

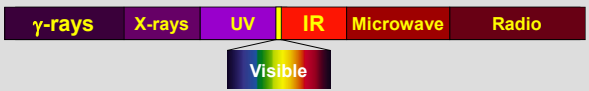
UV Spectroscopy

UV Spectroscopy

I. Introduction

A. UV radiation and Electronic Excitations

- The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole
- This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum
- For comparison, recall the EM spectrum:



- Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm
- For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV

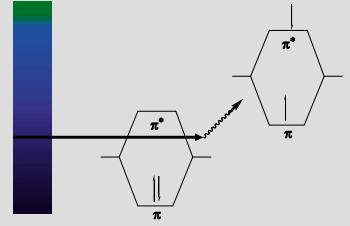
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UV Spectroscopy

I. Introduction

B. The Spectroscopic Process

- In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation
- If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed
- The remaining UV light passes through the sample and is observed
- From this residual radiation a spectrum is obtained with "gaps" at these discrete energies – this is called an *absorption spectrum*



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UV Spectroscopy

I. Introduction

C. Observed electronic transitions

- The lowest energy transition (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO)
- 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^*)
- The lowest energy occupied orbitals are typically the σ ; likewise, the corresponding anti-bonding σ^* orbital is of the highest energy
- π -orbitals are of somewhat higher energy, and their complementary anti-bonding orbital somewhat lower in energy than σ^* .
- Unshared pairs lie at the energy of the original atomic orbital, most often this energy is higher than π or σ (since no bond is formed, there is no benefit in energy)

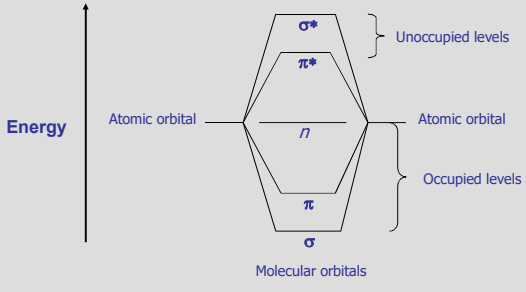
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UV Spectroscopy

I. Introduction

C. Observed electronic transitions

6. Here is a graphical representation



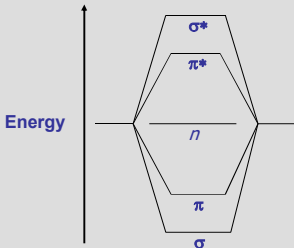
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UV Spectroscopy

I. Introduction

C. 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

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UV Spectroscopy

I. Introduction

C. Observed electronic transitions

- Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm
- Special equipment to study *vacuum* or *far UV* is required
- Routine organic UV spectra are typically collected from 200-700 nm
- 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.	180 nm ✓ - if conjugated!
$n \rightarrow \sigma^*$	O, N, S, halogens	190 nm
$n \rightarrow \pi^*$	carbonyls	300 nm ✓

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UV Spectroscopy

UV Spectroscopy

I. Introduction

D. Selection Rules

1. Not all transitions that are possible are observed
2. For an electron to transition, certain quantum mechanical constraints apply – these are called “selection rules”
3. For example, an electron cannot change its spin quantum number during a transition – these are “forbidden”
Other examples include:
 - the number of electrons that can be excited at one time
 - symmetry properties of the molecule
 - symmetry of the electronic states
4. To further complicate matters, “forbidden” transitions are sometimes observed (albeit at low intensity) due to other factors

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UV Spectroscopy

I. Introduction

E. 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, this is the case
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

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UV Spectroscopy

II. Instrumentation and Spectra

A. 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:

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UV Spectroscopy

II. Instrumentation and Spectra

A. 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

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UV Spectroscopy

II. Instrumentation and Spectra

A. 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

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UV Spectroscopy

II. Instrumentation and Spectra

B. 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; plastic and glass are only suitable for visible spectra
4. Concentration (we will cover shortly) is empirically determined

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

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UV Spectroscopy

II. Instrumentation and Spectra
 B. Instrumentation – Sample Handling

- Solvents must be transparent in the region to be observed; the wavelength where a solvent is no longer transparent is referred to as the **cutoff**
- Since spectra are only obtained up to 200 nm, solvents typically only need to lack conjugated π systems or carbonyls

Common solvents and cutoffs:

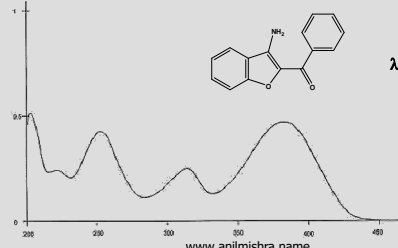
acetonitrile	190
chloroform	240
cyclohexane	195
1,4-dioxane	215
95% ethanol	205
n-hexane	201
methanol	205
isooctane	195
water	190

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UV Spectroscopy

II. Instrumentation and Spectra
 C. The Spectrum

- The x-axis of the spectrum is in wavelength; 200-350 nm for UV, 200-700 for UV-VIS determinations
- 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 "lambda max" values or λ_{max}



$\lambda_{max} =$

- 206 nm
- 317
- 376

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UV Spectroscopy

II. Instrumentation and Spectra
 C. The Spectrum

- The y-axis of the spectrum is in absorbance, A
- From the spectrometers point of view, absorbance is the inverse of transmittance: $A = \log_{10}(I_0/I)$
- From an experimental point of view, three other considerations must be made:
 - a longer **path length**, l through the sample will cause more UV light to be absorbed – linear effect
 - the greater the **concentration**, c of the sample, the more UV light will be absorbed – linear effect
 - some electronic transitions are more effective at the absorption of photon than others – **molar absorptivity**, ϵ *this may vary by orders of magnitude...*

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UV Spectroscopy

II. Instrumentation and Spectra
 C. The Spectrum

- These effects are combined into the Beer-Lambert Law: $A = \epsilon c l$
 - for most UV spectrometers, l would remain constant (standard cells are typically 1 cm in path length)
 - concentration is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M
 - molar absorptivities vary by orders of magnitude:
 - values of 10^4 - 10^6 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 unitless, so the units for ϵ are $\text{cm}^{-1} \cdot \text{M}^{-1}$ and are rarely expressed
- 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

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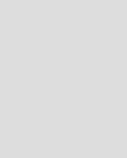
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Absorption: The Beer-Lambert Law

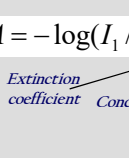
The method is used in a quantitative way to determine concentrations of an absorbing species in solution



Pierre Bouguer
(1698-1758)
Astronomer: Light is diminished as it passes through the atmosphere.



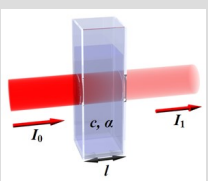
Johan Lambert
(1728-1777)
Mathematician, first to prove that π is irrational. No absorption coefficient.



August Beer (1825-1863): Added absorption coefficient and related to conc. in solution.

$$A = -\log(I_1 / I_0) = \epsilon c l$$

Extinction coefficient
Concentration
Path length



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UV Spectroscopy

II. Instrumentation and Spectra
 D. Practical application of UV spectroscopy

- UV was the first organic spectral method, however, it is rarely used as a primary method for structure determination
- It is most useful in combination with NMR and IR data to elucidate unique electronic features that may be ambiguous in those methods
- 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
- The most ubiquitous use of UV is as a detection device for HPLC; since UV is utilized for solution phase samples vs. a reference solvent this is easily incorporated into LC design

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UV Spectroscopy

Terms describing UV absorptions

1. **Chromophores:** functional groups that give electronic transitions.
2. **Auxochromes:** substituents with unshared pair e's like OH, NH, SH ..., when attached to a chromophore they generally move the absorption max. to longer λ .
3. **Bathochromic shift:** shift to longer λ , also called **red shift**.
4. **Hypsochromic shift:** shift to shorter λ , also called **blue shift**.
5. **Hyperchromism:** increase in ϵ of a band.
6. **Hypochromism:** decrease in ϵ of a band.

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UV Spectroscopy

III. Chromophores

A. 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

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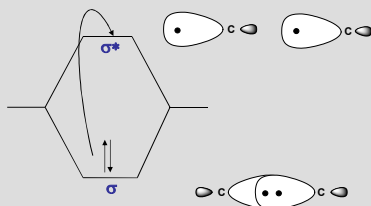
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III. Chromophores

B. Organic Chromophores

1. **Alkanes** – only possess σ -bonds and no lone pairs of electrons, so only the high energy $\sigma \rightarrow \sigma^*$ transition is observed in the far UV

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



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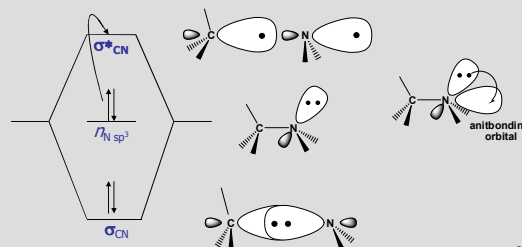
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III. Chromophores

B. Organic Chromophores

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

Note how this transition occurs from the HOMO to the LUMO



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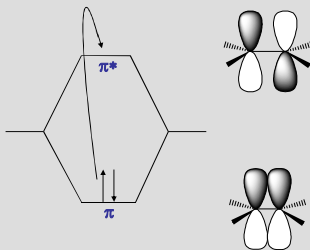
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III. Chromophores

B. 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



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UV Spectroscopy

III. Chromophores

B. 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 ($\epsilon = 15$), it is the most often observed and studied transition for carbonyls

This transition is also sensitive to substituents on the carbonyl

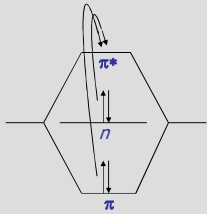
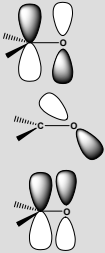
Similar to alkenes and alkynes, non-substituted carbonyls undergo the $\pi \rightarrow \pi^*$ transition in the vacuum UV (188 nm, $\epsilon = 900$); sensitive to substitution effects

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UV Spectroscopy

III. Chromophores
 B. Organic Chromophores
 4. Carbonyls – $n \rightarrow \pi^*$ transitions (~ 285 nm); $\pi \rightarrow \pi^*$ (188 nm)

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

σ_{C-O} transitions omitted for clarity

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UV Spectroscopy

CHROMOPHORE

This is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or visible region

Chromophore	Example	Excitation	λ_{max} nm	ϵ molar absorptivity	solvent
C=C	Ethene	$\pi > \pi^*$	171	15,000	Hexane
C \equiv C	1-Hexyne	$\pi > \pi^*$	180	10,000	Hexane
C=O	Ethanal	$n > \pi^*$ $\pi > \pi^*$	290 180	15 10,000	hexane Hexane
N=O	Nitromethane	$n > \pi^*$ $\pi > \pi^*$	275 200	17 5,000	ethanol Ethanol
C-X X = Br, I	Methyl bromide Methyl Iodide	$n > \sigma^*$ $n > \sigma^*$	205 255	200 360	hexane hexane

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UV Spectroscopy

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

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.

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UV Spectroscopy

AUXOCROME

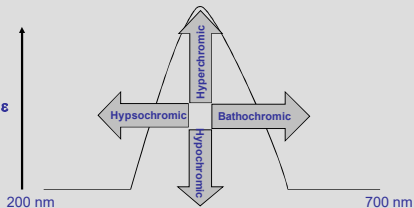
- An auxochrome is defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum.
- Some common auxochromic groups are
 - OH, –OR, –NH₂, –NHR, –NR₂, –SH

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UV Spectroscopy

III. Chromophores
 C. Substituent Effects
 General – Substituents may have any of four effects on a chromophore

- Bathochromic shift (red shift) – a shift to longer λ ; lower energy
- Hypsochromic shift (blue shift) – shift to shorter λ ; higher energy
- Hyperchromic effect – an increase in intensity
- Hypochromic effect – a decrease in intensity



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UV Spectroscopy

III. Chromophores
 C. Substituent Effects
 1. Conjugation – most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

Structure	λ_{max} nm	ϵ
<chem>H2C=CH2</chem>	175	15,000
<chem>C=CC=C</chem>	217	21,000
<chem>C=CC=CC=C</chem>	258	35,000
<chem>C=CC=CC=CC=C</chem> β -carotene	465	125,000
<chem>CH3CO</chem>	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 189	12 900
<chem>CH2=CHCO</chem>	$n \rightarrow \pi^*$ 280 $\pi \rightarrow \pi^*$ 213	27 7,100

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UV Spectroscopy

III. Chromophores
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

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UV Spectroscopy

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 \rightarrow LUMO transition is **reduced**

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UV Spectroscopy

III. Chromophores
C. Substituent Effects
2. Conjugation – Alkenes

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

Lower energy = Longer wavelengths

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UV Spectroscopy

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

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UV Spectroscopy

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

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UV Spectroscopy

IV. Structure Determination
A. Dienes
1. General Features

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

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

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UV Spectroscopy

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

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UV Spectroscopy

IV. Structure Determination

A. Dienes

1. General Features

The $\Psi_2 \rightarrow \Psi_3^*$ transition is observed as an intense absorption ($\epsilon = 20,000+$) 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:

$\lambda_{\text{max}} =$ 217 253 220 227 227 256 263 nm

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UV Spectroscopy

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)

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UV Spectroscopy

Woodward-Fieser Rules

Woodward formulated certain empirical rules for calculating the λ_{max} in case of dienes. Fieser later modified the rules. According to these rules, each type of diene has a certain fixed basic value and the value of the absorption (λ_{max} depends upon)

- The number of alkyl substituents or ring residues on the double bond.
- The number of double bonds which extend conjugation
- The presence of polar groups such as -Cl, -Br, -OR, -SR etc.

Transition Involved $\pi \rightarrow \pi^*$	Absorption
Parent value for Butadiene or a cyclic conjugated diene	217 m μ
Increment for each substituent	
Alkyl Substituent or ring residue	5 m μ
Exocyclic double bonds	5 m μ
Double bond extended conjugation	30 m μ
Auxochrome	
-OR	+6 m μ
-SR	+30 m μ
-Cl, -Br	+5 m μ
-NR ₂	+60 m μ
OCOCH ₃	0

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UV Spectroscopy

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

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UV Spectroscopy

IV. Structure Determination

A. Dienes

2. Woodward-Fieser Rules - Dienes

For example:

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

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

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UV Spectroscopy

Woodward-Fieser Rules

1
Basic Value 217 mμ
2 alkyl substituents (2 x 5) 10 mμ
Calculated value 227 mμ
Observed value 227

CH3-CH=CH-CH=CH-CH3

2
Basic Value 215 mμ
4 ring residues (4 x 5) 20 mμ
Calculated value 235 mμ
Observed value 234mμ

3
Basic Value 253 mμ
4 ring residues (4 x 5) 20 mμ
2 exocyclic double bonds(2 x 5) 10mμ
1 double bond extending conjugation 30mμ
Calculated value 313 mμ
Observed value 312mμ

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
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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): Homoannular (cisoid):



ε = 5,000 – 15,000
base λ_{max} = 214



ε = 12,000-28,000
base λ_{max} = 253

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


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

UV Spectroscopy

IV. Structure Determination

A. Dienes

3. **Woodward-Fieser Rules – Cyclic Dienes**
 For example:



1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene	heteroannular diene =	214 nm
	3 alkyl subs. (3 x 5)	+15 nm
	1 exo C=C	+ 5 nm
		234 nm
Experimental value		235 nm

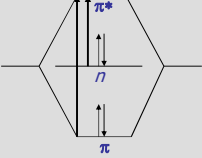
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UV Spectroscopy

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 ε, but lies outside the routine range of UV observation

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







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UV Spectroscopy

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	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
	279	
	235	
	214	It is important to note this is different from the auxochromic effect on π → π* which extends conjugation and causes a bathochromic shift
	204	
	204	In most cases, this bathochromic shift is not enough to bring the π → π* transition into the observed range

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UV Spectroscopy

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:

- the effect is more pronounced for π → π*
- if the conjugated chain is long enough, the much higher intensity π → π* band will overlap and drown out the n → π* band
- 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

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UV Spectroscopy

IV. Structure Determination
B. Enones
1. General Features
These effects are apparent from the MO diagram for a conjugated enone:

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UV Spectroscopy

WOODWARD-FIESER RULE for calculating Absorption Maximum in α,β unsaturated carbonyl compounds

1. The basic value of α,β unsaturated ketone is taken as 215m μ . The α,β unsaturated ketone may be cyclic or six membered.

•For a compound = CH-COX, a basic value is 215 m μ , if X is alkyl group
•If X=H, the basic value becomes 207m μ .
•The basic value becomes 193m μ if X is OH or OR.

2. If the double bond and the carbonyl group are contained in a five membered ring, then for such compounds the basic value becomes 202m μ .

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UV Spectroscopy

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

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UV Spectroscopy

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

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UV Spectroscopy

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

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UV Spectroscopy

IV. Structure Determination
B. Enones
2. Woodward-Fieser Rules - Enones
Some examples - keep in mind these are more complex than dienes

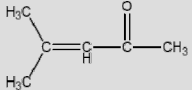
	cyclic enone = 215 nm
	2 x β -alkyl subs. (2 x 12) +24 nm
	239 nm
	Experimental value 238 nm
	cyclic enone = 215 nm
	extended conj. +30 nm
	β -ring residue +12 nm
	δ -ring residue +18 nm
	exocyclic double bond +5 nm
	280 nm
	Experimental 280 nm

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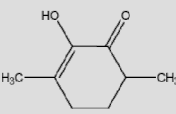
1

Basic Value	215 mμ
2β alkyl substituents (2 x 12)	24 mμ
Calculated value	239 mμ
Observed value	237 mμ



2

Basic Value	215 mμ
OH at α position	35 mμ
2β substituents (one alkyl, one ring residue)	24 mμ
Calculated value	274 mμ
Observed value	275 mμ

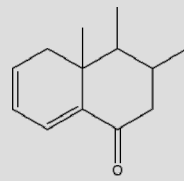


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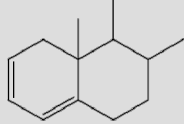
UV Spectroscopy

3

Basic Value	215 mμ
α ring residue	10 mμ
δ ring residue	18 mμ
1 exocyclic double bond	5 mμ
Homoannular conjugated diene	39 mμ
1 double bond extending conjugation	30 mμ
Calculated value	317 mμ
Observed value	319 mμ



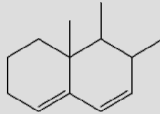
Basic Value	253 mμ
3 ring residues (3 x 5)	15 mμ
1 endo cyclic double bonds (1 x 5)	5 mμ
Calculated value	273 mμ
Observed value	274 mμ



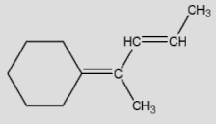
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UV Spectroscopy

Basic Value	215 mμ
3 ring residues (3 x 5)	15 mμ
1 exocyclic double bonds(1 x 5)	5 mμ
Calculated value	235 mμ
Observed value	235 mμ



Basic Value	217 mμ
2 Alkyl substituents	10 mμ
2 ring residues (2 x 5)	10 mμ
1 exocyclic double bonds	5 mμ
Calculated value	242 mμ
Observed value	242 mμ

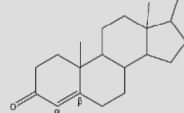


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UV Spectroscopy

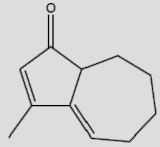
Unsaturated Ketones

Basic Value	215 mμ
2 β ring residues (2 x 12)	24 mμ
1 exocyclic double bond	5 mμ
Calculated value	244 mμ
Observed value	241 mμ



α,β-unsaturated cyclopentanone system

Basic Value	202 mμ
1 β alkyl substitution	12 mμ
1 exocyclic double bond	5 mμ
1 double bond extending conjugation	30 mμ
1 γ ring residue	18 mμ
1 δ ring residue	18 mμ
Calculated value	285 mμ
Observed value	287 mμ



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