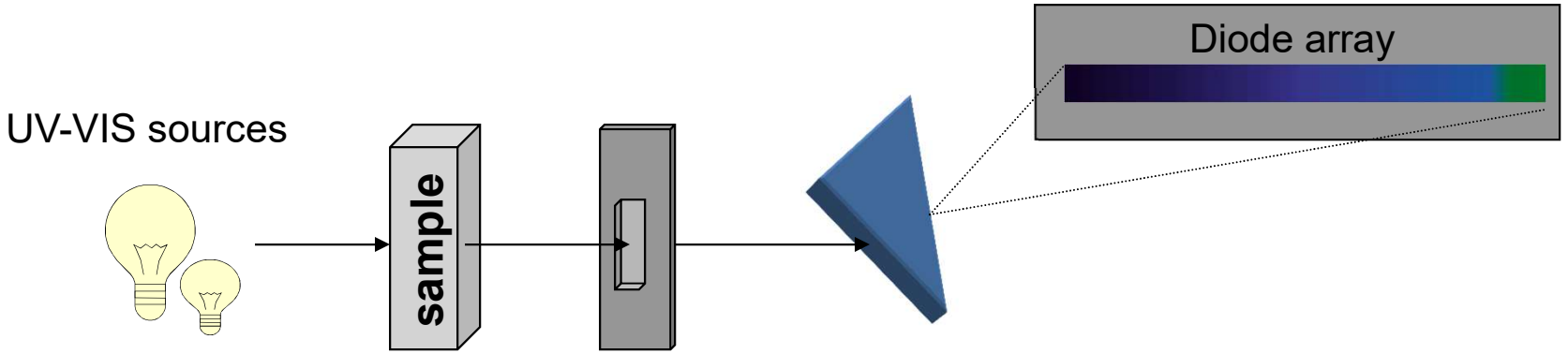
II.Instrumentation and Spectra

Instrumentation

7. As with dispersive IR, time is required to cover the entire UV-VIS band due to the mechanism of changing wavelengths

8. A recent improvement is the diode-array spectrophotometer - here a prism (dispersion device) breaks apart the full spectrum transmitted through the sample

9. Each individual band of UV is detected by a individual diodes on a silicon wafer simultaneously – the obvious limitation is the size of the diode, so some loss of resolution over traditional instruments is observed



II. Instrumentation and Spectra

Instrumentation – Sample Handling

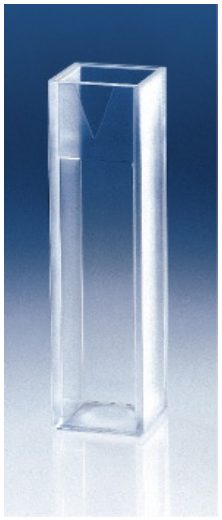
1. Virtually all UV spectra are recorded solution-phase

2. Cells can be made of plastic, glass or quartz

3. Only quartz is transparent in the full 200-700 nm range;
4. plastic and glass are only suitable for visible spectra

5. Concentration (we will cover shortly) is empirically determined

6. A typical sample cell (commonly called a ***cuvet***):



The sample cell contains a solution of the substance you are testing - usually very dilute. The solvent is chosen so that it doesn't absorb any significant amount of light in the wavelength range we are interested in (200 - 800 nm).

II. Instrumentation and Spectra

Instrumentation – Sample Handling

5. Solvents must be clear in the region to be observed; the wavelength where a solvent is no longer transparent is referred to as the cutoff

6. Since spectra are only obtained up to 200 nm, solvents typically only need to lack conjugated π systems or carbonyls

Common solvents and cutoffs:

190	acetonitrile
240	chloroform
195	cyclohexane
215	1,4-dioxane
205	95% ethanol
201	*n*-hexane
205	methanol
195	isooctane
190	water

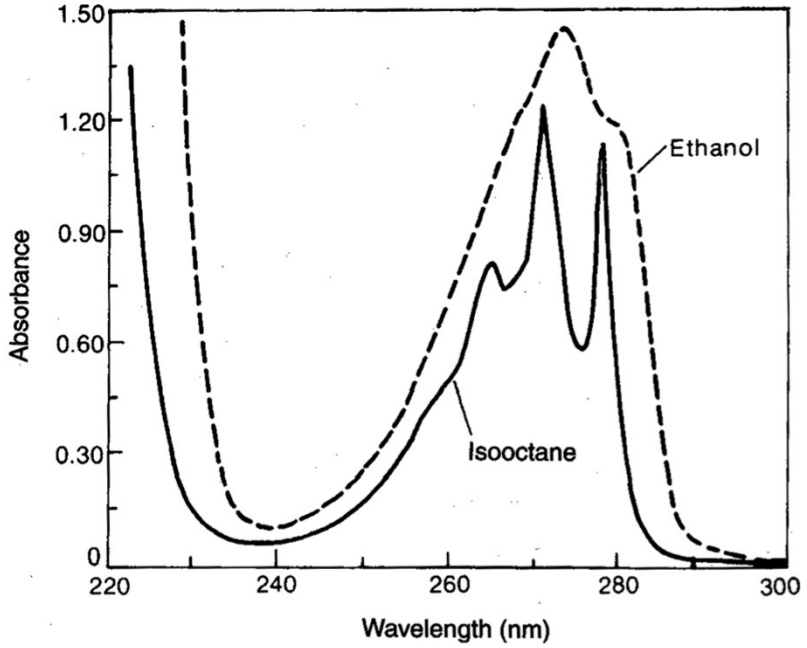
II. Instrumentation and Spectra

Instrumentation – Sample Handling

7.Additionally solvents must preserve the fine structure (where it is actually observed in UV!) where possible

8.H-bonding further complicates the effect of vibrational and rotational energy levels on electronic transitions, dipole-dipole interacts less so

9.The more non-polar the solvent, the better (this is not always possible)



Reflection and Scattering Losses

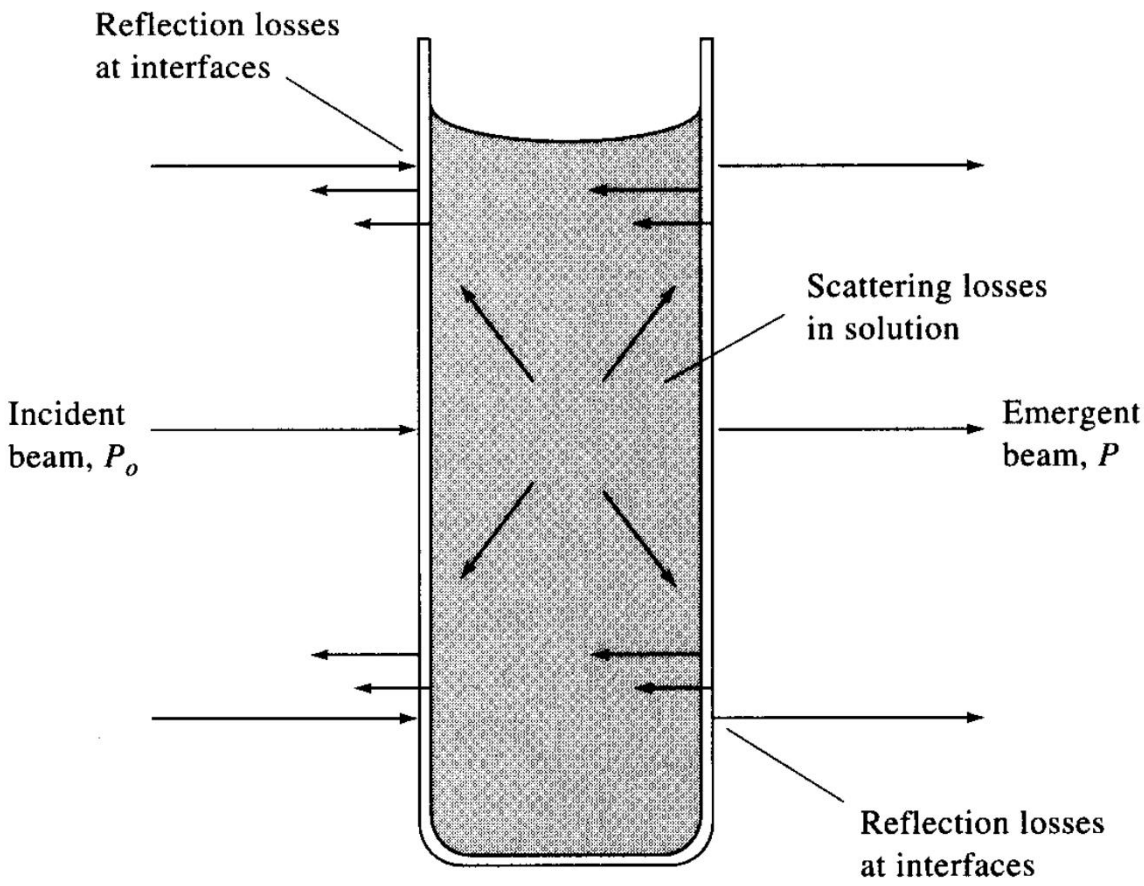


Figure 13-1 Reflection and scattering losses.

A spectrophotometer can be **either *single beam* or *double beam***. In a single beam instrument (such as the Spectronic 20), all of the light passes through the sample cell. must be measured by removing the sample. This was the earliest design and is still in common use in both teaching and industrial labs.

In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. The reference beam intensity is taken as 100% Transmission (or 0 Absorbance), and the measurement displayed is the ratio of the two beam intensities. Some double-beam instruments have two detectors (photodiodes), the sample and reference beam are measured at the same time.

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Single beam, as well as double beam instruments are now on the market. These have the advantage that they are capable of measuring a spectrum very quickly. The principles of the single beam instrument are the same as for the double beam, but data on the reference are taken first, followed by the sample. The complete spectrum can be obtained very quickly. A computer can then read the two sets of data and plot the spectrum on a chart.

This type of system can be in joint application with another technique eg. the outflow from a chromatography column is passed through a small volume cell (often less than 10-2 cm3) so that its ultraviolet/visible spectrum can be obtained as it flows through. This has several advantages:

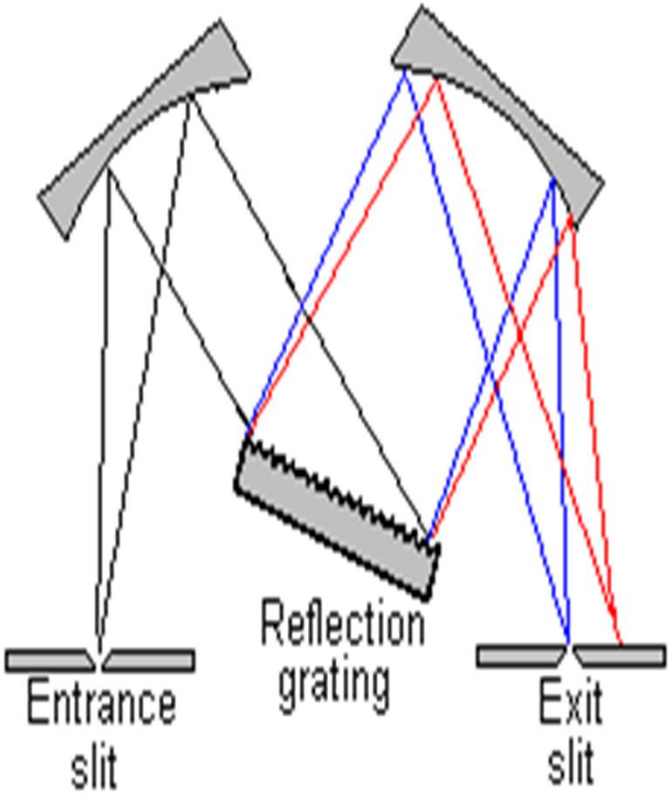
1. **The different solutes do not have to be separated and collected in individual tubes so that their spectra may be obtained successively;**
2. **each spectrum can be determined in a fraction of a second;**
3. **the spectra are stored by a computer so the spectrum of each solute can be compared with a library of known compounds**

Wavelength selector (monochromator)

All monochromators contain the following component parts;

- An entrance slit
- A collimating lens
- A dispersing device (usually a prism or a grating(
- A focusing lens
- An exit slit

Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.



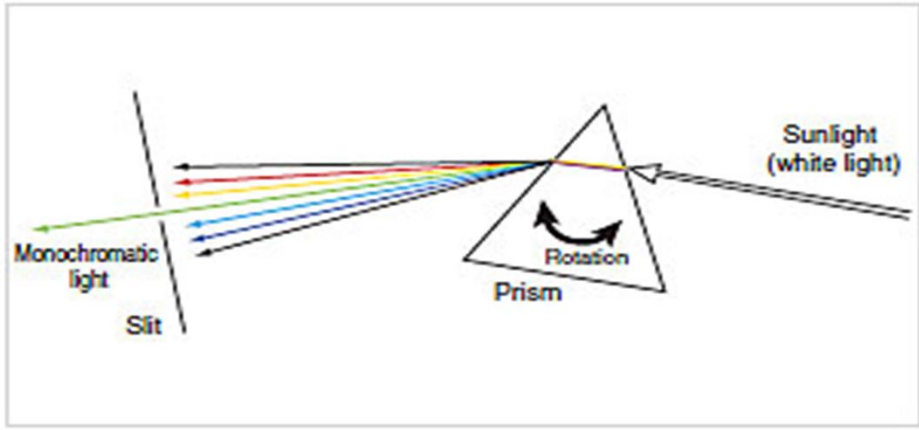


Fig.2 Prism Experiment

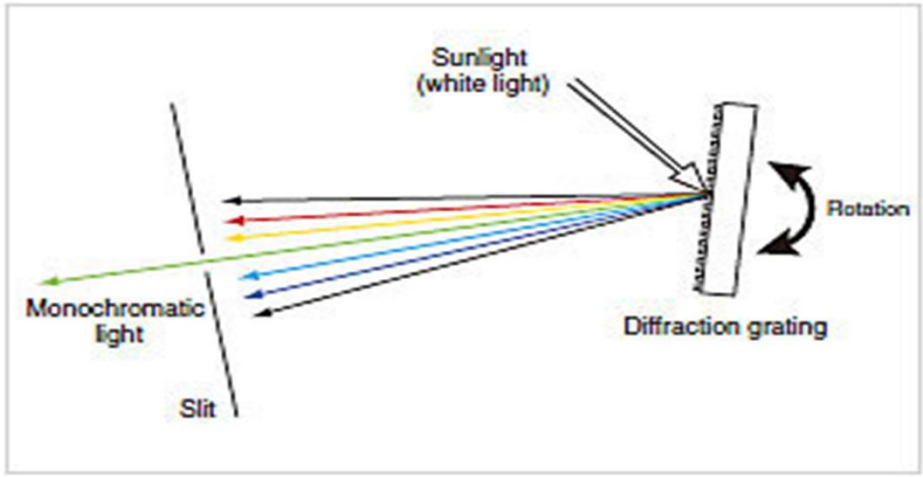


Fig.3 Using a Diffraction Grating

The Detector

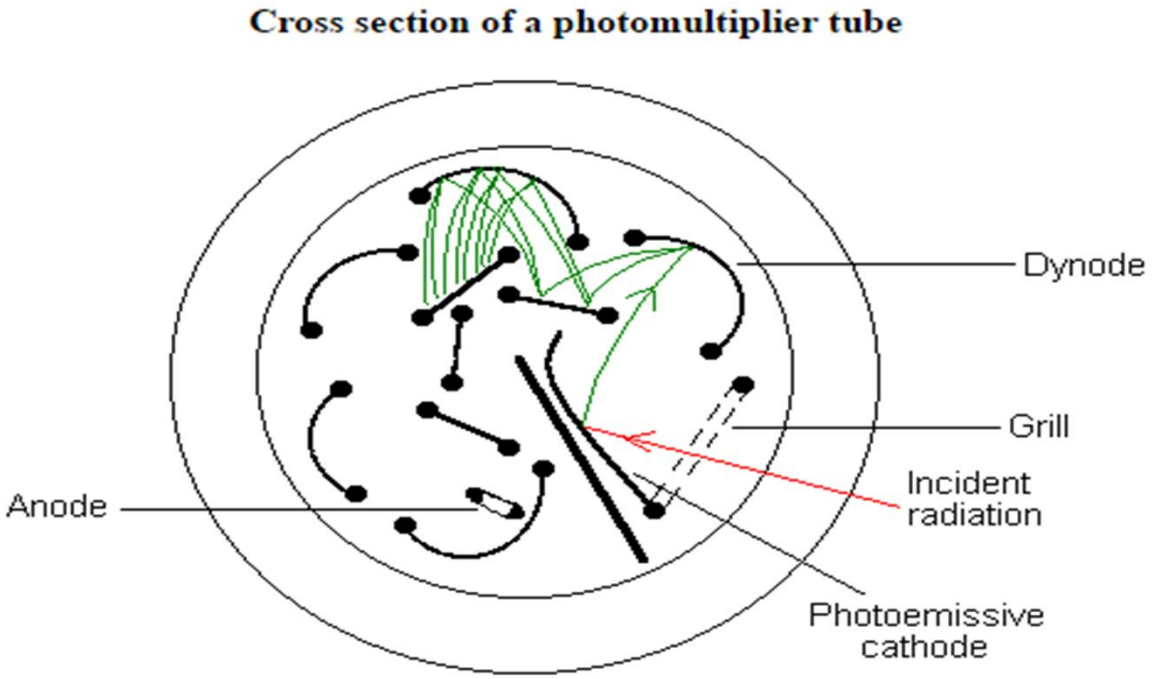
The detector converts the incoming light into a current

The detector is typically a photomultiplier tube(more specifically vacuum phototubes, are extremely sensitive detectors of light in the ultraviolet, visible, and near-infrared ranges of the electromagnetic spectrum. These detectors multiply the current produced by incident light by as much as **100 million time**), a photodiode(is a semiconductor device that converts light into current.

Single photodiode detectors and photomultiplier tubes are used with scanning monochromator, (which filter the light so that only light of a single wavelength reaches the detector at one time).

The scanning monochromator moves the diffraction grating to "step-through" each wavelength so that its intensity may be measured as a function of wavelength.

Photomultipliers are very sensitive to UV and visible radiation. They have fast response times. Intense light damages photomultipliers; they are limited to measuring low power radiation.



The detector and computer

The detector converts the incoming light into a current. The higher the current, the greater the intensity of the light. For each wavelength of light passing through the spectrometer, the intensity of the light passing through the reference cell is measured. This is usually referred to as $\mathbf{I_o}$ - that's **I** for Intensity. The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol**, I**.

If **I** is less than $\mathbf{I_o}$, then obviously the sample has absorbed some of the light. A simple bit of math's is then done in the computer to convert this into something called the ***absorbance*** of the sample - given the symbol, **A**.

The relationship between A and the two intensities is given **by:** $\mathbf{Log_{10}\ I0/I=A}$

Measurement of the spectrum

The UV/visible spectrum is usually taken on a very dilute sol. About 1mg when the compound has a molecular weight of 100 to 200 is weighted accurately and dissolved in the solvent of choice and made up for instance 100 ml. A portion of this transferred to the cell which is so made that the beam of the light passes through a 1 cm thickness. A matched cell containing pure solvent is prepared and each cell placed in the proper place in the spectrometer.

This is so arrange that the two equal beams of UV or Visible light are passed one through the solutions and the other through the pure solvent. The intensities of the transmitted beams are then compared over the whole wavelength range of the instrument. In most spectrometer there are two sources, one of white UV and one of white visible, which have to be changed when a complete scan is required

Solvent Effects

The solvent in which the absorbing species is dissolved also has an effect on the spectrum of the species. Peaks resulting from *n* to p^* transitions are shifted to shorter wavelengths (***blue shift***) with increasing solvent polarity. This arises from increased solvation of the lone pair, which lowers the energy of the *n* orbital. Often (but *not* always), the reverse (i.e. ***red shift***) is seen for p to p^* transitions.

This is caused by attractive polarization forces between the solvent and the absorber, which lower the energy levels of both the excited and unexcited states. This effect is greater for the excited state, and so **the energy difference between the excited and unexcited states is slightly reduced - resulting in a small red shift. This effect also influences *n* to p^* transitions but is over shadowed by the blue shift resulting from solvation of lone pairs.**

Example: Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (**Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.)**

Solvent polarity and pH can affect the absorption spectrum of an organic compound. **Tyrosine (4-hydroxyphenylalanine, is one of the 22 amino acids that are used by cells to synthesize proteins**), for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.

- Blue shift (n- π^*) (Hypsocromic shift)
  - Increasing polarity of solvent → better solvation of electron pairs (n level has lower E)
  - → peak shifts to the blue (more energetic)
  - 30 nm (hydrogen bond energy)

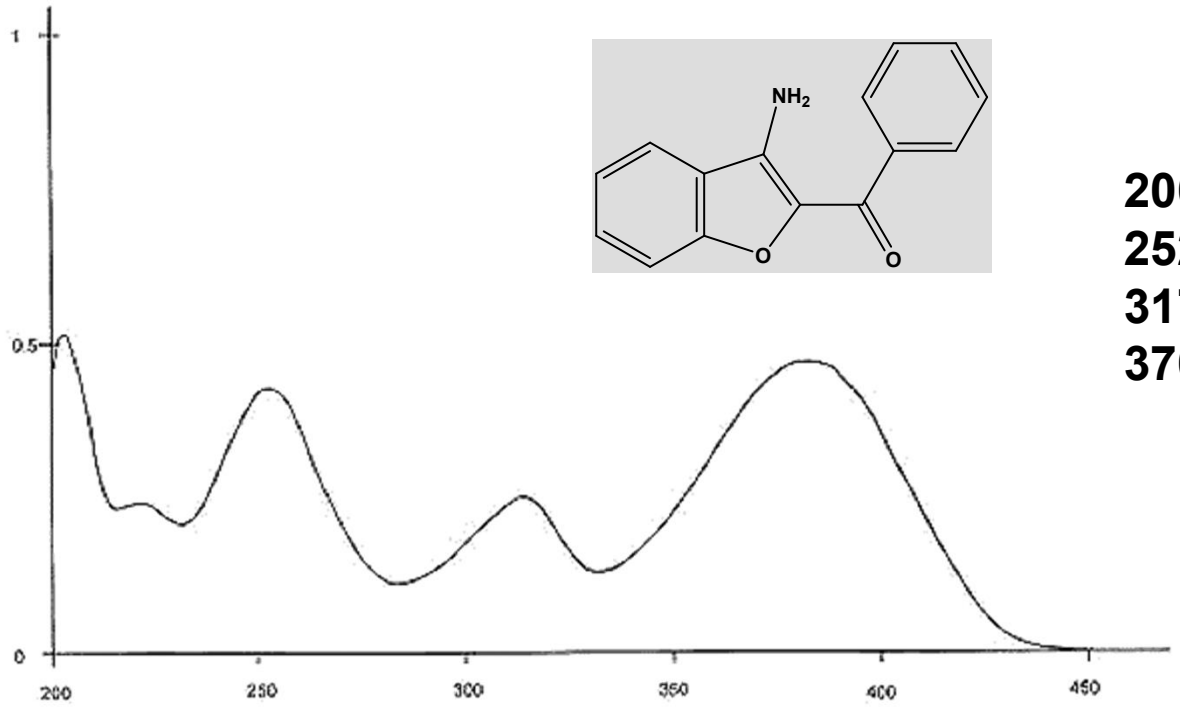
- Red shift (n- π^* and $\pi - \pi^*$) (Bathochromic shift)
  - Increasing polarity of solvent, then increase the attractive polarization forces between solvent and absorber, thus decreases the energy of the unexcited and **excited states** with the later greater
  - → peaks shift to the red
  - 5 nm

II. Instrumentation and Spectra

The Spectrum

1. The x-axis of the spectrum is in wavelength; 200-350 nm for UV, 200-700 for UV-VIS determinations

2. Due to the lack of any fine structure, spectra are rarely shown in their raw form, rather, the peak maxima are simply reported as a numerical list of "lamba max" values or λ_{max}



206 nm λ_{max} =
252
317
376

The empirical laws, Lambert's law state that the fraction of incident light absorbed is independent of the intensity of the source, while the Beer's law, state that the absorption is proportional to the number of absorbing molecules, so from these laws the remaining variable gives:

$$\text{Log} I_0/I = €.L.C$$

I_0 and I are the intensities of the incident and transmitted light respectively, L is the path length of the absorbing solutions in cm which is always equal 1 or 2 and C is the concentrations in mole/liter. The Log I_0/I is called the absorbance or optical density A, € is known as the molar extinction coefficient and has unit of $1000 cm^2/mol$.

Absorption Law:

The Beer-Lambert law states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. It is necessary to know how quickly the absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

II. Instrumentation and Spectra

The Spectrum

1. The y-axis of the spectrum is in absorbance, *A*

2. From the spectrometers point of view, absorbance is the inverse of transmittance: $A = \log_{10} (I_0/I)$

3. From an experimental point of view, three other considerations must be made:

   i. a longer *path length, l* through the sample will cause more UV light to be absorbed – linear effect

   ii. the greater the *concentration, c* of the sample, the more UV light will be absorbed – linear effect

   iii. some electronic transitions are more effective at the absorption of photon than others – *molar absorptivity,* ε

II. Instrumentation and Spectra

The Spectrum

4. These effects are combined into the Beer-Lambert Law: $A = \varepsilon c l$

i. for most UV spectrometers, l would remain constant (standard cells are typically 1 cm in path length)

ii. concentration is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M

iii. molar absorptivities vary by orders of magnitude:
values of 10^4-10^6 are termed *high intensity absorptions*
values of 10^3-10^4 are termed *low intensity absorptions*
values of 0 to 10^3 are the absorptions of *forbidden transitions*

A is unit less, so the units for ε are $\mathbf{cm^{-1} \cdot M^{-1}}$ and are rarely expressed

5. Since path length and concentration effects can be easily factored out, absorbance simply becomes proportional to ε, and the y-axis is expressed as ε directly or as the logarithm of ε

Selection Rules and Intensity

The irradiation of organic molecules may or may not give rise to excitation of electrons from one orbital (usually a lone – pair or bonding orbital) to another orbital (usually non-bonding or antibonding), it can be shown that

$\mathcal{E} = 0.87 \times 10^{-20} p.a$

P=transition probability (values from 0 to 1)

a= target area of the absorbing system (chromophore)

With common chromophore of the order 10 Aº long a transition of unit probability will have an $\mathcal{E}$ value of 10^5.

In practice, a chromophore giving rise to absorption by allowed transition will have $\mathcal{E}$ value about 10000 while those with low transition with molar extinction coefficient value equal 1000

Molar absorptivities

ε **= 8.7 x 10 ^{19} P A**

A: cross section of molecule in cm^2 (~10^{-15})

P: Probability of the electronic transition **(0-1)**

P = 0.1-1 → allowable transitions

P<0.01 → forbidden transitions

Molecular Absorption

- M + hν → M* (absorption 10^{-8} sec)
- M* → M + **heat** (relaxation process)
- M* → A+B+C (photochemical decomposition)
- M* → M + $h\nu$ (emission)

Beer's law and mixtures

- Each analyte present in the solution absorbs light!
- The magnitude of the absorption depends on its ε
- $\mathbf{A_{total} = A_1 + A_2 + \ldots + A_n}$
- $\mathbf{A_{total} = \varepsilon_1 bc_1 + \varepsilon_2 bc_2 + \ldots + \varepsilon_n bc_n}$

If $\varepsilon_1 = \varepsilon_2 = \varepsilon_n$ then immediate determination is impossible

LAMBERT-BEER LAW

Power of radiation after passing through the solvent

Power of radiation after passing through the sample solution

$$T = \frac{P_{solution}}{P_{solvent}} = \frac{P}{P_0}$$

$$A = -\log T = -\log\left(\frac{P}{P_0}\right)$$

$$A = abc = kc$$

a = absorptivi ty

b = pathlength

c = concentrat ion

The amount of absorbance

the absorbance ranges from 0 to 1, but it can go higher than that. An absorbance of **0** at some wavelength means that no light of that particular wavelength has been absorbed. **The intensities of the sample and reference beam are both the same, so the ratio I_o/I is 1. and Log_{10} of 1 is zero**. An absorbance of **1** happens when 90% of the light at that wavelength has been absorbed,which means that the intensity is 10% of what it would otherwise be.

In that case, I_o/I is 100/I0 (=10) and log_{10} of 10 is 1.

Deviations from the Beer–Lambert law

At sufficiently high concentrations, the absorption bands will saturate and show absorption destruction. The absorption peak appears to crush because close to 100% of the light is already being absorbed. **One test that can be used to test for this effect is to vary the path length of the measurement.** In the Beer-Lambert law, varying concentration and path length has an equivalent effect—diluting a solution by a factor of 10 has the same effect as shortening the path length by a factor of 10.

.

Solutions that are not homogeneous can show deviations from the Beer-Lambert law because of the phenomenon of absorption destruction. This can happen, for instance, where the absorbing substance is located within suspended particles (see Beer's law revisited, Berberan-Santos, *J. Chem. Educ.* 67 (1990) 757, and The deviations will be most noticeable under conditions of low concentration and high absorbance

Absorption Variables

Term and Symbol*	Definition	Alternative Name and Symbol
Radiant power P, P_0	Energy of radiation (in ergs) impinging on a 1-cm^2 area of a detector per second	Radiation intensity I, I_0
Absorbance A	$\log \frac{P_0}{P}$	Optical density D; extinction E
Transmittance T	$\frac{P}{P_0}$	Transmission T
Path length of radiation† b	—	l, d
Absorptivity† a	$\frac{A}{bc}$	Extinction coefficient k
Molar absorptivity‡ ϵ	$\frac{A}{bc}$	Molar extinction coefficient

*Terminology recommended by the American Chemical Society (*Anal. Chem.*, **1990,** *62*, 91).

†c may be expressed in g/L or in other specified concentration units; b may be expressed in cm or in other units of length.

‡c is expressed in mol/L; b is expressed in cm.

II. Instrumentation and Spectra

Practical application of UV spectroscopy

1.UV was the first organic spectral method, however, it is rarely used as a primary method for structure determination

2.It is most useful in combination with NMR and IR data to elucidate unique electronic features that may be ambiguous in those methods

3.It can be used to assay (via λ_{max} and molar absorptivity) the proper irradiation wavelengths for photochemical experiments, or the design of UV resistant paints and coatings

4.The most universal use of UV is as a detection device for HPLC; since UV is consumed for solution phase samples vs. a reference solvent this is easily combined into LC design

Chromophores

These words used to describe the system that containing the electrons which are responsible for the absorptions or electronic transitions and there are simple and conjugate chromophore **with common chromophore of order of 10Å long a transition unit probability will have an € value of 10^5.**

In general, the longer a particular kind of chromophore the more intense the absorptions. In practice, a chromophore giving rise to absorption by fully allowed transition will have € value greater than 10000 while those with low transitions probabilities will have € value below 100. Most of the simple and conjugated chromophores are listed below:

There are rules about which transitions are allowed and which are forbidden. These are so complicated because of the symmetry and multiplicity both of the ground state and excited state orbitals so when ε_{max} less than about 1000 are the result of forbidden transitions. Two important forbidden transitions are observed;

a) **n-π* band near 300 nm of ketones which ε value 10 – 100.**

b) **the Benzen band 260 nm with ε value 100**

that because of symmetry and by substitutions which makes the absorptions are strictly forbidden.

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

(i) $\Delta S = 0$ The Spin Rule

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

(ii) $\Delta L = +/- 1$ The Orbital Rule (Laporte)

The second rule says that if the molecule has a centre of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

III. Chromophores

Definition

1. Remember the electrons present in organic molecules are involved in covalent bonds or lone pairs of electrons on atoms such as O or N

2. Since similar functional groups will have electrons capable of discrete classes of transitions, the characteristic energy of these energies is more representative of the functional group than the electrons themselves

3. A functional group capable of having characteristic electronic transitions is called a chromophore (*color loving*)

4. Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions

5. Auxochrome: is a functional group that does not absorb in UV region but has the effect of shifting chromophore peaks to longer wavelength as well as increasing their intensity..

The longer the conjugated carbon chain in the absorbing system, the greater the intensity of the absorption. This is shown by the spectra of the polyenes CH_3-$(CH{=}CH)_n$-CH_3, where n=3,4 and 5 (*Fig. 15*).

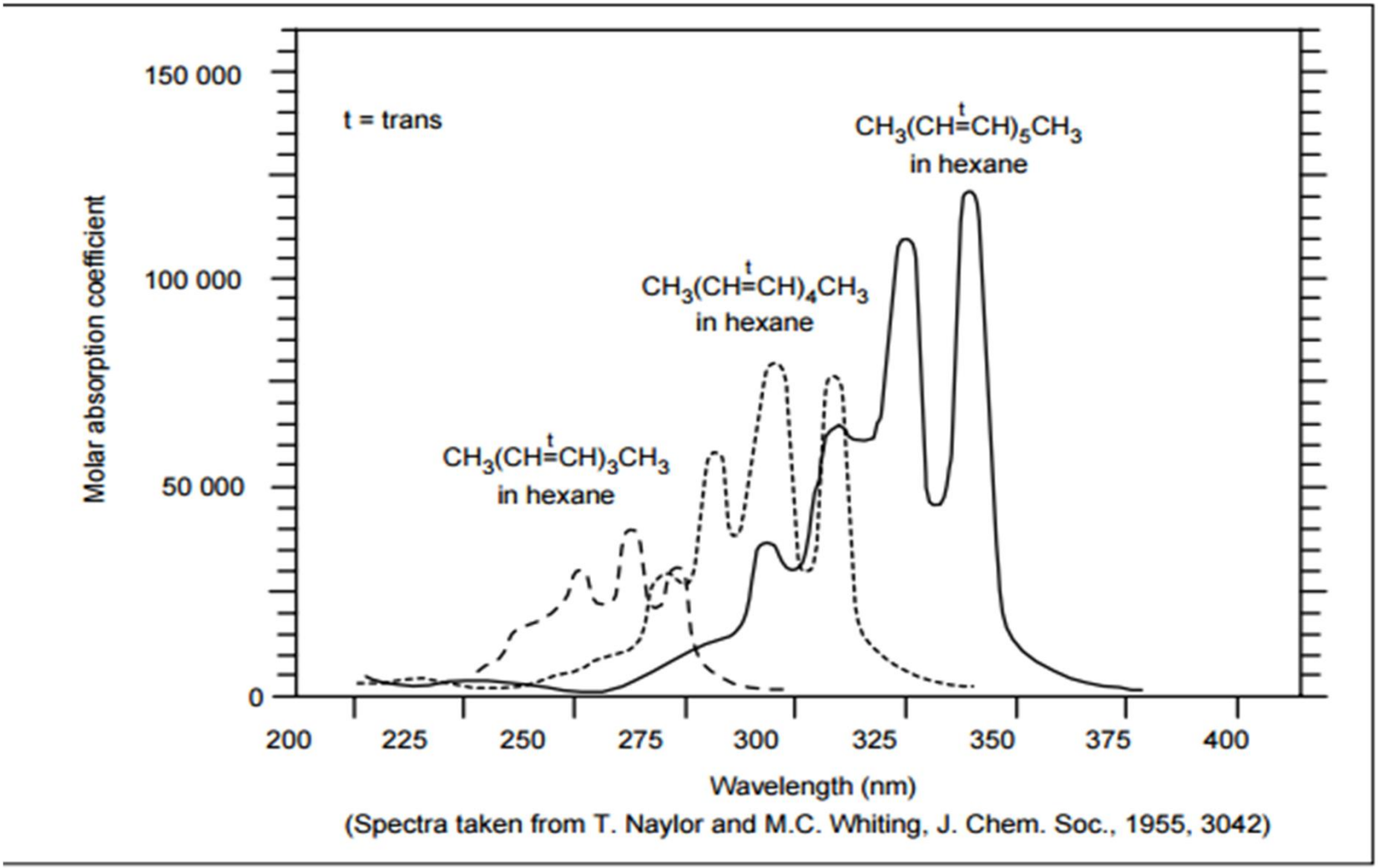
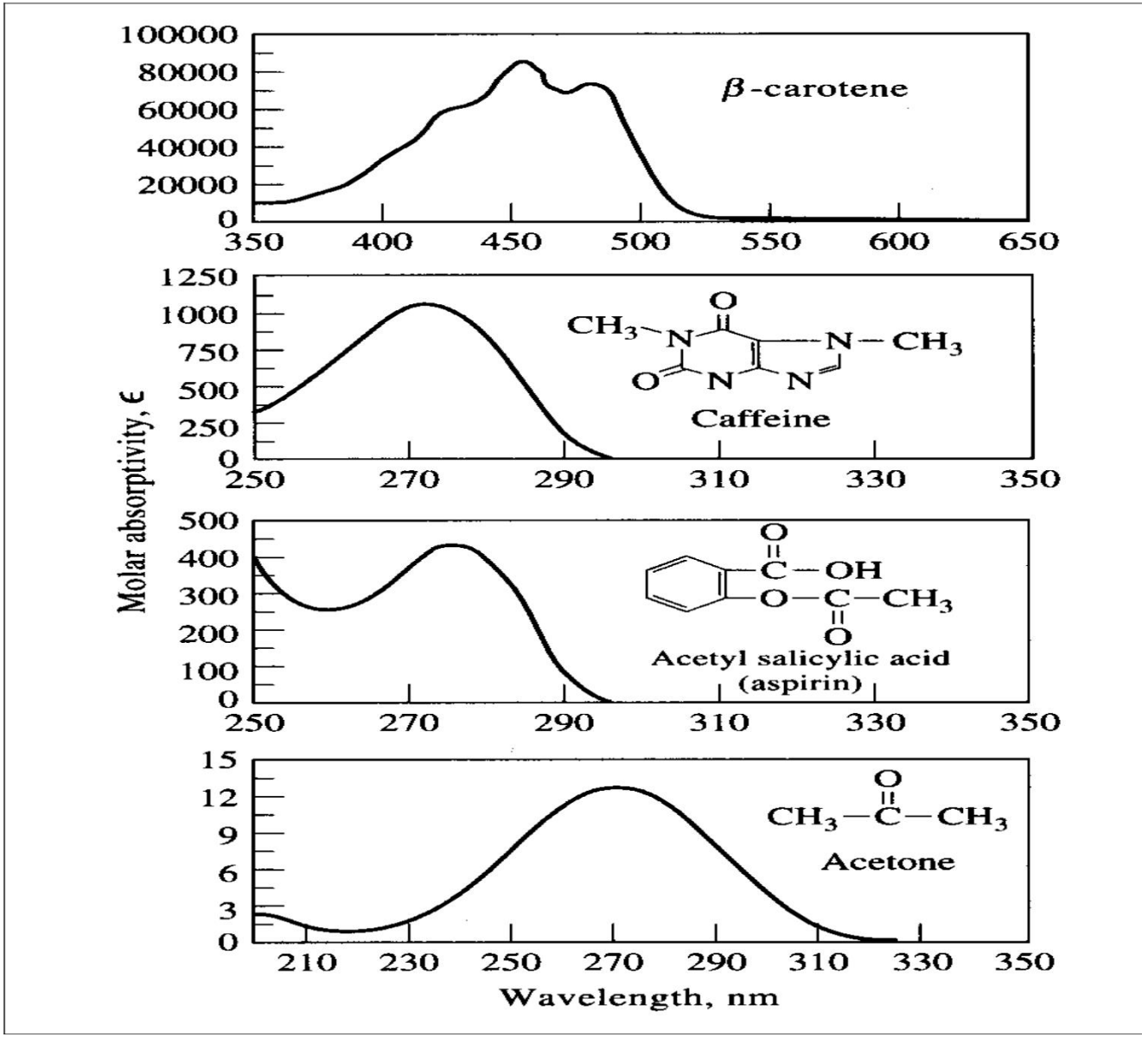


Figure 15 Ultraviolet/visible spectra of the polyenes $CH_3(CH{=}CH)_nCH_3$, where n=3,4 and 5

Typical UV Absorption Spectra

Chromophores?



Summary of transitions for organic molecules

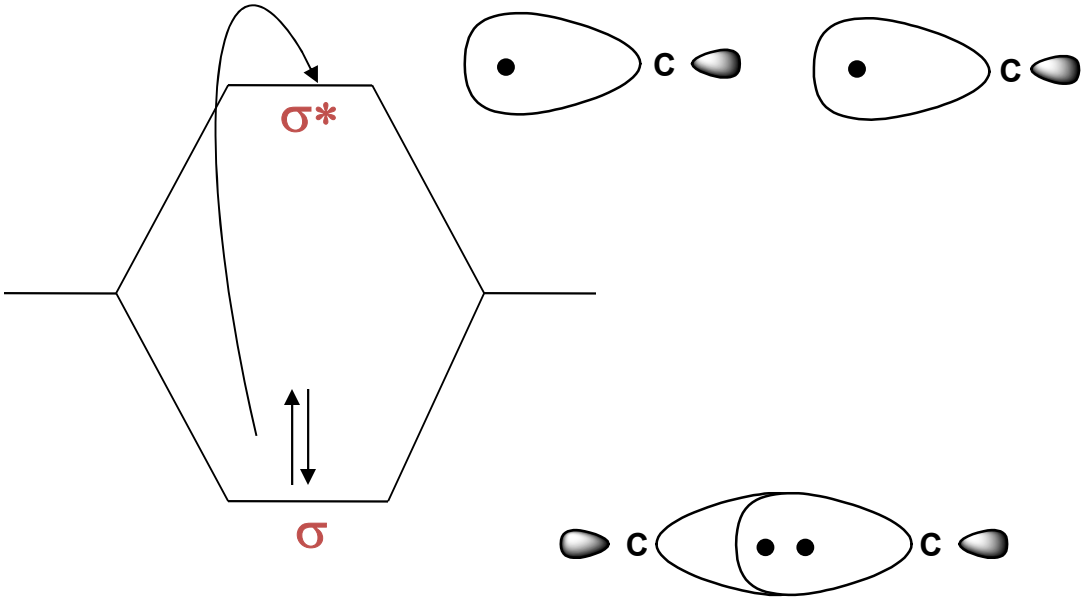
- $\sigma \rightarrow \sigma^*$ transition in vacuum UV (single bonds)
- *n* $\rightarrow \sigma^*$ saturated compounds with non-bonding electrons
- λ ~ 150-250 nm
- ε ~ 100-3000 (not strong)
- *n* $\rightarrow \pi^*$, $\pi \rightarrow \pi^*$ requires unsaturated functional groups (eq. double bonds) most commonly used, energy good range for UV/Vis
- λ ~ 200 - 700 nm
- *n* $\rightarrow \pi^*$: ε ~ 10-100
- $\pi \rightarrow \pi^*$: ε ~ 1000 – 10,000

III. Chromophores

Organic Chromophores

1.Alkanes – only posses σ-bonds and no lone pairs of electrons, so only the high energy σ → σ* transition is observed in the far UV

This transition is destructive to the molecule, causing cleavage of the σ-bond

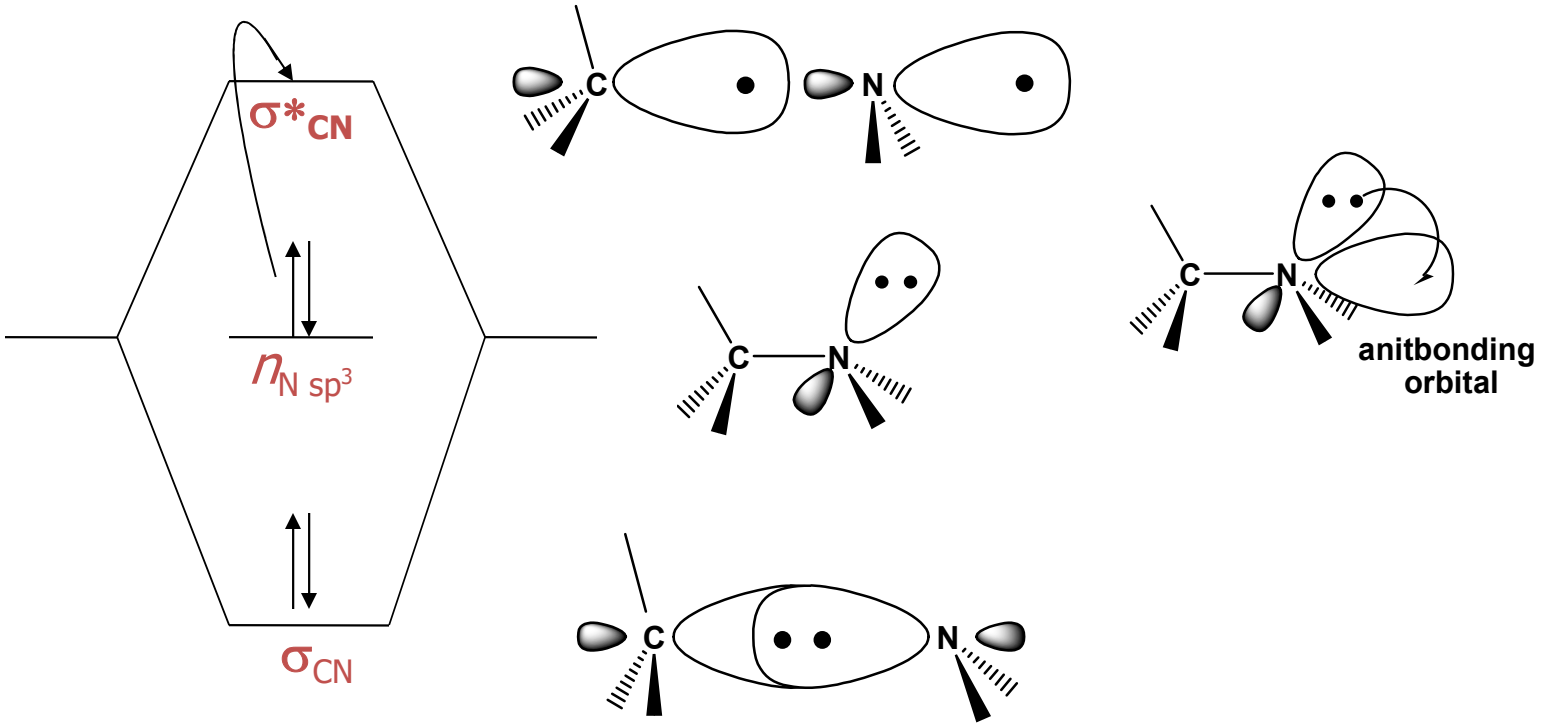


III. Chromophores

Organic Chromophores

2.Alcohols, ethers, amines and sulfur compounds – in the cases of simple, aliphatic examples of these compounds the *n* → σ* is the most often observed transition; like the alkane σ → σ* it is most often at shorter λ than 200 nm

Note how this transition occurs from the HOMO to the LUMO

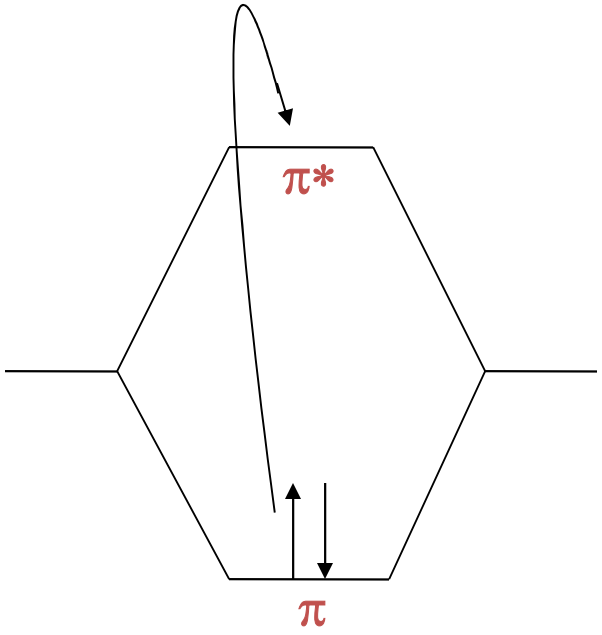


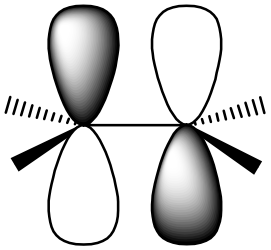
Chromophores .III

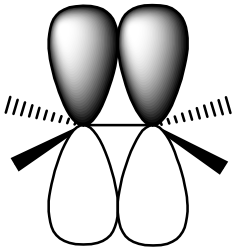
Organic Chromophores

3. Alkenes and Alkynes – in the case of isolated examples of these compounds the $\pi \rightarrow \pi^*$ is observed at 175 and 170 nm, respectively

   Even though this transition is of lower energy than $\sigma \rightarrow \sigma^*$, it is still in the far UV – however, the transition energy is sensitive to substitution







III. Chromophores

Organic Chromophores

4. Carbonyls – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transitions (~285 nm) in addition to $\pi \rightarrow \pi^*$

   Despite the fact this transition is forbidden by the selection rules (ε = 15), it is the most often observed and studied transition for carbonyls

   This transition is also sensitive to substituents on the carbonyl

   Similar to alkenes and alkynes, non-substituted carbonyls undergo the $\pi \rightarrow \pi^*$ transition in the vacuum UV (188 nm, ε = 900); sensitive to substitution effects

III. Chromophores

Organic Chromophores

4. Carbonyls – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transitions (~285 nm) in addition to $\pi \rightarrow \pi^*$

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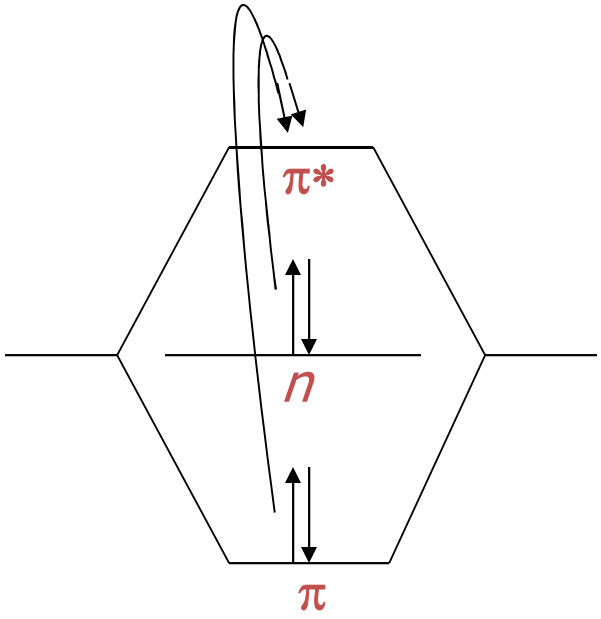
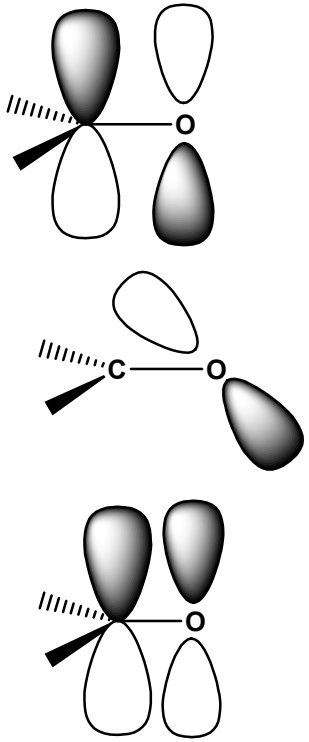
Chromophores .III

Organic Chromophores

4. Carbonyls – *n* → π* transitions (~285 nm); π → π* (188 nm)





It has been determined from spectral studies, that carbonyl oxygen more approximates *sp* rather than sp^2 !

σ_{CO} transitions omitted for clarity

III. Chromophores

C. Substituent Effects

General – from our brief study of these general chromophores, only the weak $n \rightarrow \pi^*$ transition occurs in the routinely observed UV

The attachment of substituent groups (other than H) can shift the energy of the transition

Substituents that increase the intensity and often wavelength of an absorption are called *auxochromes*

Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens

III. Chromophores

C. Substituent Effects

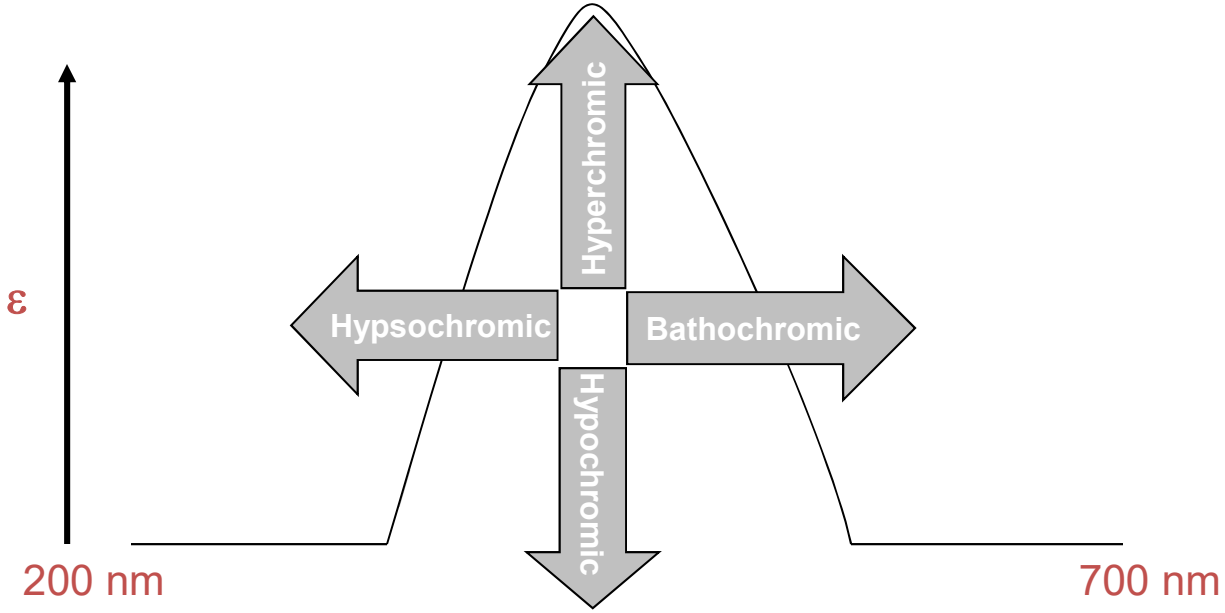
General – Substituents may have any of four effects on a chromophore

i. Bathochromic shift (red shift) – a shift to longer λ; lower energy

ii. Hypsochromic shift (blue shift) – shift to shorter λ; higher energy

iii. Hyperchromic effect – an increase in intensity

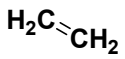
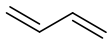
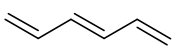
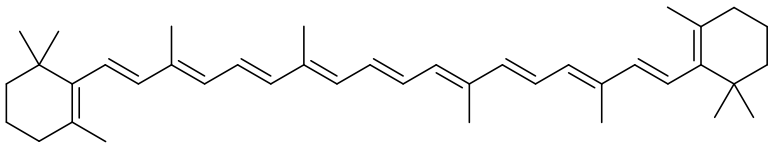
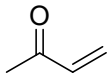
iv. Hypochromic effect – a decrease in intensity



III. Chromophores

C. Substituent Effects

1. Conjugation – most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

	ε	λ_{max} nm	
	15,000	175	
	21,000	217	
	35,000	258	
 β-carotene	125,000	465	
	12	280	$n \rightarrow \pi^*$
	900	189	$\pi \rightarrow \pi^*$
	27	280	$n \rightarrow \pi^*$
	7,100	213	$\pi \rightarrow \pi^*$

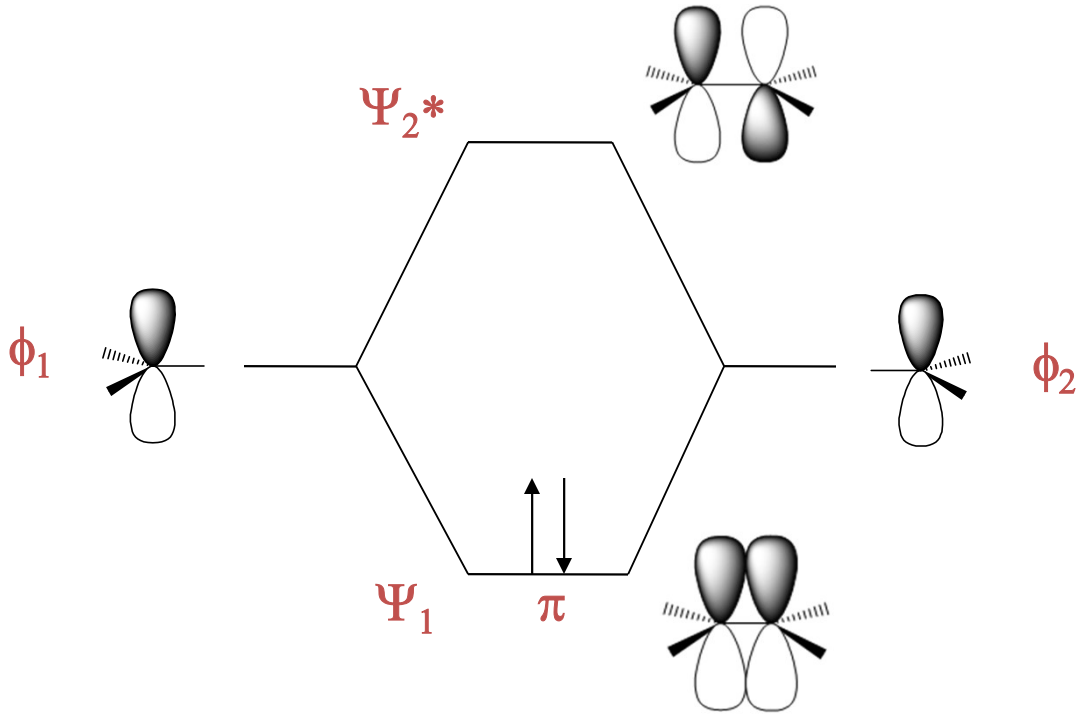
Chromophores .III

C. Substituent Effects

1. Conjugation – Alkenes

The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation

From molecular orbital (MO) theory two atomic *p* orbitals, ϕ_1 and ϕ_2 from two sp^2 hybrid carbons combine to form two MOs Ψ_1 and Ψ_2^* in ethylene

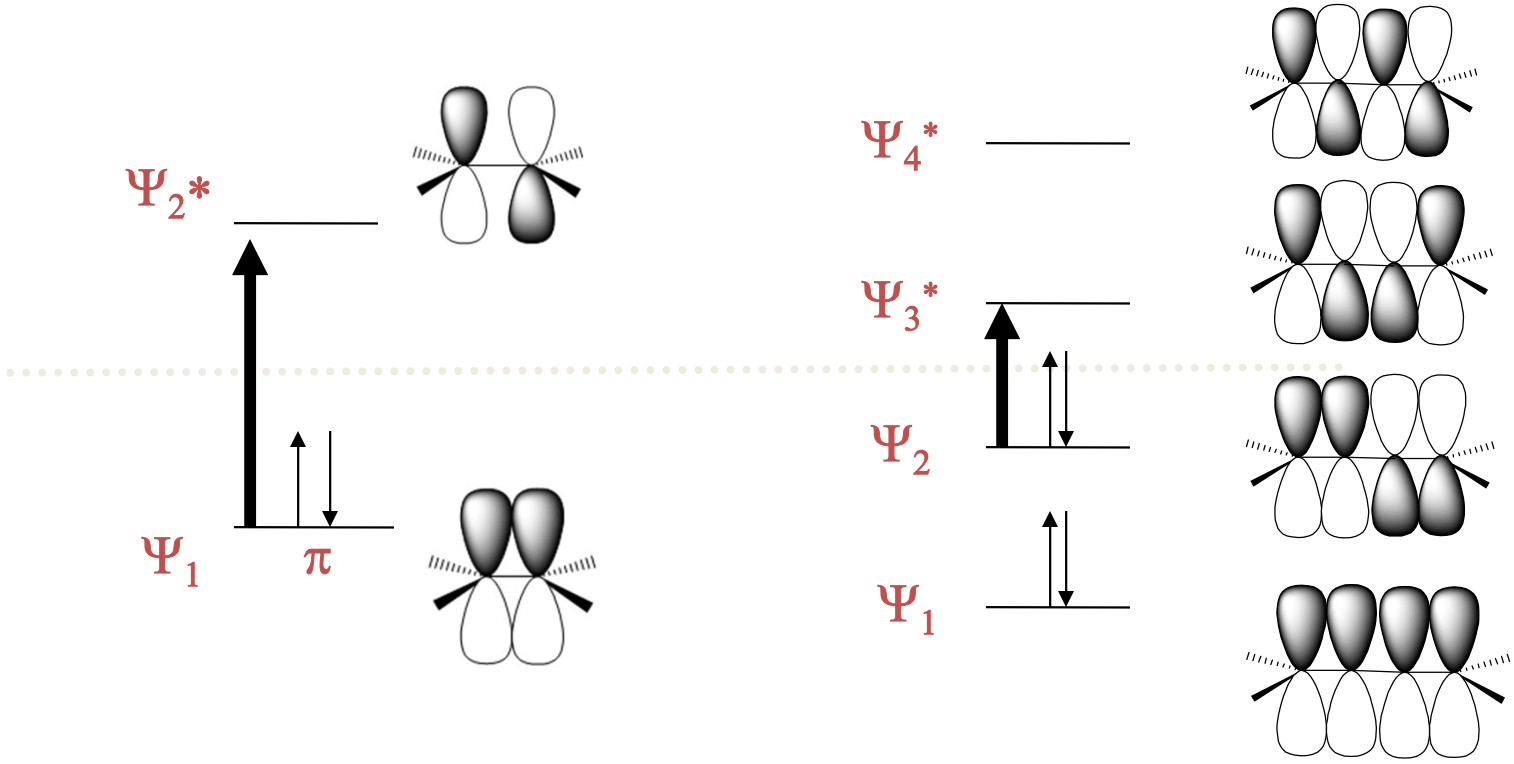


III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

When we consider butadiene, we are now mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene



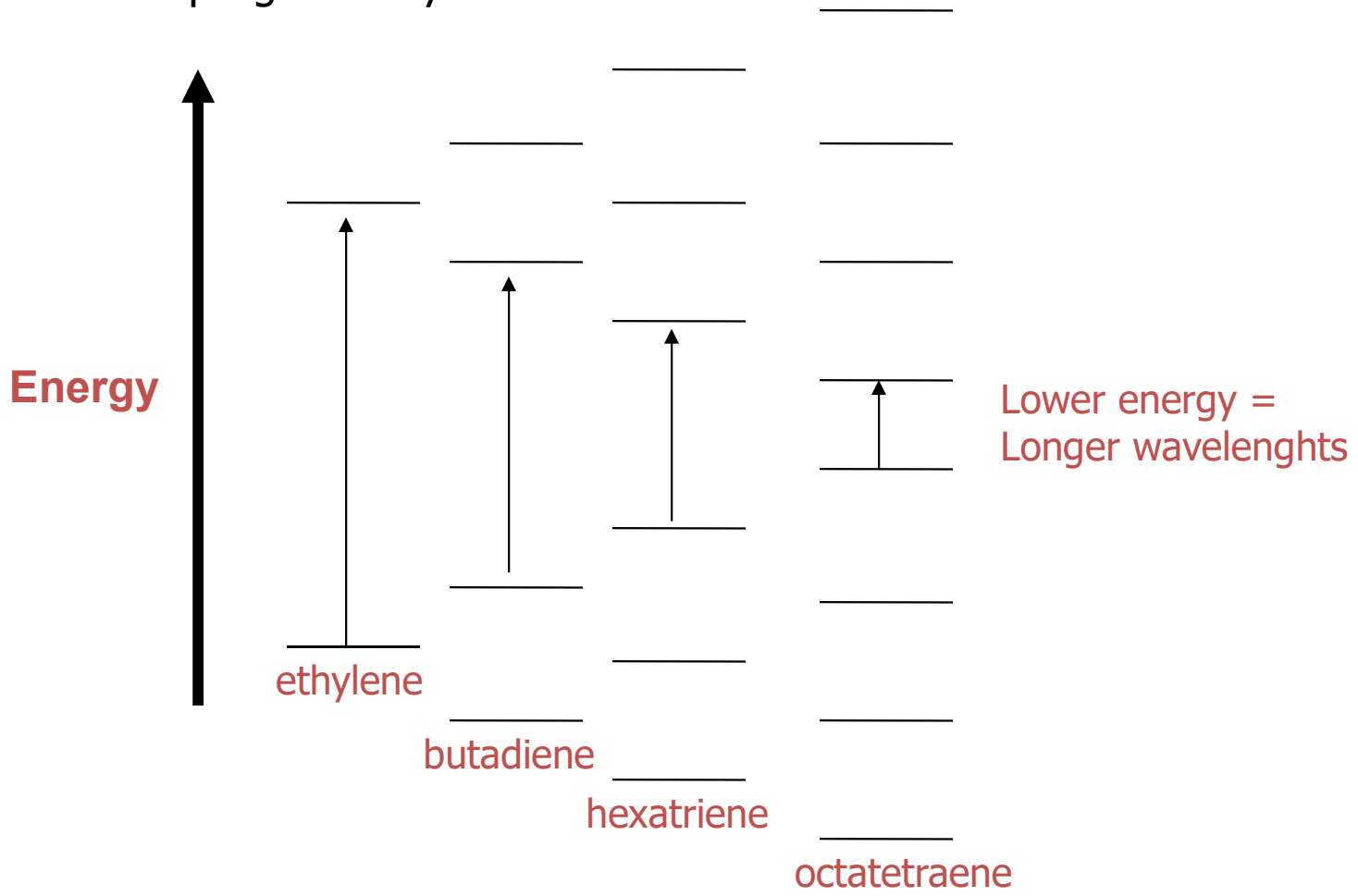
ΔE for the HOMO → LUMO transition is **reduced**

III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:



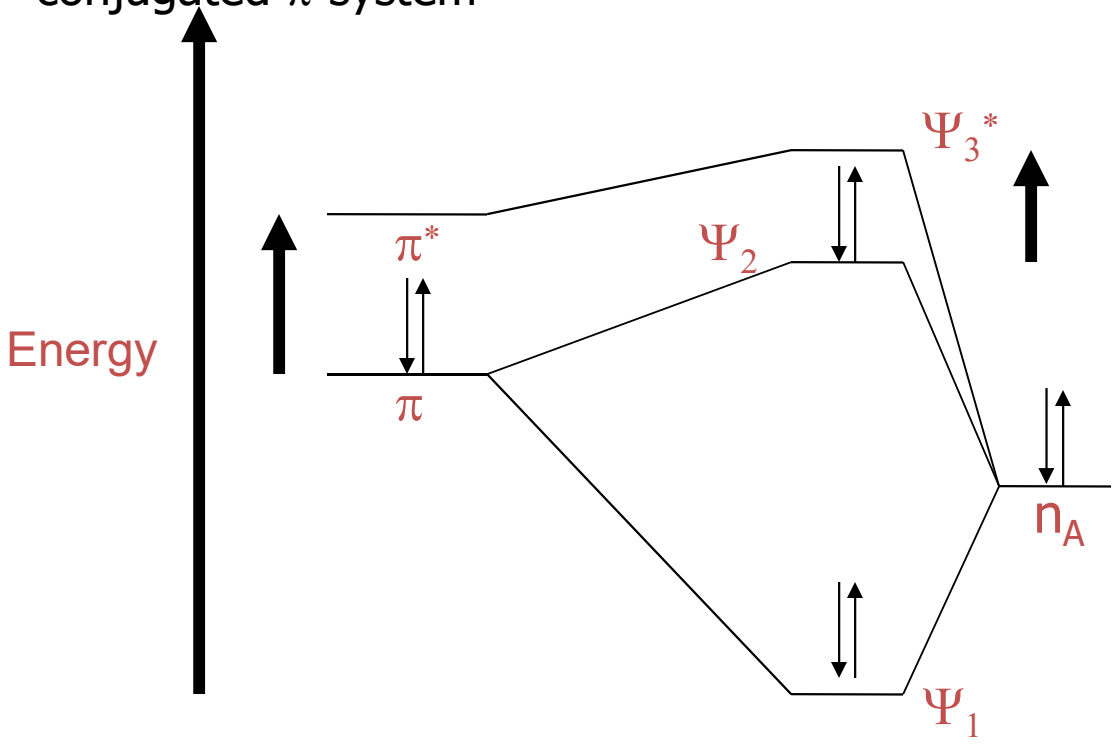
III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Similarly, the lone pairs of electrons on N, O, S, X can extend conjugated systems – auxochromes

Here we create 3 MOs – this interaction is not as strong as that of a conjugated π-system



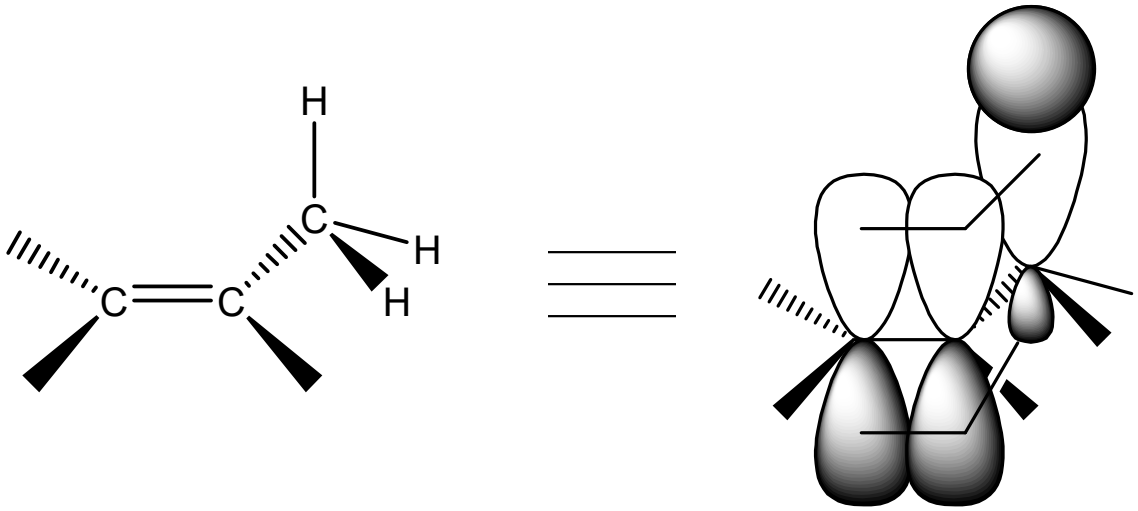
III. Chromophores

C. Substituent Effects

2. Conjugation – Alkenes

Methyl groups also cause a bathochromic shift, even though they are devoid of π- or n-electrons

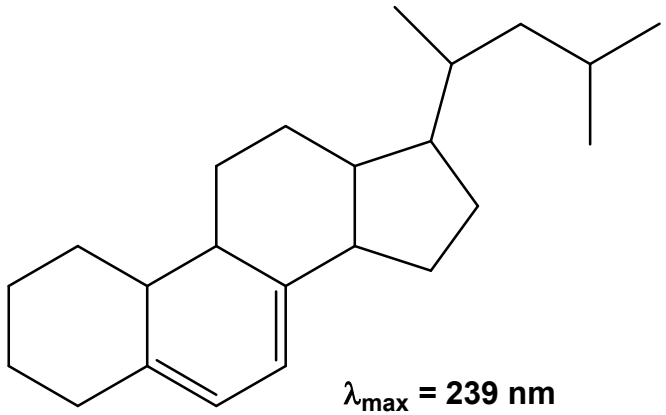
This effect is thought to be through what is termed "hyperconjugation" or sigma bond resonance



Next time – We will find that the effect of substituent groups can be reliably quantified from empirical observation of known conjugated structures and applied to new systems

This quantification is referred to as the Woodward-Fieser Rules which we will apply to three specific chromophores:

1. Conjugated dienes
2. Conjugated dienones
3. Aromatic systems



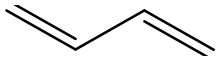
λ_{max} = 239 nm

IV. Structure Determination

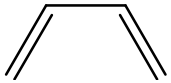
A. Dienes

1. General Features

For acyclic butadiene, two conformers are possible – s-cis and s-trans



s-trans



s-cis

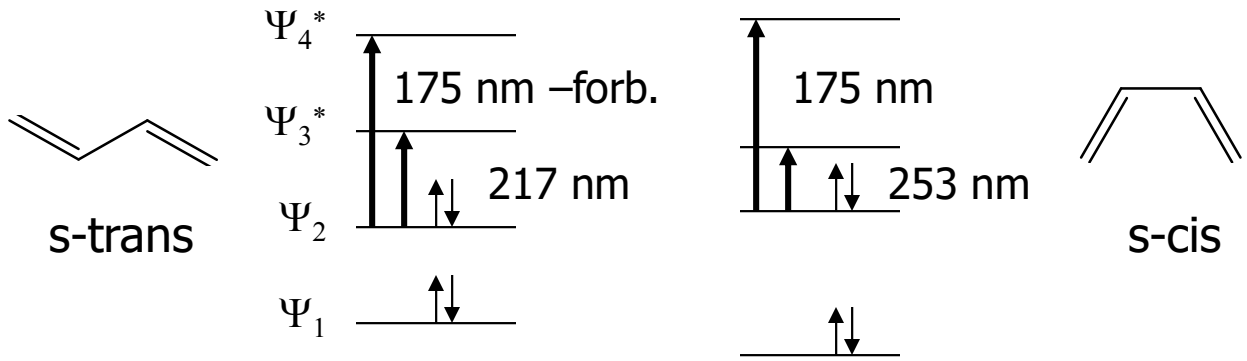
The s-cis conformer is at an overall higher potential energy than the s-trans; therefore the HOMO electrons of the conjugated system have less of a jump to the LUMO – lower energy, longer wavelength

IV. Structure Determination

A. Dienes

1. General Features

Two possible $\pi \rightarrow \pi^*$ transitions can occur for butadiene $\Psi_2 \rightarrow \Psi_3^*$ and $\Psi_2 \rightarrow \Psi_4^*$



The $\Psi_2 \rightarrow \Psi_4^*$ transition is not typically observed:

- The energy of this transition places it outside the region typically observed – 175 nm
- For the more favorable s-trans conformation, this transition is forbidden

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption

IV. Structure Determination

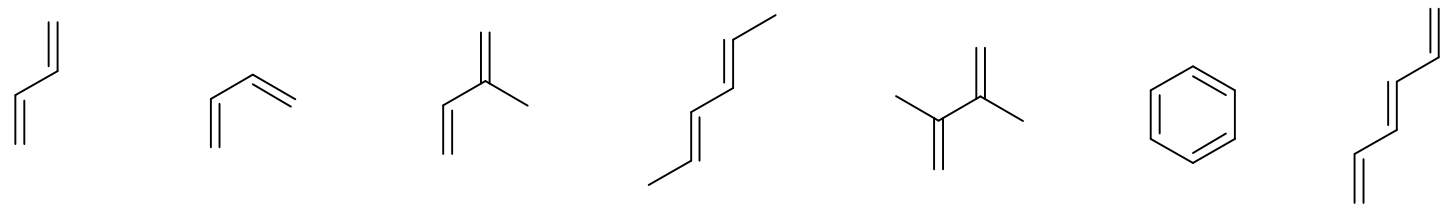
A. Dienes

1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption (e = 20,000+) based at 217 nm within the observed region of the UV

While this band is insensitive to solvent (as would be expected) it is subject to the bathochromic and hyperchromic effects of alkyl substituents as well as further conjugation

Consider:



λ_{max} =	217		253		220	227	227	256	263	nm

IV. Structure Determination

A. Dienes

2. Woodward-Fieser Rules

Woodward and the Fiesers performed extensive studies of terpene and steroidal alkenes and noted similar substituents and structural features would predictably lead to an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ electronic transition

This work was distilled by Scott in 1964 into an extensive treatise on the Woodward-Fieser rules in combination with comprehensive tables and examples – (A.I. Scott, Interpretation of the Ultraviolet Spectra of Natural Products, Pergamon, NY, 1964)

A more modern interpretation was compiled by Rao in 1975 – (C.N.R. Rao, Ultraviolet and Visible Spectroscopy, 3rd Ed., Butterworths, London, 1975)

IV. Structure Determination

A. Dienes

2. Woodward-Fieser Rules - Dienes

The rules begin with a base value for λ_{max} of the chromophore being observed:

acyclic butadiene = 217 nm

The incremental contribution of substituents is added to this base value from the group tables:

Group	Increment
Extended conjugation	+30
Each exo-cyclic C=C	+5
Alkyl	+5
-$OCOCH_3$	+0
-OR	+6
-SR	+30
-Cl, -Br	+5
-NR_2	+60

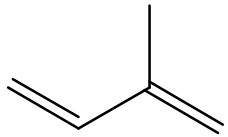
UV Spectroscopy

IV. Structure Determination

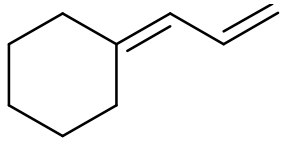
A. Dienes

2. Woodward-Fieser Rules - Dienes

For example:



217 nm Isoprene - acyclic butadiene =
+ 5 nm one alkyl subs.
222 nm
220 nm Experimental value



Allylidenecyclohexane
217 nm - acyclic butadiene =
+ 5 nm one exocyclic C=C
+10 2 alkyl subs.
nm
232 nm
237 nm Experimental value

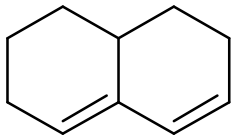
IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

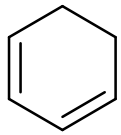
There are two major types of cyclic dienes, with two different base values

Heteroannular (transoid):



ε = 12,000 -- 28,000
base λ_{max} = 25

Homoannular (cisoid):



ε = 5,000 – 15,000
base λ_{max} = 214

The increment table is the same as for acyclic butadienes with a couple additions:

Group	Increment
Additional homoannular	+39
Where both types of diene are present, the one with the longer λ becomes the base	

UV Spectroscopy

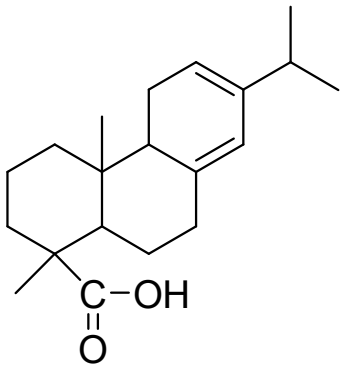
IV. Structure Determination

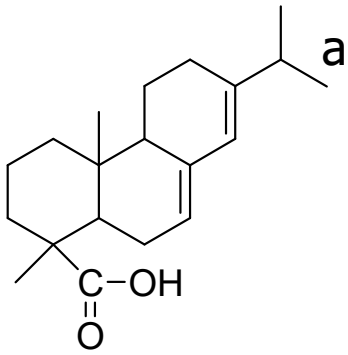
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

In the pre-NMR era of organic spectral determination, the power of the method for discerning isomers is readily apparent

Consider abietic vs. levopimaric acid:





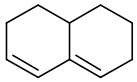
abietic acid

levopimaric acid

IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes



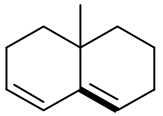
For example:

1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene

214 nm heteroannular diene =

+15 nm 3 alkyl subs. (3 x 5)

+ 5 nm 1 exo C=C



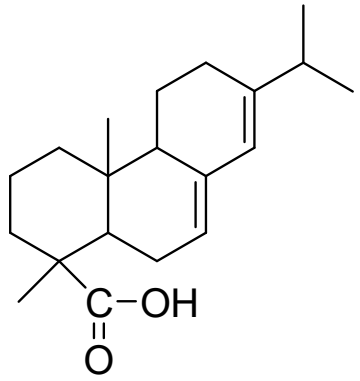
234 nm

235 nm Experimental value

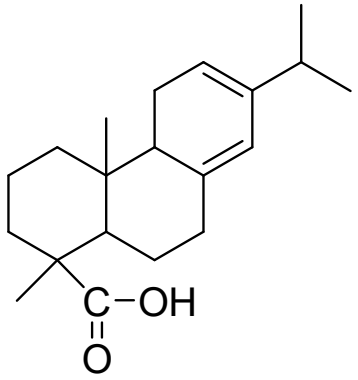
IV. Structure Determination

A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes



214 nm	heteroannular diene =
+20 nm	4 alkyl subs. (4 x 5)
+ 5 nm	1 exo C=C
239 nm	



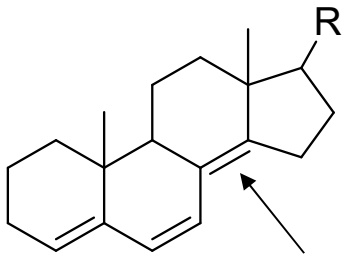
253 nm	homoannular diene =
+20 nm	4 alkyl subs. (4 x 5)
+ 5 nm	1 exo C=C
278 nm	

IV. Structure Determination

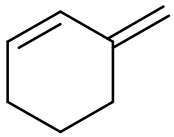
A. Dienes

3. Woodward-Fieser Rules – Cyclic Dienes

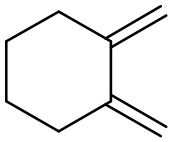
Be careful with your assignments – three common errors:



This compound has three exocyclic double bonds; the indicated bond is exocyclic to two rings



This is not a heteroannular diene; you would use the base value for an acyclic diene



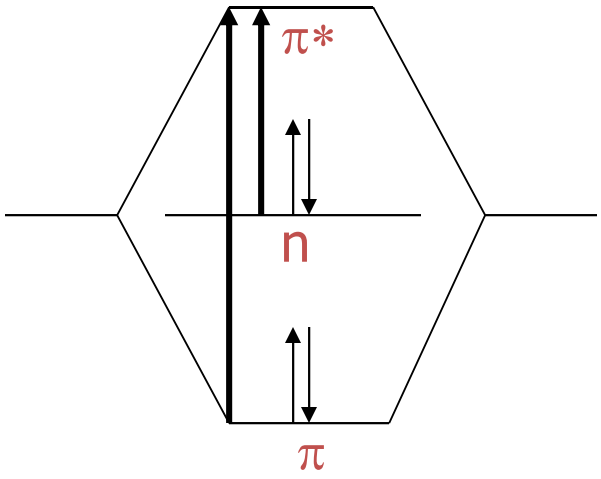
Likewise, this is not a homooannular diene; you would use the base value for an acyclic diene

IV. Structure Determination

B. Enones

1. General Features

Carbonyls, as we have discussed have two primary electronic transitions:



Remember, the π → π* transition is allowed and gives a high e, but lies outside the routine range of UV observation

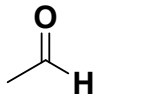
The n → π* transition is forbidden and gives a very low e, but can routinely be observed

IV. Structure Determination

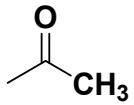
B. Enones

1. General Features

For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the n → π* transition (λ_{max}):

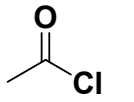


293 nm



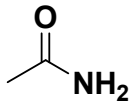
279

This is explained by the inductive withdrawal of electrons by O, N or halogen from the carbonyl carbon – this causes the n-electrons on the carbonyl oxygen to be held more firmly

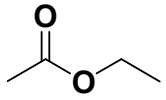


235

It is important to note this is different from the auxochromic effect on π → π* which extends conjugation and causes a bathochromic shift

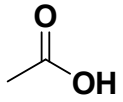


214



204

In most cases, this bathochromic shift is not enough to bring the π → π* transition into the observed range



204

IV. Structure Determination

B. Enones

1. General Features

Conversely, if the C=O system is conjugated both the n → π* and π → π* bands are bathochromically shifted

Here, several effects must be noted:

i. the effect is more pronounced for π → π*

ii. if the conjugated chain is long enough, the much higher intensity π → π* band will overlap and drown out the n → π* band

iii. the shift of the n → π* transition is not as predictable

For these reasons, empirical Woodward-Fieser rules for conjugated enones are for the higher intensity, allowed π → π* transition

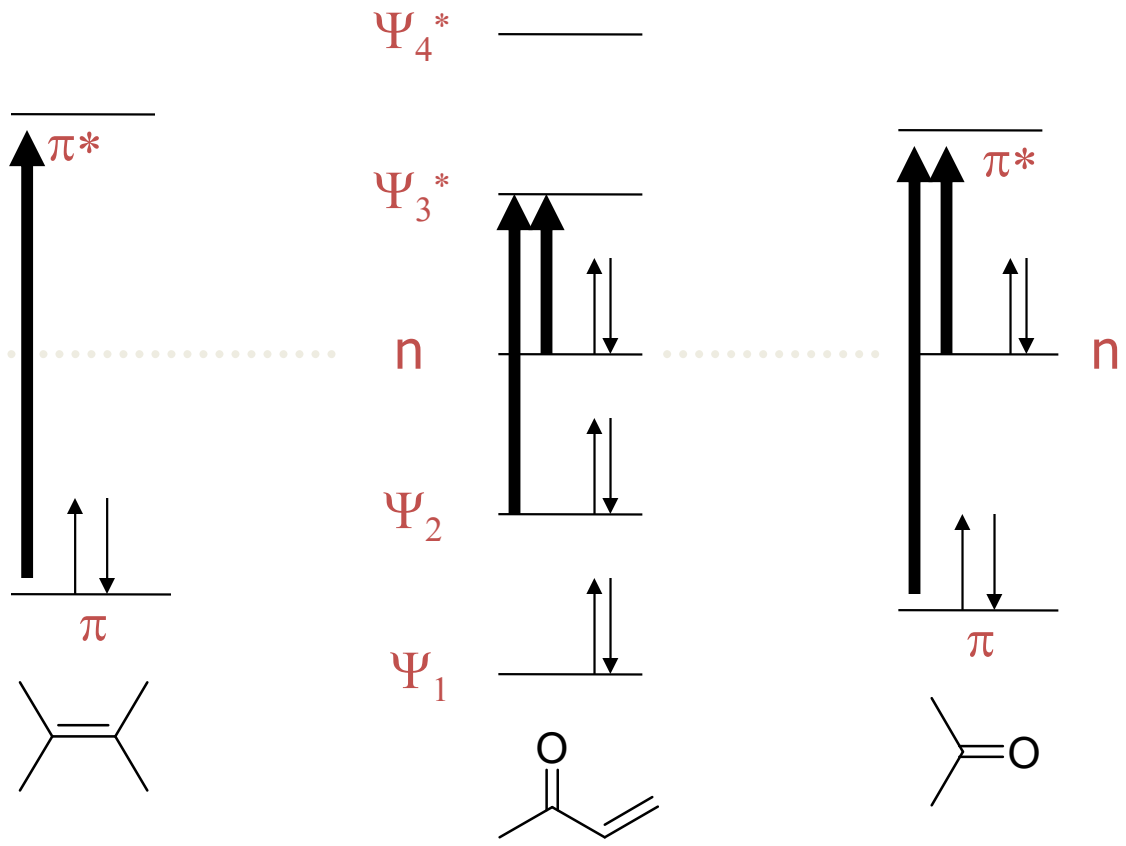
UV Spectroscopy

IV. Structure Determination

B. Enones

1. General Features

These effects are apparent from the MO diagram for a conjugated enone:



IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones

Group		Increment
6-membered ring or acyclic enone		Base 215 nm
5-membered ring parent enone		Base 202 nm
Acyclic dienone		Base 245 nm
Double bond extending conjugation		30
Alkyl group or ring residue	α, β, γ and higher	10, 12, 18
-OH	α, β, γ and higher	35, 30, 18
-OR	$\alpha, \beta, \gamma, \delta$	35, 30, 17, 31
-O(C=O)R	α, β, δ	6
-Cl	α, β	15, 12
-Br	α, β	25, 30
$-NR_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39

IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones

Aldehydes, esters and carboxylic acids have different base values than ketones

Unsaturated system	Base Value
Aldehyde	208
With α or β alkyl groups	220
With α,β or β,β alkyl groups	230
With α,β,β alkyl groups	242
Acid or ester	
With α or β alkyl groups	208
With α,β or β,β alkyl groups	217
Group value – exocyclic α,β double bond	+5
Group value – endocyclic α,β bond in 5 or 7 membered ring	+5

IV. Structure Determination

B. Enones

2. Woodward-Fieser Rules - Enones

Unlike conjugated alkenes, solvent does have an effect on λ_{max}

These effects are also described by the Woodward-Fieser rules

Solvent correction	Increment
Water	+8
Ethanol, methanol	0
Chloroform	-1
Dioxane	-5
Ether	-7
Hydrocarbon	-11

IV. Structure Determination

B. Enones

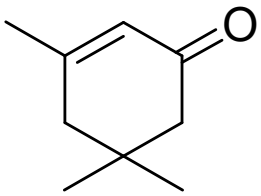
2. Woodward-Fieser Rules - Enones

Some examples – keep in mind these are more complex than dienes

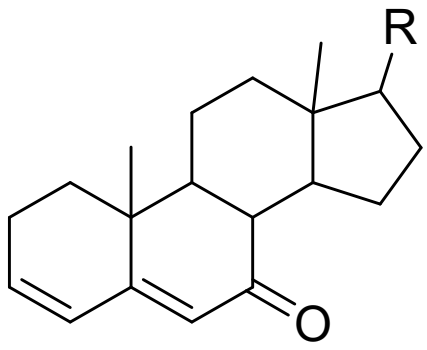
cyclic enone =	215 nm
2 x β- alkyl subs. (2 x 12)	+24 nm

239 nm

238 nm



215 nm	cyclic enone =
+30 nm	extended conj.
+12 nm	b-ring residue
+18 nm	d-ring residue
+ 5 nm	exocyclic double bond
280 nm	



280 nm Experimental

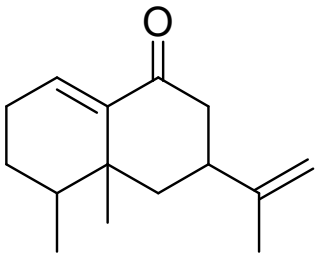
IV. Structure Determination

V.

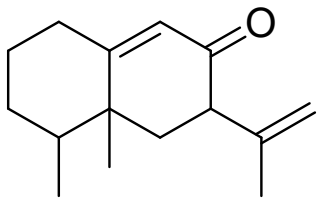
B. Enones

2. Woodward-Fieser Rules - Enones

Take home problem – can these two isomers be discerned by UV-spec



Eremophilone



allo-Eremophilone

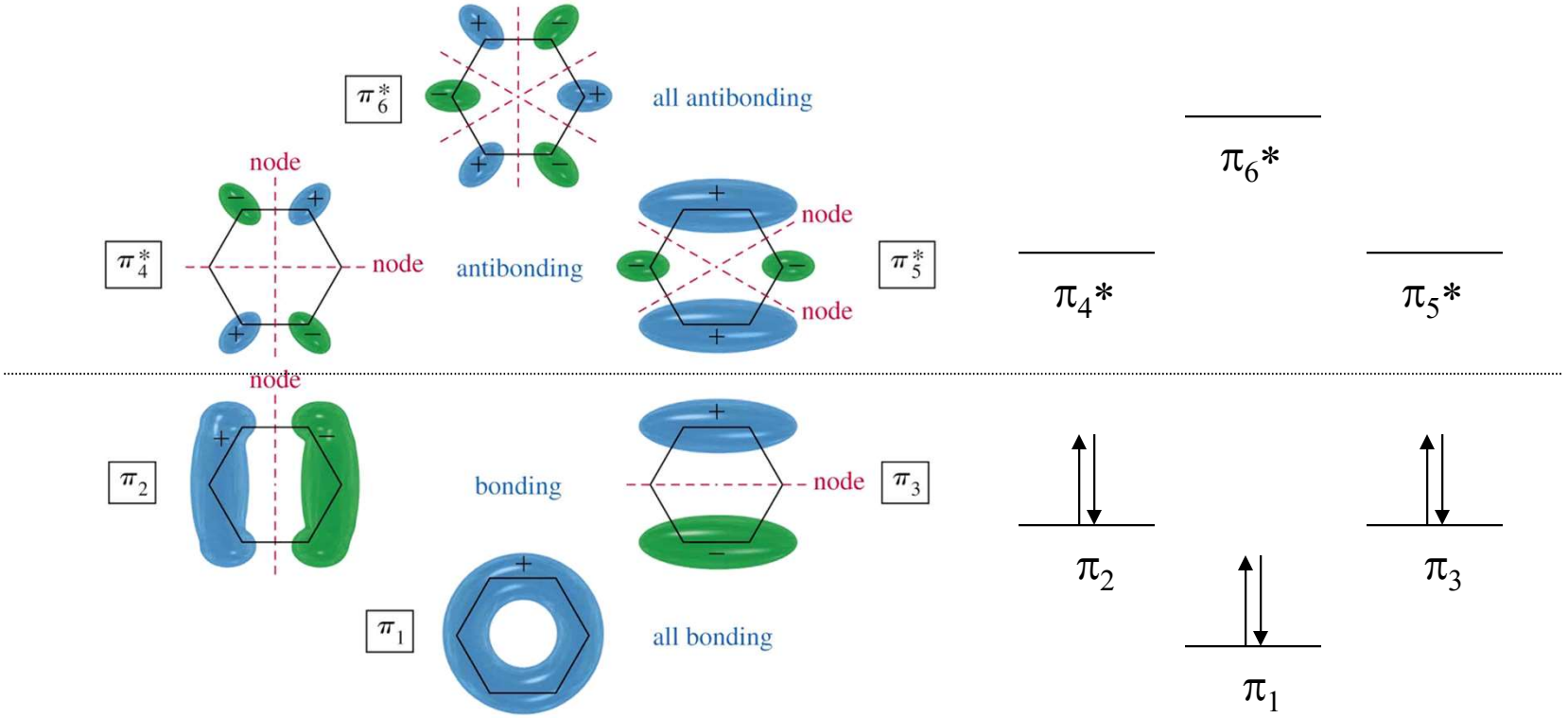
IV. Structure Determination

C. Aromatic Compounds

1. General Features

Although aromatic rings are among the most widely studied and observed chromophores, the absorptions that arise from the various electronic transitions are complex

On first inspection, benzene has six π-MOs, 3 filled π, 3 unfilled π*



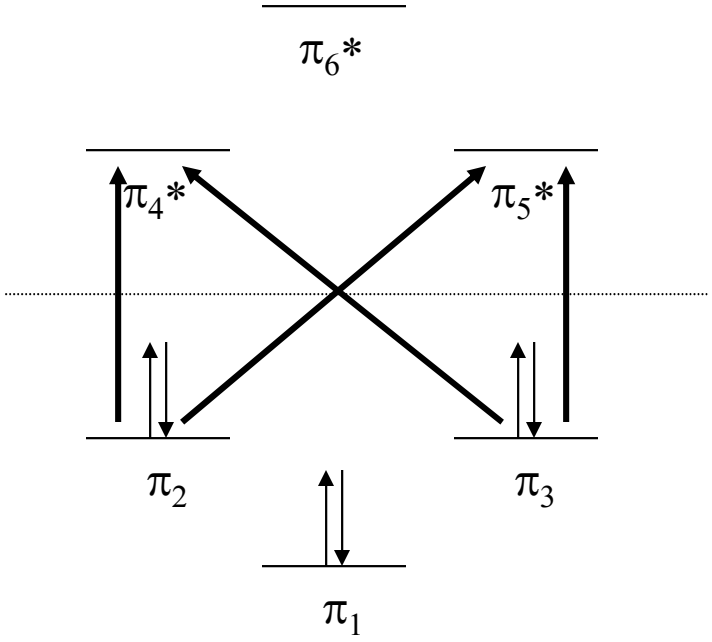
IV. Structure Determination

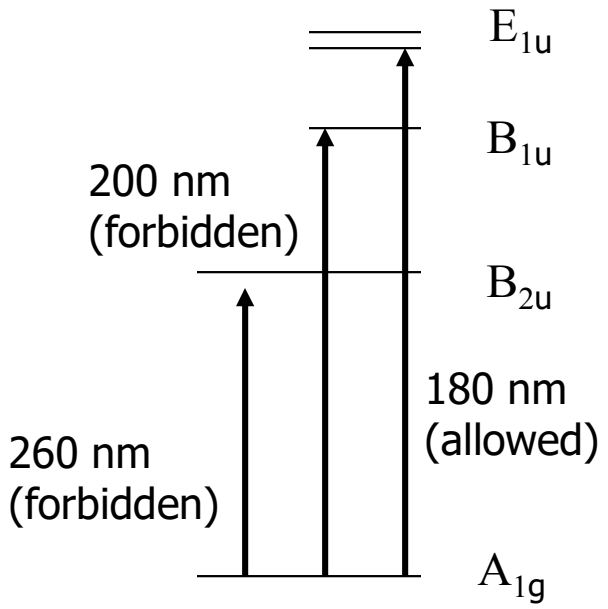
C. Aromatic Compounds

1. General Features

One would expect there to be four possible HOMO-LUMO $\pi \rightarrow \pi^*$ transitions at observable wavelengths (conjugation)

Due to symmetry concerns and selection rules, the actual transition energy states of benzene are illustrated at the right:





IV. Structure Determination

C. Aromatic Compounds

1. General Features

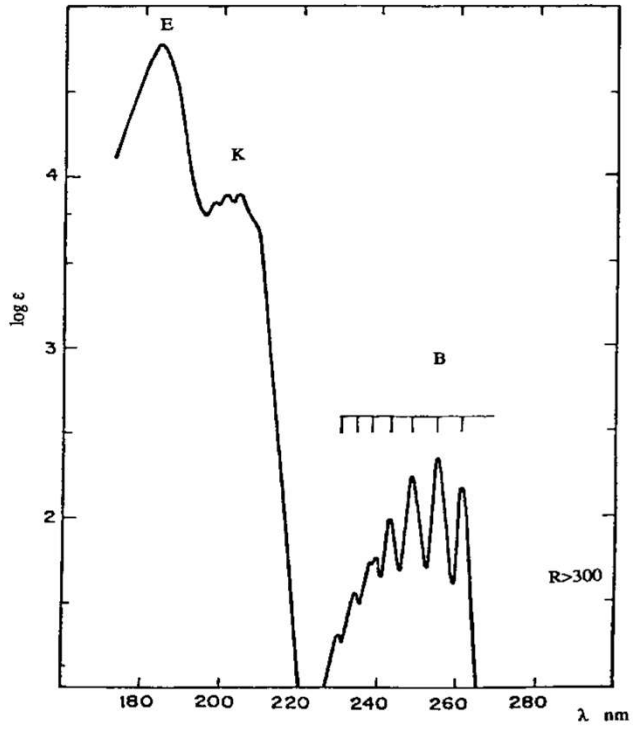
The allowed transition (ε = 47,000) is not in the routine range of UV obs. at 180 nm, and is referred to as the primary band

The forbidden transition (ε = 7400) is observed if substituent effects shift it into the obs. region; this is referred to as the second primary band

At 260 nm is another forbidden transition (ε = 230), referred to as the secondary band.

This transition is fleetingly allowed due to the disruption of symmetry by the vibrational energy states, the overlap of which is observed

in what is called fine structure



IV. Structure Determination

C. Aromatic Compounds

1. General Features

Substitution, auxochromic, conjugation and solvent effects can cause shifts in wavelength and intensity of aromatic systems similar to dienes and enones

However, these shifts are difficult to predict – the formulation of empirical rules is for the most part is not efficient (there are more exceptions than rules)

There are some general qualitative observations that can be made by classifying substituent groups –

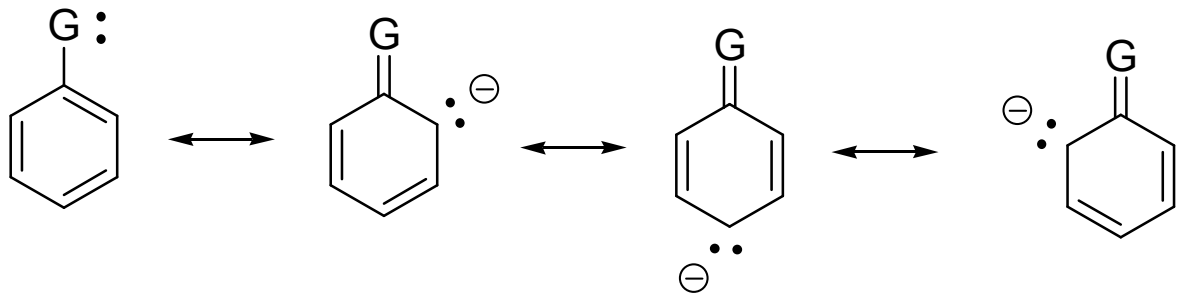
IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

a. Substituents with Unshared Electrons

- If the group attached to the ring bears n electrons, they can induce a shift in the primary and secondary absorption bands
- Non-bonding electrons extend the π-system through resonance – lowering the energy of transition $\pi \rightarrow \pi^*$
- More available n-pairs of electrons give greater shifts



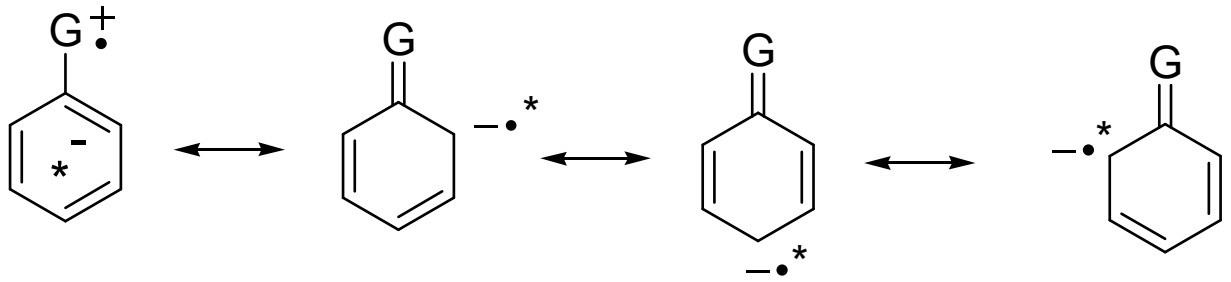
IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

a. Substituents with Unshared Electrons

- The presence of n-electrons gives the possibility of n → π^* transitions
- If this occurs, the electron now removed from G, becomes an extra electron in the anti-bonding π^* orbital of the ring
- This state is referred to as a charge-transfer excited state



IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

a. Substituents with Unshared Electrons

- pH can change the nature of the substituent group
- deprotonation of oxygen gives more available n-pairs, lowering transition energy
- protonation of nitrogen eliminates the n-pair, raising transition energy

	Primary		**Secondary**	
Substituent	λ_{max}	ε	λ_{max}	ε
-H	203.5	7,400	254	204
-OH	211	6,200	270	1,450
$-O^-$	235	9,400	287	2,600
$-NH_2$	230	8,600	280	1,430
$-NH_3^+$	203	7,500	254	169
-C(O)OH	230	11,600	273	970
$-C(O)O^-$	224	8,700	268	560

IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

b. Substituents Capable of π-conjugation

- When the substituent is a π-chromophore, it can interact with the benzene π-system
- With benzoic acids, this causes an appreciable shift in the primary and secondary bands
- For the benzoate ion, the effect of extra n-electrons from the anion reduces the effect slightly

	Primary		**Secondary**	
Substituent	λ_{max}	ε	λ_{max}	ε
-C(O)OH	230	11,600	273	970
$-C(O)O^-$	224	8,700	268	560

IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

c. Electron-donating and electron-withdrawing effects

- No matter what electronic influence a group exerts, the presence shifts the primary absorption band to longer λ
- Electron-withdrawing groups exert no influence on the position of the secondary absorption band
- Electron-donating groups increase the λ and ε of the secondary absorption band

IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

c. Electron-donating and electron-withdrawing effects

		Primary		*Secondary*	
	Substituent	λ_{max}	ε	λ_{max}	ε
Electron donating	-H	203.5	7,400	254	204
	-CH3	207	7,000	261	225
	-Cl	210	7,400	264	190
	-Br	210	7,900	261	192
	-OH	211	6,200	270	1,450
	$-OCH_3$	217	6,400	269	1,480
	$-NH_2$	230	8,600	280	1,430
Electron withdrawing	-CN	224	13,000	271	1,000
	C(O)OH	230	11,600	273	970
	-C(O)H	250	11,400		
	$-C(O)CH_3$	224	9,800		
	$-NO_2$	269	7,800		

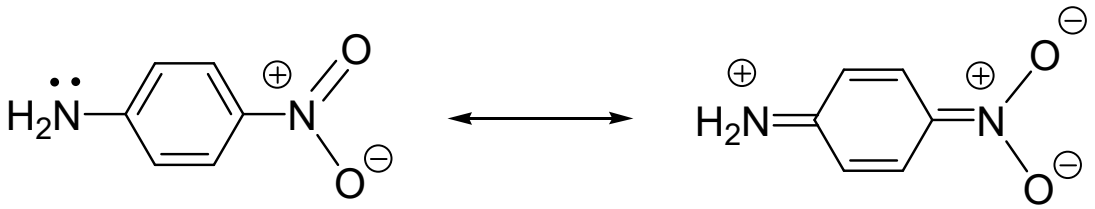
IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

d. Di-substituted and multiple group effects

- With di-substituted aromatics, it is necessary to consider both groups
- If both groups are electron donating or withdrawing, the effect is similar to the effect of the stronger of the two groups as if it were a mono-substituted ring
- If one group is electron withdrawing and one group electron donating and they are para- to one another, the magnitude of the shift is greater than the sum of both the group effects
- Consider p-nitroaniline:



IV. Structure Determination

C. Aromatic Compounds

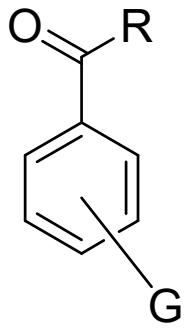
2. Substituent Effects

d. Di-substituted and multiple group effects

- If the two electonically dissimilar groups are ortho- or meta- to one another, the effect is usually the sum of the two individual effects (meta- no resonance; ortho-steric hind.)

- For the case of substituted benzoyl derivatives, an empirical correlation of structure with observed λ_{max} has been developed

- This is slightly less accurate than the Woodward-Fieser rules, but can usually predict within an error of 5 nm



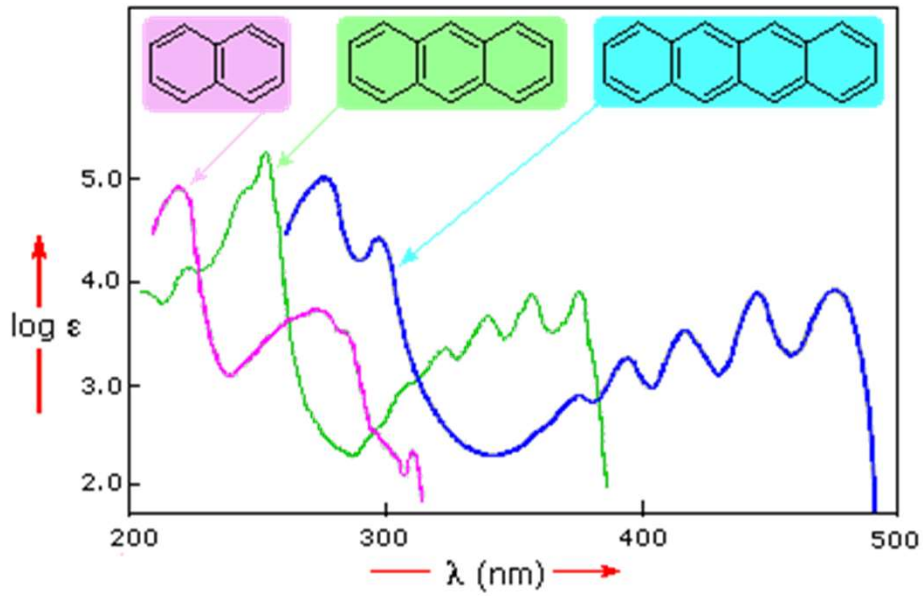
IV. Structure Determination

C. Aromatic Compounds

2. Substituent Effects

d. Polynuclear aromatics

- When the number of fused aromatic rings increases, the λ for the primary and secondary bands also increase



- For heteroaromatic systems spectra become complex with the addition of the n → π* transition and ring size effects and are unique to each case

The longer the conjugated carbon chain in the absorbing system, the greater the intensity of the absorption. This is shown by the spectra of the polyenes CH_3-$(CH{=}CH)_n$-CH_3, where n=3,4 and 5 (*Fig. 15*).

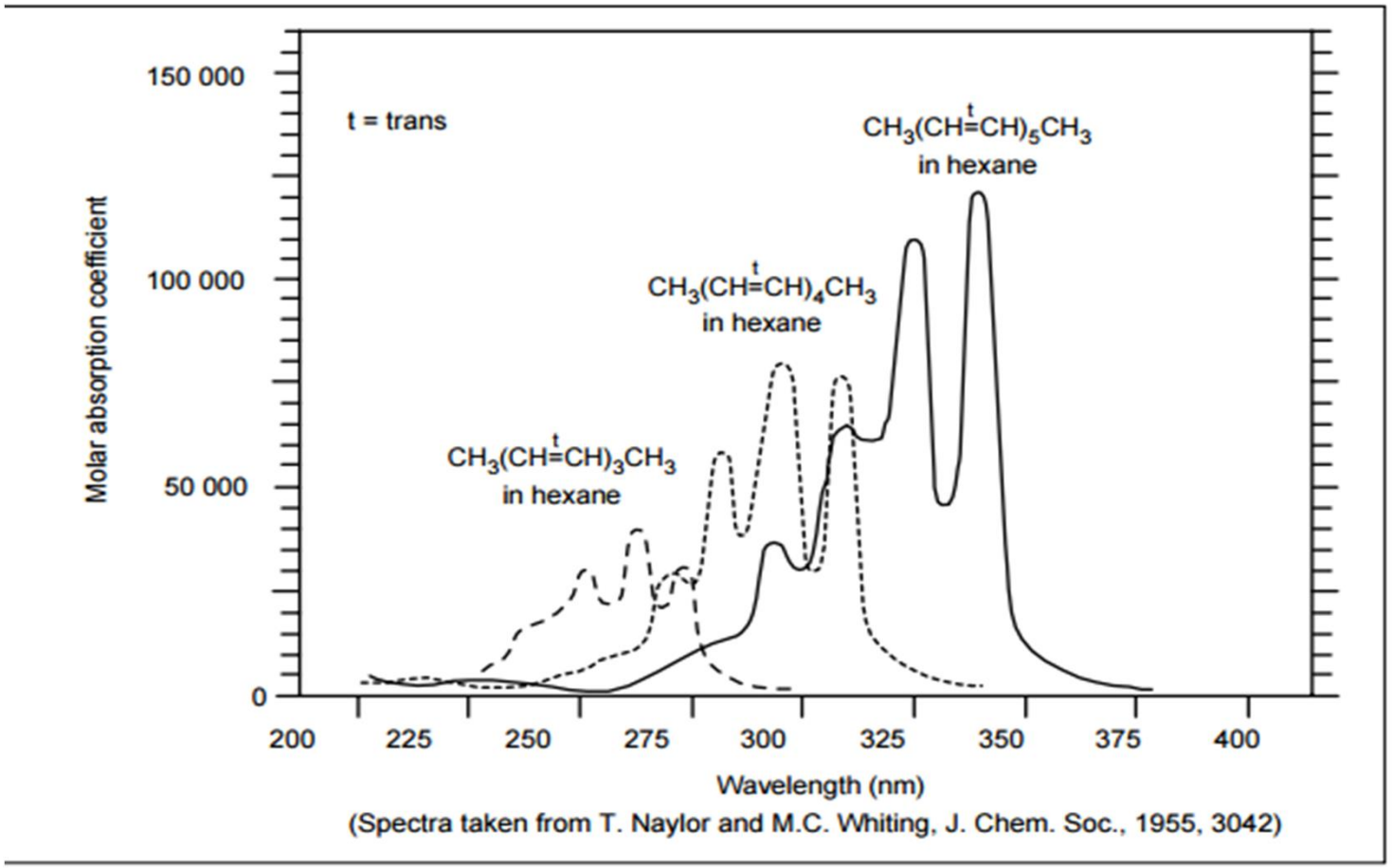


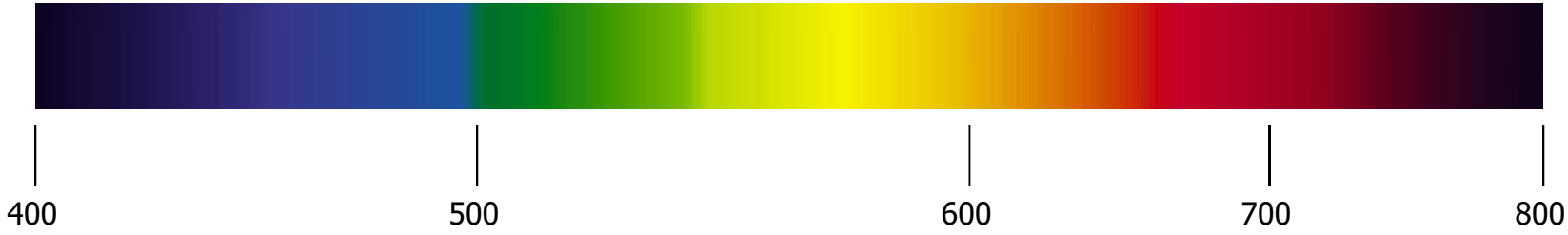
Figure 15 Ultraviolet/visible spectra of the polyenes $CH_3(CH{=}CH)_nCH_3$, where n=3,4 and 5

V. Visible Spectroscopy

A. Color

1. General

- The portion of the EM spectrum from 400-800 is observable to humans- we (and some other mammals) have the adaptation of seeing color at the expense of greater detail



	λ, nm
Violet	400-420
Indigo	420-440
Blue	440-490
Green	490-570
Yellow	570-585
Orange	585-620
Red	620-780

V. Visible Spectroscopy

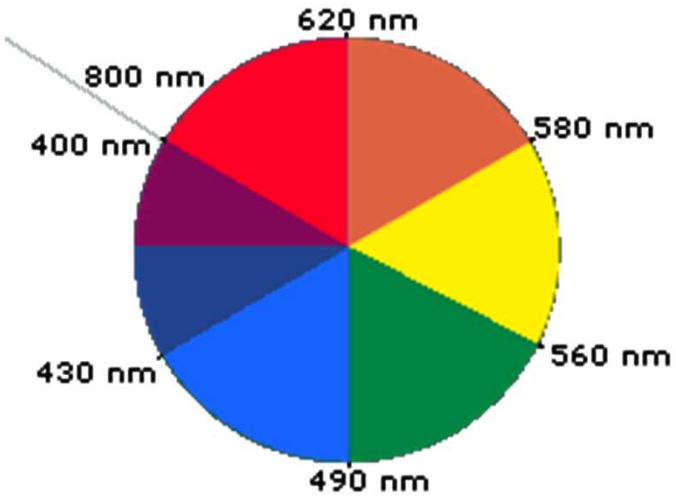
A. Color

1. General

- When white (continuum of λ) light passes through, or is reflected by a surface, those ls that are absorbed are removed from the transmitted or reflected light respectively

- What is “seen” is the complimentary colors (those that are not absorbed)

- This is the origin of the “color wheel”



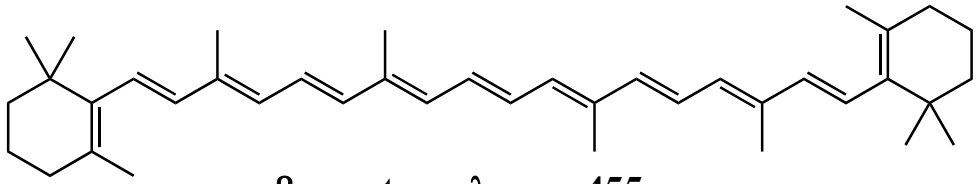
V. Visible Spectroscopy

A. Color

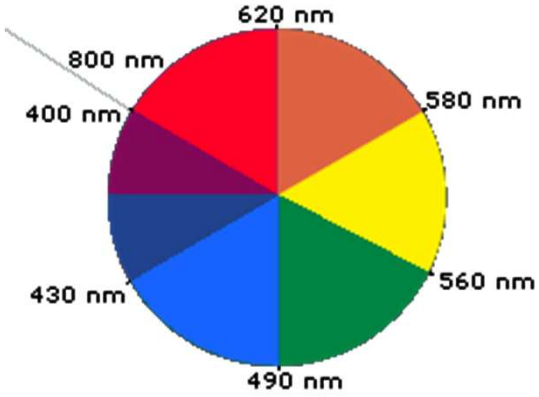
1. General

- Organic compounds that are "colored" are typically those with extensively conjugated systems (typically more than five)

- Consider β-carotene



β-carotene, λ_{max} = 455 nm



λ_{max} is at 455 – in the far blue region of the spectrum – this is absorbed

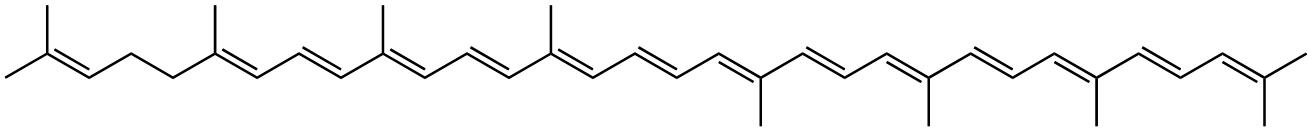
The remaining light has the complementary color of orange

V. Visible Spectroscopy

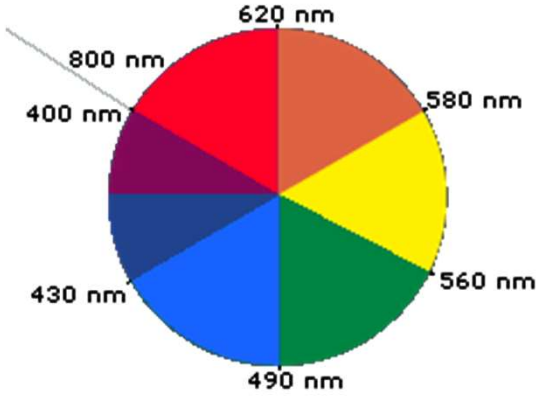
A. Color

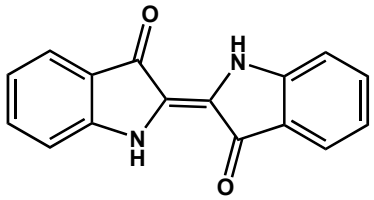
1. General

- Likewise:



lycopene, λ_{max} = 474 nm





indigo

λ_{max} for lycopene is at 474 – in the near blue region of the spectrum – this is absorbed, the compliment is now red

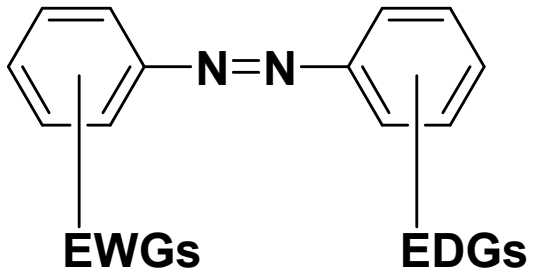
λ_{max} for indigo is at 602 – in the orange region of the spectrum – this is absorbed, the compliment is now indigo!

V. Visible Spectroscopy

A. Color

1. General

- One of the most common class of colored organic molecules are the azo dyes:



From our discussion of di-subsituted aromatic chromophores, the effect of opposite groups is greater than the sum of the individual effects – more so on this heavily conjugated system

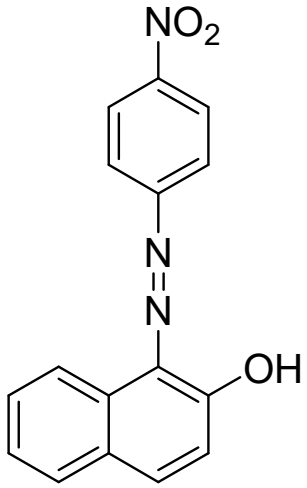
Coincidentally, it is necessary for these to be opposite for the original synthetic preparation!

V. Visible Spectroscopy

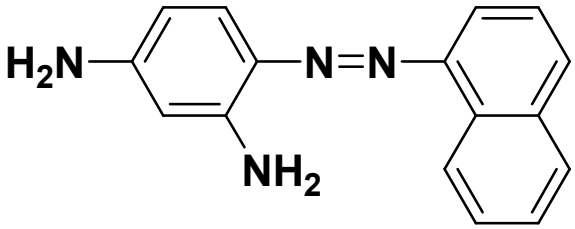
A. Color

1. General

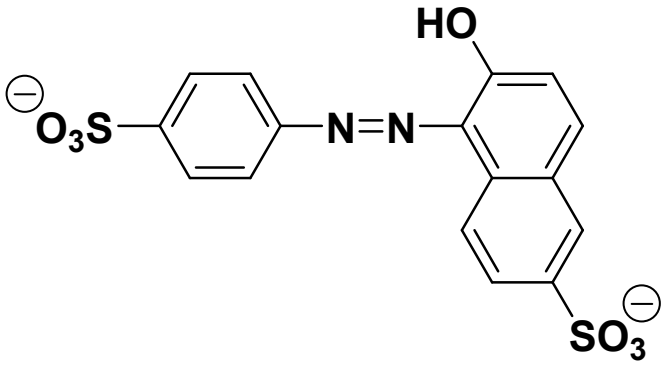
- These materials are some of the more familiar colors of our "environment"



Para Red



Fast Brown



Sunset Yellow (Food Yellow 3)

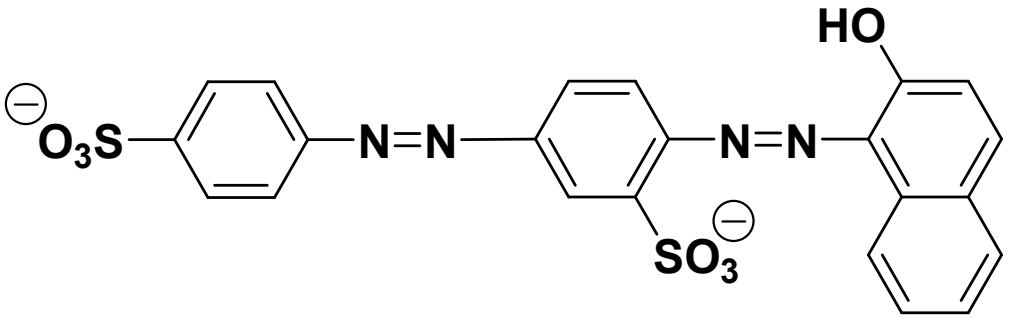
V. Visible Spectroscopy

A. Color

1. General

- In the biological sciences these compounds are used as dyes to selectively stain different tissues or cell structures

- Biebrich Scarlet - Used with picric acid/aniline blue for staining collagen, recticulum, muscle, and plasma. Luna's method for erythrocytes & eosinophil granules. Guard's method for sex chromatin and nuclear chromatin.



V. Visible Spectroscopy

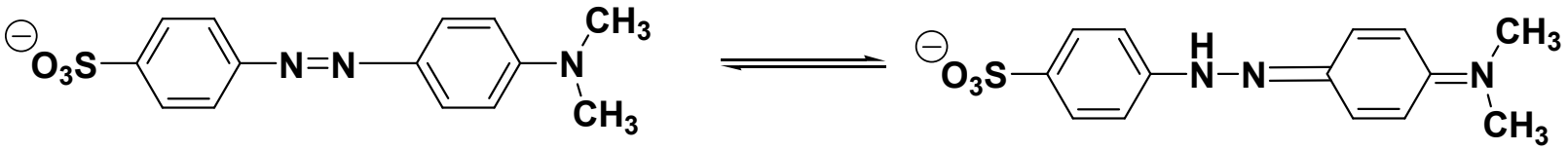
A. Color

1. General

- In the chemical sciences these are the acid-base indicators used for the various pH ranges:

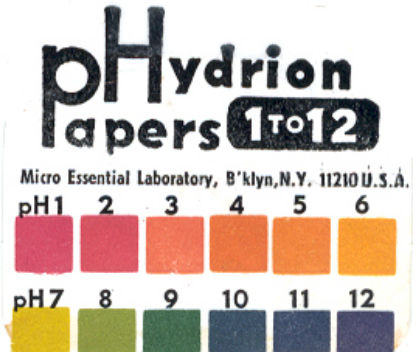
- Remember the effects of pH on aromatic substituents

Methyl Orange



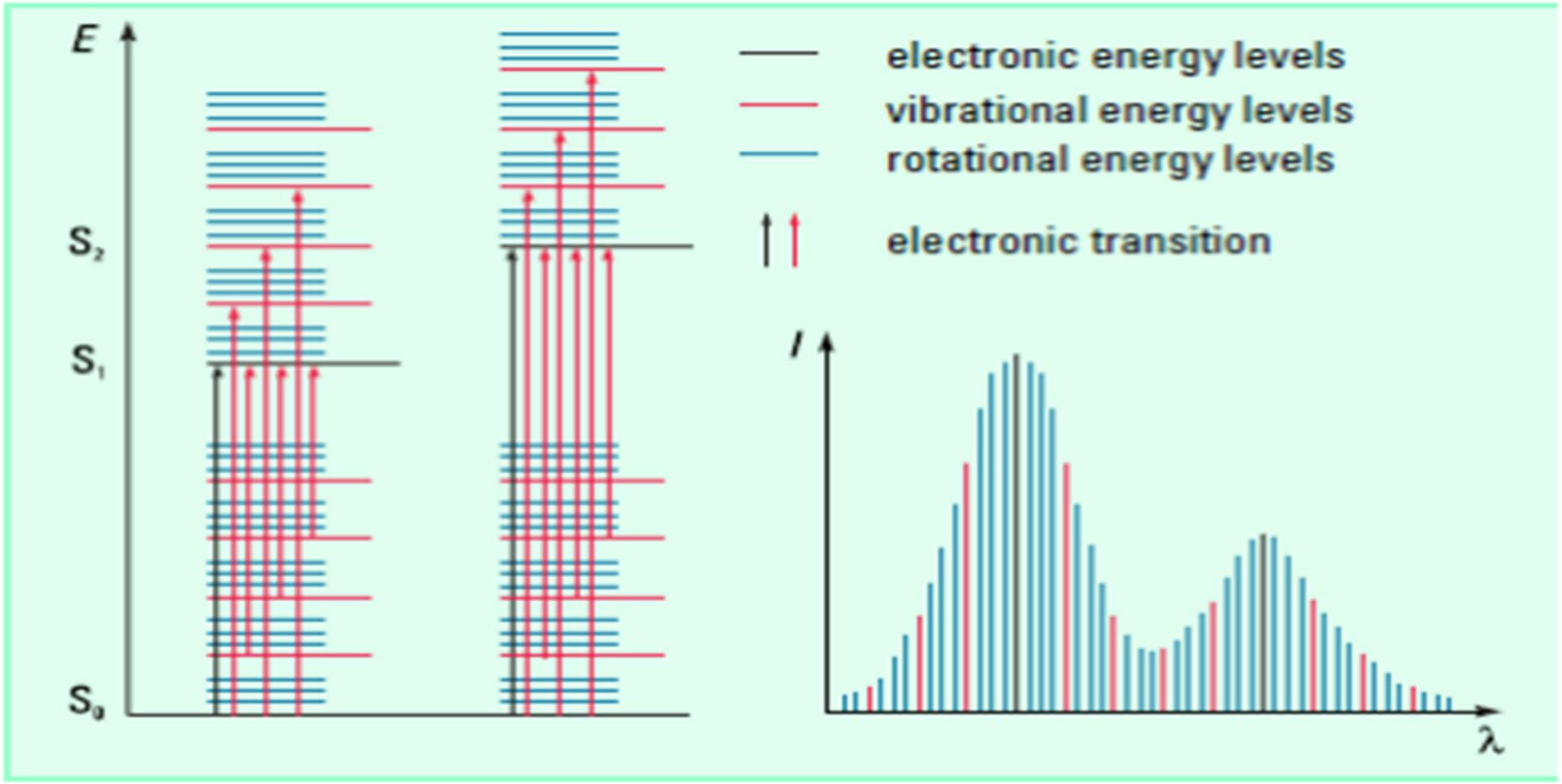
Yellow, pH > 4.4

Red, pH < 3.2



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

In molecules, vibrational and rotational energy levels are place over on the electronic energy levels. Because many transitions with different energies can occur, the bands are broadened. The broadening is even greater in solutions due to **solvent-solute interactions.**



Applications of Electronic Spectroscopy

How do we use electronic spectroscopy in chemical analysis?

The two principal applications are structure determinations and quantitative analysis. **The position and intensity of an electronic absorption band provides information as to chemical structure. Such absorptions normally are not as useful as infrared absorptions because they do not give as detailed information**. For our purposes here, the main points to remember are:

1. A weak absorption (e = 10-100) suggests an **n —->** transition of an isolated carbonyl group. If this absorption is found in the region 270-350 nm an aldehyde or ketone is probable.

2. Somewhat stronger absorptions (e = 100-4000) between 200 nm and 260 nm may correspond to $\pi \rightarrow \pi^*$ **transitions**.

3. Strong absorptions (e = 10,000-20,000) usually are characteristic of $\pi \rightarrow \pi^*$ transitions. If absorption occurs above 200 nm, a conjugated system of multiple bonds is indicated. Each additional carbon-carbon double bond shifts λ_{max} about 30 nm to longer wavelengths and increases the intensity of absorption. Conjugation also shifts λ_{max} of $\pi \rightarrow \pi^*$ transitions to longer wavelengths.

Applications of ultraviolet/visible spectroscopy In research,

ultraviolet/visible spectroscopy is used more extensively in analyzing than in identification. The trace metal content of an alloy, such as manganese in steel, can be determined by firstly reacting the sample to get the metal into solution as an ion. The ion is then complexed or made to react so that it is in a form that can be measured – eg manganese as the manganite (VII) ion.

When the spectrum is recorded, the most useful piece of information is the absorbance because if the **absorption coefficient of the chromophore** is known the concentration of the solution can be calculated, and hence the mass of the metal in the sample.

The same principle can be applied to drug metabolites. Samples are taken from various sites around the body and their solutions are analyzed to determine the amount of drug reaching those parts of the body.

Question 1.

Beer's Law states that;

1. **Absorbance is proportional to both the path length and concentration of the absorbing species**

2. Absorbance is proportional to the log of the concentration of the absorbing species

3. Absorbance is equal to P_0 / P

Questions 2.

UV-Vis. Spectroscopy of organic compounds is usually concerned with which electronic transition(s)?

1.s to s^*

2. *n* to s^*

3. *n* to p^* and p to p^*

Question

Molar absorptivity's of compounds showing charge transfer absorption are

a) **Small**
b) **b) Moderate**
c) **c) Large**

Question

Peaks resulting from *n* to p* transitions are shifted to shorter wavelengths (*blue shift*) with increasing solvent polarity.
True or false?

Questions

1. What are the main components of a UV-Vis absorption instrument?

2. What sources are used in UV-Vis spectroscopy? Describe their act characteristics.

3. What is a chromophore?

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

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

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

7. $\pi-\pi*$Transition is the most suitable and useful transition in UV-Vis Spectroscopy. Why?

8. What are the effects of conjugation and aromaticity on UV-Vis absorption spectroscopy?

Solvent effects:

π – π*, the frank – condon principle state that during the electronic transition, atoms do not move, electrons however, including those of the solvent molecules may recognize. **Most transitions result in an excited state is more polar than the ground state so the dipole – dipole interactions with the solvent will therefore lower the energy of exited state more than of the ground states** so there is a small red shift of order 10 to 20 nm in going from hexane to ethanol as a polar solvents.

n – π*, the weak transitions of oxygen in the ketones so the solvent effect in opposite direction in which **solvent can make hydrogen bonding to the carbonyl group in the excited state**. In hexane solution the absorbance of acetone is at 279 nm ($\mathcal{E} = 15$) where as in aqueous solution absorbed at 264.5 nm so the shift is blue shift.

Definitions:

Red shift or bathochromic shift effect:-

A shift of an absorption maximum towards longer wavelength, **it may be produced by a change of medium or by present of an auxochrome.** The Auxochrome is a substituent on a chromophore which leads to red shifts for example the conjugations of the lone pair on the hetro atom (NH_2) with the aromatic ring, in that case the hetro atom extend the chromophore to gives new chromophore.

Blue shift or hypsochromic effect:

A shift towards shorter wavelength and this may be cause **by change of medium and also such phenomena as the removed of conjugation of the lone pair of electrons** of aniline with π-bond system.

Hypochromic effect:- An effect leading to decrease the absorption intensity.

Hyperchromic effect: An effect leading to increase the absorptions intensity

Isosbestic point:- a point common to all curves produced in the spectra of compound taken at several PH values.

Factors affecting the absorptions

The steric effect in (1) cause absorption at 10 nm longer wavelength than (2)

$(CH_3)_3CCH_2COCH_3$ (1) CH_3COCH_3 (2)

and has a slightly higher extinction coefficient in which depends on p (the probability) and a (chromophore length). While the replacement of halogen, amino, hydroxyl or alkoxy groups on the carbonyl group results in very significant displacement of absorption from n – π* transition

X-CO-R

X shift to short wavelength (λ) (high energy) because of X = OR group donate electron to practically +ve charge on the carbon atom and entire decrease the possibility of excitation of electrons from the oxygen of carbonyl group to the π* orbitals so it need more energy (blue shift).

Searching for chromophore:-

There are no easy rules or set procedure for identifying of chromophore, there are too many factors affect the spectrum in which the structure can be found.

The complexity and the extent to which the spectrum influences on the visible region. A spectrum with many bands stretching into visible shows the presence of long conjugated or polycyclic aromatic chromophore, a compounds giving spectrum with only one band or only few bands below about 300 nm probably contains only two or three conjugate unit.

Simple chromophore such **as dienes or tri and α, β- unsaturated ketones have** $\mathcal{E}$ **values 10,000 to 20,000**, so the longer simple conjugate system (usually also the longestλ_{max}) with correspondingly high $\mathcal{E}$ values.

Very low intensity of bands in 270 – 350 nm, for n - π* with $\mathcal{E}$ **values 10 to 100, for ketone transition in which (forbidding transitions),**

The transitions with $\mathcal{E}$ values 1000 – 10000 almost always shows presence of aromatic system.

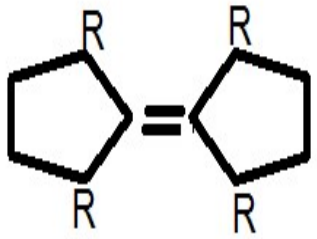
Steric effect is also important

Steric hindrance to coplannarity about the double bond as in (x) below

Mild steric effect to coplannarity about single bond has only small effect on the position and intensity of absorption.

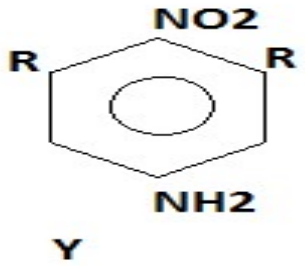
Medium steric effect about single bond as in (y) gives rise to decrease in intensity but also lead to red or blue shift

(x)



R is bulky group

(y)



Y

In (y) when R= CH_3 the absorption is 385 nm ($\mathcal{E}$ 4840) when R = H the absorption is 375 nm ($\mathcal{E}$ 16000)

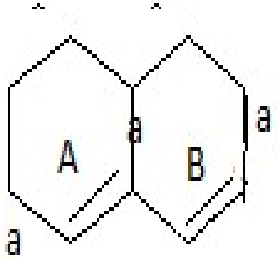
Extreme steric hindrance to coplanarity about a single bond.

Such compd. **showed no maximum in the accessible uv. region but on hydrolysis give the absorption, this because the steric prevents the conjugation**

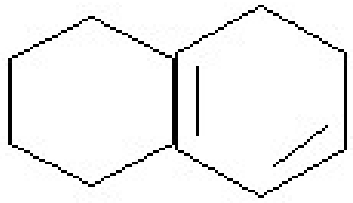
Conjugated dienes:

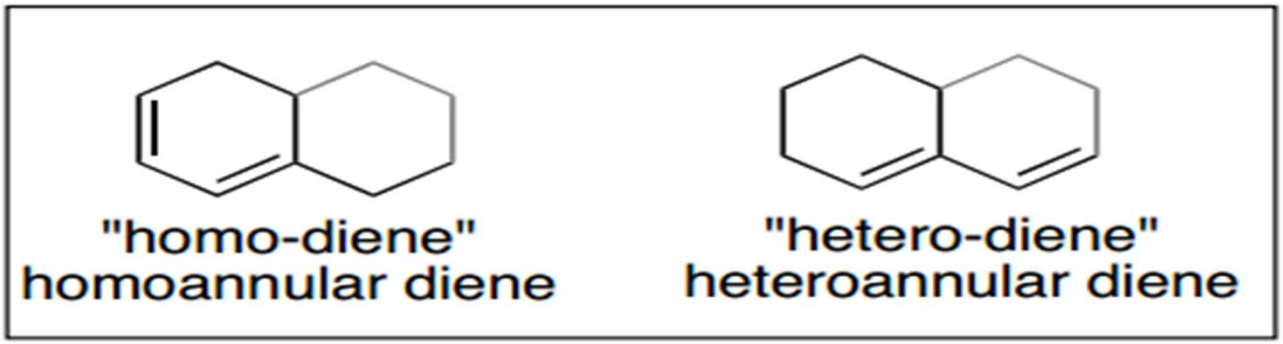
The energy levels of butadiene have been illustrated in slide No. 58, the transition y give rise to strong absorption at 217 nm $\mathcal{E} = 21000$. Alkyl substitution extends the chromophore in the sense that there is small interaction between σ-bonded electrons of the alkyl group and π-bond system so there is small red shift in going from isolated double bond to a conjugated diene. **Fortunately the effect of alkyl substituent in dienes at least is additive and few rules used to predict the position of absorption in open chain & six membered ring dienes**. Open chain dienes exist in normally s-trans conformation, while homoannuular dienes must be in s-ciss conformation; these conformations are in 1&2.

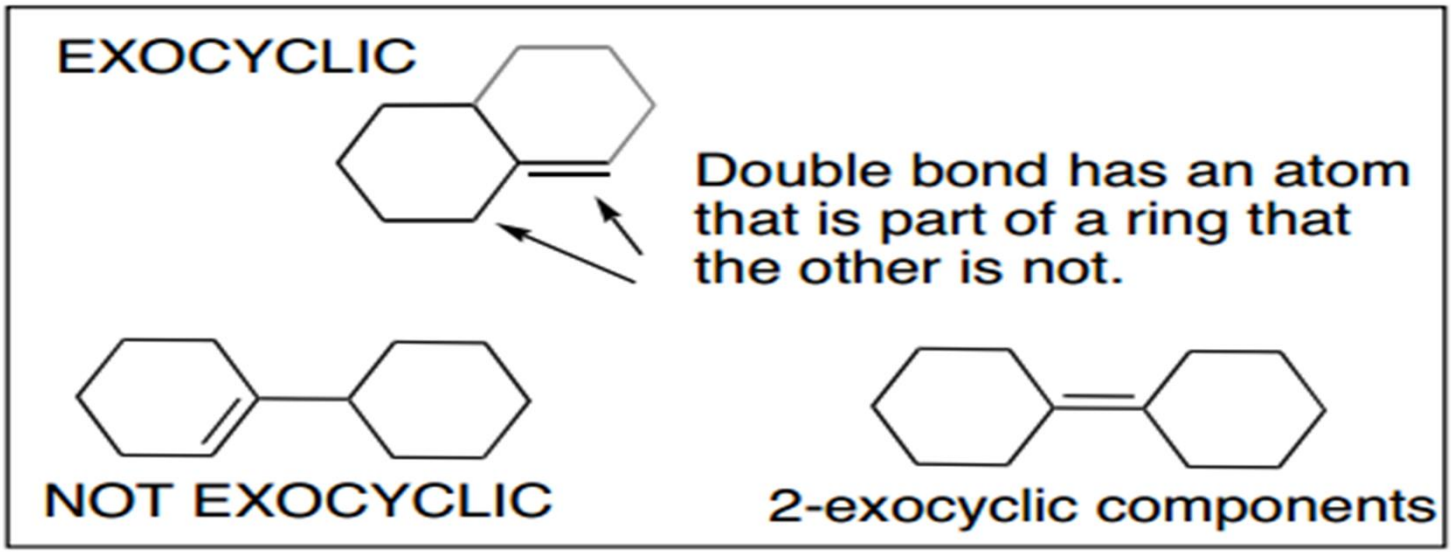
(1)



(2)




"homo-diene"
homoannular diene
"hetero-diene"
heteroannular diene


EXOCYCLIC
Double bond has an atom that is part of a ring that the other is not.
NOT EXOCYCLIC
2-exocyclic components

Each type of diene or triene system is having a certain fixed value at which absorption takes place; this constitutes the ***Base value or Parent value***. The contribution made by various alkyl substituents or ring residue, double bond extending conjugation and polar groups such as –Cl, -Br etc are added to the basic value to obtain λ_{max} for a particular compound.

I) CONJUGATED DIENE CORRELATIONS:

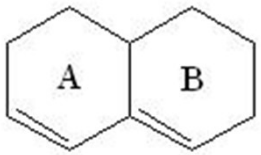
a) Homoannular Diene:- Cyclic diene having conjugated double bonds in same ring.

b) Heteroannular Diene:- Cyclic diene having conjugated double bonds in different rings.

c) Endocyclic double bond:- Double bond present in a ring.

d) Exocyclic double bond: - Double bond in which one of the doubly bonded atoms is a part of a ring system.

Here Ring A has one exocyclic and endocyclic double bond. Ring B has only one endocyclic double bond.



The rules for open chain and six-membered ring dienes were made by **Woodward** in 1941 then modified by **Fieser** and by **Scot** as a result of experience so for example compound (1) would be calculated to have a $\lambda_{\max}$ equal to 234 nm.

Parent value = 214 nm

Three ring residues (a) = 3 x 5 = 15 nm

one exocyclic double bond (the bond is exocyclic to ring B) = 5 nm

Total = 234 nm

The observed value is 235 nm $\varepsilon = 19000.$

Rules for dienes and triene absorption:

Value assigned to parent heteroannular or open chain diene = 214 nm

Value assigned to parent homoannular diene = 253 nm

Addition for:-

Each alkyl substituent or ring residue = 5 nm

The exocyclic double bond = 5 nm Double bond extension = 30 nm

Auxochrome – O Acyl = 0 O Alkyl = 6

S Alkyl = 30 Cl , -Br= 5 nm

M alkyls = 60 nm

By similar calculation for compd. (2) would be expected to have λ_{max} 273 nm and actually have one at 275 nm through ethanol as a solvent.

However, there are a large number of exceptions to the rules such as distortion of the chromophore may lead to **red or blue** shift depending on the nature of the distortion. The strained molecule of compd. Compd. (3) has a maximum at 245.5 nm while the usual value gives 229 nm, the diene (4) might be expected to have λ_{max} 273 nm but the distortion of the chromophore with loss of conjugation cause λ_{max} to 220 nm.

Compd. (5) absorbed at 248nm, changing of the ring size also lead to departures from the predicated value of 263 nm as follows.

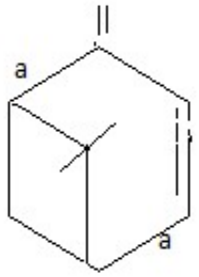
Cyclopentadiene 238.5 nm ($\mathcal{E}$ 3400)

Cycloheptadiene 248 nm ($\mathcal{E}$ 7500)

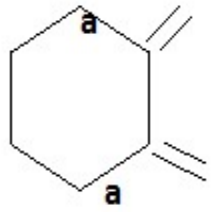
Cyclohexadiene 256 nm ($\mathcal{E}$ 800)

Compd.3 =229nm and obs.248nm

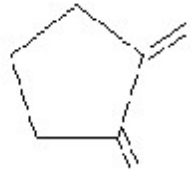
Compd. 4=234nm and obs. 220nm



3



4



5

Ex.

For compound No. 3

Parent value = 214 nm, 2 ring residue (a) = 2x5 = 10 nm, exocyclic double bond= 5, Total = 229 nm, Observed = 245.5 nm

That is because of strain

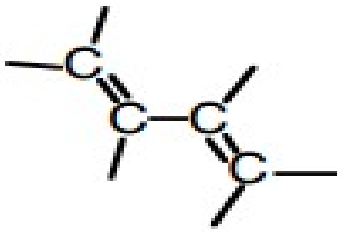
Compound. No. 4

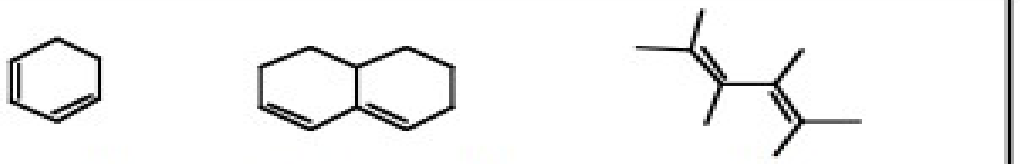
parent value = 214 nm, Two exocyclic double bond = 10 nm

Two ring residue = 10 nm, Total = 234 nm, Observed = 220 nm

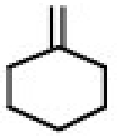
Woodward-Fieser Rules for Dienes

	Homoannular	Heteroannular
Parent	λ=253 nm	λ=214 nm =217 (acyclic)
Increments for:		
Double bond extending conjugation	+30	
Alkyl substituent or ring residue	+5	
Exocyclic double bond	+5	
Polar groupings:		
-OC(O)CH3	+0	
-OR	+6	
-Cl, -Br	+5	
-NR2	+60	
-SR	+30	





Homoannular heteroannular acyclic

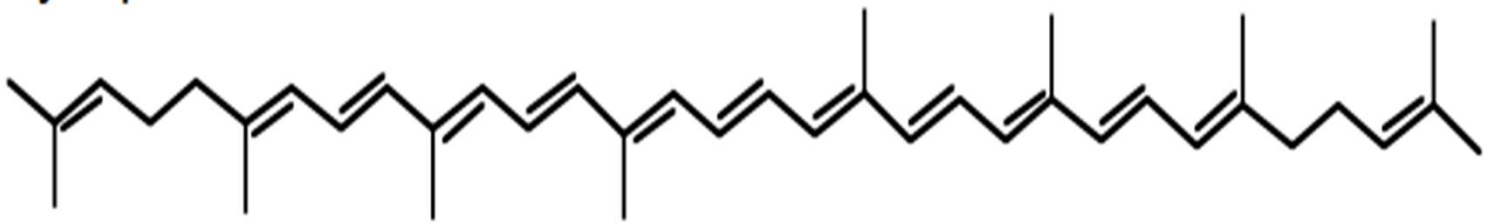


exocyclic

For more than 4 conjugated double bonds:

$\lambda_{max} = 114 + 5(\#\text{ of alkyl groups}) + n(48.0\text{-}1.7n)$

Lycopene:

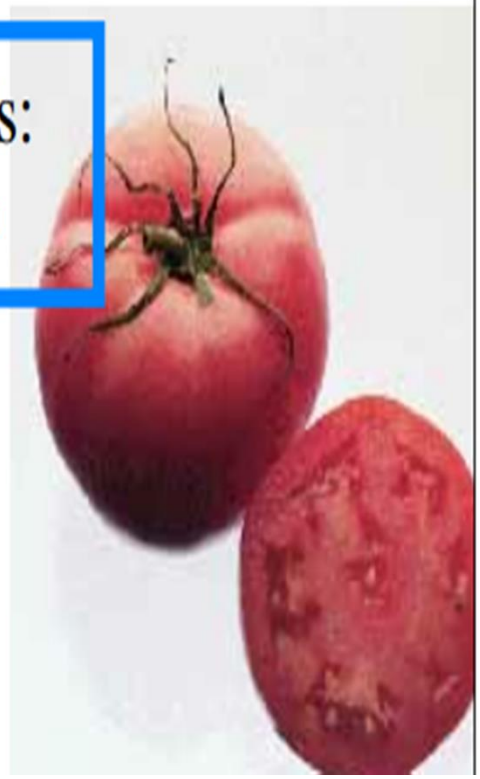


For more than 4 conjugated double bonds:

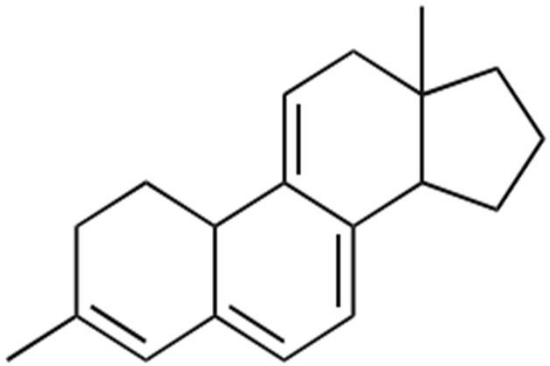
$\lambda_{max} = 114 + 5(\#\text{ of alkyl groups}) + n(48.0\text{-}1.7n)$

$\lambda_{max} = 114 + 5(8) + 11*(48.0\text{-}1.7*11) = 476$ nm

λ_{max}(Actual) = 474.



ght, the visible spectrum



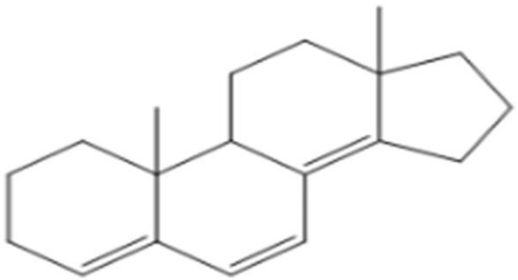
Base(homodiene)	
253	
2 DBE	60
6 alkyls	30
3 exocyclic olefins	15
	358 nm

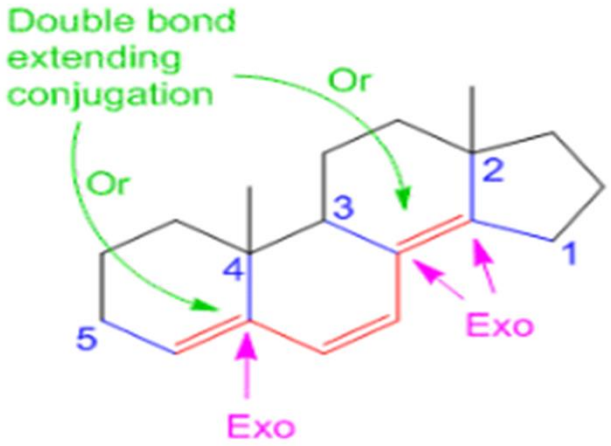
TABLE 7.5

Rules of Diene Absorption[a]

Base value for heteroannular diene	214
Base value for homoannular diene	253
Increments for	
Double bond extending conjugation	+30
Alkyl substituent or ring residue	+5
Exocyclic double bond	+5
Polar groupings: OAc	+0
OAlk	+6
SAlk	+30
Cl, Br	+5
$N(Alk)_2$	+60
Solvent correction[b]	+0
	λ_{calc} = Tota

[a]See L. M. Fieser and M. Fieser, *Steroids*. New York: Reinhold 1959, pp. 15–24; R. B. Woodward, *J. Am. Chem. Soc.*, **63**, 112 (1941); **64**, 72, 76 (1942); A. I. Scott, *Interpretation of the Ultraviole Spectra of Natural Products*. New York: Pergamon (Macmillan) 1964.





Name of Compound	10,13-dimethyl-2,3,9,10,11,12,13,15,16,17-decahydro-1H-cyclopenta[a]phenanthrene
Woodward Component	**Contribution**
Core- Transoid/Heteroannular	+ 215 nm
Substituents- 5 alkyl groups	5 x 5 = + 25 nm
1 Double bond extending conjugation	+ 30 nm
Other Effects- 3 Exocyclic Double Bond	+ 15 nm
Calculated λmax	**285 nm**
Observed λmax	283 nm

Homoannular and hetroannular

dinene

Component	Contribution
Core- Homoannular/Cisoid diene	+ 253 nm
Substituents– 5 alkyl substituents	5 x 5 = + 25 nm
Double bond extending conjugation	+ 30 nm
Other Effects- 3 Exocyclic double bonds	3 x 5 = + 15 nm
Calculated λ_{max}	**323 nm**

Ketones and Aldehydes n –π* transitions

Saturated ketones & aldehydes shows a weak symmetry forbidden band in the rang 275 – 295 nm ($\mathcal{E} - 20$) due to excitation of an oxygen lone-pair of electrons to the anti-bonding π-orbital of the carbonyl group, aldehydes and the more heavily substituted ketones absorb at the upper end of this rang. **In simple unconjugated carbonyl group has absorption either around 190 nm due to n-σ* and in the region around 300 nm due to n-π* as weak forbidden transition 275 – 295 nm ($\mathcal{E}$ 20).**

Polar substituent on the α-carbon atom raise when axial or lower when equatorial to extremes of this rang 275-295 nm when carbonyl group is substituted by auxochrome as in acid or an amide so the π* is raised but n-level left un – ulter so transition is n-π* and these compounds is shifted to 200 – 215 nm range.

The position and intensity of n-π* bond also influence by solvent due to hydrogen bonding in the ground state relative to excited state.

Rules of ketones or aldehydes containing carbonyl group conjugated with other double bond (α,β – unsaturated carbonyl group). π-π* transitions (allowed) in α,β-unsaturated ketones and aldehyde absorption)

Parant value for α,β-unsaturated six ring or a cyclic ketones = 215 nm

Parant value for α,β-unsaturated five- ring ketones = 205 nm

Parant value for α,β-unsaturated aldehyde = 210 nm

--C=C—-C=C—-C=O

δ ℘ B α

α, β UNSATURATED CARBONYL COMPOUNDS OR KETONES:

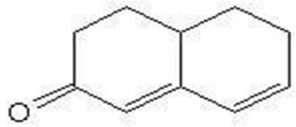
1. Base value:
   a) Acyclic α, β unsaturated ketones = 215 nm
   b) 6 membered cyclic α, β unsaturated ketones = 215 nm
   c) 5 membered cyclic α, β unsaturated ketones = 205 nm
   d) α, β unsaturated aldehydes = 210 nm
   e) α, β unsaturated carboxylic acids & esters = 195 nm
2. Alkyl substituent or Ring residue in α position = 10 nm
3. Alkyl substituent or Ring residue in β position = 12 nm
4. Alkyl substituent or Ring residue in γ and higher positions = 18 nm
5. Double bond extending conjugation = 30 nm
6. Exocyclic double bonds = 5 nm
7. Homodiene compound = 39 nm
8. Polar groups: a) –OH in α position = 35 nm –OH in β position = 30 nm

–OH in δ position = 50 nm b) –OAc in α, β, γ, δ positions = 6 nm c) –OMe in α position = 35 nm

–OMe in β position = 30 nm –OMe in γ position = 17 nm –OMe in δ position = 31 nm

d) –Cl in α position = 15 nm –Cl in β position = 12 nm e) –Br in α position = 25 nm –Br in β position = 30 nm

f) –NR_2 in β position = 95 nm



Eg:

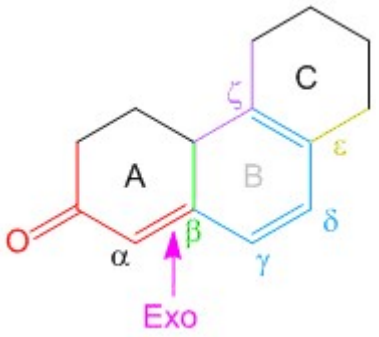
Base value = 215 nm β- Substituents = 1 x 12 = 12 nm δ- Substituents = 1 x 18 = 18 nm

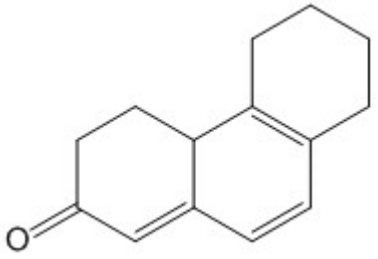
Double bond extending conjugation =1 x 30 = 30 nm Exocyclic double bond = 5 nm

λ_{max} = 279 nm

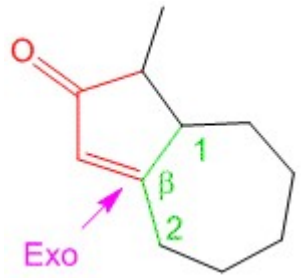
•

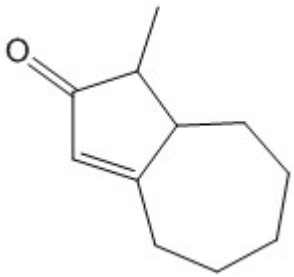
Name of Compound	4,4a,5,6,7,8-hexahydrophenanthren-2(3H)-one
Component	**Contribution**
Core- cyclohexenone	+ 215 nm
Substituents at α-position:	0
Substituents at β-position: 1 alkyl group	+ 12 nm
Substituents at γ-position:	0
Substituents at δ-position:	0
Substituents at ε-position: 1 alkyl group	+ 18 nm
Substituents at ζ-position: 2 alkyl group	2 x 18 = + 36 nm
Other Effects: 2 Double bonds extending conjugation Homoannular Diene system in ring B 1 Exocyclic double bond	2 x 30 = + 60 nm + 39 nm + 5 nm
Calculated λ_{max}	**381 nm**
Observed λ_{max}	388 nm



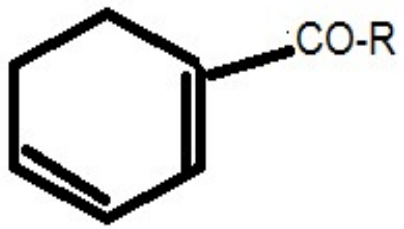


Name of Compound	1-methyl-4,5,6,7,8,8a-hexahydroazulen-2(1H)-one
Component	**Contribution**
Core- cyclopentenone	+ 202 nm
Substituents at α-position	0
Substituents at β-position- 2 alkyl groups	2 x 12= + 24 nm
Other Effects- 1 Exocyclic Double Bond	+ 5 nm
Calculated λ_{max}	**231 nm**
Observed λ_{max}	226 nm





Additions:



Double bond extension = 30 nm

Alkyl or ring residue for

α=10 nm β=12 nm ℘=18 nm or higher

Auxochroms

OH α= 35 nm, β…….30 nm, σ……..50 nm

OCH_3 α = 35 nm, β =30 nm, ℘= 17 nm, σ =31 nm

Cl α=15 nm, β =12 nm

Br α=23 nm, β =30 nm NR_2 β~95 nm

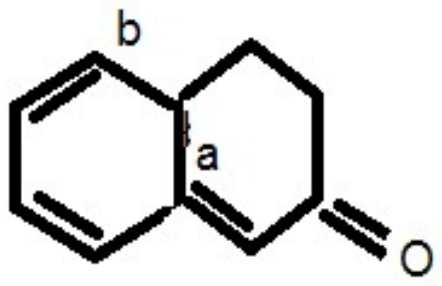
Exocyclic double bond (six member ring or less to which the double bond is = 5 nm

Homodiene compound if found = 39 nm

Ex.: $(CH_3)_2CCHCOCH_3$

Parant = 215 nm, Two β-substituents = 2x12 = 24 nm

Total = 239 nm, Observed = 237 nm



Parant = 215 nm,

β-ring residue (a) = 12 nm,

ω-ring residue(b) = 18 nm

two double bond extension = 2x30=60

one exocyclic double bond = 5nm,

homodiene or homoannular = 39 nm,

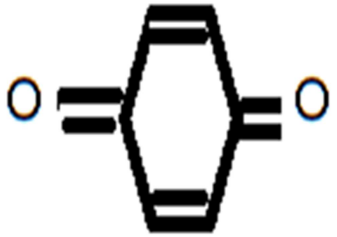
Total=349, Observed = 348

$$\varepsilon = 11000$$

The presence of a weak band in the range 275 – 295 nm region is positive identification of ketone or aldehyde carbonyl group and nitro group shows similar band of course impurities must be absent. In α-diketons R-CO-CO-R, there are two n-π* transitions one appeared at 290 nm $\mathcal{E} = 30$ and the second in the 340 – 440 range ($\mathcal{E} = 10 - 30$) which stretches to visible region to gives yellow colour.

In Quinone's also there is colors due to n-π* transitions

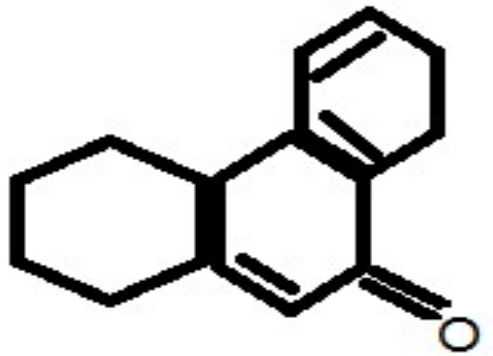
λ_{max}=253 ($\mathcal{E}$ 2500)
= 263 ($\mathcal{E}$ 23500)
= 398 (69000)



λ_{max}=242 nm
= 281nm
= 434 nm

Cross-conjugated system:

In this system the absorption observed due to the most highly substituted chromophore (the longest one)



Parant = 215 nm, α-residue = 10 nm alkyl, βresidue=12 nm

σ-residue =18 nm, one extension = 30 nm, homoannular = 39

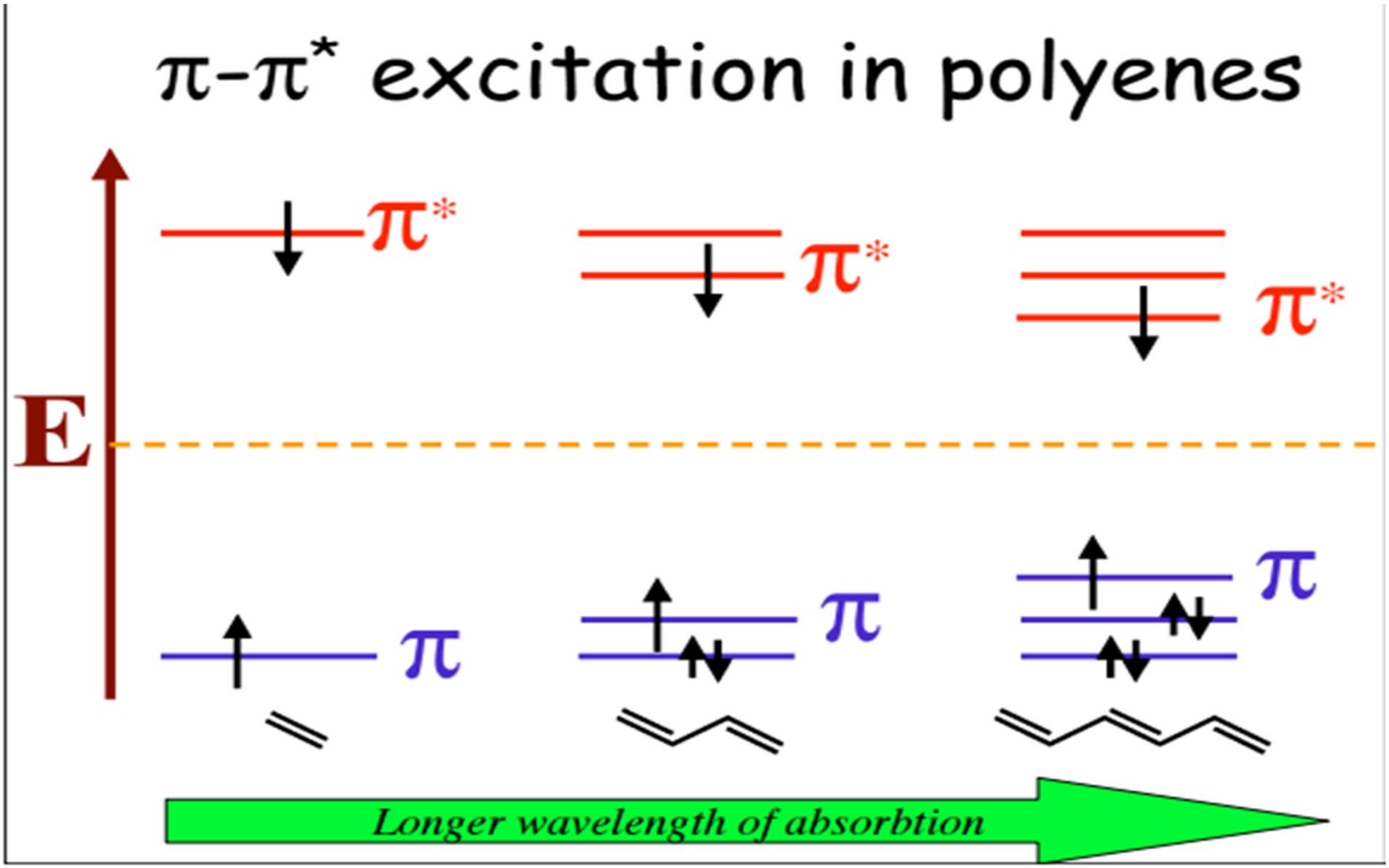
Total = 324 nm, Observed = 327nm

Note:

For unsaturated acids, esters, nitriles and amides follow a trend similar to that of ketones but slightly shorter wavelength. The molar excitation coefficients are usually above 10000

Aromatic system

Benzene ring absorbed at 184 ($\mathcal{E}$ 60000) & 203.5 ($\mathcal{E}$ 7400) and 254 ($\mathcal{E}$ 204) nm in hexane solution. When the aromatic ring is substituted by alkyl groups, the symmetry is lowered, when the ring substituted by lone –pair donating or by π-bonded system the chromophore is extended so the conjugated increased. The main band of Benzene ring appear at 203.5 nm (this band called k-band) effectively moved to longer λ than (β-band) which is originally at 254 nm


π-π* excitation in polyenes
E
π*
π*
π*
π
π
π
Longer wavelength of absorbtion

In case of disubstituted benzene ring in which the electron donating group in complemented by electron with drawing carbonyl group such as.

RC_6H_4-CO-X

X= alkyl, H, OH, OAlkyl

refer to the strongest band in the region so the calculation based on parent value with increments for each substituent.

Poly substituted ring should be treated with caution, practically when the substitution might lead to steric effect which preventing coplanarity of the carbonyl group and the ring. In the absences of steric hindrance to coplainarity, the calculated values are usually within 5 nm of the observed value

Rules for the principle band of substituted Benzene derivatives

$R - C_6H_4 - COX$

Parant chromophore orientation λ in EtOH

x=alkyl or ring residue ……246

x=H ……..250

x=OH, O alkyl ……230

Addition for each substituent

R=alkyl or ring residue o-, m-…3, p….10

R=OH, OMe, O alkyl o-, m- ……7, p…..25

R= O^- ……..o- …..11, m-….20, p-…..78

R=NH_2…….o-, m- --- 13, p…58

R=Cl……..o, m------ 0, P….0

R=Br…….o, m- ----- 2, P----15

R=NMe_2……..o , m- 20, P-----85

Other electron with drawing groups e.g. nitriles and nitro compounds show similar trends but with different and less well documented substituted effect.

There is red shift in the main absorption band compare to the effect of either substituent separately due to the extension of chromophore

When two groups are situated at ortho or meta to each other or when is para disposed group are not complementary so the observed spectrum is closer to that of separated non interacting chromophore

Polycyclic aromatic hydrocarbons

Their spectra are usually complicated and for that reason are useful as fingerprints, the spectra of a typical series naphthalene, anthracene & naphthacene here.

Naphthalene(1), Anthracene (2), Naphthacene (3)

$\lambda_{\max}$ 480 nm ($\mathcal{E}11000$) for Naphthancen to give yellow color

Compds (1) & (2) are not observed at visible region

pentacene $\lambda_{\max}$580 nm ($\mathcal{E}$ 12000) blue color

Question:. why Naphthacene is yellow & why pentacene is blue?

Hetroatomic compounds

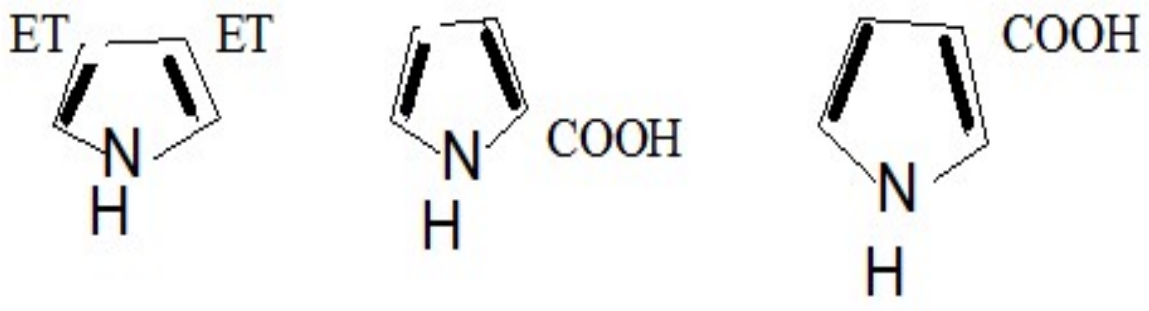
The range of heter-oaromatic compounds is too great. In general they resemble the spectra of their corresponding hydrocarbons. The hetro-atom whether like that in a pyrrole or that in pyridine

Pyrrole pyridine

Lead to pronounced substituent effects which depend on electron donating or withdrawing effect of the substituent and the hetro atom and or their orientation.

ex. simple pyrrole and pyrrole with an electron withdrawing substituent have different absorption because of the conjugation of the lone pair on the nitrogen atom through the pyrrole ring to the carbonyl group which increase the chromophore then red shift take place

203nm	262nm	245nm
€= 5670	12000	4800



In (2) the withdrawing group at ortho-position while in (3) at meta position so the conjugation in (3) is weak. In case of potentially tautomeric molecules the change in the absorption maxima with the change of PH is due to sometime to change in the chromophore as a result of the tautomerism and some time to simple protonation or deprotonation. **The change in the absorption is very important diagnostically in order to find the stable tautomeric species**

Electronic (Absorption) Spectra of 3d Transition Metal Complexes

1. Introduction

1.1. Types of spectra

Spectra are broadly classified into two groups: (i) emission spectra and (ii) absorption spectra.

i- Emission spectra are of three kinds **(a) continuous spectra, (b) band spectra and (c) line spectra**.

a. Continuous spectra: **Solids like iron or carbon emit** continuous spectra when they are heated until they light. Continuous spectrum is due to the thermal excitation of the molecules of the substance.

b. Band spectra: The band spectrum consists of a number of bands of different colours separated by dark regions. Band spectrum **is emitted by substances in the molecular state when the thermal excitement of the substance is not quite sufficient to break the molecules into continuous atoms**

c. Line spectra: A line spectrum consists of bright lines in different regions of the visible spectrum against a dark background. All the lines do not have the same intensity. The number of lines, their nature and arrangement depends on the nature of the substance excited. **Line spectra are emitted by vapours of elements.** No two elements do ever produce similar line spectra .

ii. **Absorption spectra**: When a substance is placed between a light source and a spectrometer, the substance absorbs certain part of the spectrum. This spectrum is called the absorption spectrum of the substance

Electronic absorption spectrum is of two types.

d-d spectrum and charge transfer spectrum.

d-d spectrum deals with the electronic transitions within the d-orbitals.

In the charge transfer spectrum, electronic transitions occur from metal ligand MLCT or vice versa LMCT.

Electronic spectra of transitions metal complexes and electronic absorption spectroscopy requires consideration of the following principles:

a. **Franck-Condon Principle**: Electronic transitions occur in a very short time (about 10-15sec.) and hence the atoms in a molecule do not have time to change position significantly during electronic transition .So the molecule will find itself with the same molecular configuration and hence the vibrational kinetic energy in the exited state remains the same as it had in the ground state at the moment of absorption

b. Electronic transitions between vibrational states:

Frequently, transitions occur from the ground vibrational level of the ground electronic state to many different vibrational levels of particular excited electronic states.. Since all the molecules are present in the ground vibrational level, nearly all transitions that give rise to a peak in the absorption spectrum will arise from the ground electronic state.

If the different excited vibrational levels are represented as υ1, υ2, etc., and the ground state as υ0, the fine structure in the main peak of the spectrum is assigned to υ0 → υ0 , υ0 → υ1, υ0 → υ2 etc., vibrational states. The υ0 → υ0 transition is the lowest energy transition

C. Symmetry requirement:

This requirement is to be satisfied for the transitions discussed above. Electronic transitions occur between split 'd' levels of the central atom giving rise to so called d-d or ligand field spectra. The spectral region where these occur durations the near infrared, visible and U.V. region. Ultraviolet UV, Visible Vis and Near infrared NIR

(50,000 – 26300) (26300 -12800) (12800 -5000) cm respectively

(200 – 380) (380 -780) (780 – 20000) nm respectively

3. Russel-Saunders or L-S coupling scheme :

An orbiting electronic charge produces magnetic field perpendicular to the plane of the orbit. Hence the orbital angular momentum and spin angular momentum have corresponding magnetic vectors. As a result, both of these momenta couple magnetically to give rise to total orbital angular momentum. There are two schemes of coupling: Russel Saunders or **L-S coupling and j-j coupling**.

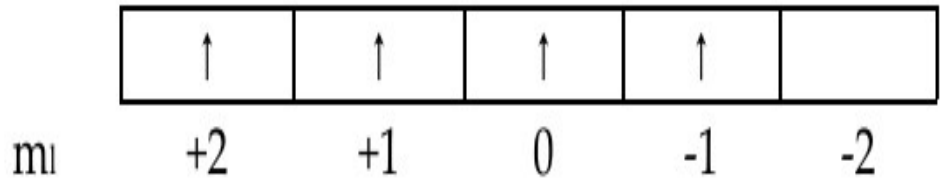
a. The individual spin angular momenta of the electrons, **si**, each of which has a value of **± ½**, combine to give a resultant spin angular momentum (individual spin angular momentum is represented by a lower case symbol whereas the total resultant value is given by a upper case symbol).

a. The individual spin angular momenta of the electrons, si, each of which has a value of ± ½, combine to give a resultant spin angular momentum (individual spin angular momentum is represented by a lower case symbol whereas the total resultant value is given by a upper case symbol). Electronic (Absorption) Spectra of 3d Transition Metal Complexes 5 is=S Two spins of each ± ½ could give a resultant value of S =1 or S= 0; similarly a resultant of three electrons is 1 ½ or ½ .The resultant is expressed in units of h/2 π. The spin multiplicity s given by (2S+1). Hence, If n is the number of unpaired electrons, spin multiplicity is given by n + 1

b. The individual orbital angular momenta of electrons, **li**, each of which may be 0, 1 ,2, 3 , 4 ….. in units of **h/2π** for s, p, d, f, g, …..orbit respectively, combine to give a resultant orbital angular momentum, **L** in units of **h/2π**. **∑li = L** The resultant **L** may be once again **0, 1, 2, 3,4**…. which are referred to as **S, P, D, F G**,…respectively in units of **h/2π**.The orbital multiplicity is given by **(2L+1).** 0 1 2 3 4 5 S P D F G H

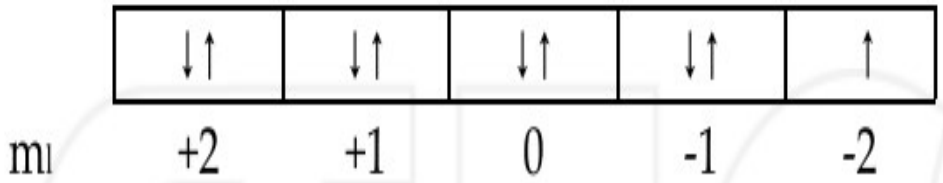
c. Now the resultant S and L couple to give a total angular momentum, **J**. Hence, it is not surprising that **J** is also quantized in units of **h/2π**.The possible values of **J** quantum number are given as **J = L + S , L + S - 1 , L + S - 2 , L + S - 3 , ….. L - S** , The symbol | | indicates that the absolute value **(L – S)** is employed, i.e., no regard is paid to ± sign. Thus **for L = 2 and S = 1, the possible J states are 3, 2 and 1 in units of h/2π**.

For d^4 configuration:



Hence, L = 3 -1 = 2 i.e., D; S = 2; 2S+1 = 5; and J = L- S = 0; Term symbol = $^5D_0$

For d^9 configuration:

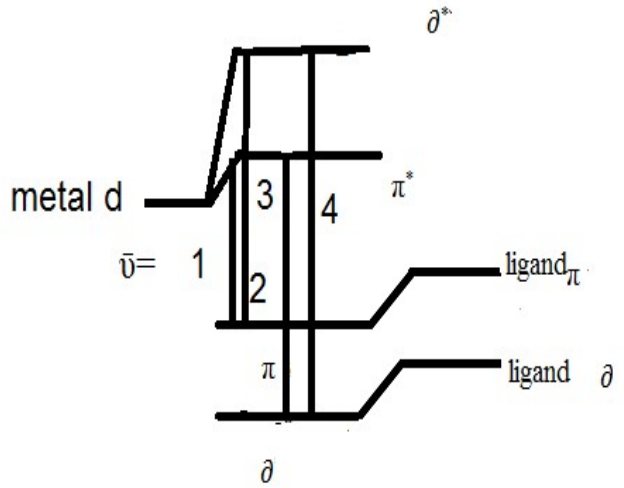


Hence, L = +2+1+0-1 = 2 i.e., D ; S = 1 /2 ; 2S+1 = 2 ; and J = L+ S = 3/2 ; Term symbol = $^2D_{5/2}$

Charge Transfer

The charge distribution is considerably different in ground and excited states and so they called charge transfer transitions and in most cases CT processes are higher energy than d-d transitions thus usually lie at the extreme blue shift end of the visible spectrum, or in the ultraviolet region and also all (CT) transitions observed are fully allowed transitions, hence they are strong and the molar extinctions coefficient are typically more than 10^3. There are of course many forbidden CT transitions that give rise to weak bands, there are seldom observed because they are converted up by strong CT bands.

There are four types of transitions that would be expected as above so the ῡ1 type of transition is the lowest energy, ῡ2 should give lowest energy CT bands in t_2g^6 PtX_6^{-2} type since the transitions from mainly non-bonding levels to anti-bonding one and the band should be fairly broad, ῡ3 expected to be broad and weak and not observed and ῡ4 observed in few cases but in most cases they must lie beyond the range of observations.



Charge-transfer occurs often in inorganic ligand chemistry involving metals. Charge-transfer complexes are formed by weak association of molecules or molecular sub-groups, one acting as an electron donor and another as an electron acceptor. The association does not constitute a strong covalent bond and is subject to significant temperature, concentration, and host, e.g., solvent, dependencies

The charge-transfer association occurs in a chemical equilibrium with the independent donor (D) and acceptor (A) molecules:

Depending on the direction of charge transfer, they are classified as either ligand-to-metal (LMCT) or metal-to-ligand (MLCT) charge transfer.. The charge-transfer complex (CT complex) or electron-donor-acceptor complex is an association of two or more molecules, or of different parts of one large molecule, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor

The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and is thus much weaker than covalent forces. Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electro-magnetic spectrum, which produces the characteristic intense color for these complexes. These optical absorption bands are often referred to as *charge-transfer bands* (CT bands). Optical spectroscopy is a powerful technique to characterize charge-transfer bands. Charge-transfer complexes exist in many types of molecules, inorganic as well as organic, and in solids, liquids, and solutions. In inorganic chemistry, most charge-transfer complexes involve electron transfer between metal atoms and ligands.

The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal in character and those that are predominantly ligand in character. If the transfer occurs from the MO with ligand-like character to the metal-like one, the complex is called a ligand-to-metal charge-transfer (LMCT) complex. If the electronic charge shifts from the MO with metal-like character to the ligand-like one, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, a MLCT results in oxidation of the metal center, whereas a LMCT results in the reduction of the metal center. Resonance Raman spectroscopy is also a powerful technique to assign and characterize charge-transfer bands in these complexes

Charge-transfer complexes are identified by:

Color: The color of CT complexes is reflective of the relative energy balance resulting from the transfer of electronic charge from donor to acceptor.

Solvatochromism: (is the ability of a chemical substance to change color due to a change in solvent polarity. Negative solvatochromism corresponds to hypsochromic shift (or blue shift) with increasing solvent polarity. The corresponding bathochromic shift (or red) is termed positive solvatochromism. The sign of the solvatochromism depends on the difference in dipole moment between the ground and excited states of the chromophore). In solution, the transition energy and therefore the complex color varies with variation in solvent permittivity, indicating variations in shifts of electron density as a result of the transition.

Intensity: CT absorptions bands are intense and often lie in the ultraviolet or visible portion of the spectrum. For inorganic complexes, the typical molar absorptivity's, ε, are about 50000 L mol^{-1} cm^{-1}, that are three orders of magnitude higher than typical ε of 20 L mol^{-1} cm^{-1} or lower, for d-d transitions (transition from t_{2g} to e_g). This is because the CT transitions are spin-allowed and Laporte-allowed so $\Delta s = 0$ and $\Delta L = \pm 1$. However, d-d transitions are only spin-allowed; they are Laporte-forbidden.

Color of charge-transfer complexes

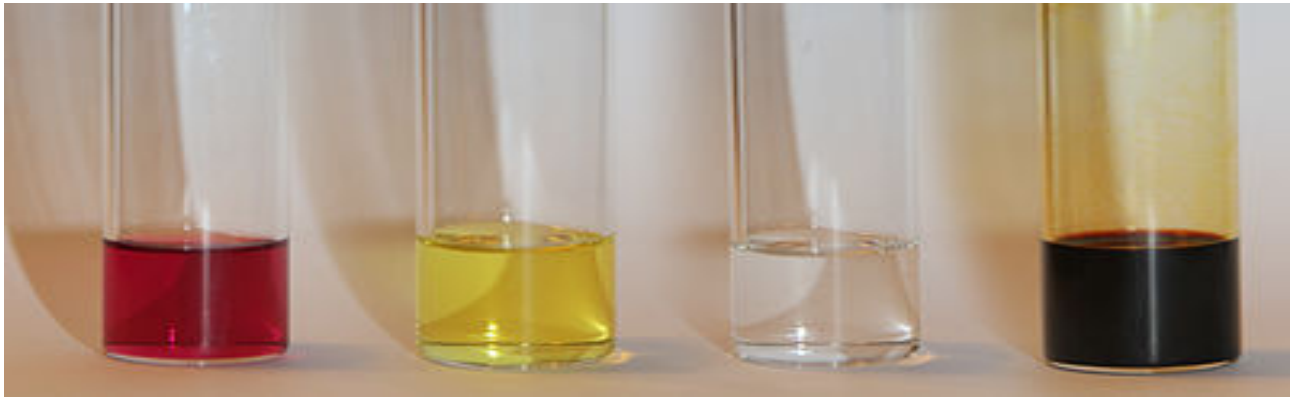


Fig. 1 I_2•PPh_3 charge-transfer complexes in CH_2Cl_2. From left to right:

(1) I_2 dissolved in dichloromethane - no CT complex. (2) A few seconds after excess PPh_3 was added - CT complex is forming. (3) One minute later after excess PPh_3 was added, the CT complex $[Ph_3PI]^+I^-$ has been formed. (4) Immediately after excess I_2 was added, which contains $[Ph_3PI]^+[I_3]^-$.

Many metal complexes are colored due to d-d electronic transitions. Visible light of the correct wavelength is absorbed, promoting a lower d-electron to a higher excited state. This absorption of light causes color. These colors are usually quite faint, however.
This is because of two selection rules:

The spin rule: $\Delta S = 0$

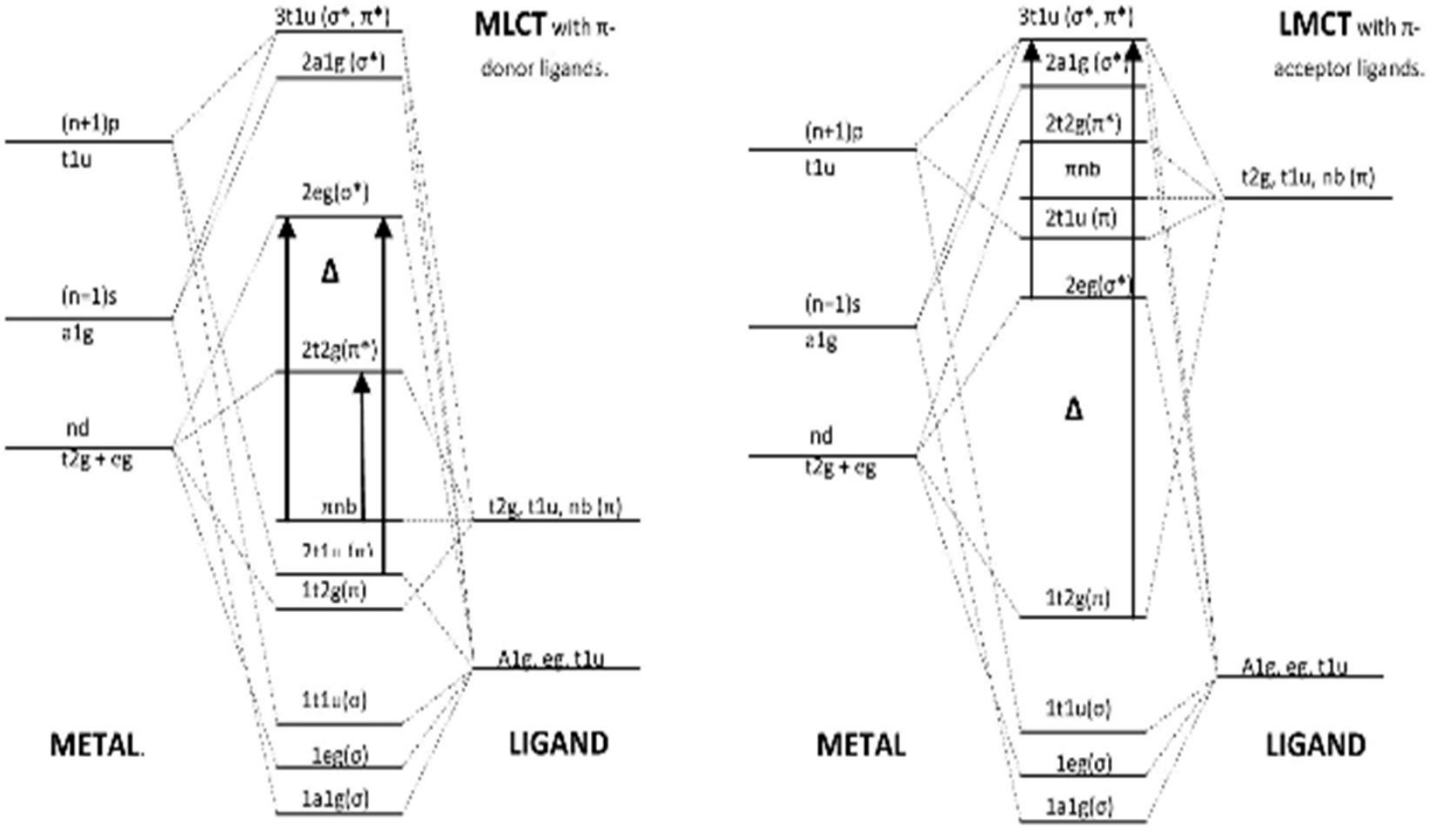
On promotion, the electron should not experience a change in spin. Electronic transitions that experience a change in spin are said to be *spin-forbidden*.

Laporte's rule: $\Delta L = \pm 1$

d-d transitions for complexes that have a center of symmetry are forbidden - *symmetry-forbidden* or *Laporte-forbidden*.

Inorganic Molecule Spectra

Speaking of transition probabilities in organic molecules is a good seq way into interpreting the spectra of inorganic molecules. Three types of transitions are important to consider are Metal to Ligand Charge Transfer (MLCT), Ligand to Metal Charge Transfer (LMCT), and d-d transitions. To understand the differences of these transitions we must investigate where these transitions originate. To do this, we must define the difference between pi accepting and pi donating ligands:



Orgel Diagrams

Orgel diagrams are correlation diagrams which shows the relative energies of electronic terms in transition metal complexes, much like Tanabe-Sugano diagrams. They are named after their creator, Leslie Orgel. Orgel diagrams are restricted to only show weak field (i.e. high spin) cases, and offer no information about strong field (low spin) cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams; also, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a Tanabe-Sugano diagram. Orgel diagrams will, however, show the number of spin allowed transitions, along with their respective symmetry descriptions. In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram, with the terms due to that electronic configuration in a ligand field at each side

- There are two Orgel diagrams, one for d^1, d^4, d^6, and d^9 configurations and the other with d^2, d^3, d^7, and d^8 configurations.

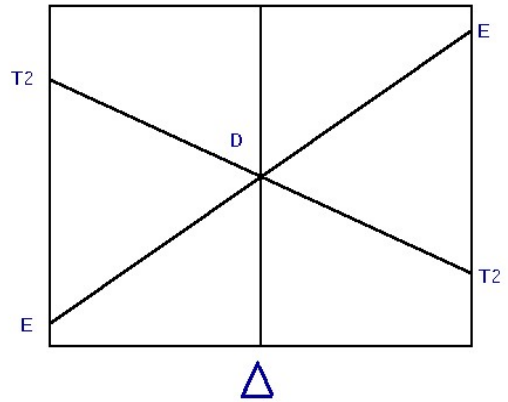


Figure 1: D Orgel Diagram

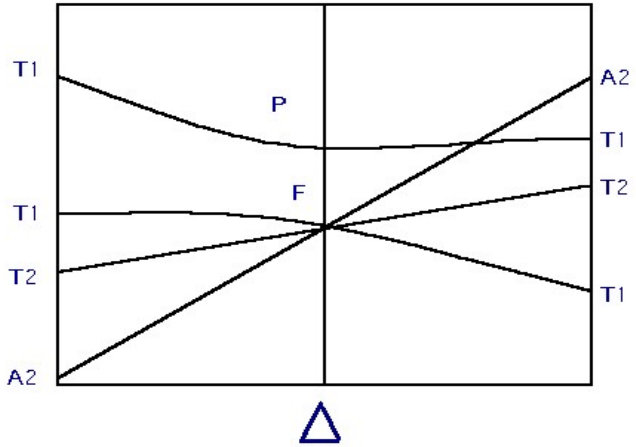
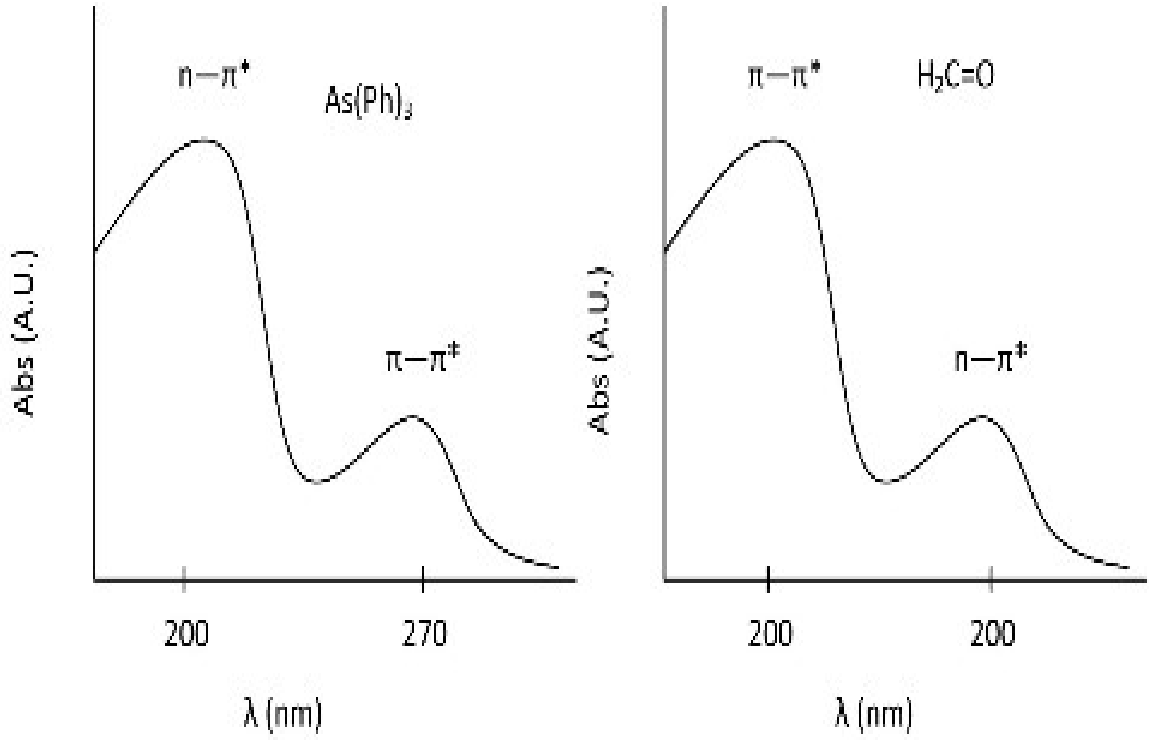


Figure 2: F and P Orgel Diagram

Organic Molecule Spectra

From the example of benzene, we have investigated the characteristic pi to pi* transitions for aromatic compounds. Now we can move to other organic molecules, which involves n to pi* as well as pi to pi*. Two examples are given below:



The highest energy transition for both of these molecules has an intensity around 10,000 cm^{-1} and the second band has an intensity of approximately 100 cm^{-1}. In the case of formaldehyde, the n to pi* transition is forbidden by symmetry where as the pi to pi* is allowed. The opposite is true for $As(Ph)_3$ and the difference in molar absorptivity is evidence of this.

1. What are the effects of conjugation and aromaticity on UV-Vis absorption spectroscopy?

Conjugation of double bonds decreases the energy required for the π–π* and thus increases its absorptivity. In addition, the absorption wavelength is shifted to longer λ's (a bathochromic shift). Aromaticity results in asimilar effect like conjugation but to a much larger extent.

2. Why do many transition and inner transition metals absorb in the UV-Vis, although they lack π 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.

3. 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 λ 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.

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4. 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 acids and bases can be also titrated photometrically

5. 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

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6. 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

7.Express the following absorbance in terms of percent transmittance:

a 0.051

b 0.918

c 0.379

d 0.261

e 0.485

f 0.072

$A = \log Po/P = \log 1/T = - \log T$

$T = 10\text{-}A$

8. Convert the following transmittance data to absorbance:

a 0.255

b 0.567

c 0.328

d 0.036

e 0.085

$A = -\log T$

A solution containing 4.48 ppm $KMnO_4$, had a % transmittance of 30.9% in a 1.00 cm cell at 520 nm. Calculate the molar ahsorptivity of $KMnO_4$, at 520 nm.

$A = \varepsilon bc$

mmol $KMnO_4$/mL = (4.48 mg $KMnO_4$/1000 mL) x (mmol $KMnO_4$/158 mg $KMnO_4$) = 2.84x10-5M T = 0.309

$A = -\log T = -\log 0.309 = 0.510$

0.510 = ε* 1.00 cm 2.84x15mol/L ε= 1.80x104L mol-1cm-1

A solution containing the complex formed between Bi(III) and thiourea has a molar absorptivity 9.32 X 103L mol-1cm-1at 470 nm.

(a) What is the absorbance of a 6.24x10-5M solution of the complex at 470 nm in a 1.00 cm cell?

(b) What is the percent transmittance of the solution described in (a)?

(c) What is the molar concentration of the complex in a solution that has the

absorbance described in (a) when measured at 470 nmin a 5.00 cm cell

A = εbc

a. A = 9.32x103* 1.00 * 6.24x10-5

= 0.582

b. T = 10-A

T = 10-0.582

= 0.262

%T = 0.262x100% = 26.2%

c. A = εbc

0.582 = 9.32x103* 5.00 * c

c = 1.25x10-5M

13-8. At 580 nm. which is the wavelength of its maximum absorption. the complex Fe(SCN)2+has a molar absorptivity of 7.00x103 L cm-1mol-1. Calculate

(a) the absorbance of a 2.50x10-5M solution of the complex at 580 nm in a 1.00-cm cell

(b) the absorbance of a solution in a 2.00 cm cell in which the concentration of the complex is one half that in (a).

(c) the percent transmittance of the solutions described in (a) and (b).

(d) the absorbance of a solution that has half the transmittance of that described in (a).

a. $A = \varepsilon bc$

$A = 7.00x103*1.00*2.50x10-5$

$= 0.175$

b. $A = \varepsilon bc$

$A = 7.00x103*2.00*1.25x10-5$

$= 0.175$

c. Ta= 10-A= 10-0.175= 0.668

Tb= 10-0.175= 0.668

d. T = 0.668/2 = 0.334

A = -log T = -log 0.334 = 0.476

Describe the differences between the following and list any particular advantages possessed by one over the other.

(a) hydrogen and deuterium discharge lamps as sources for ultraviolet radiation.

(b) filters and monochromators as wavelength selectors.

(c) photovoltaic cells and phototubes as detectors for electromagnetic radiation.

(d) photodiodes and photomultiplier tubes.

(e) double-beam-in-space and double-beam-in-time spectrophotometers.

(f) spectrophotometers and photometers.

(g) single-beam and double-beam instruments for absorbance measurements.

(h) conventional and multichannel spectrophotometers.

answer.

a. deuterium lamp contains deuterium while a hydrogen lamp contain hydrogen. Deuterium lamps produce radiation of higher intensity and are the most common sources in the ultraviolet.

b. Filters transmit bands of radiation that may vary from 5-250 nm. They also attenuate incident radiation and have applications in quantitative analysis where resolution is not crucial. Monochromators produce radiation of high resolution and can be used for both qualitative and quantitative analysis.

c. Phototubes have higher sensitivities and great reliability but require a power supply. A photovoltaic cell has a lower sensitivity, and suffers from weakness but has the advantage of exclusion of the need for a power supply.

d. Phototubes are less sensitive since a phototube contains a single photo emissive surface. The dark current is low in phototubes. Photomultiplier tubes are superior to phototubes in sensitivity but are far more expensive and suffer from dark currents.

e. A photometer is an instrument which uses a filter as a wavelength selector or a laser without a wavelength selector. A colorimeter is a photometer used in the visible as samples must be colored