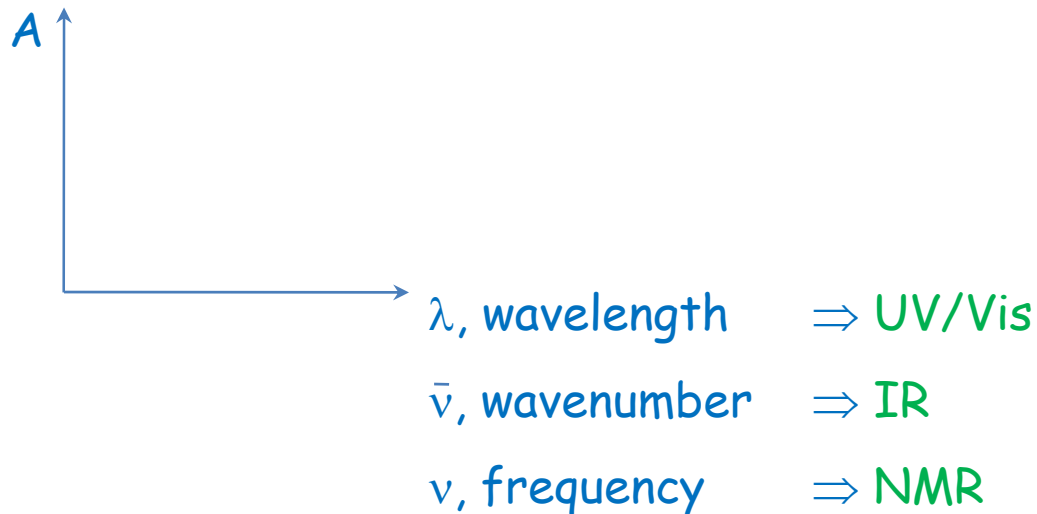


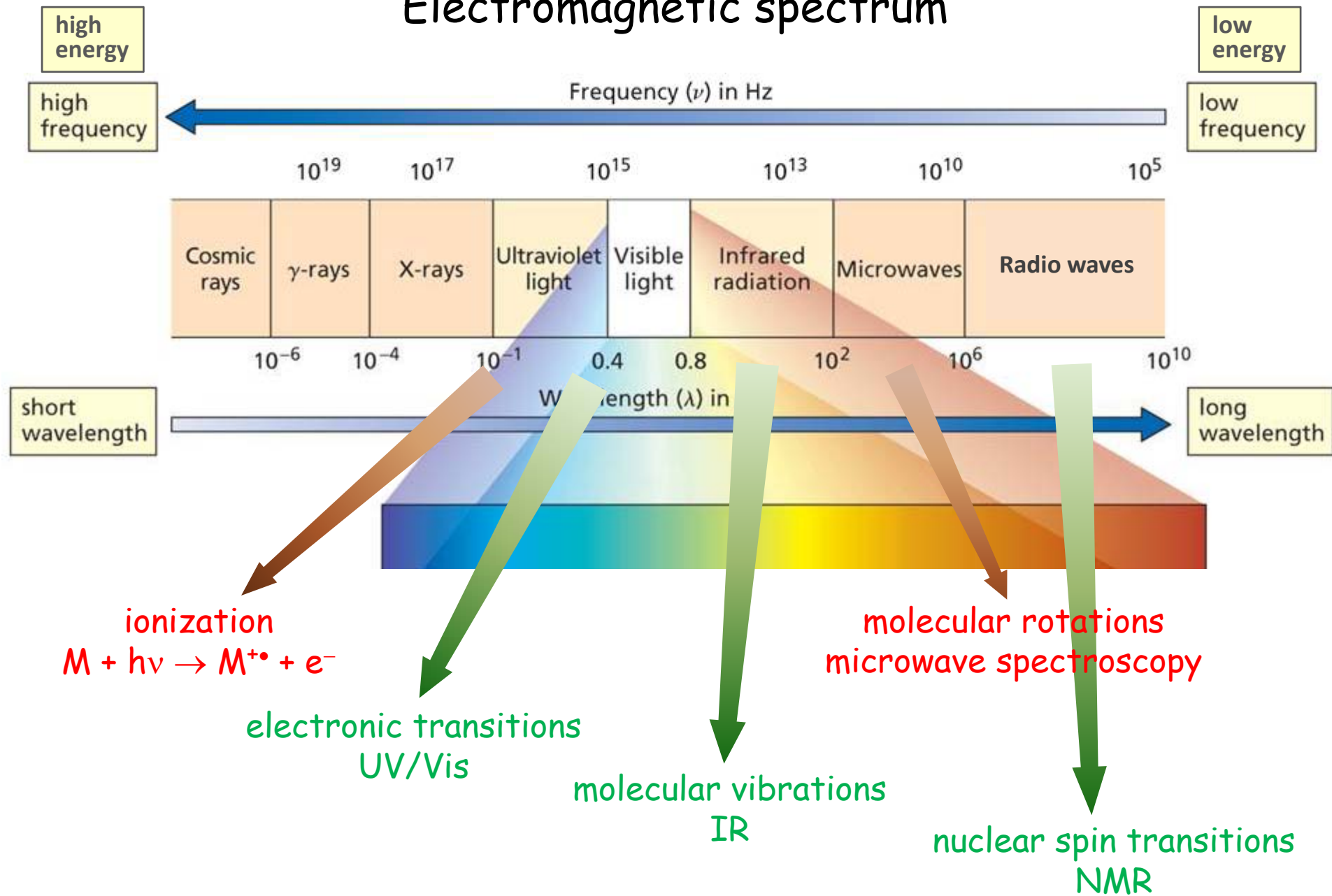
# Interlude on Spectroscopy

“interaction of radiation with matter”

- type of interaction depends on the energy of the radiation
- use of the full electromagnetic spectrum is possible
- interaction happens through absorption
- spectrum is a plot of the absorption as a function of the energy used

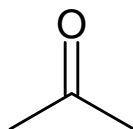


# Electromagnetic spectrum



# Chapter 2. Ultraviolet (and visible) spectroscopy

## electronic transitions



- which transitions?  
wavelength and intensity,  $\lambda_{\max}$  and  $\epsilon$
- what happens if we change the molecule?  
substituent effects on  $\lambda_{\max}$  and  $\epsilon$
- laws for the prediction of  $\lambda_{\max}$  in conjugated alkenes and ketones

Reading:

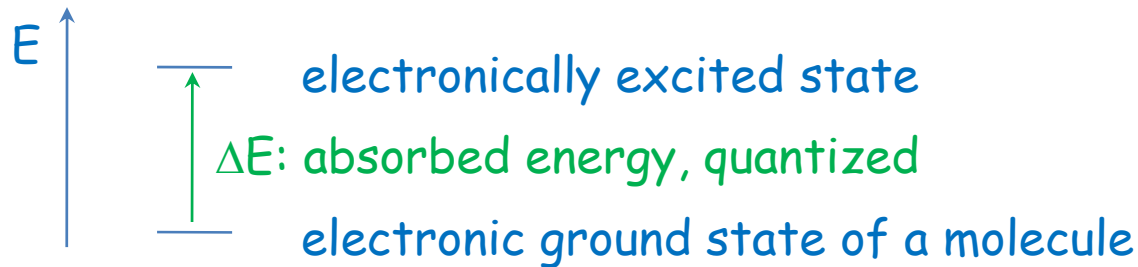
Pavia

Chapter 7

Don't need 7.13, 7.14D and E, 7.15

# 1. General

- range of radiation:  $\approx 200 - 800 \text{ nm}$
- absorption leads to excitation of electrons



**Question:** How large is the energy gap needed (let's say at 200 nm) and what does that imply for the population of the two states?

Planck's law

$$E = h\nu = h \frac{c}{\lambda} = 6.6 \cdot 10^{-34} \text{ Js} \cdot \frac{3 \cdot 10^8 \text{ m/s} \cdot 10^9 \text{ nm/m}}{200 \text{ nm}} = 9.9 \cdot 10^{-19} \text{ J}$$

Boltzmann distribution

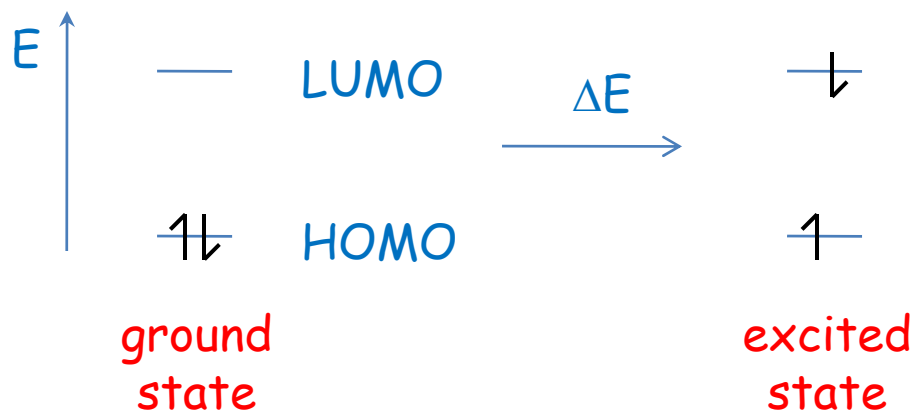
$$\frac{N_u}{N_l} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{9.9 \cdot 10^{-19} \text{ J}}{1.38 \cdot 10^{-23} \text{ J/K} \cdot 298 \text{ K}}} = 0 \Rightarrow \text{read: "1 upper over all lower":}$$

all molecules are in their electronic ground state

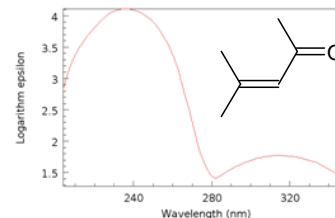
## 2. Nature of electronic excitations

### A. Electronic states

- electronic levels for the lowest-energy transition are HOMO and LUMO



- $E$  is quantized: only a specific  $\Delta E$  leads to this promotion
  - $\Rightarrow$  we should observe a line spectrum
  - $\Rightarrow$  true for an atom, but not for a molecule
  - $\Rightarrow$  a molecule vibrates and rotates



## 2. Nature of electronic excitations continued

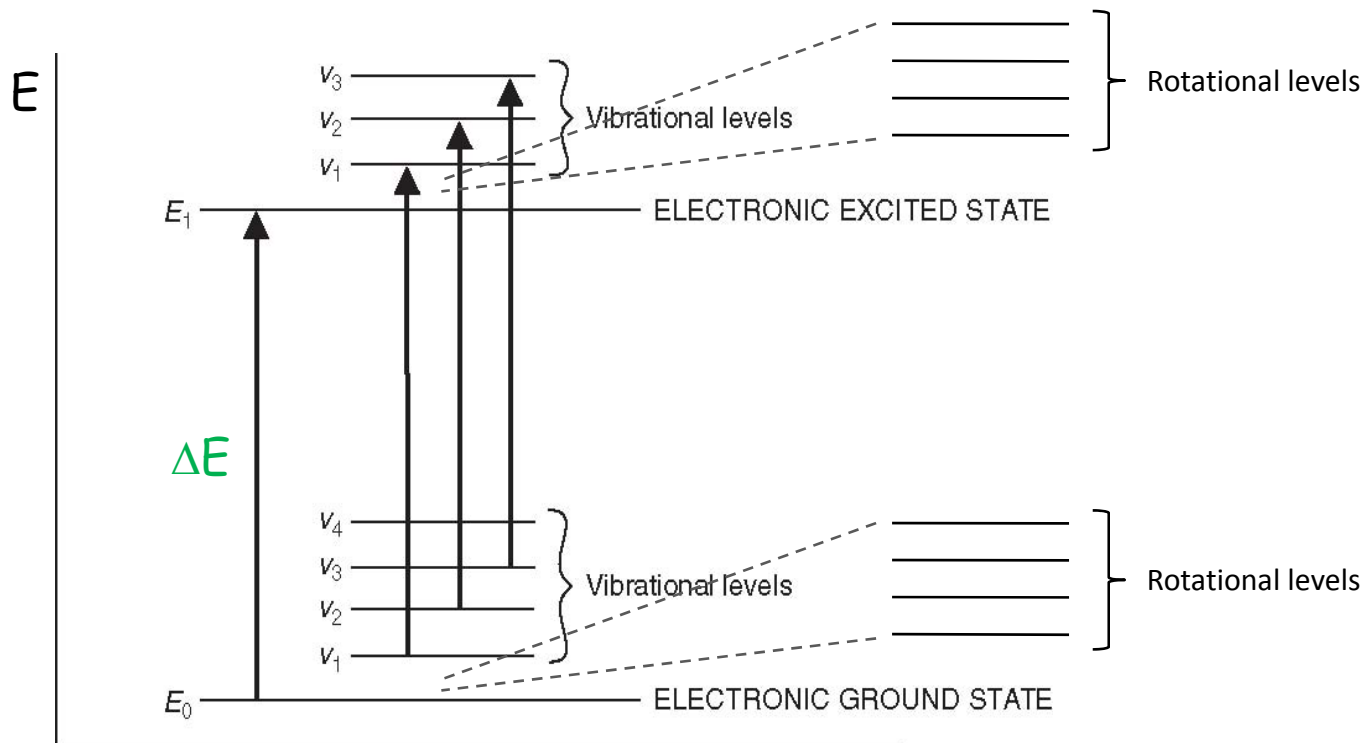
### A. Electronic states

- every electronic state possesses vibrational and rotational states

$\lambda$ : nm

$\mu\text{m}$

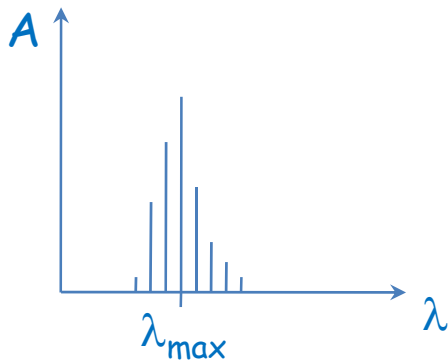
cm



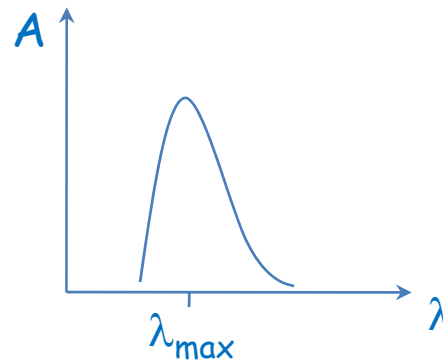
## 2. Nature of electronic excitations continued

### A. Electronic states

⇒ leads to line broadening: all  $\Delta E$  are similar but slightly different



(wavelength for  
maximum  
absorption)

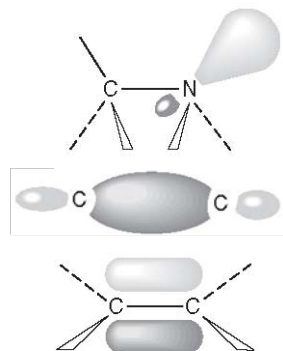


observed band  
due to poor  
resolution

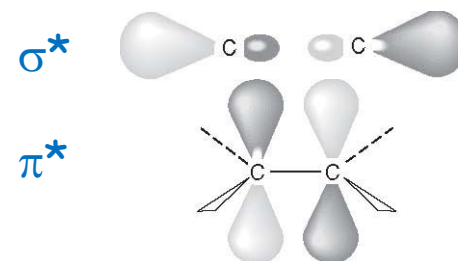
## 2. Nature of electronic excitations continued

### B. Molecular orbitals

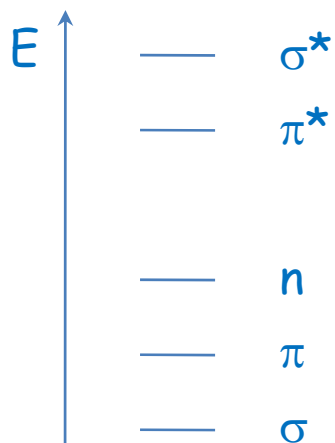
- occupied MOs  $n$



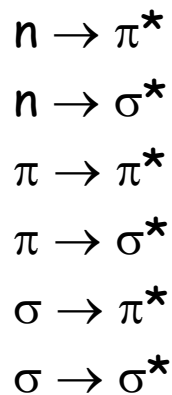
- unoccupied MOs



- general orbital diagram



possible transitions:



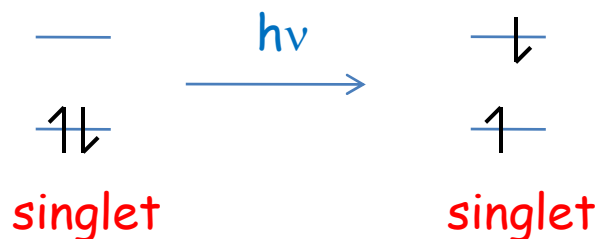
molecules?



### 3. Selection rules

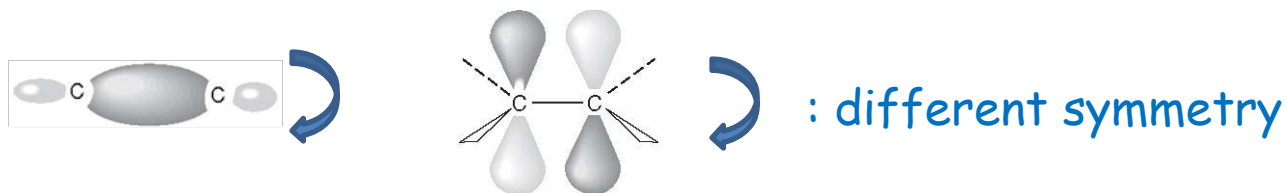
- govern which transitions are allowed, which forbidden
- allowed transition is observed
- forbidden transition is either not observed or very weak

- the promoted electron does not change spin



- only *one* electron is excited

- transitions between orbitals of different symmetry are forbidden



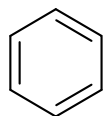
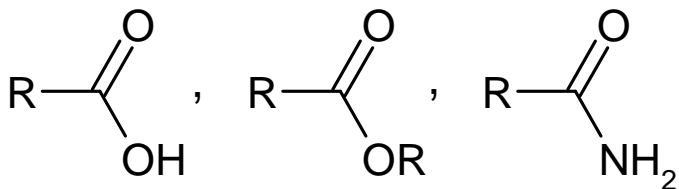
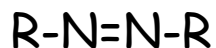
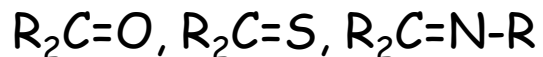
$\Rightarrow \pi \rightarrow \pi^*$  allowed

$\Rightarrow n \rightarrow \pi^*$  forbidden, but observed

## 4. Chromophores

- group of atoms that makes an absorption possible (at least two)

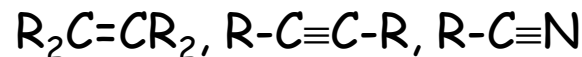
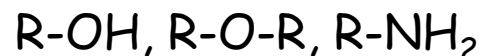
important chromophores



(aromatics in general)

less important chromophores

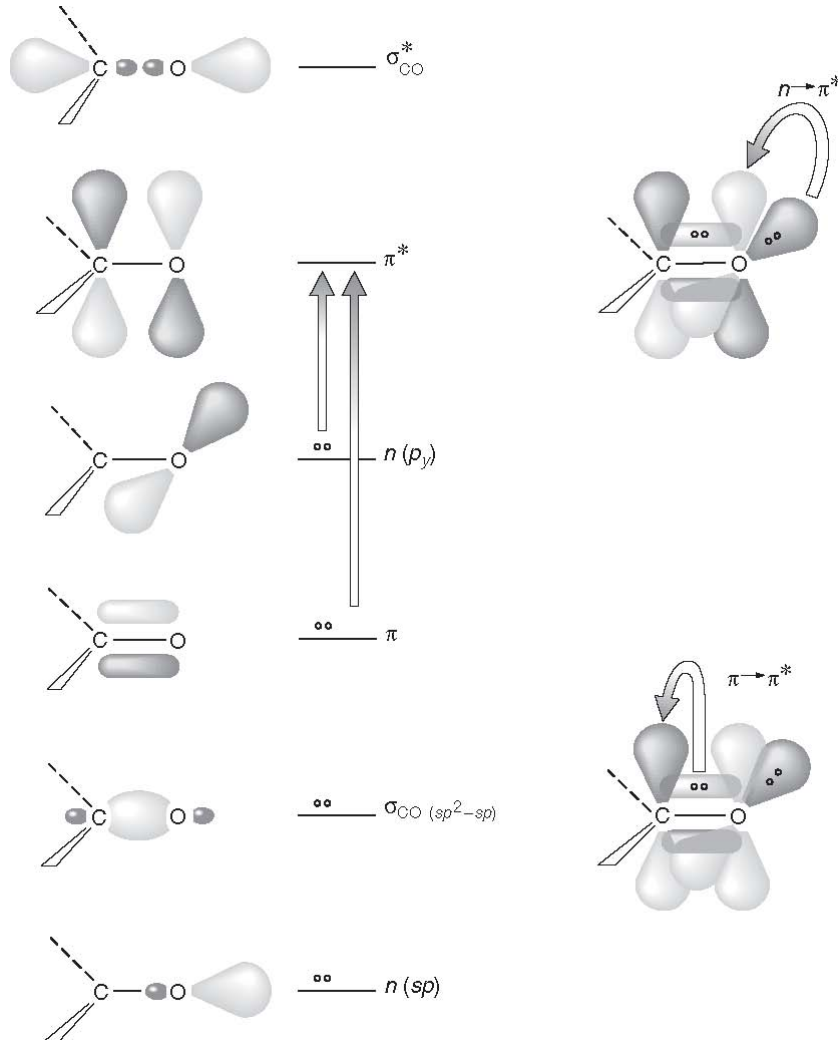
(first  $\lambda_{\max}$  too small/short)



see Table 7.3

# 4. Chromophores continued

- probably the best-studied chromophore is the carbonyl group

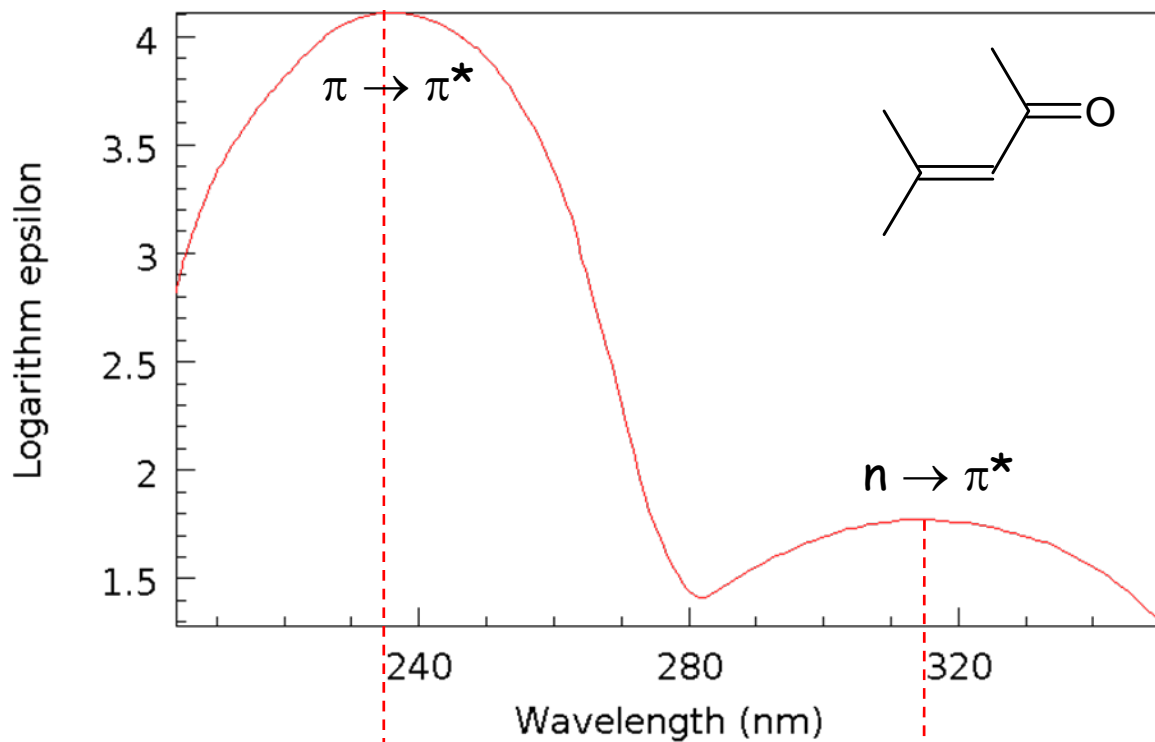


280-290 nm  
but  
forbidden,  
low intensity

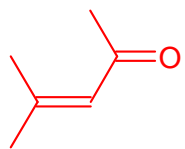
180-190 nm  
allowed,  
high intensity,  
but too short to be observed!

## 4. Chromophores continued

- "typical" UV-Vis spectrum of a carbonyl compound



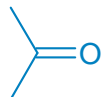
What is this?  
C=O plus C=C?



235 nm

315 nm

$\pi \rightarrow \pi^*$  becomes observable



189 nm

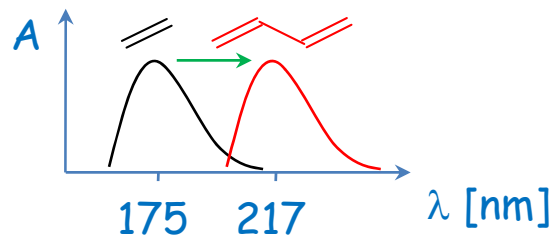
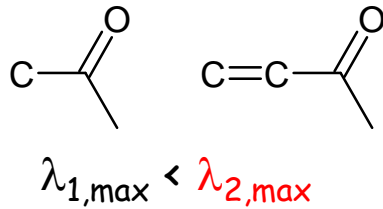
280 nm

# 4. Chromophores continued

- the combination of chromophores leads to shifts in band intensity:
  - increased: hyperchromic effect
  - decreased: hypochromic effect

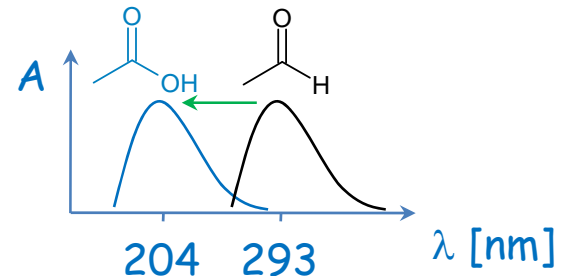
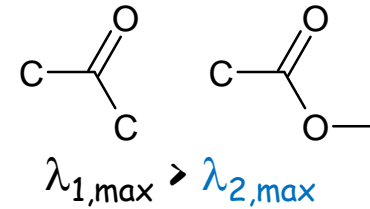
wavelength: increased: longer  $\lambda_{\max}$ :

- bathochromic effect
- **red shifted  $\pi \rightarrow \pi^*$  band**
- less energetic light
- through conjugation



wavelength: decreased: shorter  $\lambda_{\max}$ :

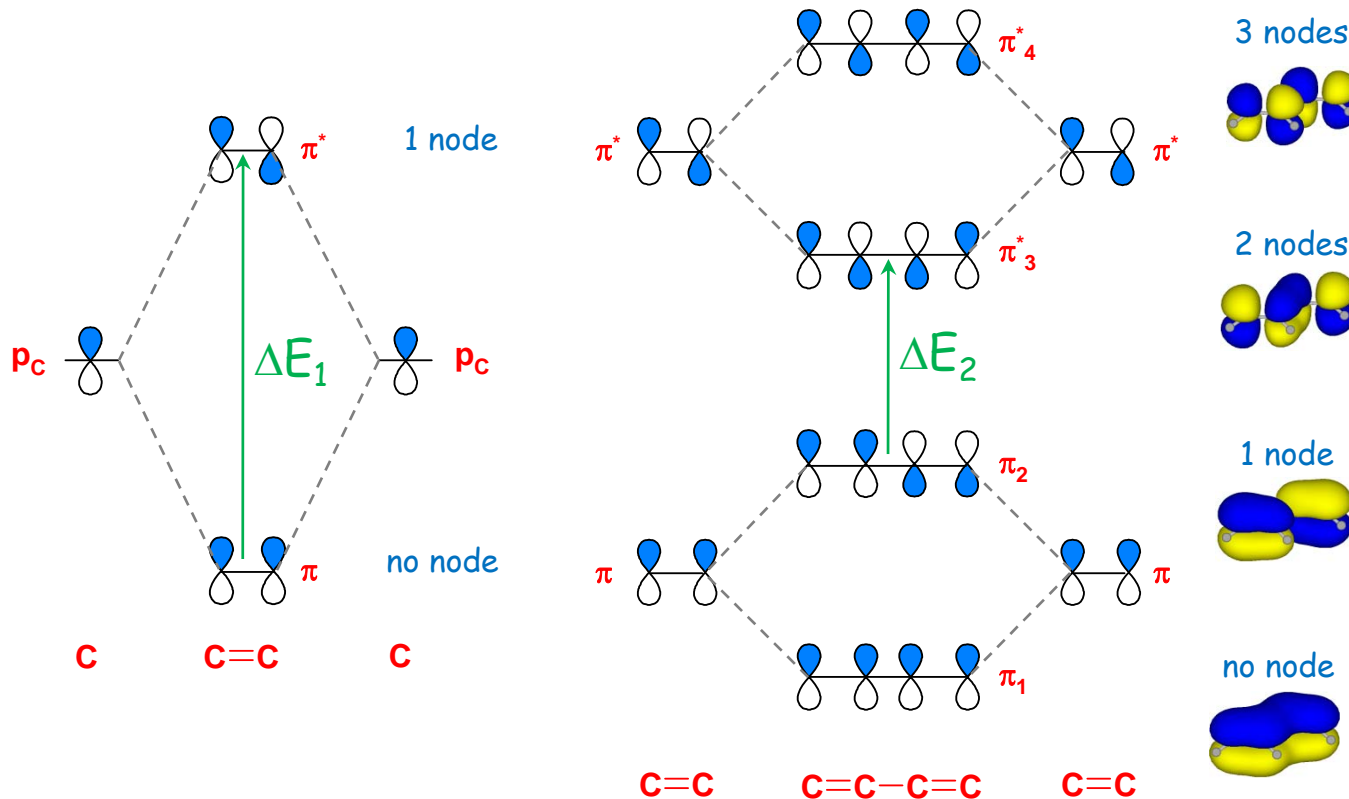
- hypsochromic effect
- **blue shifted  $n \rightarrow \pi^*$  band**
- more energetic light
- through heteroatoms



# 4. Chromophores continued

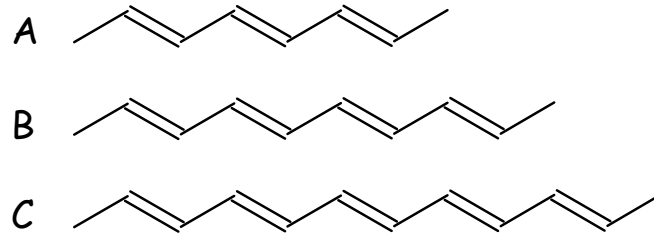
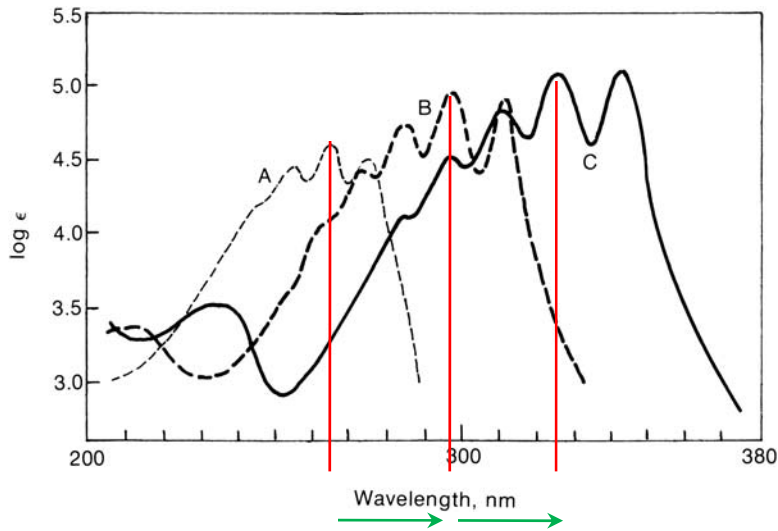
- reason for a **red shifted**  $\pi \rightarrow \pi^*$  band through conjugation:  
HOMO - LUMO gap becomes smaller upon conjugation
- acyclic conjugated:

MO (interaction) diagram for the  $\pi$ -orbitals of ethene and butadiene  
 LCAO principle: linear combinations of atomic orbitals (p only)



# 4. Chromophores continued

- the **red shift** through conjugation can be dramatic:



β-carotene

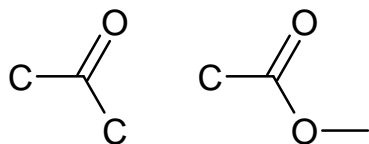


$$C_{40}H_{56}: U = 40 + 1 - \frac{1}{2}(56 - 0) = 41 - 28 = 13, 11 \text{ conjugated } C=C \Rightarrow \lambda_{\max} 465 \text{ nm}$$

orange!

## 4. Chromophores continued

- reason for a red shifted  $\pi \rightarrow \pi^*$  band through conjugation
- reason for a blue shifted  $n \rightarrow \pi^*$  band through heteroatoms:  
inductive effect: energy of  $n_O$  is lowered
- $\pi \rightarrow \pi^*$  still shows a bathochromic shift:  
 $\pi$ -system is still extended through the heteroatom



$$n \rightarrow \pi^* \quad \lambda_{1,\max} > \lambda_{2,\max}$$

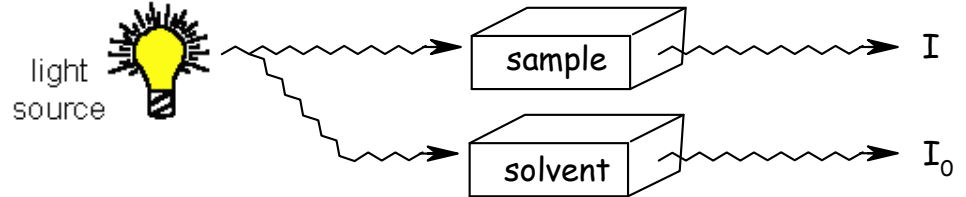
$$\pi \rightarrow \pi^* \quad \lambda_{1,\max} < \lambda_{2,\max}$$



# 5. Absorption

- follows the Lambert-Beer law

$$A = \log\left(\frac{I_0}{I}\right) = \epsilon cl$$

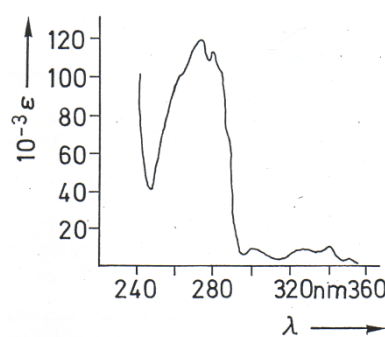
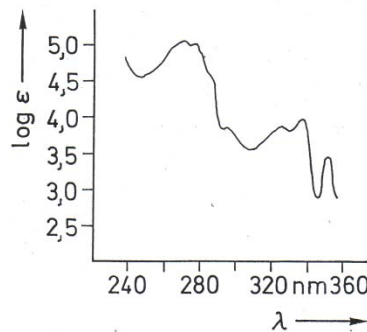
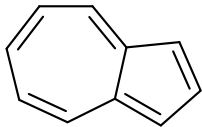


- $\epsilon$  is determined by the size of the absorbing system  
probability of the transition

$\epsilon < 1000 \Rightarrow \log \epsilon \approx 2-3$ : low intensity absorption

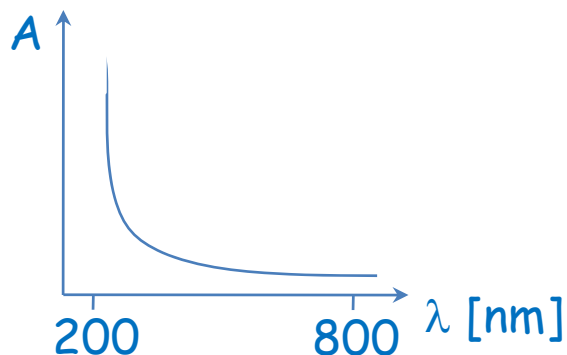
$\epsilon \gg 1000 \Rightarrow \log \epsilon \approx 4-5$ : high intensity absorption

- plotted is  $A$  or  $\epsilon$  or  $\log \epsilon$



## 6. Materials

- **Central question:** Where does the material absorb?
- **solvent:** - should be transparent in the region of interest  
- "ideal" UV-Vis spectrum:



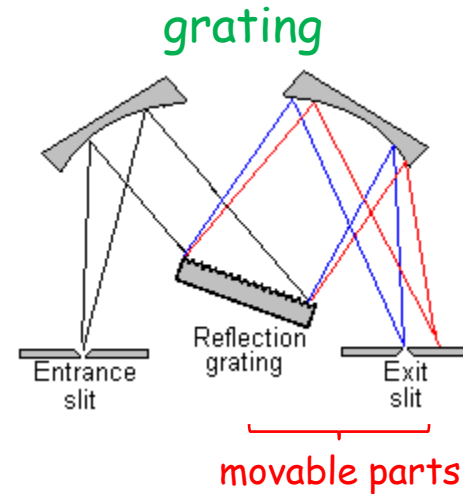
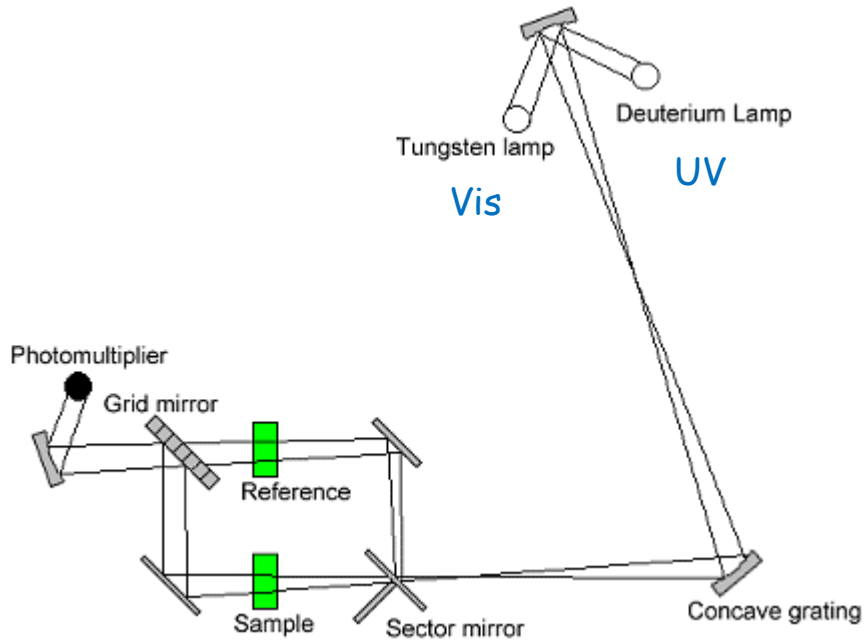
short-wavelength cutoff:  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{CN}$  190 nm  
 $\text{CHCl}_3$  240 nm

see Table 7.1

- **cuvette:** **quartz**, transparent to  $\approx 200$  nm  
**polymer**, transparent to  $\approx 220$  nm (PMMA)  
**optical glass**, transparent to only  $\approx 350$  nm

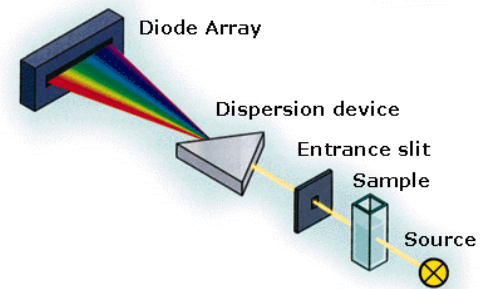
# 7. Spectrometer

- Beam in a UV-Vis spectrometer



<http://teaching.shu.ac.uk/hwb/chemistry/tutorials/molspec/uvvisab3.htm>

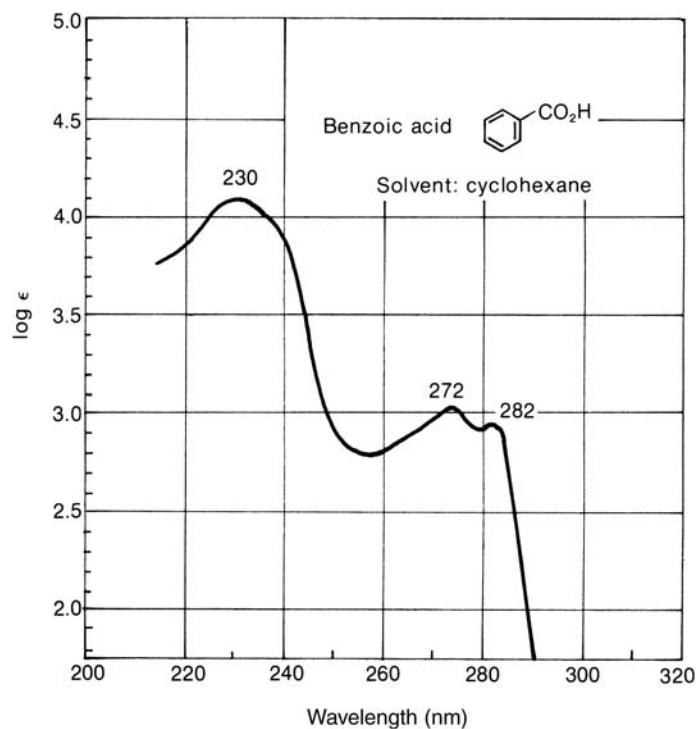
Diode-array spectrophotometer  
no movable parts:  
faster



<http://www.gmi-inc.com/Categories/spectrophotometers.htm>

## 8. Spectrum

- UV-Vis spectra are often not published
- x-y data of the extrema are reported instead



Info from this spectrum **reported**:

$\lambda_{\max}$	230 nm	log $\epsilon$	4.2
	272		3.1
	282		2.9

Info from this spectrum **gained**:

- no long-wavelength absorption:  
not highly conjugated
- longer-wavelength low intensity:  
probably forbidden, possibly  $n \rightarrow \pi^*$
- shorter-wavelength high intensity:  
probably allowed, possibly  $\pi \rightarrow \pi^*$

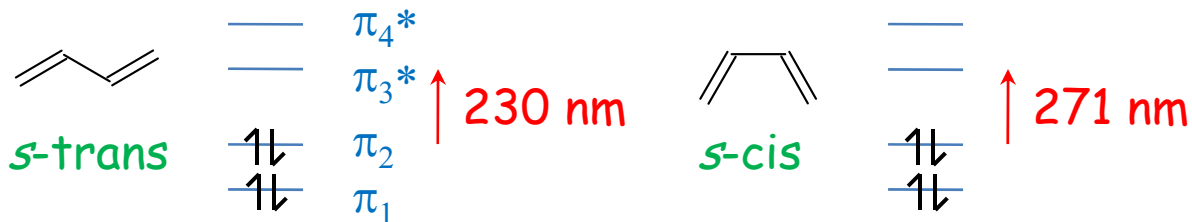
## 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions

### I. Dienes and higher conjugated C=C

Why do we write  and not  ? Conformation matters!

- acyclic dienes

butadiene



Interesting, but *s-cis* is not usually important in acyclic systems!

- cyclic dienes



- use Woodward-Fieser rules to predict  $\lambda_{\max}$

# 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

## I. Dienes and higher conjugated C=C

R.B. Woodward  
Nobel Prize 1965



Woodward-Fieser rules

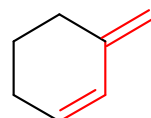
- calculate  $\lambda_{\max}$  from a base value...



acyclic (*s*-trans)

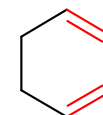
base value [nm]

214



transoid

214



cisoid

253

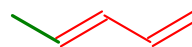
- ...plus increments for structural features...



another  
conjugated C=C

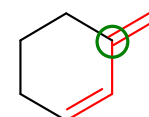
increment [nm]

30



alkyl group or  
ring residue

5



exocyclic C=C

5

- ...plus increments for other substituents

see Table 7.5

# 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

## I. Dienes and higher conjugated C=C

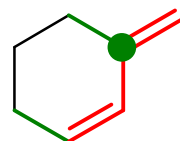
### Examples



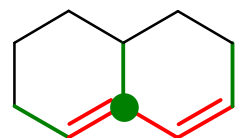
$$214 + 5 = 219 \text{ nm}$$



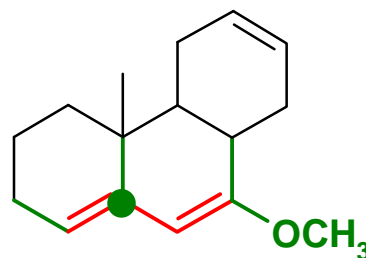
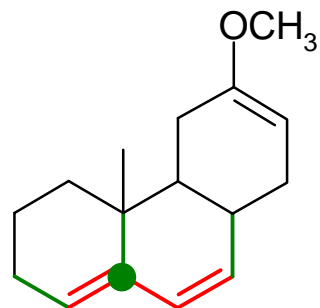
$$214 + 30 = 244 \text{ nm}$$



$$214 + 2 \times 5 + 5 = 229 \text{ nm}$$



$$214 + 3 \times 5 + 5 = 234 \text{ nm}$$



$$234 + 6 = 240 \text{ nm}$$

Colour code:

base system

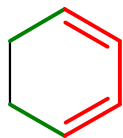
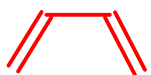
increments

not important  
for absorption

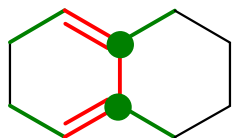
# 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

## I. Dienes and higher conjugated C=C

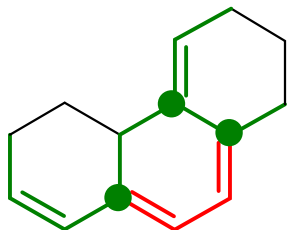
### Examples



$$253 + 2 \times 5 = 263 \text{ nm}$$



$$253 + 4 \times 5 + 2 \times 5 = 283 \text{ nm}$$



$$253 + 2 \times 30 + 5 \times 5 + 3 \times 5 = 353 \text{ nm}$$

Colour code:

base system

increments

not important  
for absorption

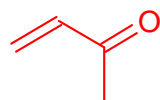


# 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

## II. Enones and higher conjugated C=O (ketones only)

### Woodward rules

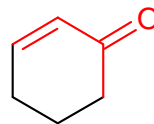
- calculate  $\lambda_{\max}$  from a base value...



acyclic (*s*-trans)

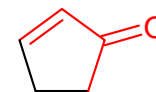
215

base value [nm]



6-membered ring

215



5-membered ring

202

- ...plus increments for structural features...

another  
conjugated C=C

30

increment [nm]

alkyl group or  
ring residue

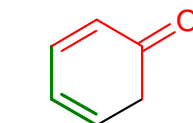
in  $\alpha$  10

in  $\beta$  12

in  $\gamma$ ... 18

exocyclic  
C=C

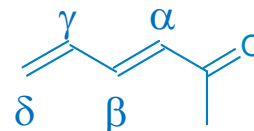
5



homocyclic  
(cisoid) diene

39

- ...plus increments for other substituents

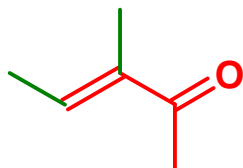
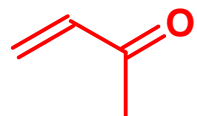


see Table 7.7

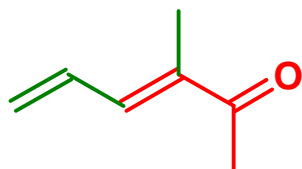
# 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

## II. Enones and higher conjugated C=O

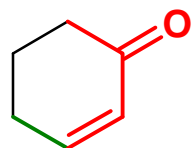
### Examples



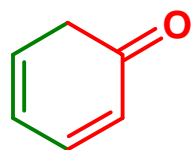
$$215 + 10 + 12 = 237 \text{ nm}$$



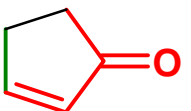
$$215 + 30 + 10 = 255 \text{ nm}$$



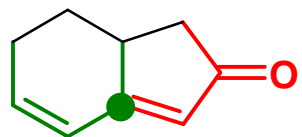
$$215 + 12 = 227 \text{ nm}$$



$$215 + 30 + 39 + 18 = 302 \text{ nm}$$



$$202 + 12 = 214 \text{ nm}$$



$$202 + 30 + 12 + 18 + 5 = 267 \text{ nm}$$

Colour code:

base system

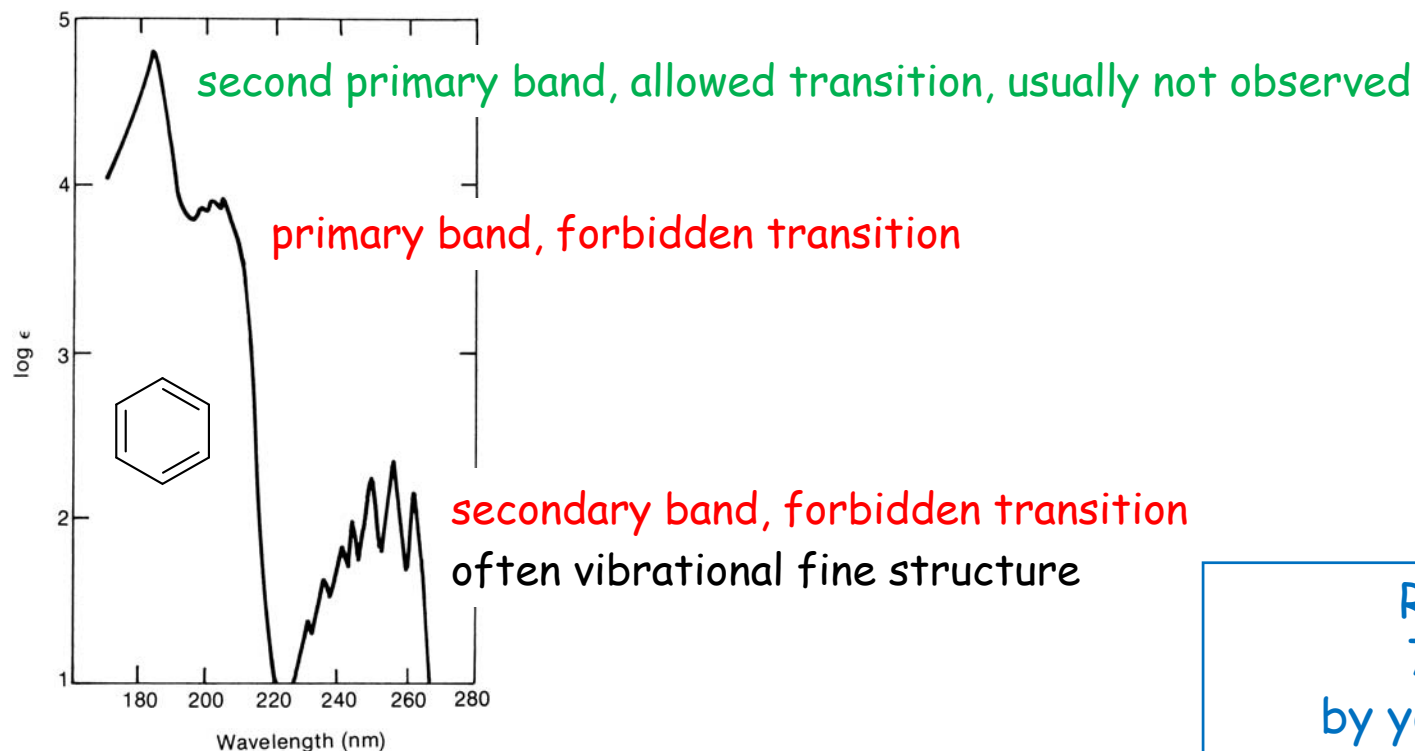
increments

not important  
for absorption

## 9. Prediction of $\lambda_{\max}$ of $\pi \rightarrow \pi^*$ transitions continued

### III. Aromatic compounds

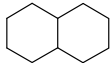
- good chromophore: 3 conjugated C=C, cis, in one ring



Read  
7.14  
by yourself,  
focus on conjugation  
issues

- conjugation effects as discussed earlier
- no quantitative treatment:  $\lambda_{\max}$  not easy to predict for substitution

## Example

An alkene  $C_{12}H_{16}$  and an unsaturated ketone  $C_{11}H_{14}O$ , both almost identical in structure (  ), show UV absorptions at 269 and 286 nm, respectively.

Give their structures.