

Chemistry 1B-AL, Fall 2016

Topics 19-20- Spectroscopy

Topics 19-20
Spectroscopy
Fall 2016

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SPECTROSCOPY:
short wavelength regions
ESCA (photoelectron) and UV

handout

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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. Show what type of information technique is used to determine each of the variables

Wavelength	Wavenumber	Frequency	Energy	Photon Momentum
10 ¹² m	10 ¹⁶ m ⁻¹	3 × 10 ¹⁴ s ⁻¹	2 × 10 ⁻¹⁸ J	1.3 × 10 ⁻²⁷ kg m s ⁻¹
10 ¹¹ m	10 ¹⁷ m ⁻¹	3 × 10 ¹⁵ s ⁻¹	2 × 10 ⁻¹⁷ J	1.3 × 10 ⁻²⁶ kg m s ⁻¹
10 ¹⁰ m	10 ¹⁸ m ⁻¹	3 × 10 ¹⁶ s ⁻¹	2 × 10 ⁻¹⁶ J	1.3 × 10 ⁻²⁵ kg m s ⁻¹
10 ⁹ m	10 ¹⁹ m ⁻¹	3 × 10 ¹⁷ s ⁻¹	2 × 10 ⁻¹⁵ J	1.3 × 10 ⁻²⁴ kg m s ⁻¹
10 ⁸ m	10 ²⁰ m ⁻¹	3 × 10 ¹⁸ s ⁻¹	2 × 10 ⁻¹⁴ J	1.3 × 10 ⁻²³ kg m s ⁻¹
10 ⁷ m	10 ²¹ m ⁻¹	3 × 10 ¹⁹ s ⁻¹	2 × 10 ⁻¹³ J	1.3 × 10 ⁻²² kg m s ⁻¹
10 ⁶ m	10 ²² m ⁻¹	3 × 10 ²⁰ s ⁻¹	2 × 10 ⁻¹² J	1.3 × 10 ⁻²¹ kg m s ⁻¹
10 ⁵ m	10 ²³ m ⁻¹	3 × 10 ²¹ s ⁻¹	2 × 10 ⁻¹¹ J	1.3 × 10 ⁻²⁰ kg m s ⁻¹
10 ⁴ m	10 ²⁴ m ⁻¹	3 × 10 ²² s ⁻¹	2 × 10 ⁻¹⁰ J	1.3 × 10 ⁻¹⁹ kg m s ⁻¹
10 ³ m	10 ²⁵ m ⁻¹	3 × 10 ²³ s ⁻¹	2 × 10 ⁻⁹ J	1.3 × 10 ⁻¹⁸ kg m s ⁻¹
10 ² m	10 ²⁶ m ⁻¹	3 × 10 ²⁴ s ⁻¹	2 × 10 ⁻⁸ J	1.3 × 10 ⁻¹⁷ kg m s ⁻¹
10 ¹ m	10 ²⁷ m ⁻¹	3 × 10 ²⁵ s ⁻¹	2 × 10 ⁻⁷ J	1.3 × 10 ⁻¹⁶ kg m s ⁻¹

2. How are IR and UV spectra recorded?

3. What are the main differences between IR and UV spectra?

4. How are IR and UV spectra recorded?

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

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

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

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 (R)
3×10^6	10^{11}	microwave	microwave ESR	rotations of molecules and flipping unpaired electron spins in external magnetic field
3×10^8	10^8	radiowave	NMR (MRI)	flipping of nuclear spins in an external magnetic field

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spectroscopic excitations: ESCA

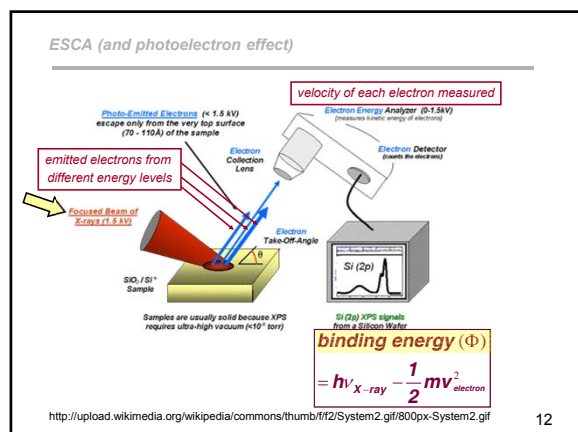
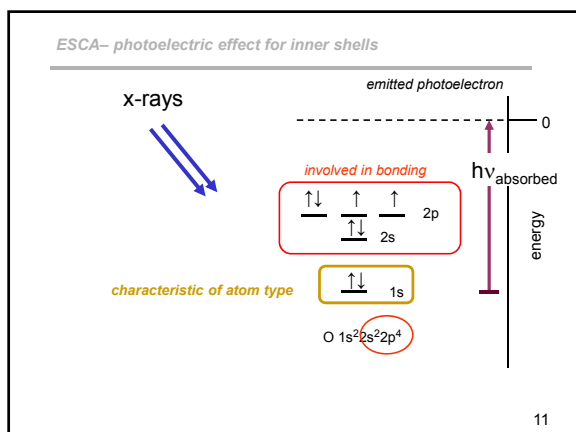
λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)

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ESCA

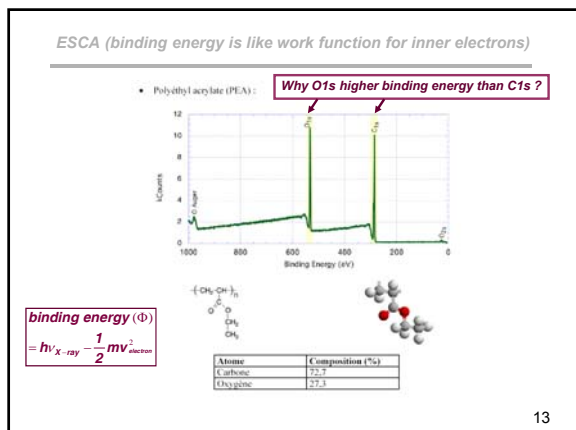
Electron Spectroscopy for Chemical Analysis

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spectroscopic excitations: ESCA

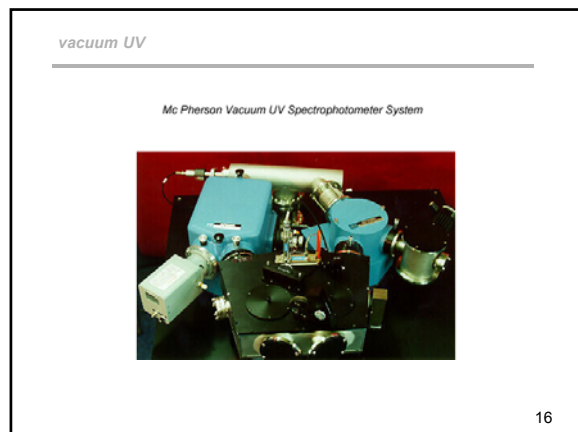
λ (nm)	ν (sec ⁻¹)	radiation	technique	molecular excitation
.3	10^{18}	x-rays	ESCA	excitation of inner shells breaking of bonds (x-ray damage)

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vacuum UV

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

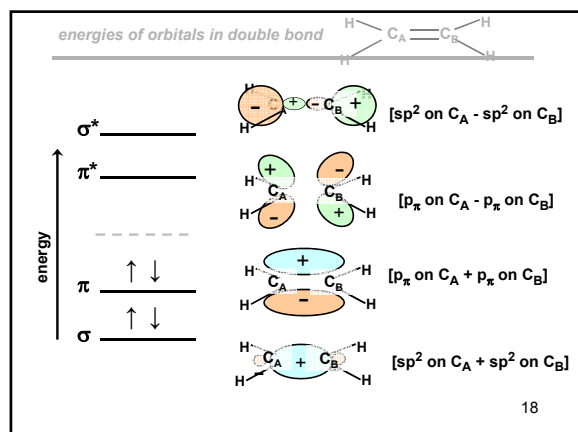
15



excited-state orbitals in polyatomic molecules

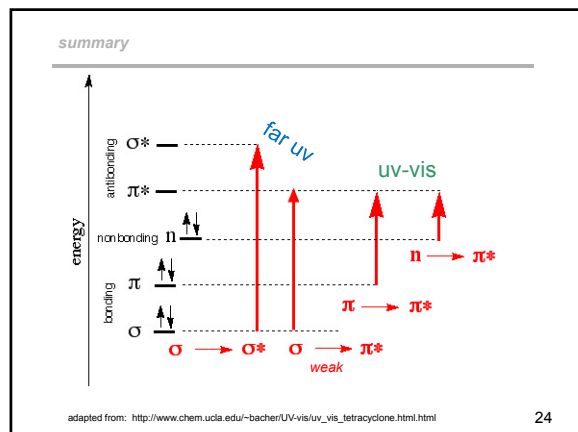
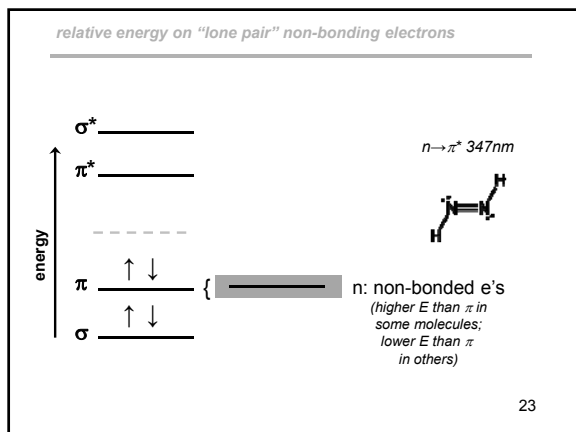
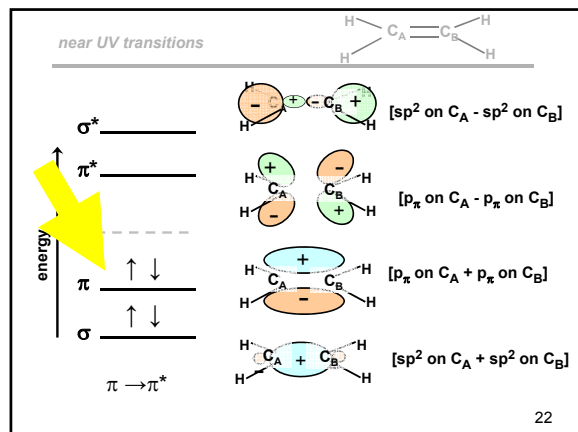
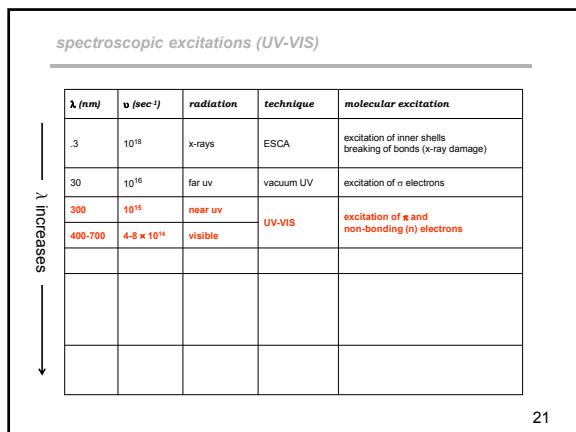
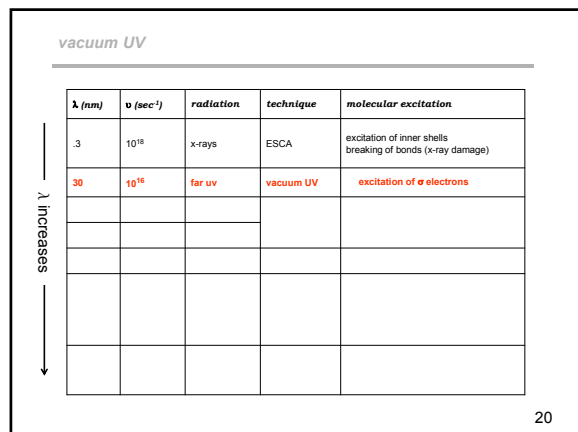
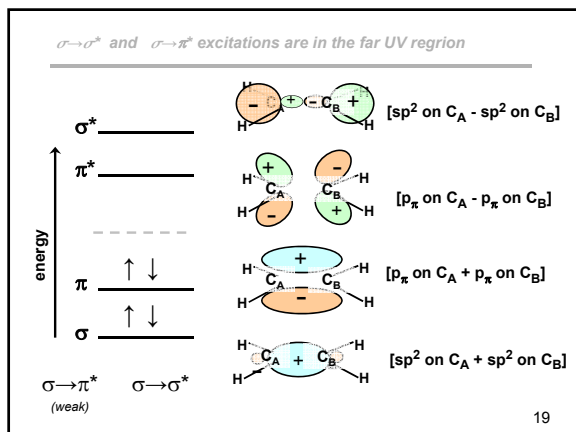
- destructive interference leads to antibonding orbitals which are not usually occupied in the ground state of molecules but which may become occupied upon excitation of electrons by light
- types of antibonding orbitals:
 - CH_4 : $\sigma^* = \text{sp}^3$ on C - 1s on H
 - C_2H_4 : $\sigma^* = \text{sp}^2$ on C_A - sp^2 on C_B
 - $\pi^* = p_\pi$ on C_A - p_π on C_B

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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)
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		

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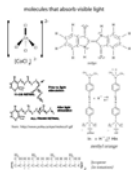
UV-VIS spectrometers (Chem 1M/1N exps. #9 and #11)



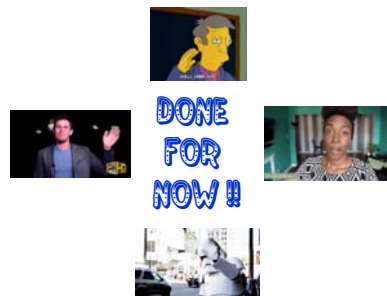
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continue in next class: absorptions in the visible region

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



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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.

electronic transition **HOMO** → **LUMO**

Highest Occupied Molecular Orbital → Lowest Unoccupied Molecular Orbital

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

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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

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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)
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)

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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

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

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

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 $\tilde{\nu}$)

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vibrational frequencies of homonuclear diatomic molecules and ions

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

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

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

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

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vibrational motion in molecules (H₂O)

wave number
 $\tilde{\nu} = \frac{1}{\lambda_{cm}} [\tilde{\nu}] = cm^{-1}$
 $E = hc\tilde{\nu} \quad c = 2.99792 \times 10^{10} cm \text{ sec}^{-1}$

Characteristic Vibrations of H₂O

$\nu_1 = 3657 \text{ cm}^{-1}$ $\nu_2 = 1648 \text{ cm}^{-1}$

$\nu_3 = 3200 \text{ cm}^{-1}$

ORIGINALLY FROM: http://www.gps.caltech.edu/~edwin/MoleculeHTML/H2O_html/H2O_page.html → 37

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: blmo@hydrogen.cchem.berkeley.edu 38

IR spectrometer

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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: $E_{C \equiv C} > E_{C=C} > E_{C-C}$ 41

IR spectra

Acetone IR spectrum

Ethanol IR spectrum

3-hydroxy-2-butanone IR spectrum

C—H ~3200 cm⁻¹

C=O ~1700 cm⁻¹

O—H ~3600 cm⁻¹

→ → 42

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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)
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

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radiowave

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 × 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 ⁸	10 ⁶	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

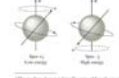
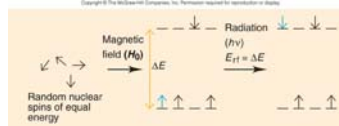


FIGURE 14.16

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

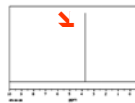


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identifying equivalent and non-equivalent protons

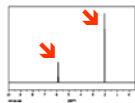
to 'flip' hydrogen atoms (nuclei) in different chemical environments requires slightly different energies (chemical shift)

1,2 dichloroethane 1H NMR



(all H equivalent,
H₂C1C-
1 peak
one 'chemical shift')

1,1 dichloroethane 1H NMR



(two H environments,
HCl₂C- and -CH₃
2 peaks
two 'chemical shifts')

Spectra from: <http://www.ahf.org/ROES/2002/chem1.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

$E_{in} = h\nu_{in}$ $E_{out} = h\nu_{out}$
 excited ground
 $(\nu_{out} \leq \nu_{in})$
 $(\lambda_{out} \geq \lambda_{in})$
 time $\sim 10^{-12}$ to 10^{-9} sec
 (fluorescence stops soon after exciting light is turned off)

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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

$E_{in} = h\nu_{in}$
 excited ground
 radiationless decay
 thermal energy

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phosphorescence

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

$E_{in} = h\nu_{in}$ $E_{out} = h\nu_{out}$
 excited intermediate state ground
 nonradiative decay
 slow spin flip
 $(\nu_{out} < \nu_{in})$
 $(\lambda_{out} > \lambda_{in})$
 time $\sim 10^{-3}$ 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

$$\text{luciferin} + \text{luciferase} + \text{ATP} \longrightarrow \text{luciferyl adenylate-luciferase} + \text{pyrophosphate}$$

$$\text{luciferyl adenylate-luciferase} + \text{O}_2 \longrightarrow \text{oxyluciferin} + \text{luciferase} + \text{AMP} + \text{light}$$

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chemiluminescence: light sticks

The luciferin chain decomposes into two carbon dioxide molecules

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

<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 dirofagellates may work. As dirofagellates float, mechanical stimulation generated by the movement of surrounding water sends electrical impulses around an internal compartment within the organism, called a vesicle—which holds an abundance of protons. These electrical impulses open so-called voltage-sensitive proton channels that connect the vesicle to tiny pockets dotting the vesicle membrane, known as scintillons.

Once opened, the voltage-sensitive proton channels may funnel protons from the vesicle into the scintillons. Protons entering the scintillons then activate luciferase-3 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 dirofagellates.

<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

$\text{Ni}(\text{NH}_3)_6\text{Br}_2$ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

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

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d-Orbitals and ligand Interaction (octahedral field)

$\text{Ni}(\text{NH}_3)_6\text{Cl}_2 \xrightarrow{\text{H}_2\text{O}} [\text{Ni}(\text{NH}_3)_6]^{2+} (\text{aq}) + 2\text{Cl}^- (\text{aq})$

$\text{Ni}^{2+} [\text{Ar}]3d^8$

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](http://chem.com/IB/ibfiles/periodicity/per_ppt/Crystal_field_theory.ppt)

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absorption of visible light in octahedral transition metal complexes

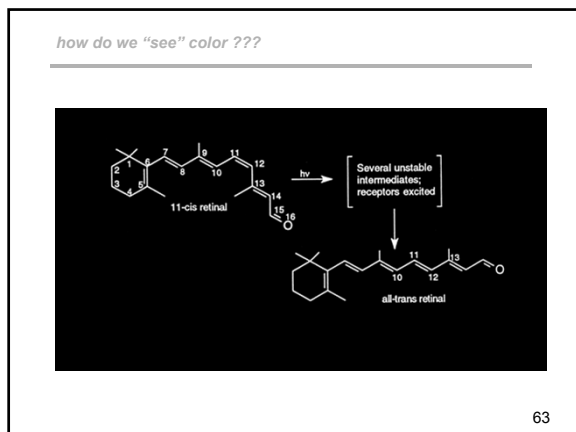
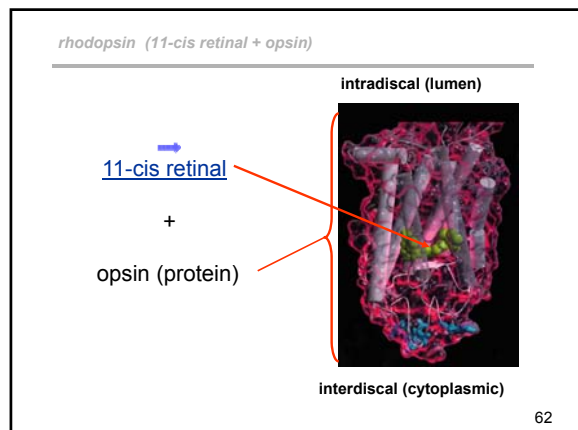
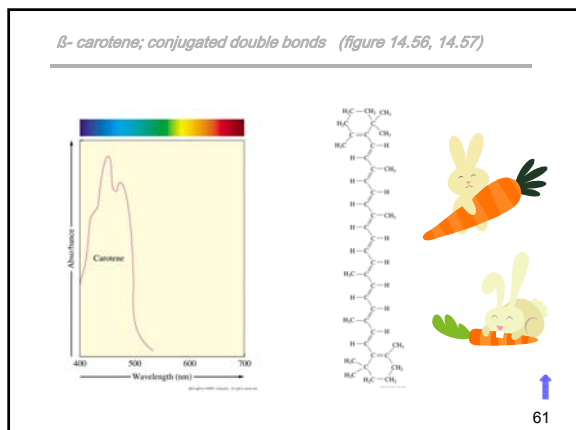
$[\text{Ni}(\text{NH}_3)_6]^{2+}$

- 3d orbitals all have same energy in $\text{Ni}^{2+} (\text{g})$
- 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

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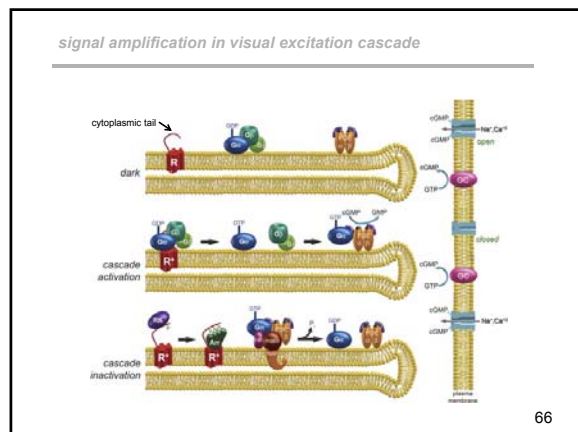
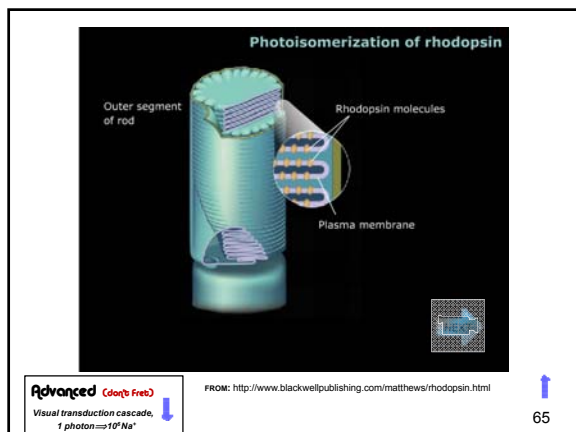
Topics 19-20- Spectroscopy



AHA! that's what its all about

The graphic features the text "CHEMISTRY 1B-AL FALL 2016" in blue. Below the text is a chemical reaction showing the photoisomerization of 11-cis retinal to all-trans retinal, with the reaction arrow labeled $h\nu$. The graphic also includes a small image of a person's face and a logo for "HODGKIN'S".

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