

Topics 19-20

Spectroscopy

Fall 2016

SPECTROSCOPY:
short wavelength regions
ESCA (photoelectron) and UV

handout

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)



Spectroscopy Handout

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

λ (nm)	ν (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	$4-8 \times 10^{14}$	visible		
3000	10^{13}	infra-red	IR	vibrational excitations (IR)
3×10^6	10^{11}	microwave	microwave	rotations of molecules and
			ESR	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

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:
- Fluorescence
 - Phosphorescence
 - Radiationless decay
 - Chemiluminescence

clicker questions worksheet 11, sections I-II.3



Chemistry 1B-AL Fall 2016, Study Guide and Worksheet XI

Learning Objectives and Worksheet XI

Chemistry 1B-AL Fall 2016

Lectures (19-20) Spectroscopy

The material on spectroscopy will be taken from a number of sources and will not specifically follow the presentation in Zumdahl. It will be especially important to pay close attention to the handouts, worksheets, videos, and class presentations.

Understanding the electronic structure of atoms and bonding in molecules has been a primary focus of our work so far in Chemistry 1B. It is a very, very, nice story, but how can one experimentally verify that these abstract concepts actually occur in nature? Spectroscopy provides a primary experimental tool for investigating molecular structure. Additionally, other phenomena arising from the interaction of light (radiation) with matter are of wide ranging importance.

I. Basic Concepts of Spectroscopy

1. Know the names of the major types of electromagnetic radiation ranging from long wavelengths, corresponding to _____ frequencies, to short wavelengths corresponding to _____ frequencies.



HWRE: 64

related videos:
<https://youtu.be/OQWTC9TRtUM>

2. The relationship between the wavelength and frequency of electromagnetic radiation is: _____.
3. The energy of a quantum of radiation is related to its frequency and wavelength by _____.
4. The position and intensity of a spectral absorption cannot only reveal information about the structure of a molecule, but the intensity contains information on the _____ of the compound (think Beer's Law).

1



HWRE: 65

- ii. Semantically, why is spectroscopy using far ultraviolet wavelengths called vacuum UV spectroscopy? _____
 - iii. What type of electronic excitations are caused by absorption of far UV radiation? _____
3. Near Ultraviolet
 - i. What type of electronic excitations are caused by radiation in the near ultraviolet (~300 nm)? _____

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet XI

Chemistry 1B-AL Fall 2016, Study Guide and Worksheet XI

II. Types of spectroscopy corresponding to differing regions of the electromagnetic spectrum

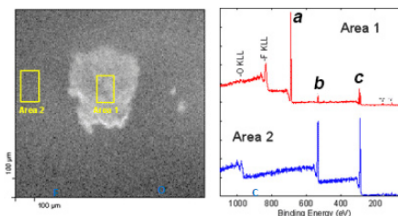
1. X-rays



HWRE: 65

- i. Generally, what two things might occur when x-rays interact with a molecule

- ii. In _____ spectroscopy, the binding energy of an inner shell electron is determined by knowing the energy of the X-ray photon and measuring the _____ of the inner shell electron which is ejected.
- iii. This type of spectroscopy is used to _____.
- iv. ESCA spectra were obtained for a surface putatively containing only carbon and oxygen compounds. However fluorine contamination was observed in Area 1, while Area 2 remained uncontaminated. In the ESCA spectrum for Area 1, identify which peak corresponds to ejection of 1s inner shell electrons from O, F, or C:
 a. _____ b. _____ c. _____



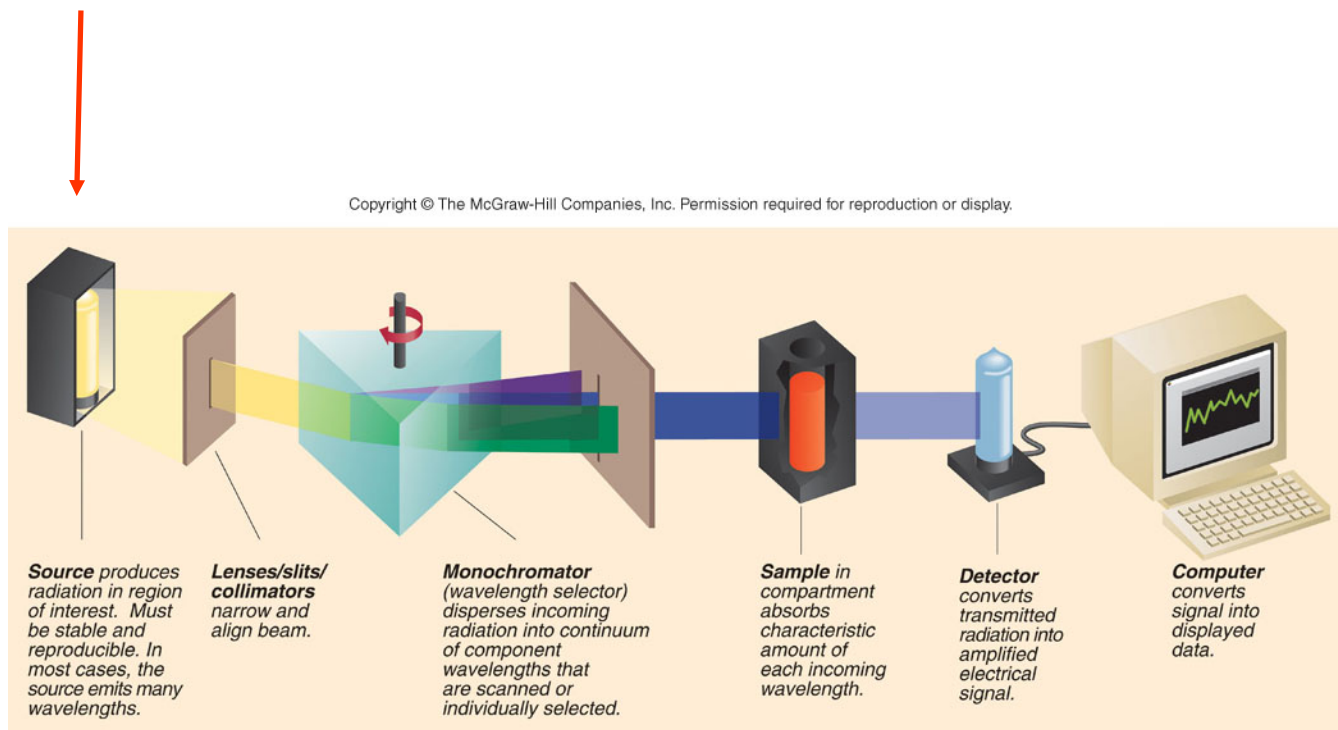
Why does the atom that you identified for peak a have the greatest 1s binding energy (~650 eV)? _____

2. Far Ultraviolet

- i. Semantically, why is the spectral region with 200-300 nm called the 'far' ultraviolet vis a vis the 'near' ultraviolet with 300-400 nm?

2

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



spectroscopic excitations ($E = h\nu = hc/\lambda$; $\lambda\nu = c$)

λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation

spectroscopic excitations ($E = h\nu = hc/\lambda$; $\lambda\nu = c$)

λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
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3 × 10 ⁹	10 ⁸	radiowave	NMR (MRI)	flipping of nuclear spins in an external magnetic field

↑ increases ↓ energy decreases

spectroscopic excitations: ESCA

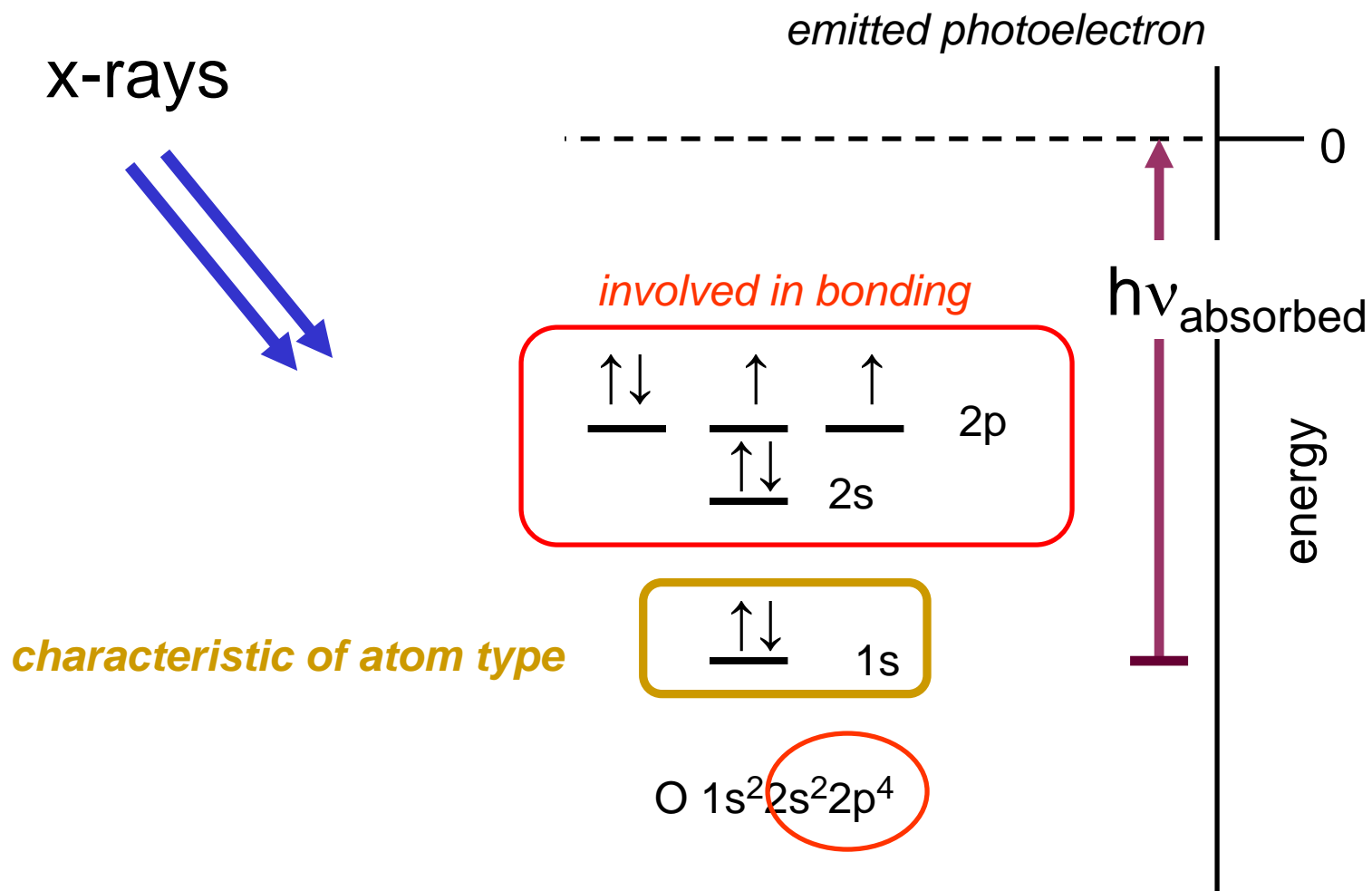
|
□ increases
|
↓

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

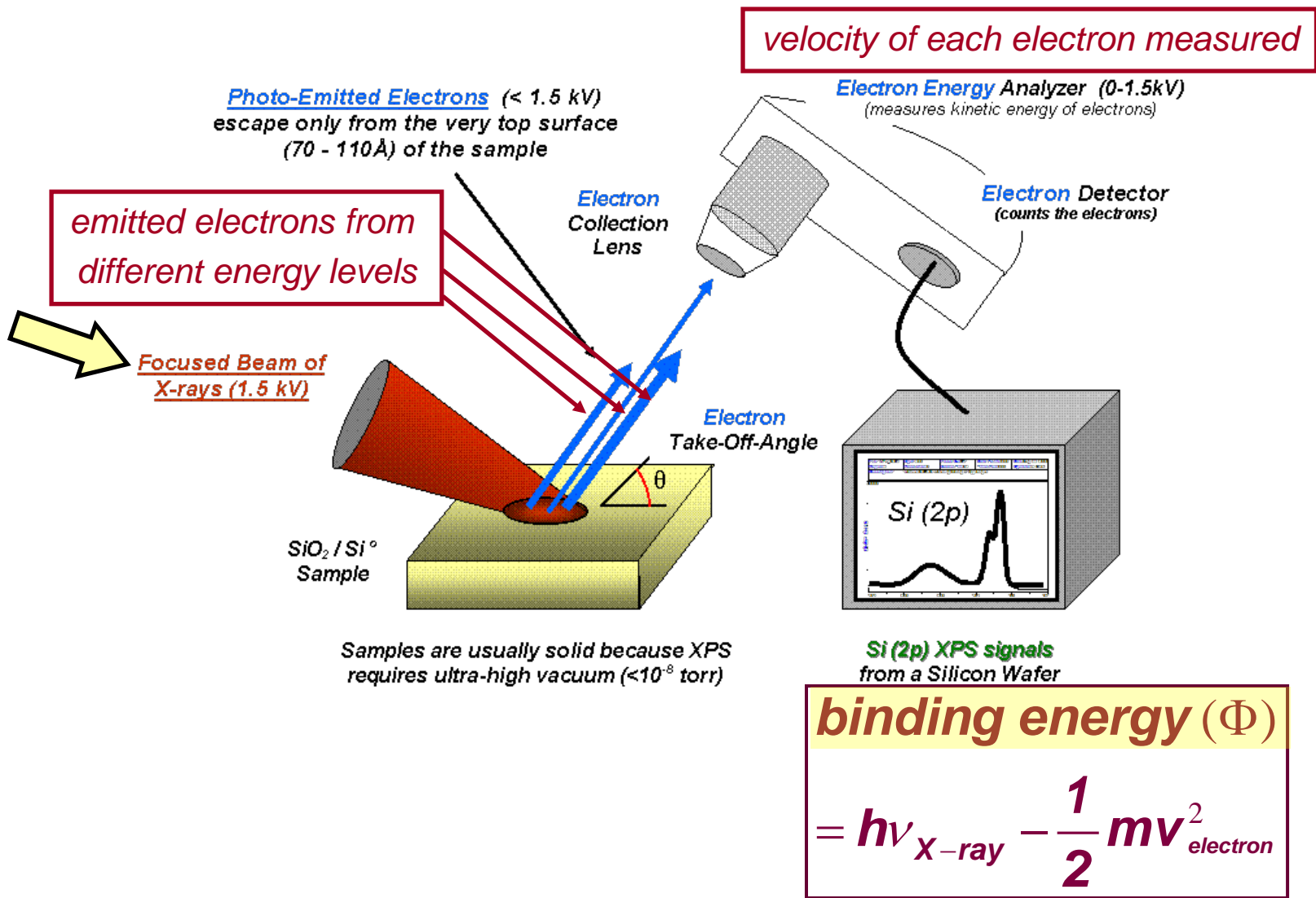
Electron Spectroscopy for Chemical Analysis



ESCA – photoelectric effect for inner shells



ESCA (and photoelectron effect)

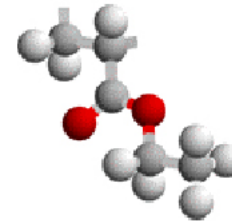
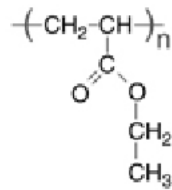
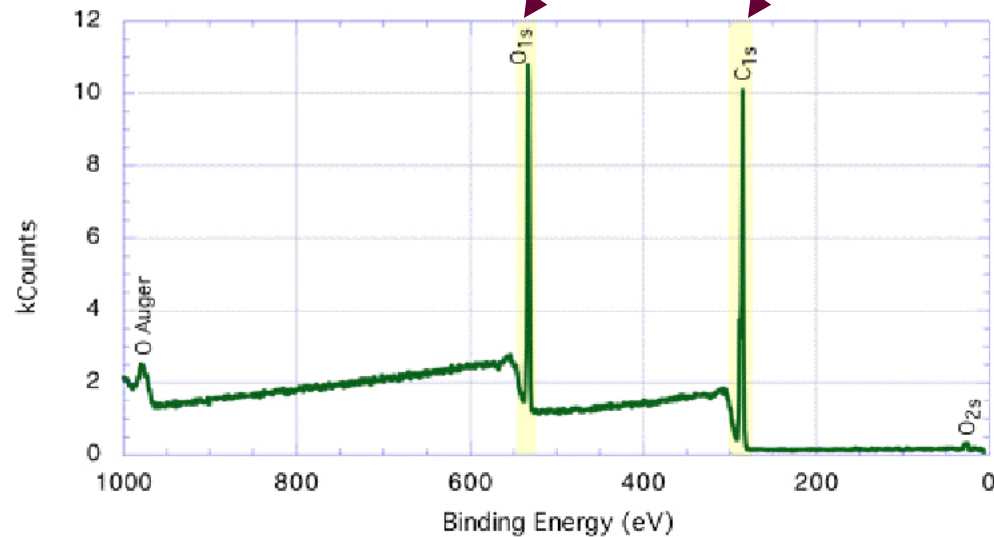


Samples are usually solid because XPS requires ultra-high vacuum (<10⁻⁸ torr)

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

- Polyéthyl acrylate (PEA) :

Why O1s higher binding energy than C1s ?



binding energy (Φ)

$$= h\nu_{X\text{-ray}} - \frac{1}{2}mv_{\text{electron}}^2$$

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

spectroscopic excitations: ESCA

↑
□ increases
↓

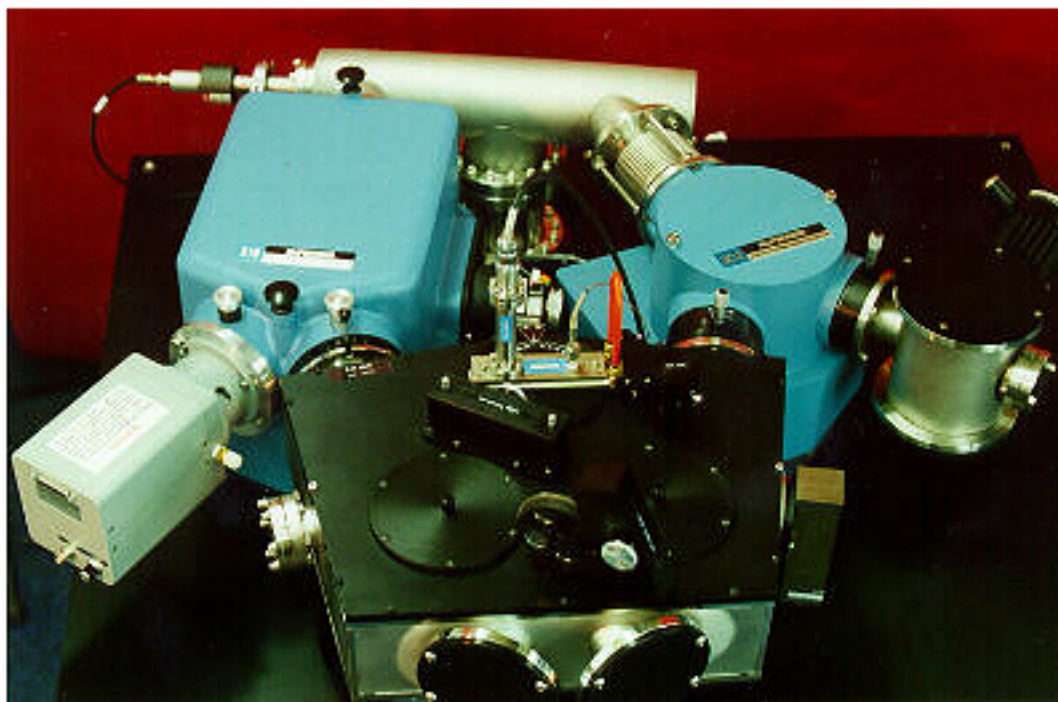
λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
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vacuum UV

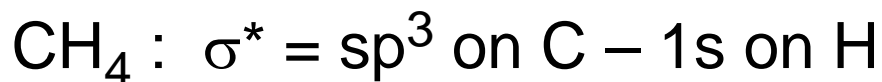
↑
□ increases
↓

λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
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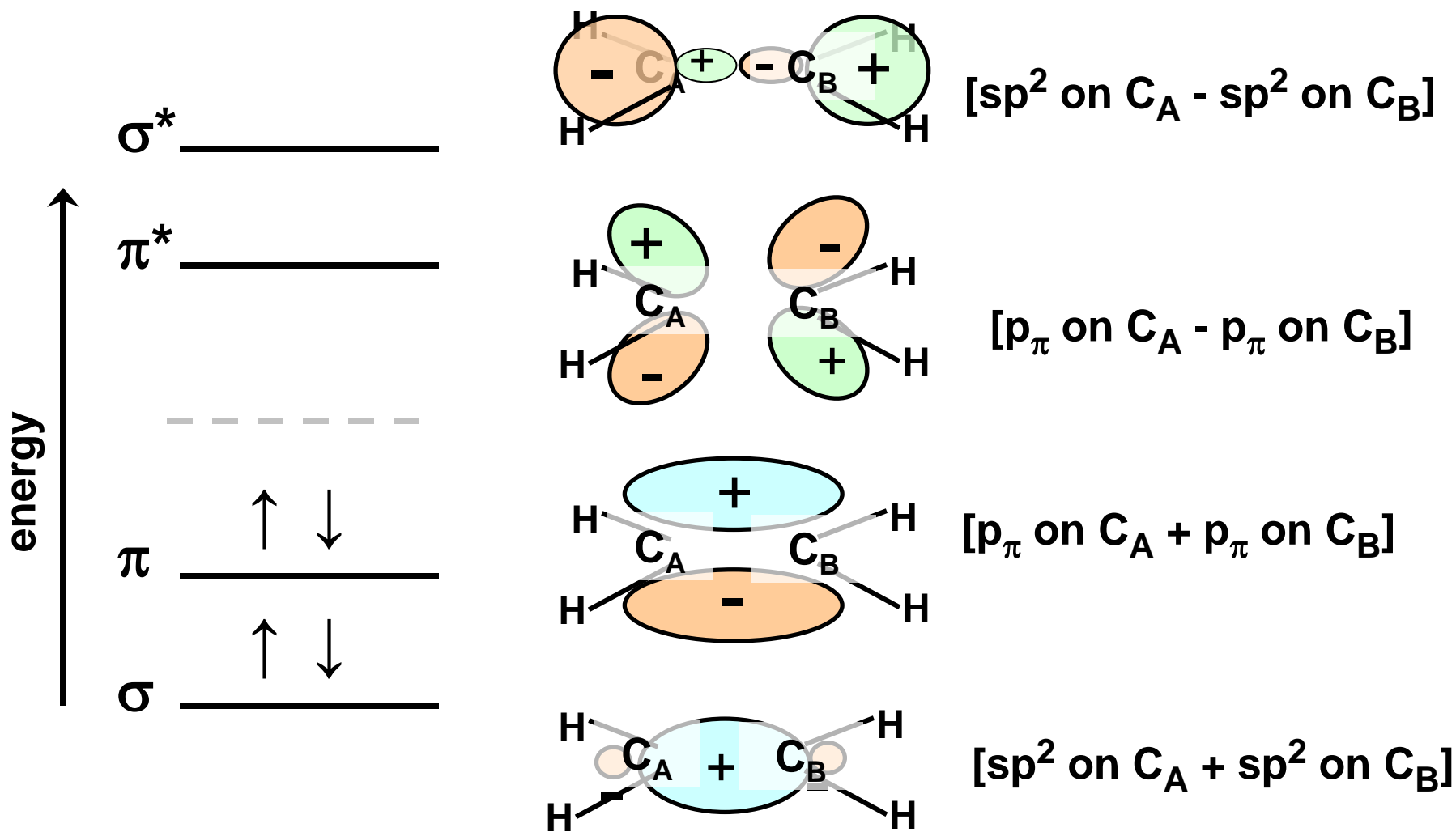
Mc Pherson Vacuum UV Spectrophotometer System



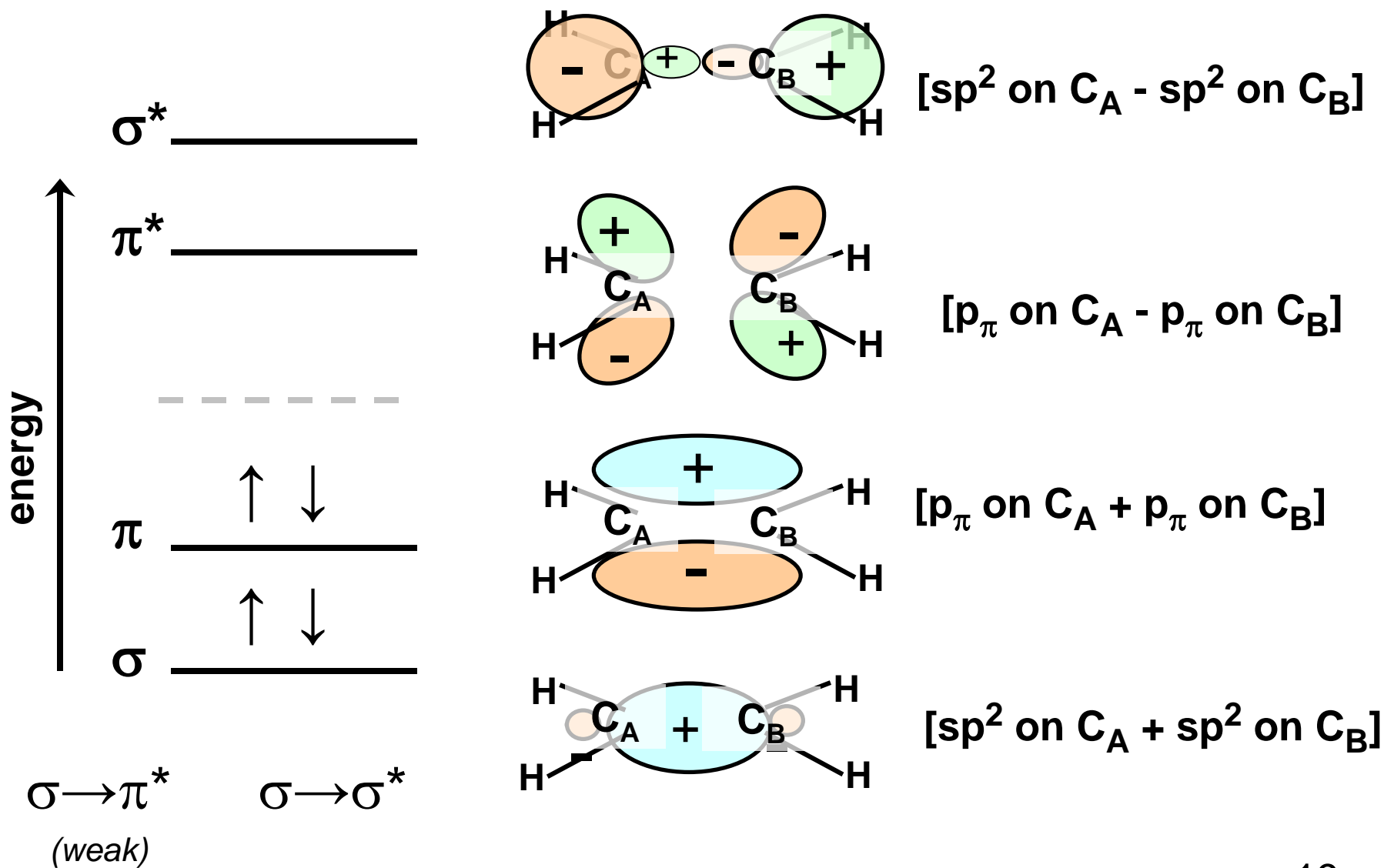
- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light
- types of antibonding orbitals:



energies of orbitals in double bond



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



vacuum UV

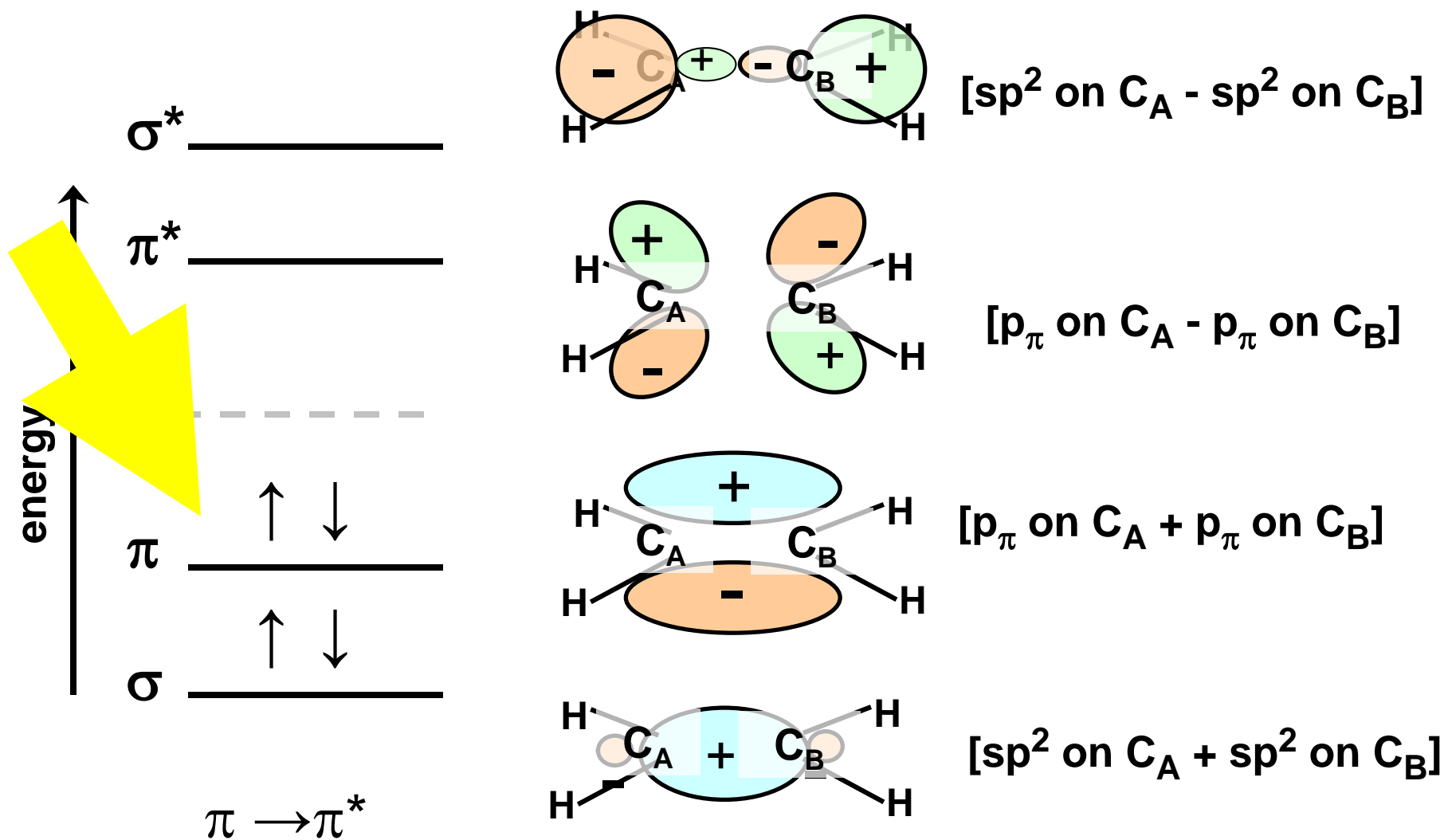
↑
□ increases
↓

λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
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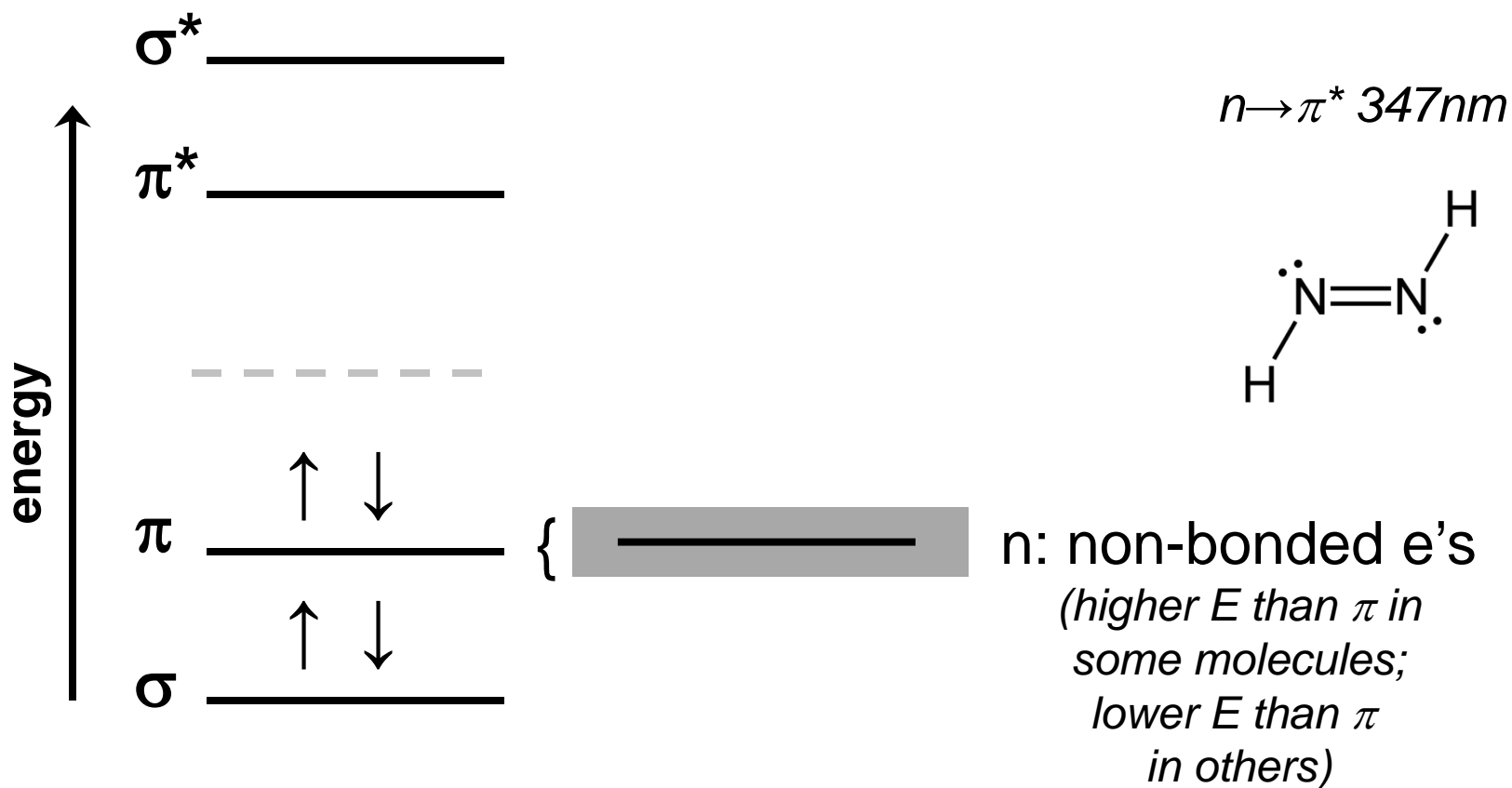
spectroscopic excitations (UV-VIS)

λ (nm)	ν (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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400-700	4-8 × 10¹⁴	visible		

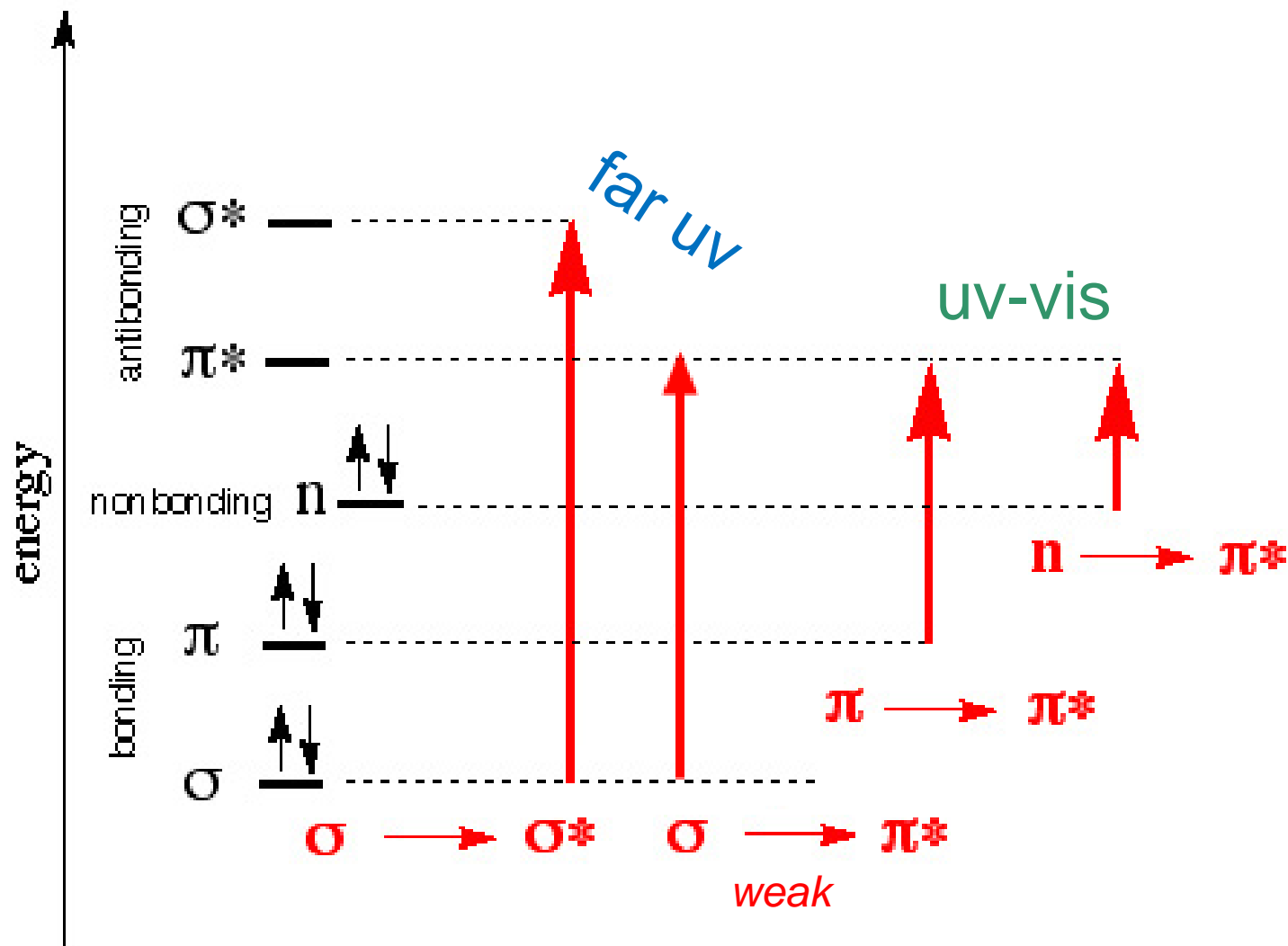
near UV transitions



relative energy on "lone pair" non-bonding electrons



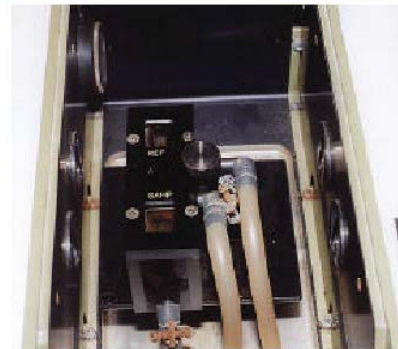
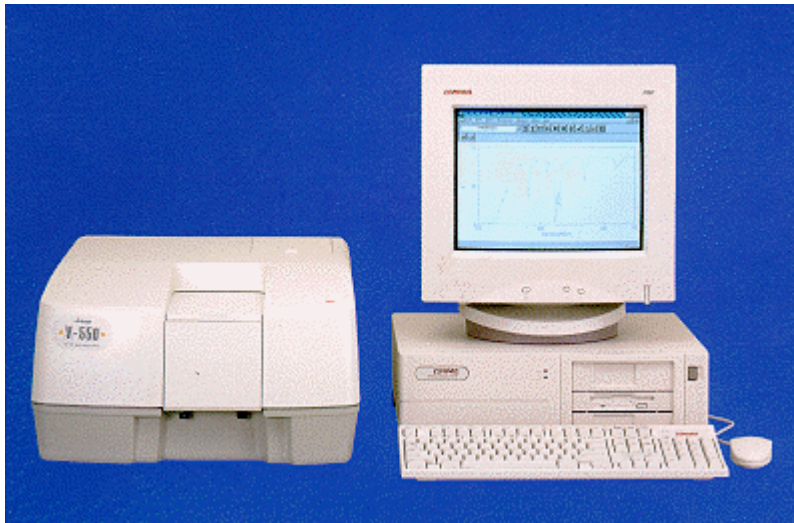
summary



spectroscopic excitations (UV-VIS)

λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
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UV-VIS spectrometers (Chem 1M/1N expts. #9 and #11)



sample container

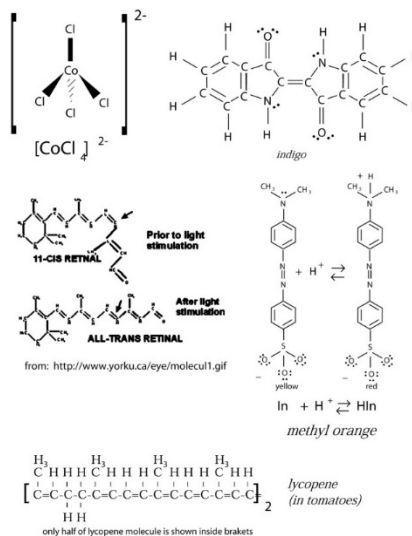


cuvets

continue in next class: absorptions in the visible region

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

molecules that absorb visible light





DONE
FOR
NOW !!





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

flip class



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



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.

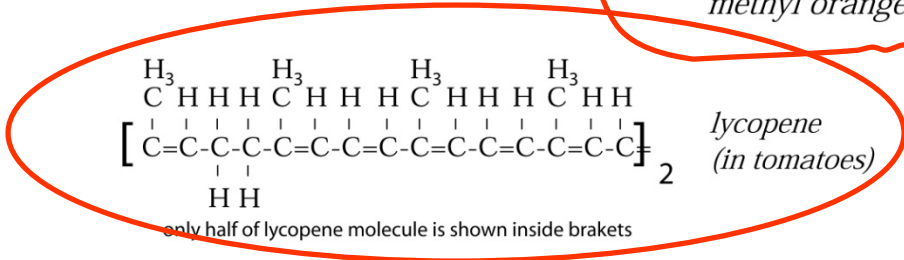
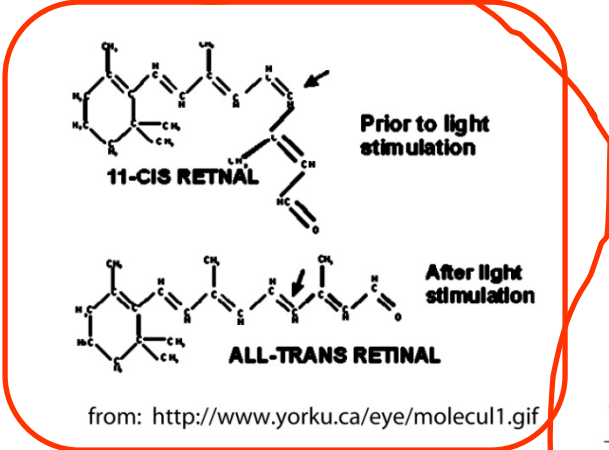
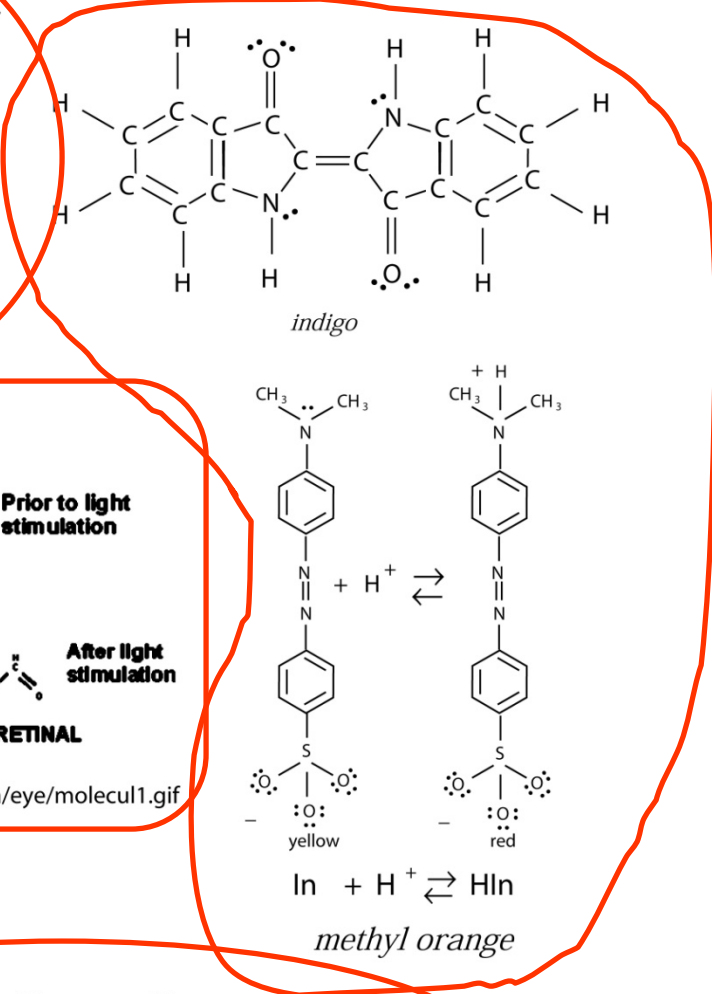
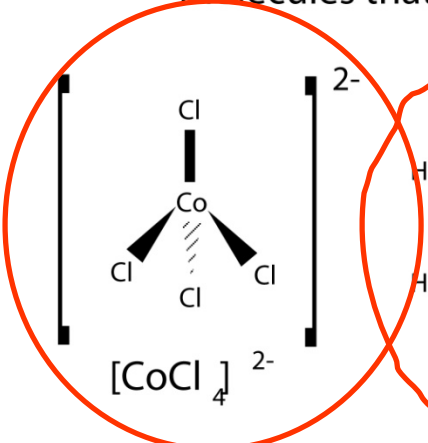


Highest **O**ccupied **M**olecular **O**rbital \rightarrow **L**owest **U**noccupied **M**olecular **O**rbital

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

molecules that absorb visible light

Br₂(g), I₂(g), NO₂



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) $n \rightarrow \pi^*$

$\pi \rightarrow \pi^*$ in molecules with **conjugated** pi-systems

rhodopsin, the molecule most important to seeing color

spectroscopic excitations

λ (nm)	ν (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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400-700	$4-8 \times 10^{14}$	visible		
3000	10^{13}	infra-red	IR	vibrational excitations (IR)

diatomic molecules (vibrating and rotating)



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

wave number

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

new 'unit'

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

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

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

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

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

vibrational frequencies of homonuclear diatomic molecules and ions

wave number
larger $\tilde{\nu} \Rightarrow$ higher energy photon

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

- mass of atoms (lighter \square higher $\tilde{\nu}$)
- strength of bond (tighter 'spring' \square 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. \square greater frequency

b.o.

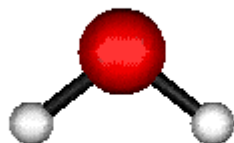
$\tilde{\nu}$

vibrational motion in molecules (H_2O)

wave number

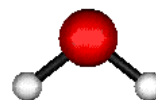
$$\tilde{\nu} = \frac{1}{\lambda_{cm}} \quad [\tilde{\nu}] = cm^{-1}$$

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

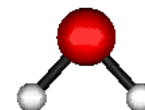


Characteristic Vibrations of H_2O

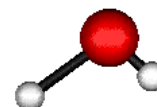
$\nu_1 = 3835 \text{ cm}^{-1}$



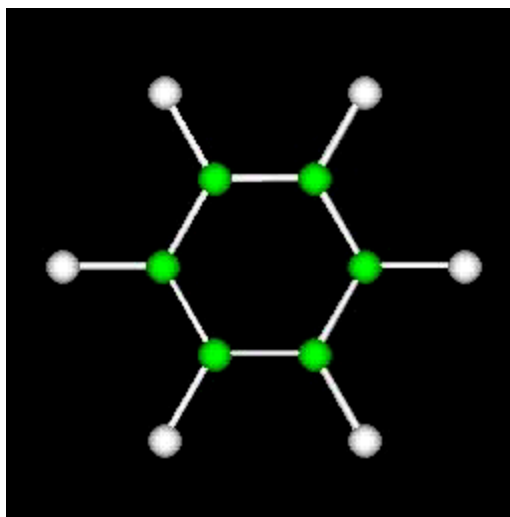
$\nu_2 = 1648 \text{ cm}^{-1}$



$\nu_3 = 3939 \text{ cm}^{-1}$

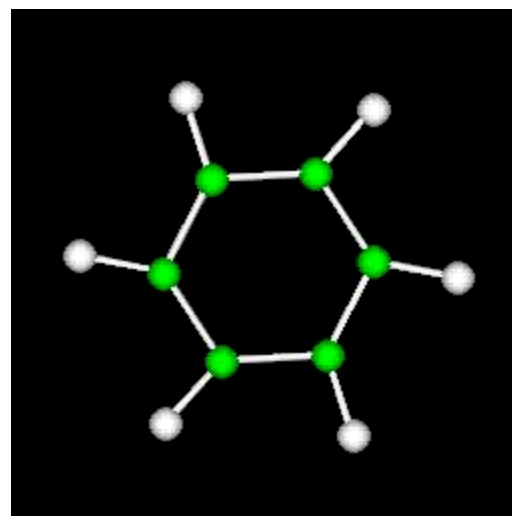
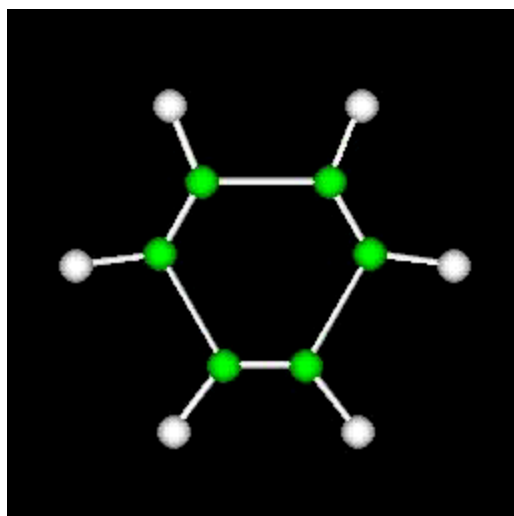


vibrational motions in molecules (benzene)

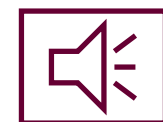


breathing (stretching) mode

asymmetric stretching mode



Chubby Checkers
twisting mode



**American
Bandstand**

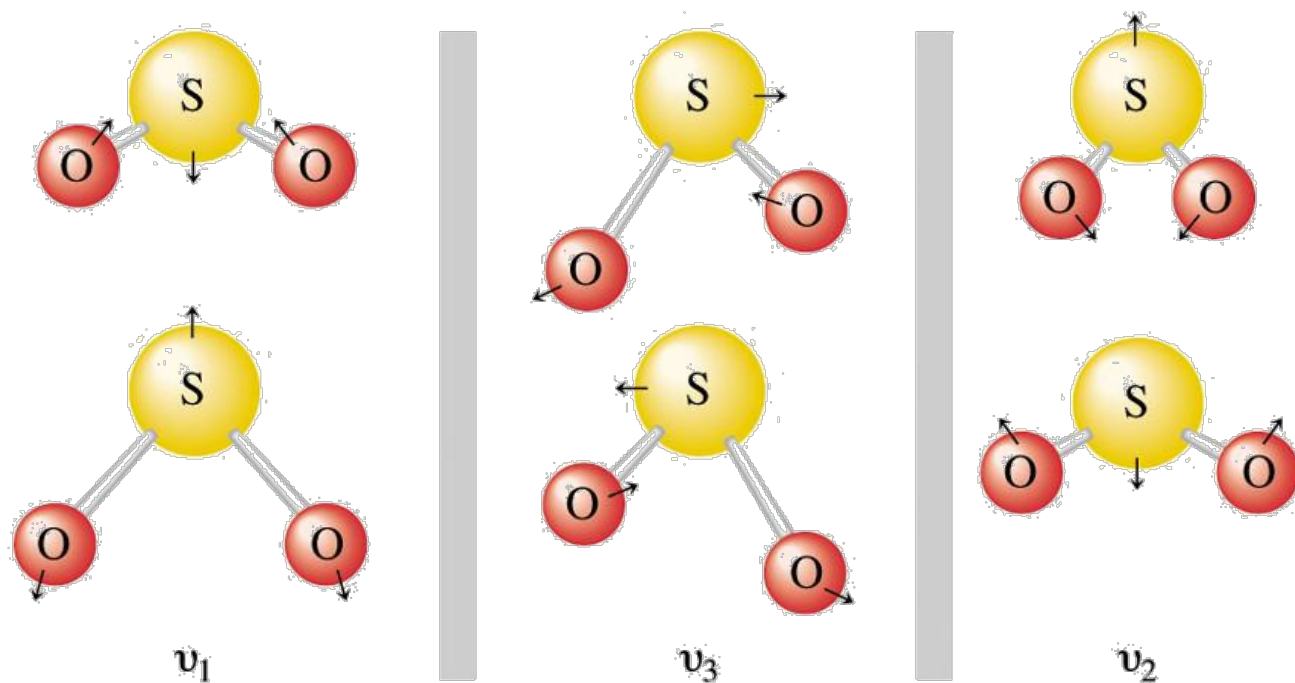


IR spectrometer



infrared vibrational spectroscopy (fig. 14.60)

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



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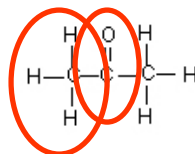
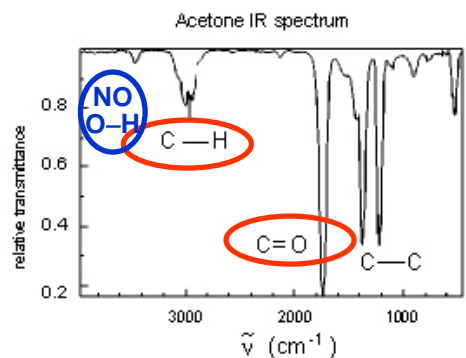
group frequencies

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

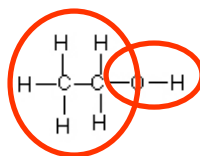
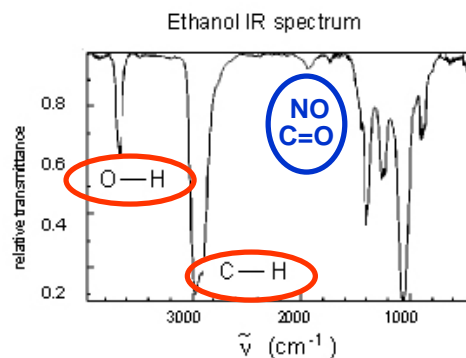
Bond	Characteristic Frequency (approximate) $\tilde{\nu}$ (cm^{-1}) [E = $hc\tilde{\nu}$]	λ (nm)
C – C	1000-1400	10000-7140
C = C	1600	6250
C \equiv C	2100	4760
C – O	1100	9090
C = O	1800	5880
C – H	2800-3200	3125
O – H	3600	2770

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

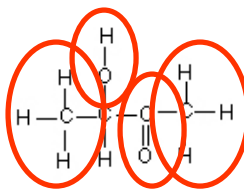
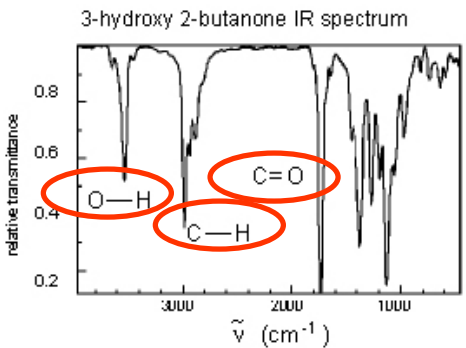
IR spectra



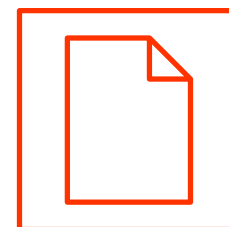
C-H $\sim 3200 \text{ cm}^{-1}$



C=O $\sim 1700 \text{ cm}^{-1}$



O-H $\sim 3600 \text{ cm}^{-1}$



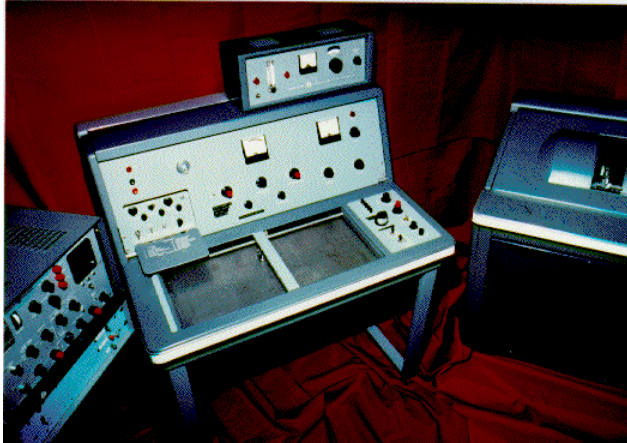
spectroscopic excitations

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radiowave

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3000	10 ¹³	infra-red	IR	vibrational excitations (IR)
3 \times 10 ⁶	10 ¹¹	microwave	microwave ESR	rotations of molecules and flipping unpaired electron spins in external magnetic field
3 \times 10⁹	10⁸	radiowave	NMR (MRI)	flipping of nuclear spins in an external magnetic field

NMR (MRI) spectrometers



NMR- WHY?

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

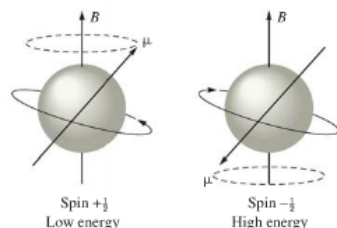


FIGURE 14.62

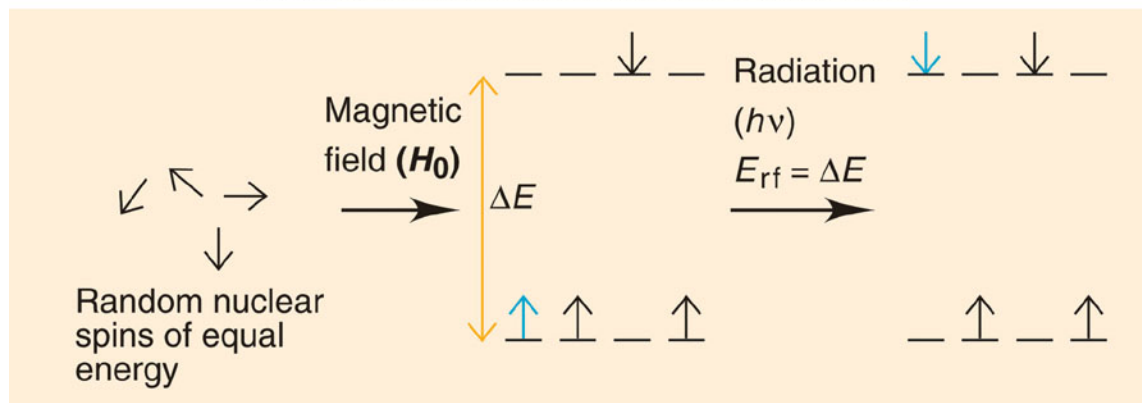
Representations of the two spin states of the proton interacting with a large, steady magnetic field B .

electron ~650 x stronger magnet

*The nucleus does not literally spin, although we often picture it that way. Nuclear "spin," like electron "spin," is simply a name for a property called spin angular momentum.

- in an external magnetic field, spin up \uparrow and spin down \downarrow 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

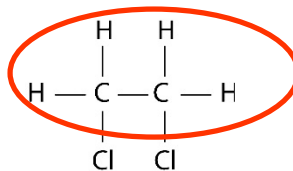
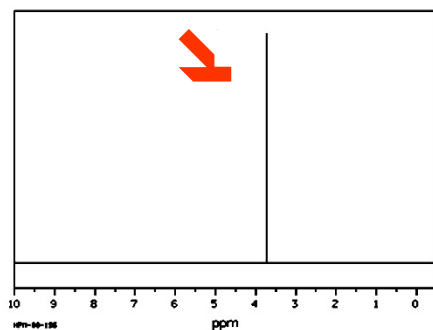
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identifying equivalent and non-equivalent protons

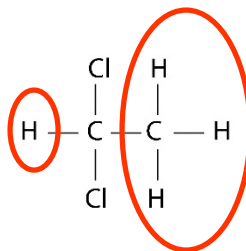
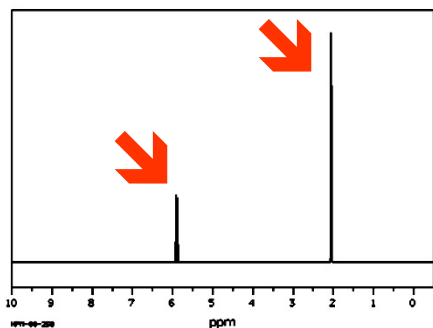
to 'flip' hydrogen atoms (nuclei) in different chemical environments requires slightly different energies (chemical shift)

1,2 dichloroethane HNMR



(all H equivalent,
 $\text{H}_2\text{ClC}-$
1 peak
one 'chemical shift')

1,1 dichloroethane HNMR

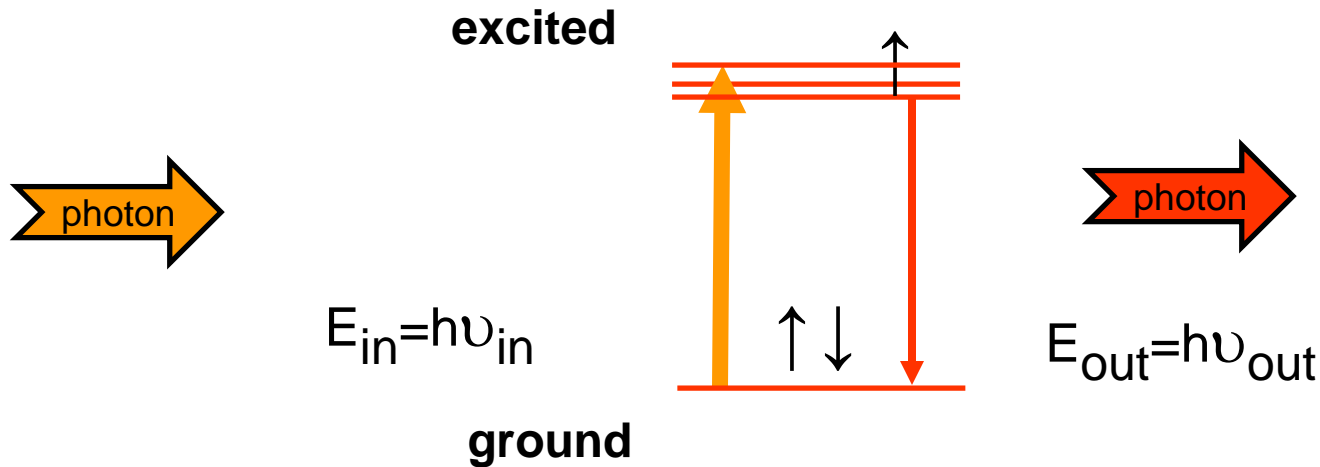


(two H environments,
 $\text{HCl}_2\text{C}-$ and $-\text{CH}_3$
2 peaks
two 'chemical shifts')

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

will get plenty in o-chem

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



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

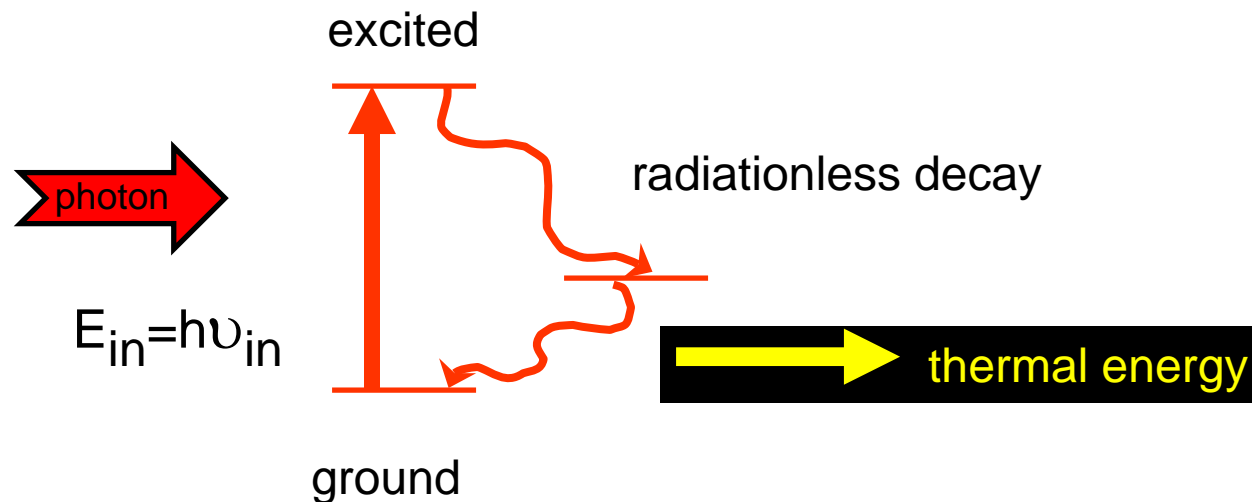
$$(\lambda_{out} \geq \lambda_{in})$$

time $\sim 10^{-12}$ to 10^{-9} sec

(fluorescence stops soon after exciting light is turned off)

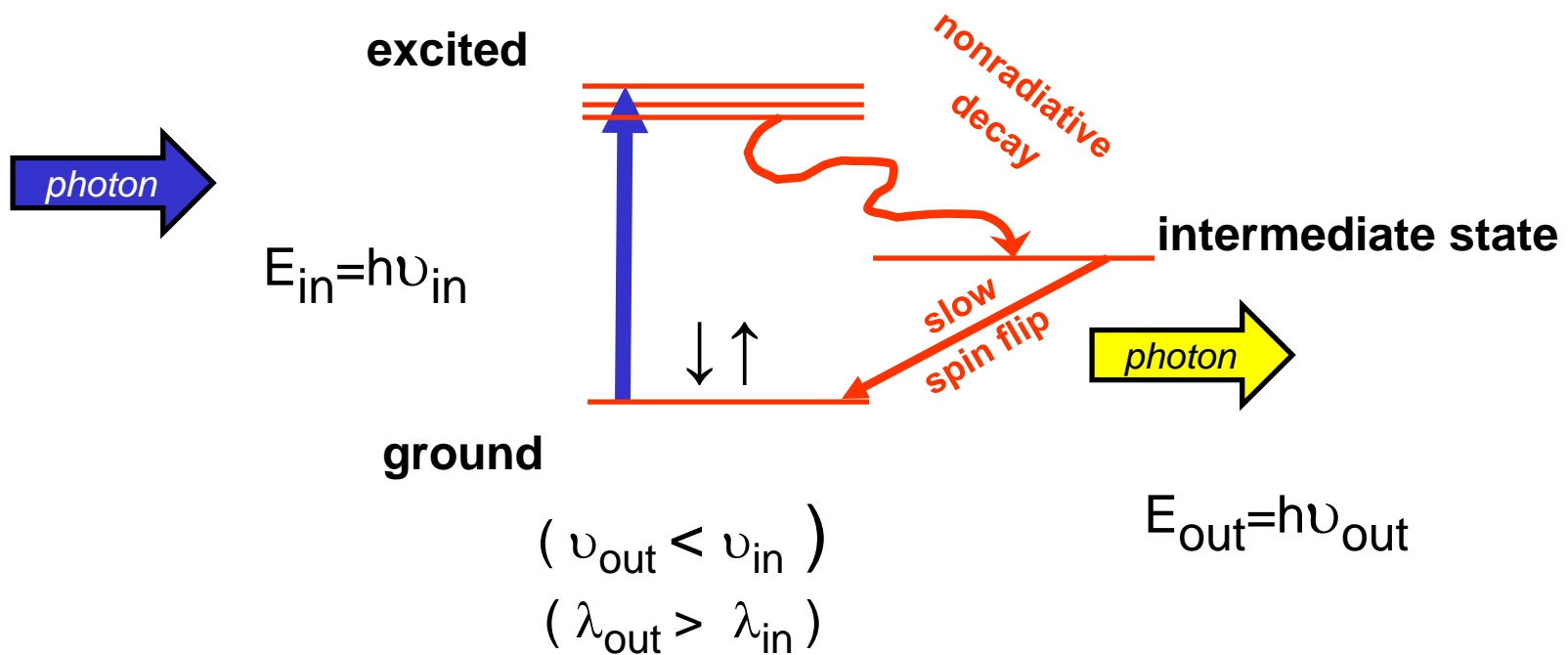
vocabulary: radiationless decay (nonradiative decay)

- **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



phosphorescence

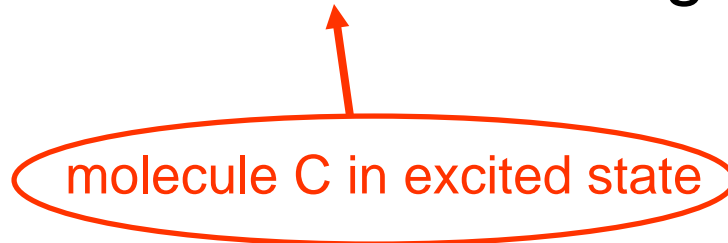
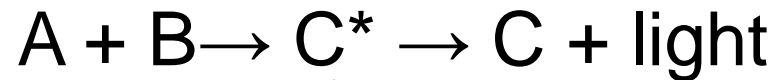
phosphorescence- 'slow' return to ground state by emission of photon from intermediate state



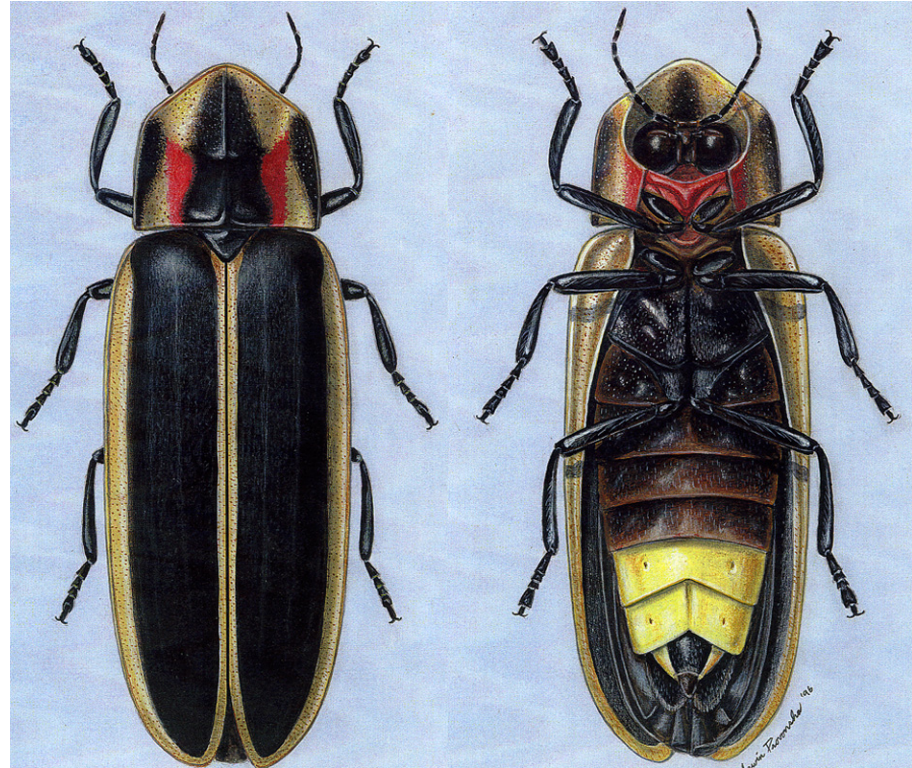
time $\sim 10^{-3}$ to 10 sec and longer

(phosphorescence continues after exciting light is turned off)

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



chemiluminescence: fireflies



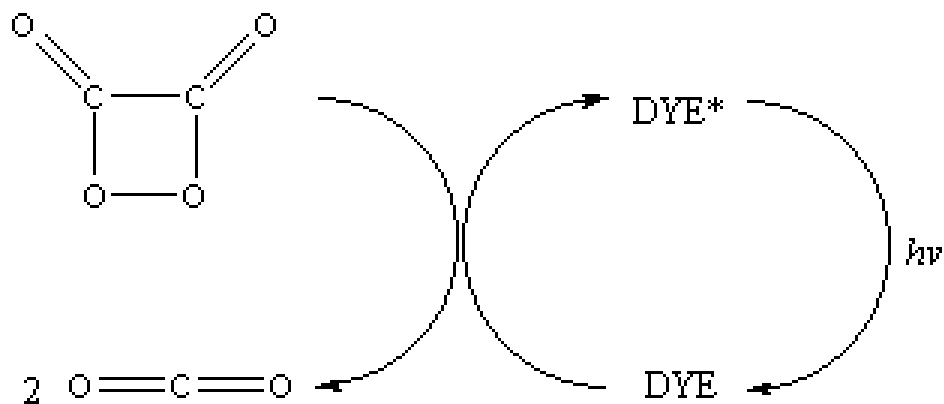
chemiluminescence: fireflies



**luciferin + luciferase + ATP \longrightarrow
luciferyl adenylate-luciferase + pyrophosphate**

**luciferyl adenylate-luciferase + O₂ \longrightarrow
oxyluciferin + luciferase + AMP + light**

chemiluminescence: light sticks

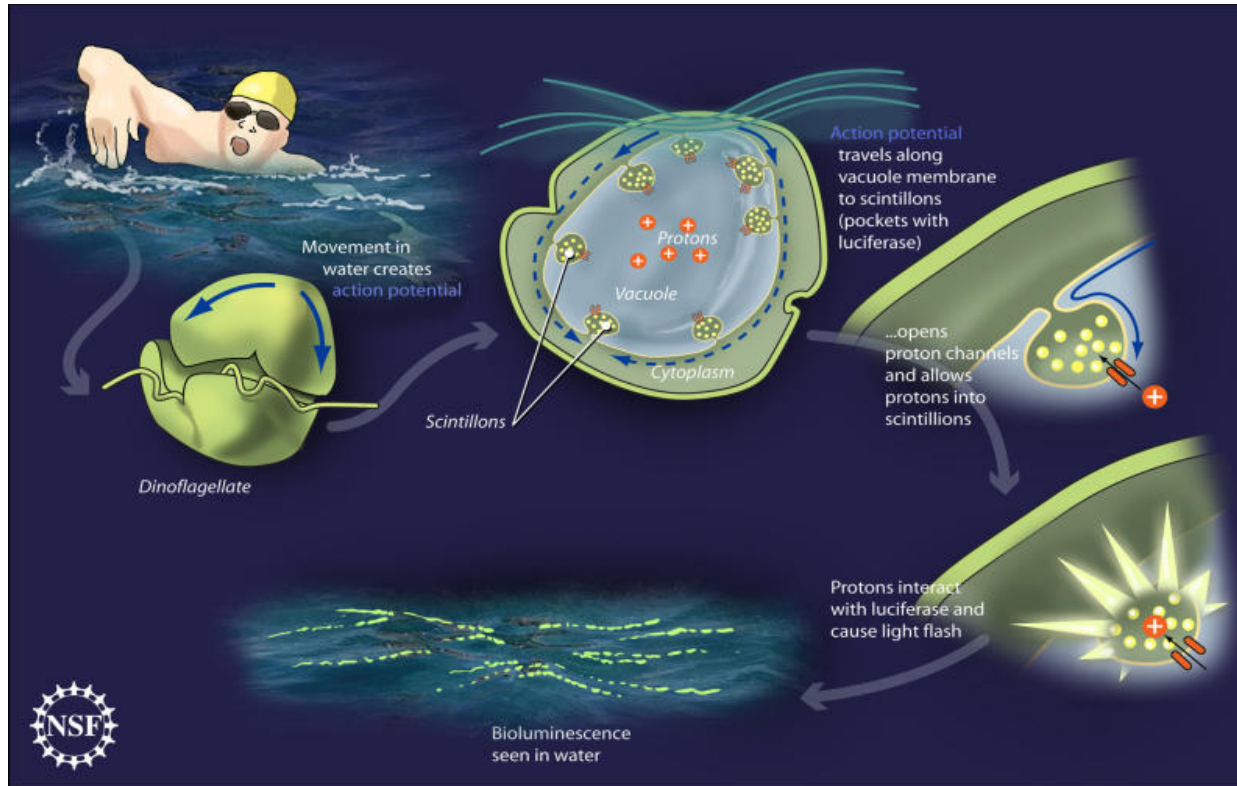


The intermediate
decomposes into two
carbon dioxide molecules

The fluorescer is excited; light
is given off as the excited state
returns to the ground state

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

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/2011/10/11019190823.htm>

end of lectures
on
spectroscopy

colored transition metal complexes- glazes



$\text{Ni}(\text{NH}_3)_6\text{Br}_2$

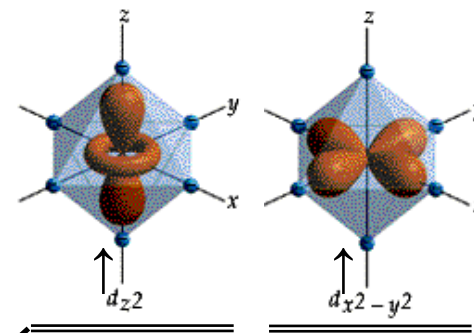
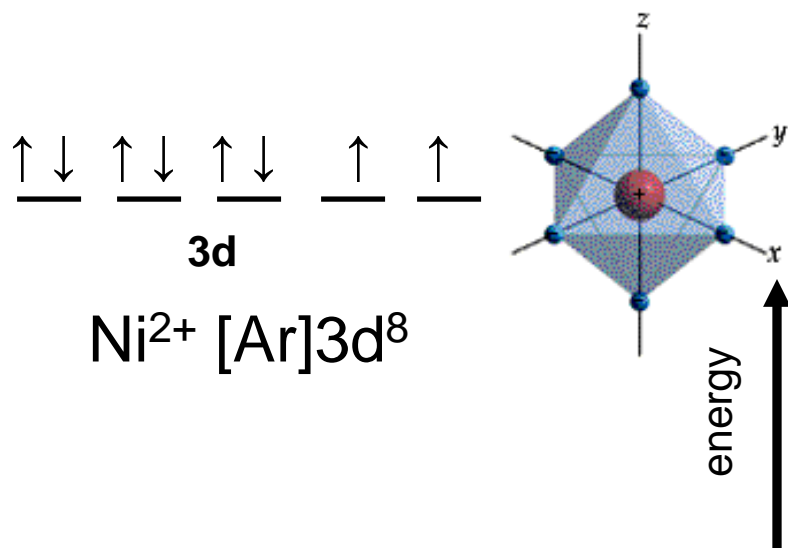
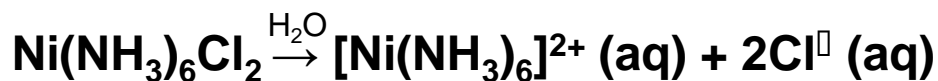
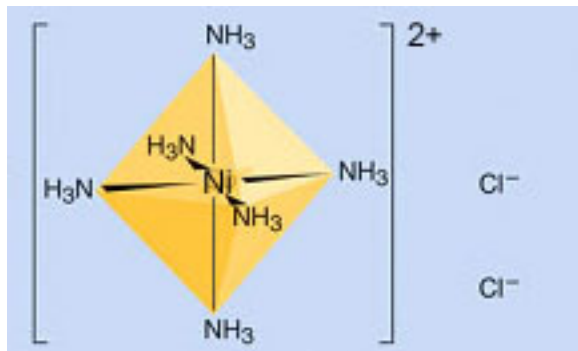


$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

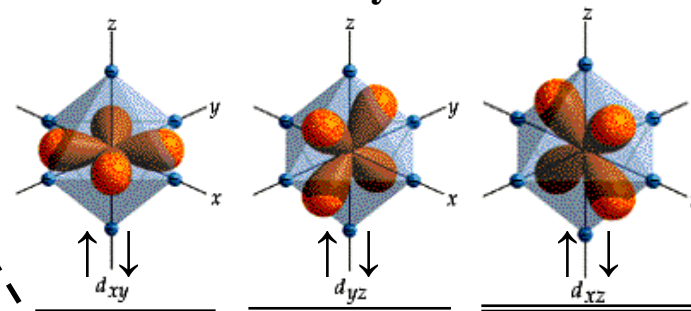


$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

d-Orbitals and ligand Interaction (octahedral field)

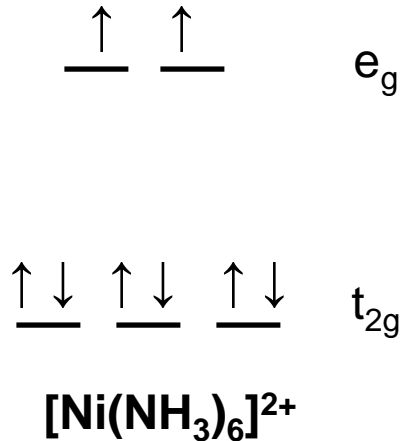
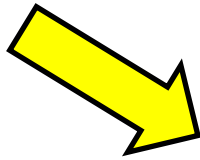


d-orbitals pointing directly at axis are affected most by electrostatic interaction



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

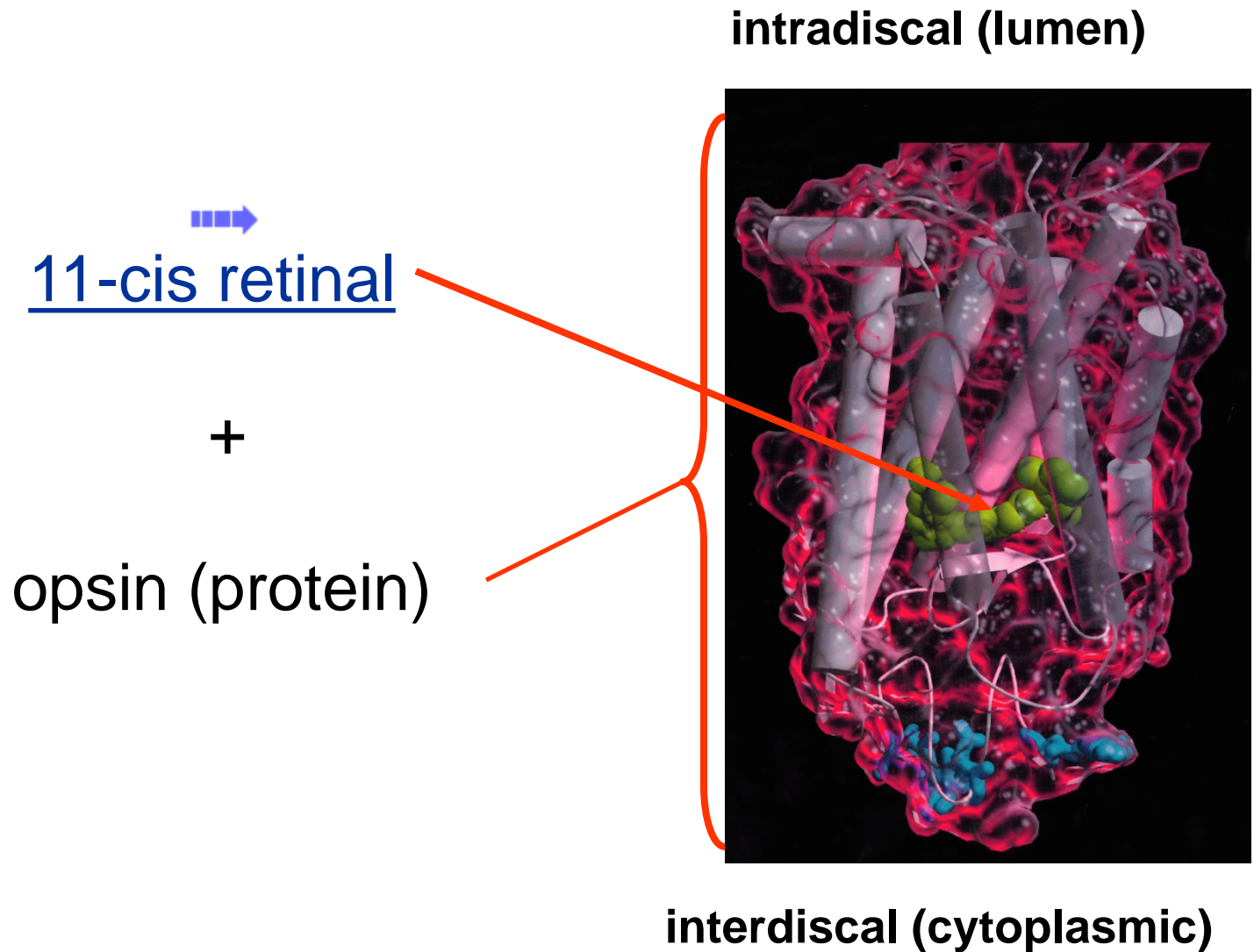
absorption of visible light in octahedral transition metal complexes



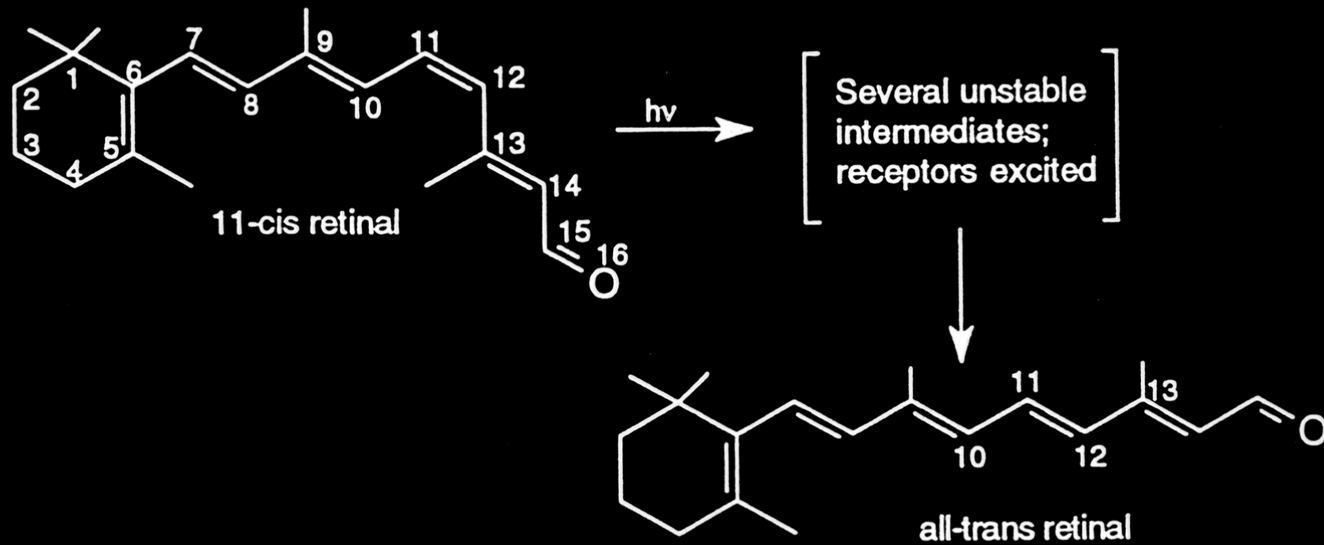
- 3d orbitals all have same energy in Ni^{2+} (g)
- presence of 6NH_3 cause “splitting of the energies of the 3d-orbitals into two levels in $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ”
- visible light causes electronic transitions between the two levels resulting in ‘colored’ transition metal complexes



rhodopsin (11-cis retinal + opsin)

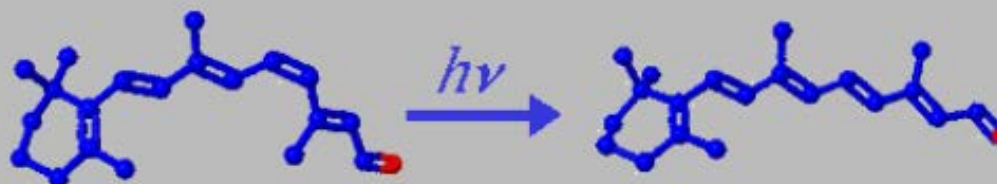


how do we “see” color ???



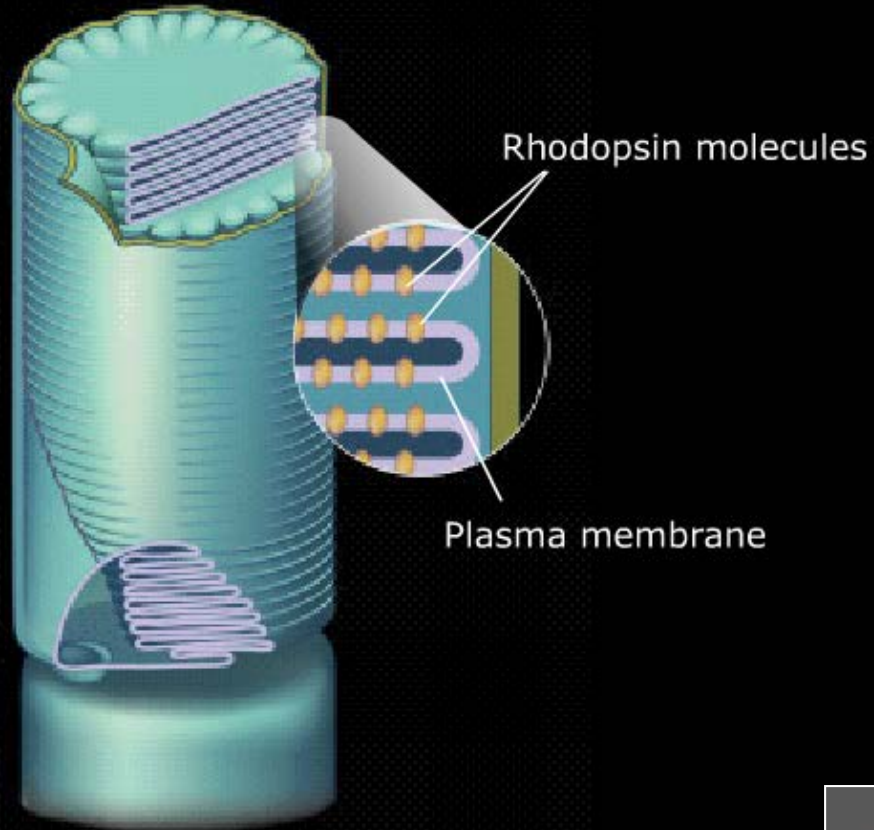
AHA! that's what its all about

CHEMISTRY 1B-AL FALL 2016



Photoisomerization of rhodopsin

Outer segment
of rod



Advanced (don't fret)

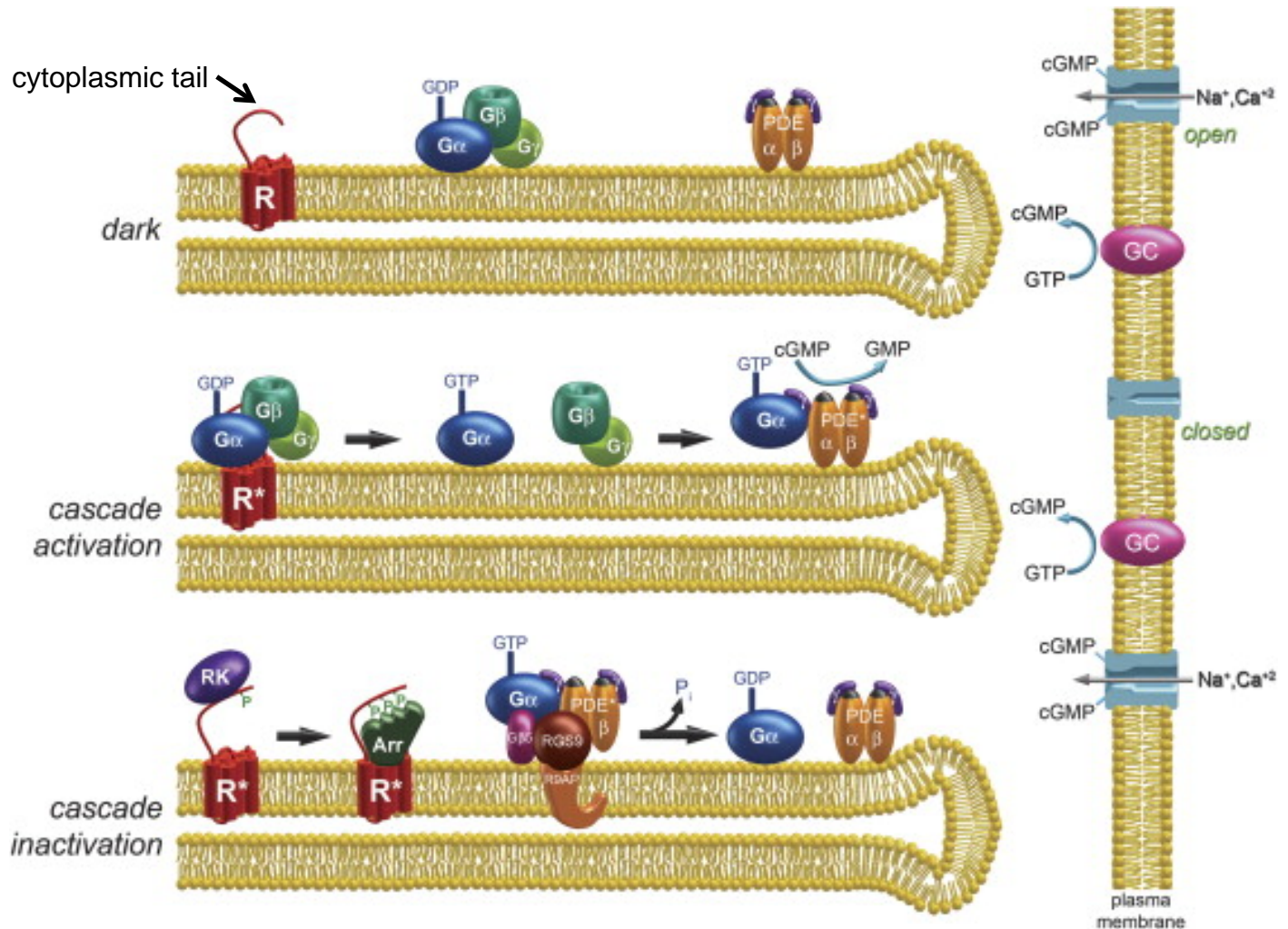
Visual transduction cascade,
1 photon \rightarrow 10^6 Na⁺



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

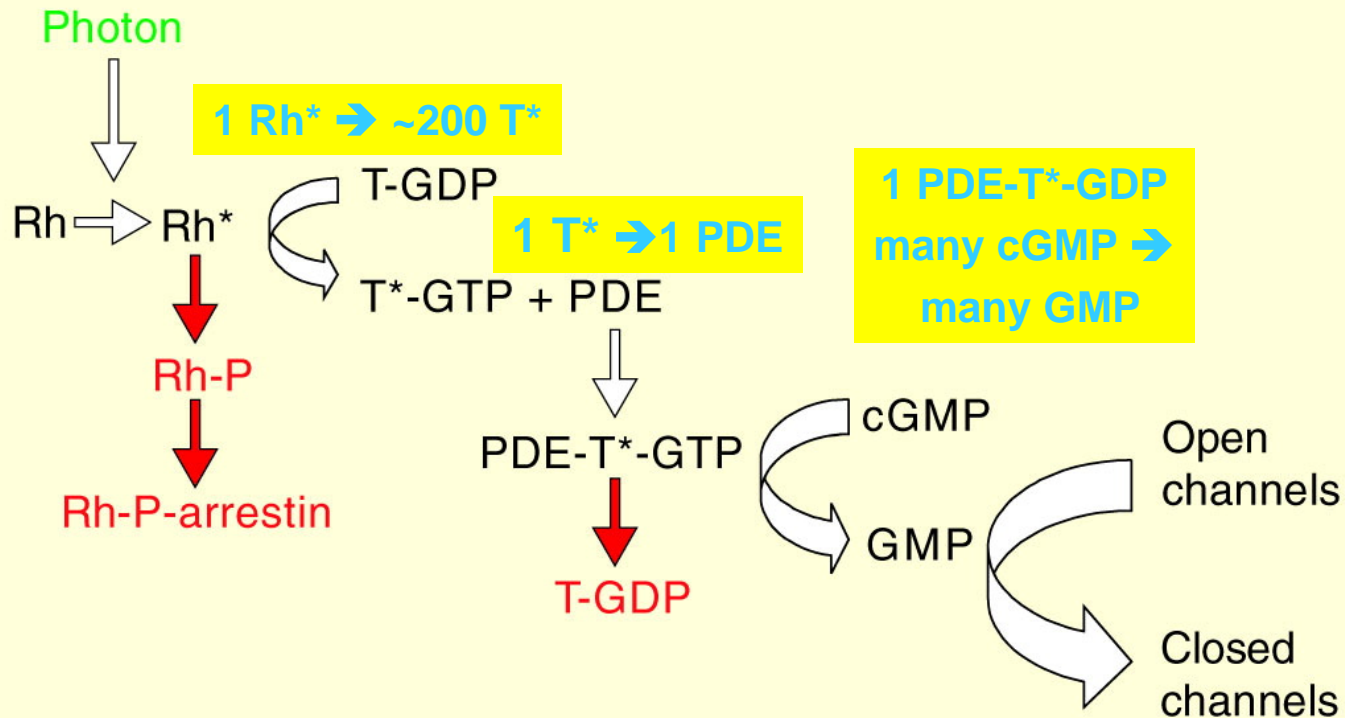


signal amplification in visual excitation cascade



amplification

1 photon



closes
200 Na⁺ channels
10⁶ Na⁺ ions

erent Biology



summary

