Topics 19-20

Spectroscopy

Fall 2016

1

SPECTROSCOPY:

short wavelength regions

ESCA (photoelectron) and UV

handout

2

Chemistry 1B-AL, Fall 2016
Topics 19-20- Spectroscopy

alert

approach for spectroscopy

- material not straight from text chapter
- must FOLLOW videos, “lectures”, handout and worksheet
- (WA) HW is from SAMPLE FINAL QUESTIONS on spectroscopy
- for discussion group (M-Tu 28-29 November): **inquiry exercise Galen Gorski (UCSC graduate student EarthSci, ISEE)**

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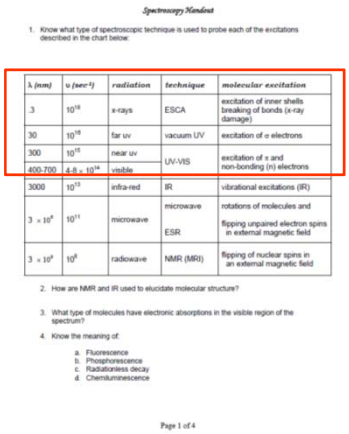
spectroscopy handout



Spectroscopy Handout

1. Know what type of spectroscopic technique is used to probe each of the excitations described in the chart below:

λ (nm)	υ (sec⁻¹)	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons
300	10^{15}	near uv	UV-VIS	excitation of π and non-bonding (n) electrons
400-700	$4\text{-}8 \times 10^{14}$	visible		
3000	10^{13}	infra-red	IR	vibrational excitations (IR)
3×10^{8}	10^{11}	microwave	microwave	rotations of molecules and
			ESR	flipping unpaired electron spins in external magnetic field
3×10^{6}	10^{8}	radiowave	NMR (MRI)	flipping of nuclear spins in an external magnetic field

2. How are NMR and IR used to elucidate molecular structure?

3. What type of molecules have electronic absorptions in the visible region of the spectrum?

4. Know the meaning of:
   a. Fluorescence
   b. Phosphorescence
   c. Radiationless decay
   d. Chemiluminescence

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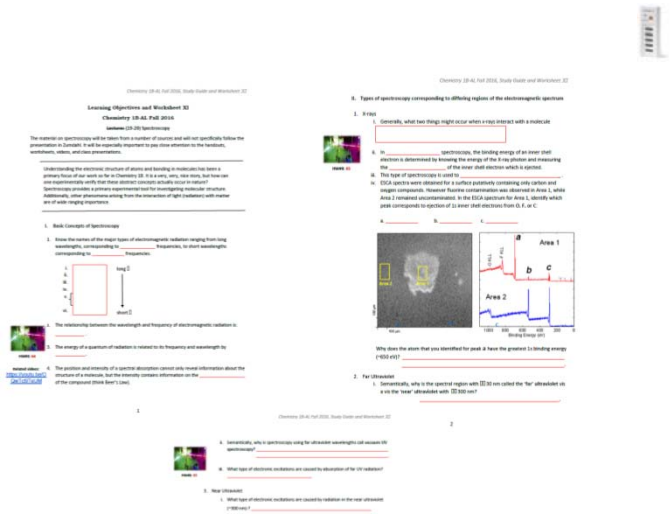
Chemistry 1B-AL, Fall 2016
Topics 19-20- Spectroscopy

clicker questions worksheet 11, sections I-II.3



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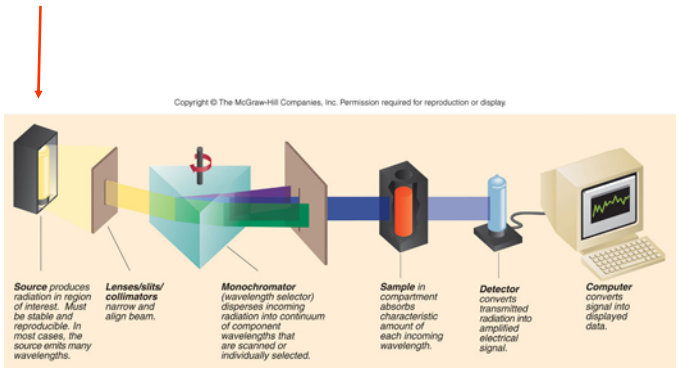
spectroscopic principles (Chem 1M/1N exps. #6, #9 and #11)



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spectroscopic excitations ***(E = hυ = hc/λ ; λυ = c)***

λ *(nm)*	υ *(sec^{-1})*	*radiation*	*technique*	*molecular excitation*

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spectroscopic excitations ***(E = hυ = hc/λ ; λυ = c)***

λ increases ↓

λ *(nm)*	υ *(sec^{-1})*	*radiation*	*technique*	*molecular excitation*
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
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3 × 10^{6}	10^{11}	microwave	microwave ESR	rotations of molecules and flipping unpaired electron spins in external magnetic field
3 × 10^{9}	10^{8}	radiowave	NMR (MRI)	flipping of nuclear spins in an external magnetic field

↓ energy decreases

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spectroscopic excitations: ESCA

λ increases ↓

λ (nm)	υ (sec^{-1})	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)

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ESCA

Electron Spectroscopy for Chemical Analysis

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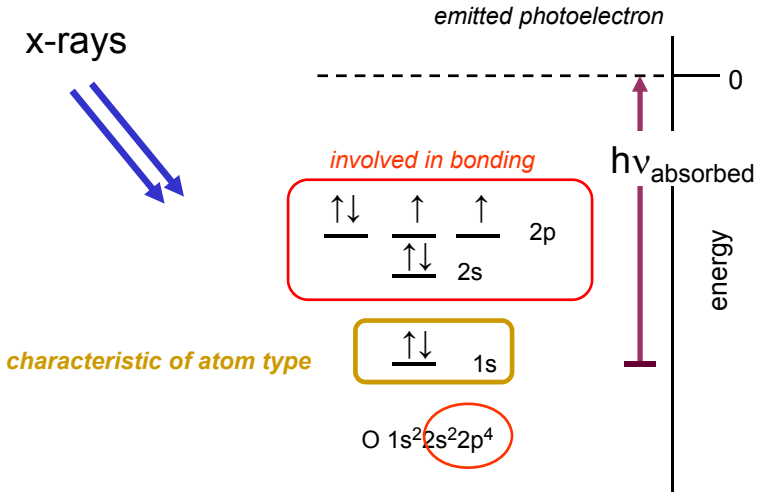
ESCA– photoelectric effect for inner shells



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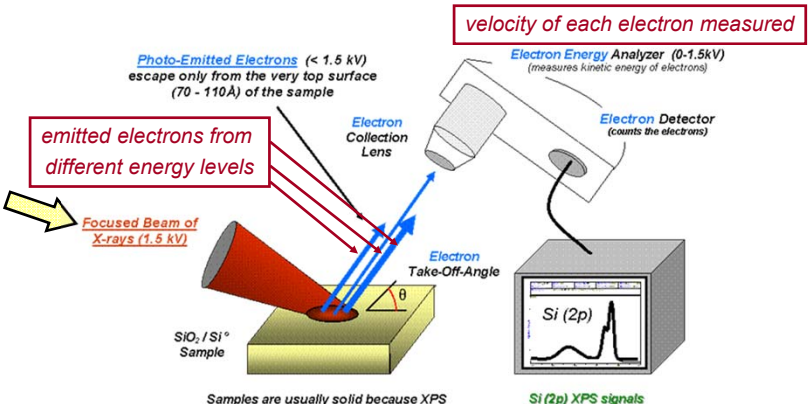
ESCA (and photoelectron effect)



$$\text{binding energy } (\Phi) = h\nu_{x-ray} - \frac{1}{2} m v^2_{electron}$$

http://upload.wikimedia.org/wikipedia/commons/thumb/f/f2/System2.gif/800px-System2.gif

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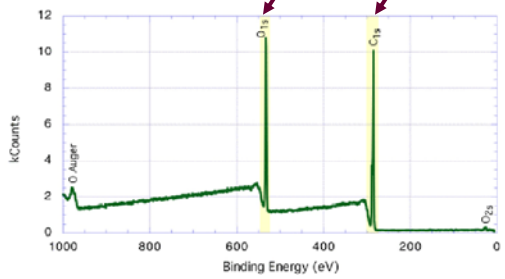
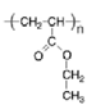
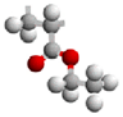
ESCA (binding energy is like work function for inner electrons)

- Polyéthyl acrylate (PEA) :

Why O1s higher binding energy than C1s ?







$$\textit{binding energy}\ (\Phi) = h\nu_{X-ray} - \frac{1}{2}mv^2_{electron}$$

Atome	Composition (%)
Carbone	72,7
Oxygène	27,3

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spectroscopic excitations: ESCA

λ (nm)	*υ (sec⁻¹)*	*radiation*	*technique*	*molecular excitation*
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)

λ increases ↓

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vacuum UV

λ increases

λ (nm)	υ (sec^{-1})	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons

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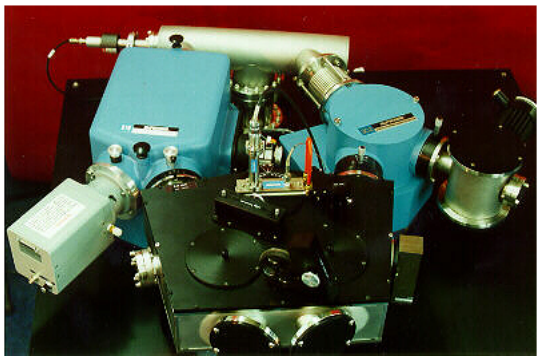
vacuum UV

Mc Pherson Vacuum UV Spectrophotometer System



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excited-state orbitals in polyatomic molecules

- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light
- types of antibonding orbitals:

CH_4 : $\sigma^* = sp^3$ on C – 1s on H
C_2H_4: $\sigma^* = sp^2$ on C_A – sp^2 on C_B
$\pi^* = p_\pi$ on C_A – p_π on C_B

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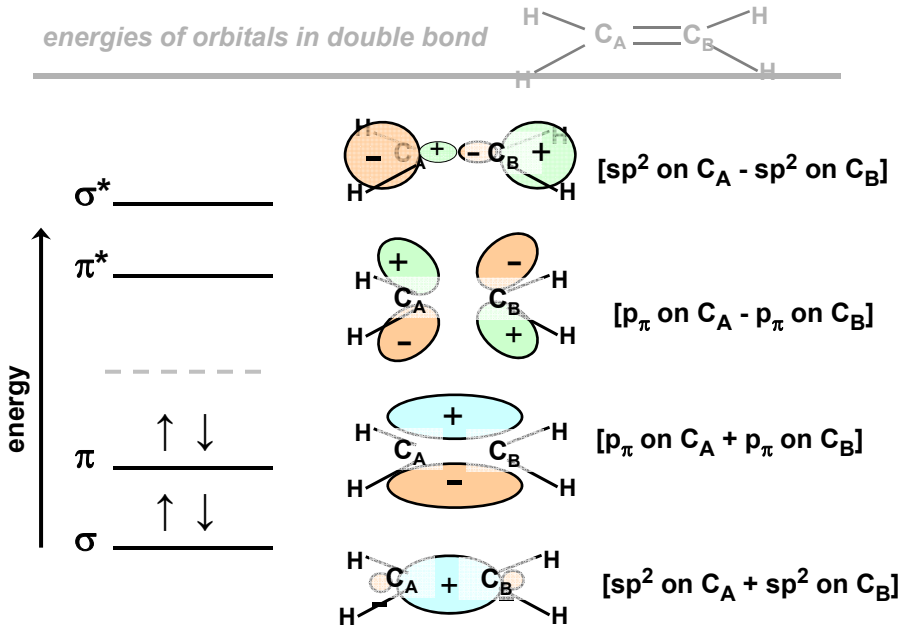
energies of orbitals in double bond



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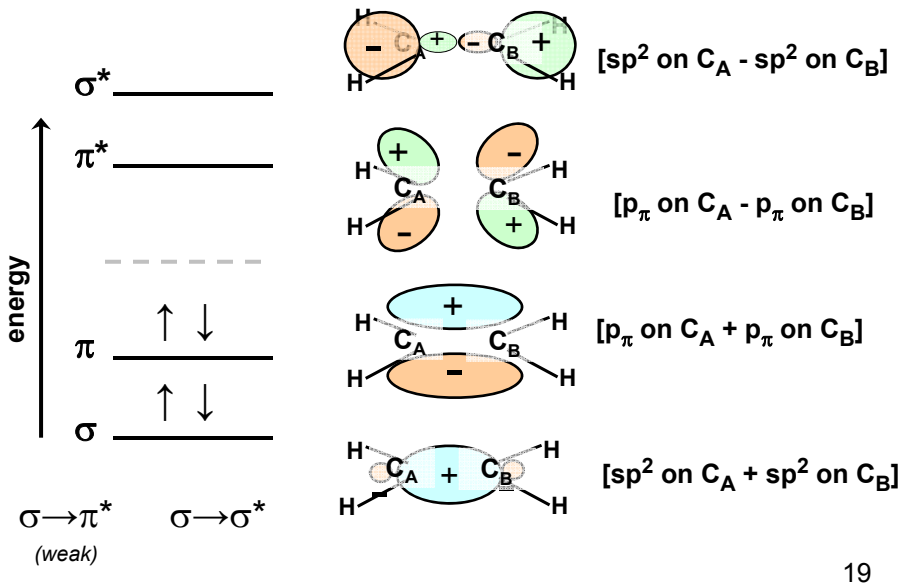
$\sigma\rightarrow\sigma^*$ and $\sigma\rightarrow\pi^*$ excitations are in the far UV regrion



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vacuum UV

λ increases

λ (nm)	*υ (sec⁻¹)*	*radiation*	*technique*	*molecular excitation*
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons

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spectroscopic excitations (UV-VIS)

λ increases

λ (nm)	υ (sec^{-1})	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons
300	10^{15}	near uv	UV-VIS	excitation of π and non-bonding (n) electrons
400-700	$4\text{-}8 \times 10^{14}$	visible		

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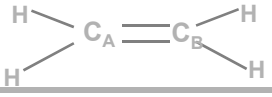
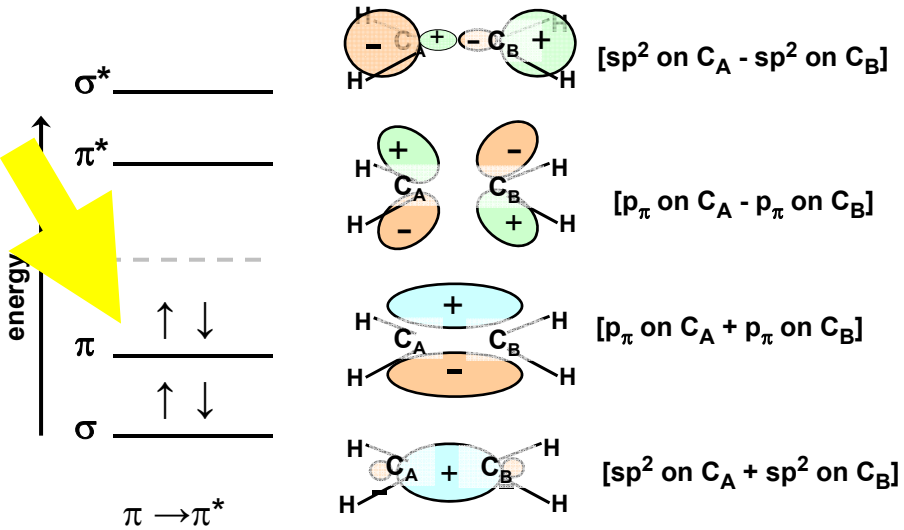
near UV transitions





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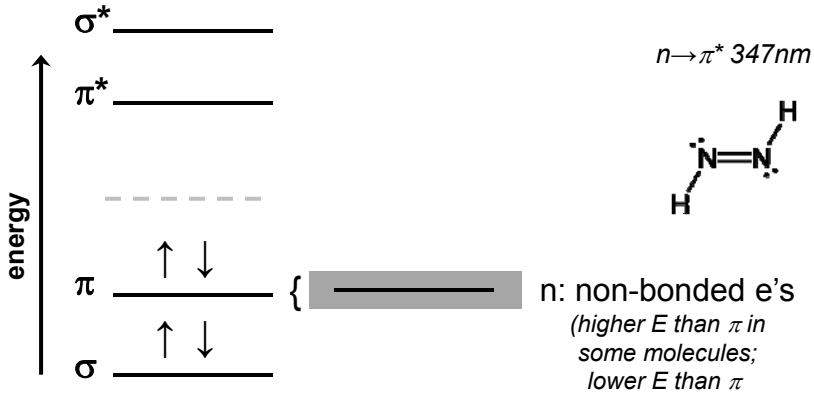
relative energy on "lone pair" non-bonding electrons



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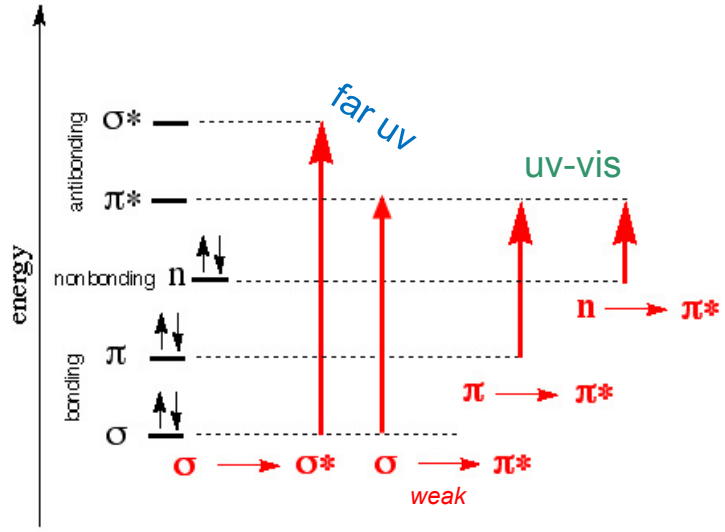
summary



adapted from: http://www.chem.ucla.edu/~bacher/UV-vis/uv_vis_tetracyclone.html.html

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spectroscopic excitations (UV-VIS)

λ (nm)	*υ (sec^{-1})*	*radiation*	*technique*	*molecular excitation*
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons
300	**10^{15}**	**near uv**	**UV-VIS**	**excitation of π and non-bonding (n) electrons**
400-700	**4-8 × 10^{14}**	**visible**		

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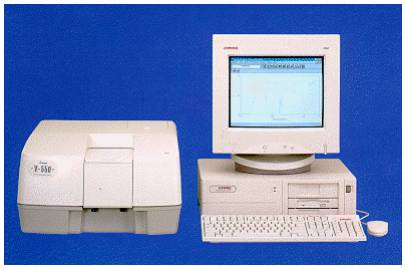
UV-VIS spectrometers (Chem 1M/1N exps. #9 and #11)



sample container

cuvets

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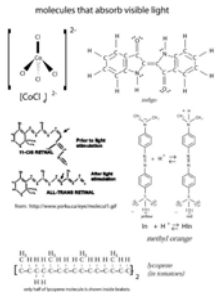
continue in next class: absorptions in the visible region

why do objects appear colored ?? (previously)
what molecules absorb visible light ??



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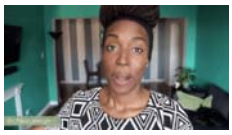
DONE FOR NOW !!



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this video on short wavelength spectroscopic techniques was extracted from a full lecture length movie produced for a previous UCSC CHEM1B

flip class

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HW 9-10

this week
WebAssign HW9
spectroscopy problems from sample final *(conceptual)*
due Tuesday November 29

next week
WebAssign HW10
kinetics calculations
(last WebAssign)
due Sunday December 4

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why do objects appear colored?

why do objects appear colored ??

low energy electronic absorptions in the 'visible' region of electromagnetic spectrum result in the reflection (transmission) of wavelengths of the **complementary** color.

Highest **O**ccupied **M**olecular **O**rbital → **L**owest **U**noccupied **M**olecular **O**rbital

absorbs photon of energy $h\nu = E_{LUMO} - E_{HOMO}$

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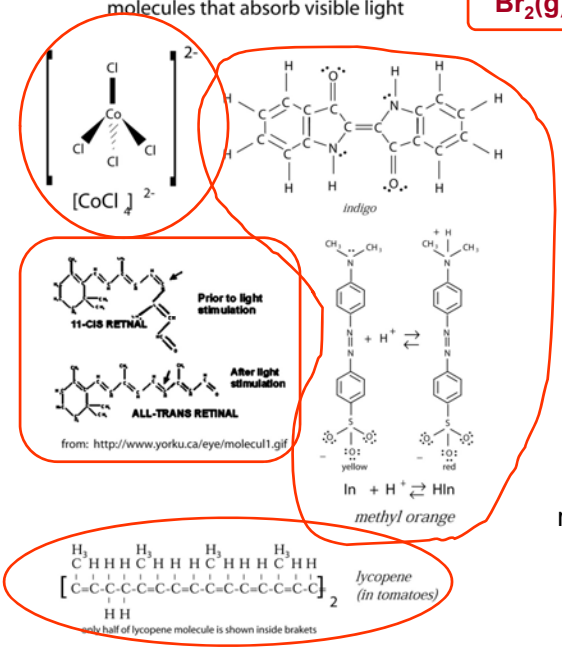
molecules that absorb visible light



$Br_2(g)$, $I_2(g)$, NO_2

closely spaced HOMO and LUMO due to d-orbital m.o.s or open shells (unpaired e's)

transition metal complex ions

octahedral complex $t_{2g} \rightarrow e_g$

(lone-pair) n → π*

π → π* in molecules with conjugated pi-systems

rhodopsin, the molecule most important to seeing color

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spectroscopic excitations

λ *(nm)*	υ *(sec^{-1})*	*radiation*	*technique*	*molecular excitation*
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons
300	10^{15}	near uv	UV-VIS	excitation of π and non-bonding (n) electrons
400-700	4-8 × 10^{14}	visible		
3000	**10^{13}**	**infra-red**	**IR**	**vibrational excitations (IR)**

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diatomic molecules (vibrating and rotating)

http://www.tau.ac.il/~phchlab/experiments_new/LIF/theory.html

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vibrations

new 'unit'

wave number

$$\tilde{\nu} = \frac{1}{\lambda_{cm}} = \frac{\nu}{c} \quad [\tilde{\nu}] = cm^{-1}$$

$E = hc\tilde{\nu}$ $c = 2.99792 \times 10^{10}\ cm\ sec^{-1}$

larger $\tilde{\nu}$ ⇒ higher energy photon

larger $\tilde{\nu}$ ⇒ higher energy vibration

vibrational frequency ($\tilde{\nu}$) depends on

- mass of atoms (lighter ⟹ higher $\tilde{\nu}$)
- strength of bond (tighter 'spring' ⟹ higher $\tilde{\nu}$)

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vibrational frequencies of homonuclear diatomic molecules and ions

wave number

larger $\tilde{\nu}$ ⇒ higher energy photon

vibrational frequency ($\tilde{\nu}$) depends on

- mass of atoms (lighter ⟹ higher $\tilde{\nu}$) ☑
- strength of bond (tighter 'spring' ⟹ higher $\tilde{\nu}$) ☑

Molecule	Bond Order	Vibrational frequency (cm^{-1})
H_2	1	4400
Li_2	1	351
C_2	2	1781
N_2	3	2358
N_2+	2.5	2207
O_2	2	1580
O_2+	2.5	1905
F_2	1	917

low mass

vibrational frequency follows bond order

greater b.o. ⟹ greater frequency

b.o. *$\tilde{\nu}$*

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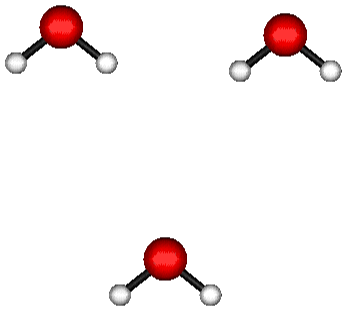
vibrational motion in molecules (H_2O)

wave number

$$\tilde{\nu} = \frac{1}{\lambda_{cm}} \quad [\tilde{\nu}] = cm^{-1}$$

$$E = hc\tilde{\nu} \quad c = 2.99792 \times 10^{10}\ cm\ sec^{-1}$$



Characteristic Vibrations of H_2O

$n_1 = 3835\ cm^{-1}$ $n_2 = 1648\ cm^{-1}$

$n_3 = 3939\ cm^{-1}$

ORIGINALLY FROM: http://www.gps.caltech.edu/~edwin/MoleculeHTML/H2O_html/H2O_page.html

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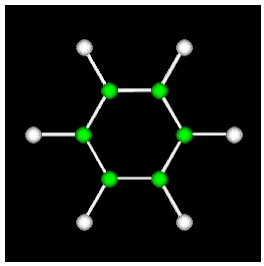
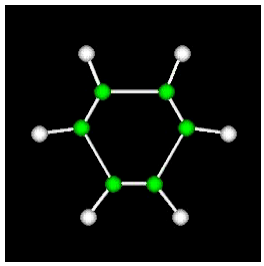
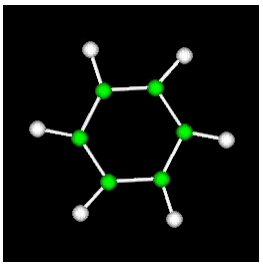
vibrational motions in molecules (benzene)



breathing (stretching) mode

asymmetric stretching mode





Chubby Checkers twisting mode

American Bandstand

http://chemistry.berkeley.edu/links/vibrations.html

Movies provided courtesy: timro@hydrogen.cchem.berkeley.edu

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IR spectrometer

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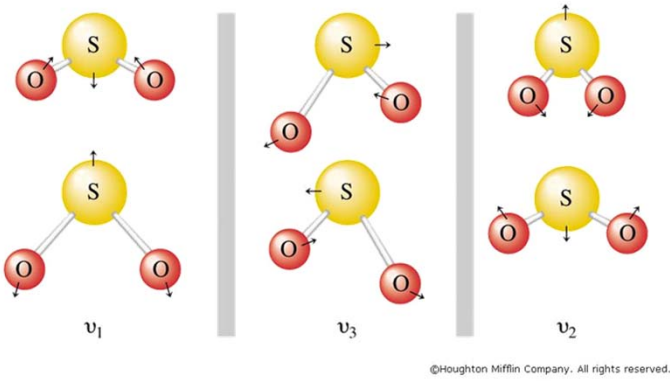
infrared vibrational spectrocopy (fig. 14.60)

photons at infrared wavelengths excite the vibrational motion of atoms in a molecule



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group frequencies

- different types of bonds require different energy photons for vibrational excitation
- a given bond type will have a similar absorption energy in various molecules

Bond	Characteristic Frequency (approximate) $\tilde{\nu}$ (cm^{-1}) [$E = hc\tilde{\nu}$]	λ (nm)
C — C	1000-1400	10000-7140
C = C	1600	6250
C ≡ C	2100	4760
C — O	1100	9090
C = O	1800	5880
C — H	2800-3200	3125
O — H	3600	2770

note energy to excite bond vibration: $E_{C\equiv C} > E_{C=C} > E_{C-C}$

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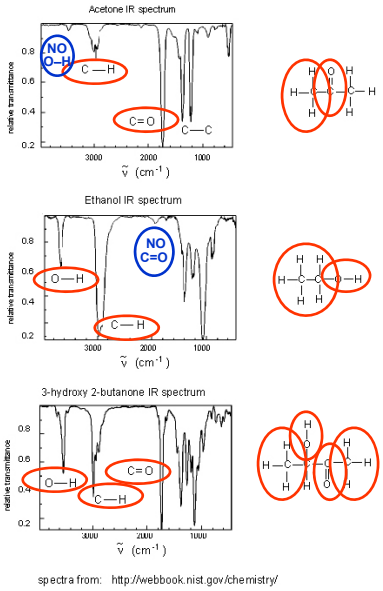
IR spectra



C — H ~3200 cm^{-1}

C=O ~1700 cm^{-1}

O-H ~3600 cm^{-1}

spectra from: http://webbook.nist.gov/chemistry/

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spectroscopic excitations

λ (nm)	υ (sec^{-1})	radiation	technique	molecular excitation
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400-700	4-8 × 10^{14}	visible		
3000	10^{13}	infra-red	IR	vibrational excitations (IR)
3 × 10^{6}	**10^{11}**	**microwave**	**microwave ESR**	**rotations of molecules and flipping unpaired electron spins in external magnetic field**

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radiowave

λ (nm)	υ (sec^{-1})	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)
30	10^{16}	far uv	vacuum UV	excitation of σ electrons
300	10^{15}	near uv	UV-VIS	excitation of π and non-bonding (n) electrons
400-700	4-8 × 10^{14}	visible		
3000	10^{13}	infra-red	IR	vibrational excitations (IR)
3 × 10^{6}	10^{11}	microwave	microwave ESR	rotations of molecules and flipping unpaired electron spins in external magnetic field
3 × 10^{9}	**10^{8}**	**radiowave**	**NMR (MRI)**	**flipping of nuclear spins in an external magnetic field**

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NMR (MRI) spectrometers

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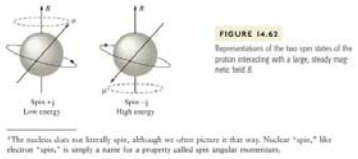
NMR- WHY?

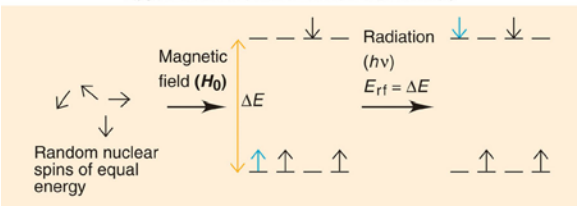
- protons (hydrogen nuclei), like electrons, behave as if they were tiny magnets



electron ~650 x stronger magnet

- in an external magnetic field, spin up ↑ and spin down ↓ will have different energies

- in NMR spectroscopy, photons in the radiowave region have the correct energy to cause a hydrogen nucleus to flip its spin



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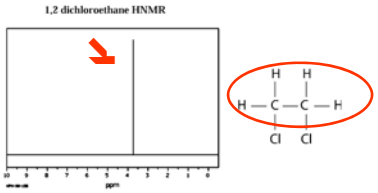
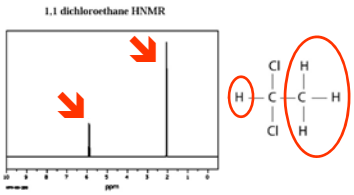
identifying equivalent and non-equivalent protons

to 'flip' hydrogen atoms (nuclei) in different chemical environments requires slightly different energies (chemical shift)



(all H equivalent, H_2ClC– 1 peak one 'chemical shift')



(two H environments, HCl_2C– and $–CH_3$ 2 peaks two 'chemical shifts')

spectra from: http://www.aist.go.jp/RIODB/SDBS/menu-e.html

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not responsible for spin-spin coupling (pp. 703-704)

will get plenty in o-chem

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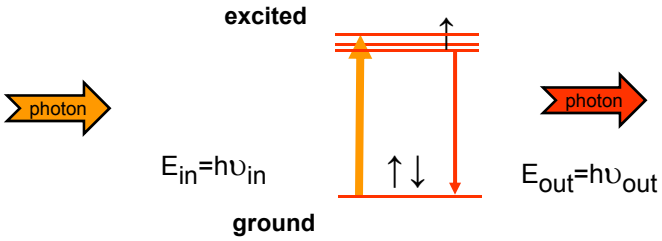
vocabulary: fluorescence

- fluorescence- emission of radiation (almost) directly from the excited state



$(\upsilon_{out} \leq \upsilon_{in})$

$(\lambda_{out} \geq \lambda_{in})$

time ~ 10^{-12} to 10^{-9} sec

(fluorescence stops soon after exciting light is turned off)

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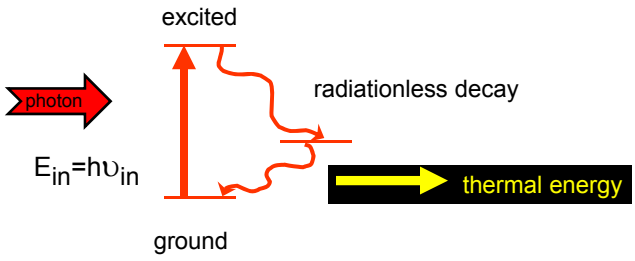
vocabulary: radiationless decay (nonradiative decay)

- radiationless decay- transition from a higher to a lower energy state with a loss of energy in the form of heat rather than emission of a photon



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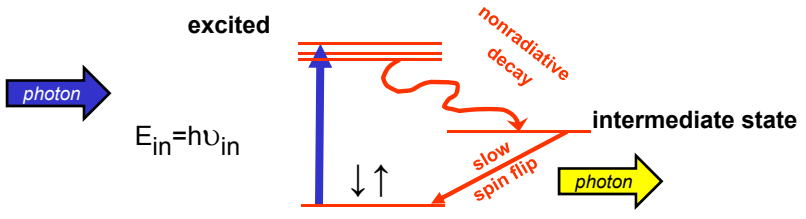
phosphorescence

phosphorescence- 'slow' return to ground state by emission of photon from intermediate state



$E_{in}=h\upsilon_{in}$

$E_{out}=h\upsilon_{out}$

$(\upsilon_{out} < \upsilon_{in})$

$(\lambda_{out} > \lambda_{in})$

time ~ 10^{-3} to 10 sec and longer

(phosphorescence continues after exciting light is turned off)

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chemiluminescence

chemiluminescence- light given off when chemical reaction leaves products in excited states and then the product fluoresces

$$A + B \rightarrow C^* \rightarrow C + \text{light}$$

molecule C in excited state

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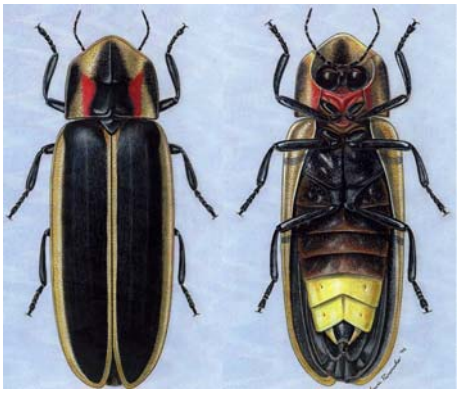
chemiluminescence: fireflies



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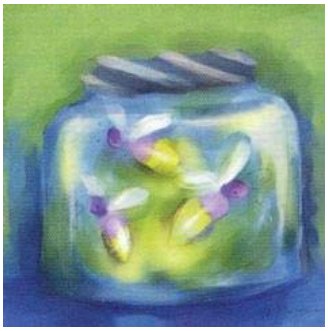
chemiluminescence: fireflies



luciferin + luciferase + ATP ⟶
luciferyl adenylate-luciferase + pyrophosphate

luciferyl adenylate-luciferase + O2 ⟶
oxyluciferin + luciferase + AMP + light

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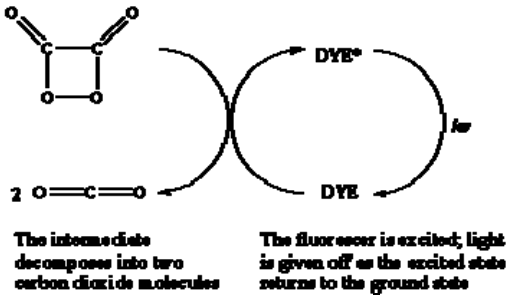
chemiluminescence: light sticks



http://www.sas.upenn.edu/~mtc/Lightstick.html

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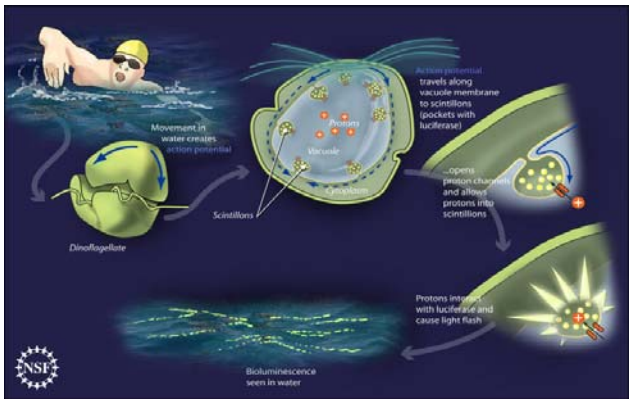
bioluminescence

Bioluminescence: Explanation for Glowing Seas Suggested



According to the study, here is how the light-generating process in dinoflagellates may work: As dinoflagellates float, mechanical stimulation generated by the movement of surrounding water sends electrical impulses around an internal compartment within the organism, called a vacuole--which holds an abundance of protons. These electrical impulses open so-called voltage-sensitive proton channels that connect the vacuole to tiny pockets dotting the vacuole membrane, known as scintillons.

Once opened, the voltage-sensitive proton channels may funnel protons from the vacuole into the scintillons. Protons entering the scintillons then activate luciferase--a protein, which produces flashes of light, that is stored in scintillons. Flashes of light produced by resulting luciferase activation would be most visible during blooms of dinoflagellates.

http://www.sciencedaily.com/releases/2011/10/111019190823.htm

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end of lectures

on

spectroscopy

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colored transition metal complexes- glazes

$Ni(NH_3)_6Br_2$

$CoCl_2 \cdot 6H_2O$

$NiSO_4 \cdot 6H_2O$

http://woelen.scheikunde.net/science/chem/elem/metalsalts.jpg

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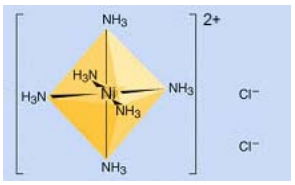
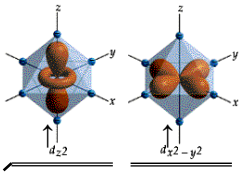
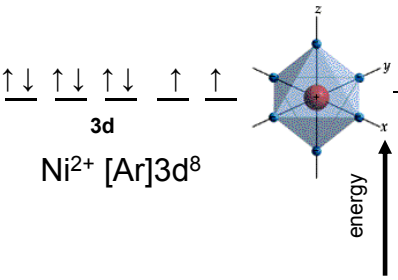
d-Orbitals and ligand Interaction (octahedral field)

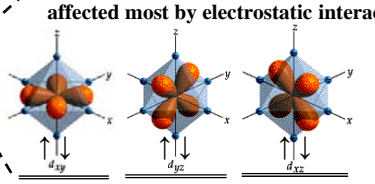


$Ni(NH_3)_6Cl_2 \xrightarrow{H_2O} [Ni(NH_3)_6]^{2+}(aq) + 2Cl^-(aq)$



d-orbitals pointing directly at axis are affected most by electrostatic interaction

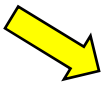


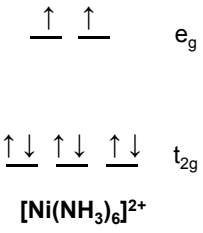


d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

ibchem.com/IB/ibfiles/periodicity/per_ppt/**Crystal_field_theory**.ppt 59

absorption of visible light in octahedral transition metal complexes





$[Ni(NH_3)_6]^{2+}$

- 3d orbitals all have same energy in Ni^{2+} (g)
- presence of $6NH_3$ cause "splitting of the energies of the 3d-orbitals into two levels in $[Ni(NH_3)_6]^{2+}$
- visible light causes electronic transitions between the two levels resulting in 'colored' transition metal complexes

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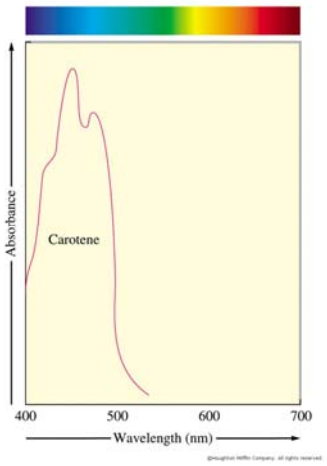
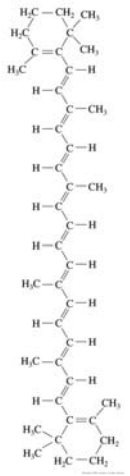
ß- carotene; conjugated double bonds (figure 14.56, 14.57)





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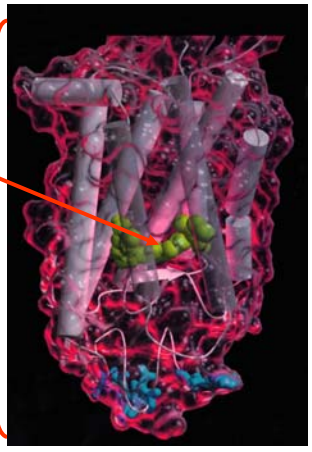
rhodopsin (11-cis retinal + opsin)

intradiscal (lumen)

11-cis retinal

+

opsin (protein)



interdiscal (cytoplasmic)

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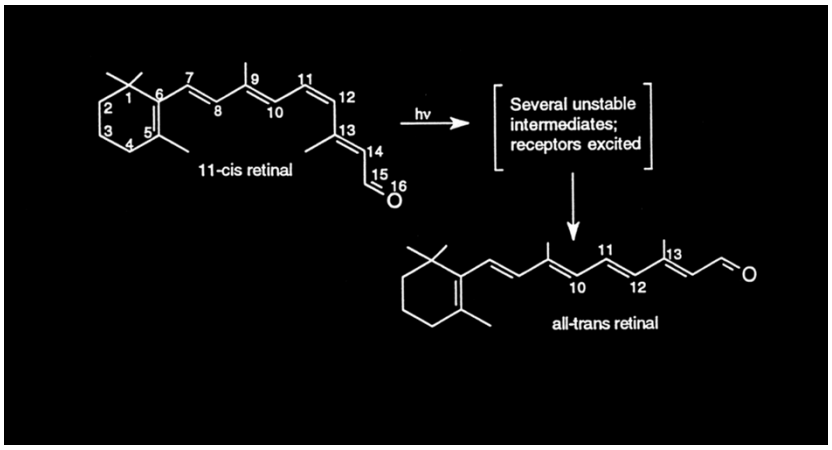
how do we "see" color ???



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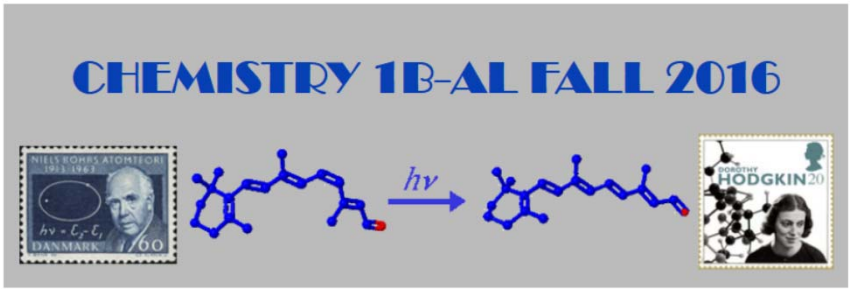
AHA! that's what its all about



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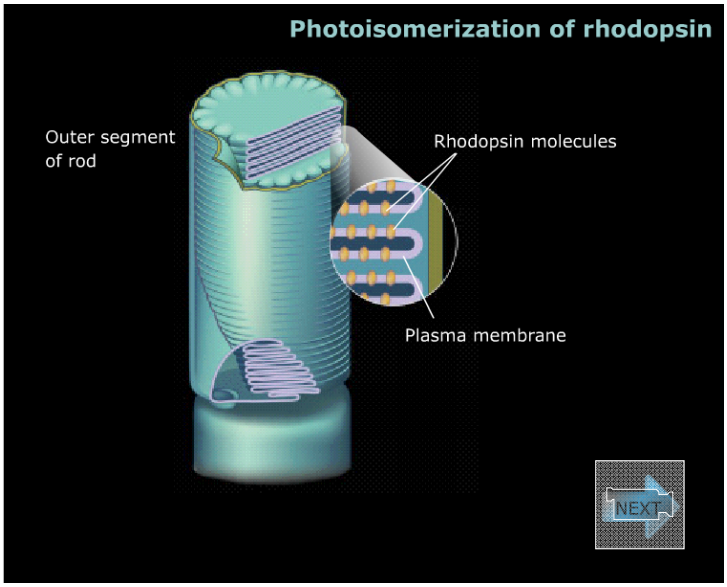

Advanced (don't fret)

Visual transduction cascade, 1 photon⟹10^6 Na^+

FROM: http://www.blackwellpublishing.com/matthews/rhodopsin.html

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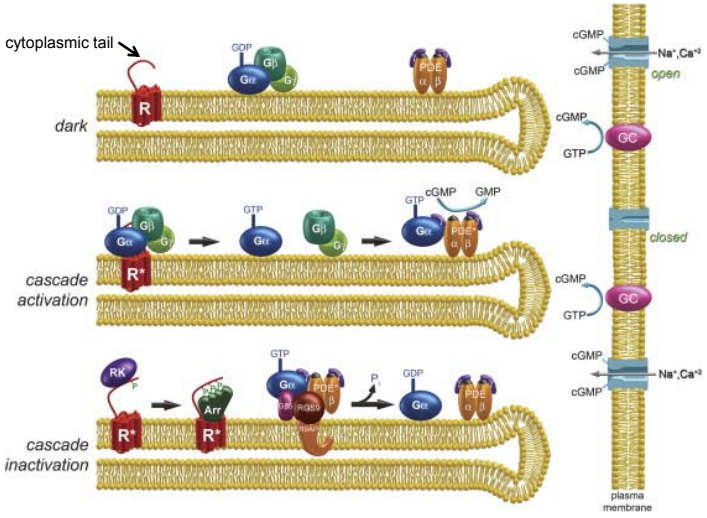
signal amplification in visual excitation cascade



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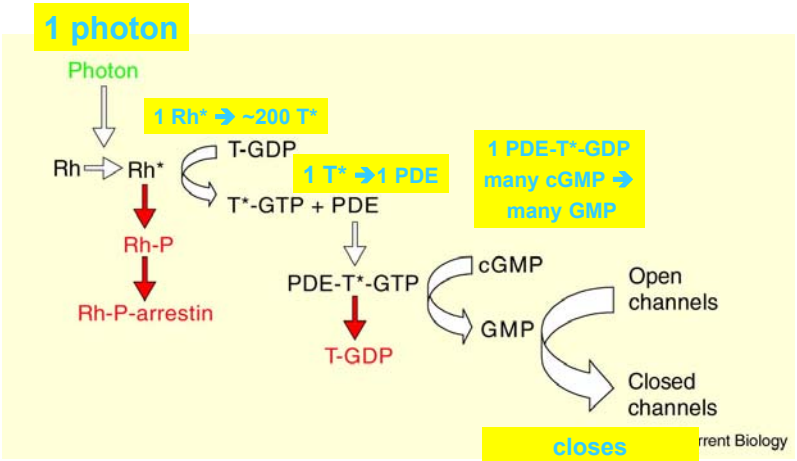
amplification



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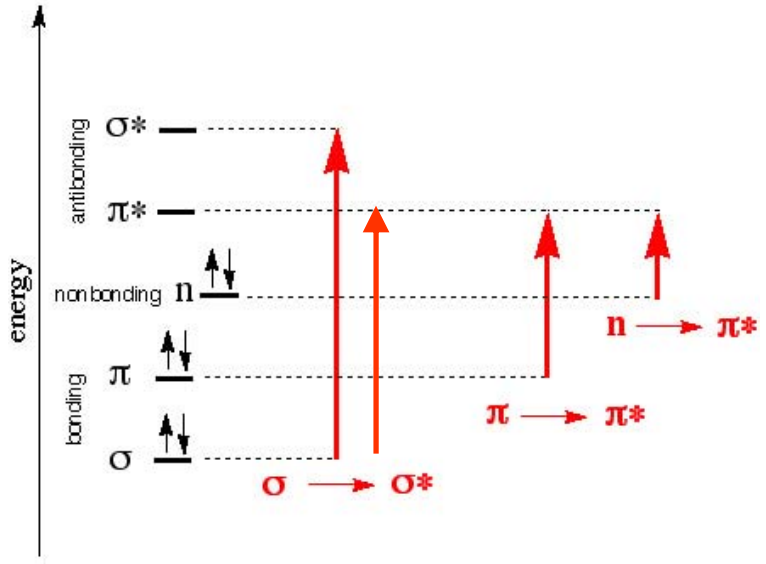
summary



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