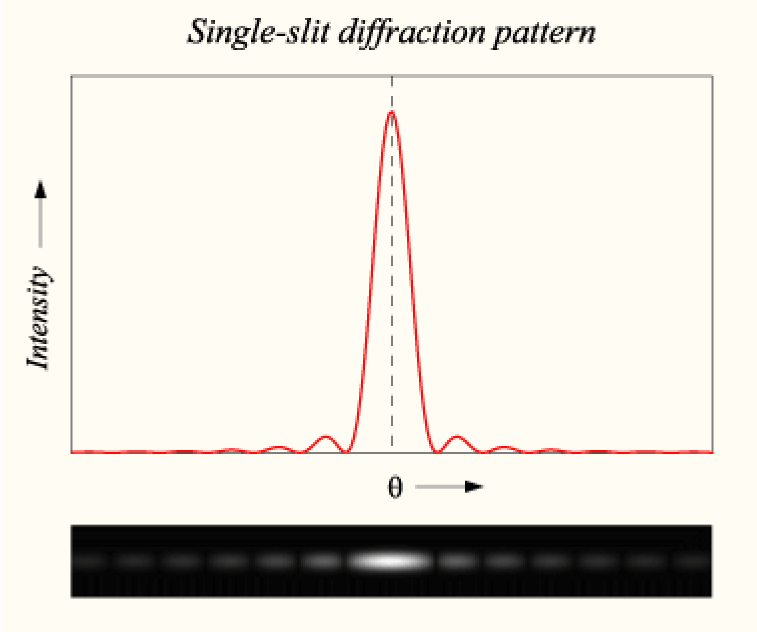
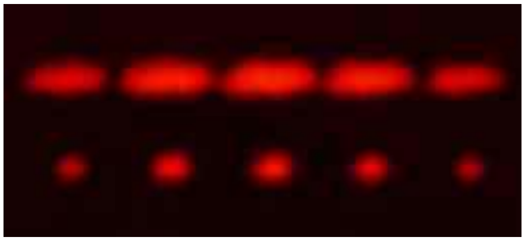
1. UV-vis spectrometer
   1.1. Grating spectrometer –
   1.2. Single slit: $I_\theta = I_0\left[\frac{sin\left(\pi\frac{d}{\lambda}sin\theta\right)}{\pi\frac{d}{\lambda}sin\theta}\right]^2$
      1.2.1. I_θ – diffracted intensity at θ relative to un-diffracted beam
      1.2.2. I_0 - intensity of light at slit, d = slit width, λ = wavelength
      1.2.3. http://en.wikipedia.org/wiki/File:Diffraction1.png



   1.3. Multi-slit grating: $\sin\theta_m + \sin\theta_i = m\lambda/d$
      1.3.1. Angle of diffracted intensity maximum - θ_m
      1.3.2. θ_i – incident angle, d = distance between slits, m is an integer
      1.3.3. Equation true for any number of slits, but “spots are narrower” for more slits and intensity spreads out
      1.3.4. http://en.wikipedia.org/wiki/File:Diffraction2vs5.jpg, two slits and 5 slits



1.4. for eq 1.3 let $\theta_i = 0$: $\sin\theta_m = m\lambda/d$

  1.4.1. locates spot positions not intensities

  1.4.2. Different wavelengths are diffracted at different angles

    1.4.2.1. Where would blue be in pattern above?

  1.4.3. Distance between slits are large (~10^{-3} cm) compared to wavelength (2-7×10^{-7} cm)

  1.4.4. λ/d is small, so θ_m is small

  1.4.5. Place detector far away from grating to get good separation of wavelengths

  1.4.6. : $\sin\theta_m + \sin\theta_i = m\lambda/d$, keep θ_m constant, scan θ_i to detect different wavelengths

1.5. UV-Vis spec grating - Instrumentation.pdf

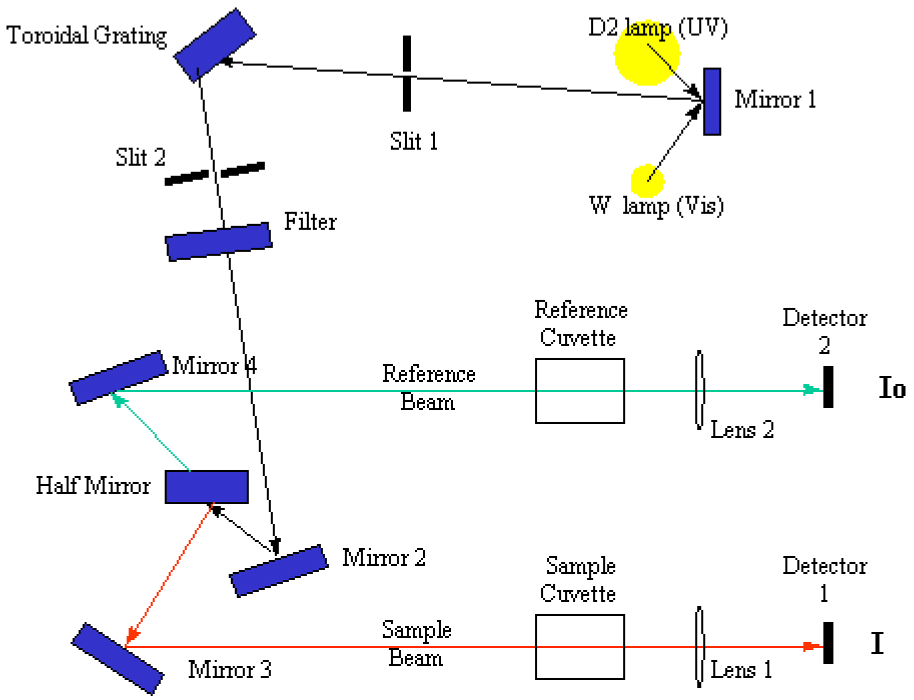
  1.5.1. Photomultiplier tube sensitive to all wavelengths

  1.5.2. Grating is scanned so that only small range of frequency enters at one time

  1.5.3. Photomultiplier tube – record current as a function of time

  1.5.4. Alternately samples two beams – difference spectrum

1.6. Dual beam – dual detector

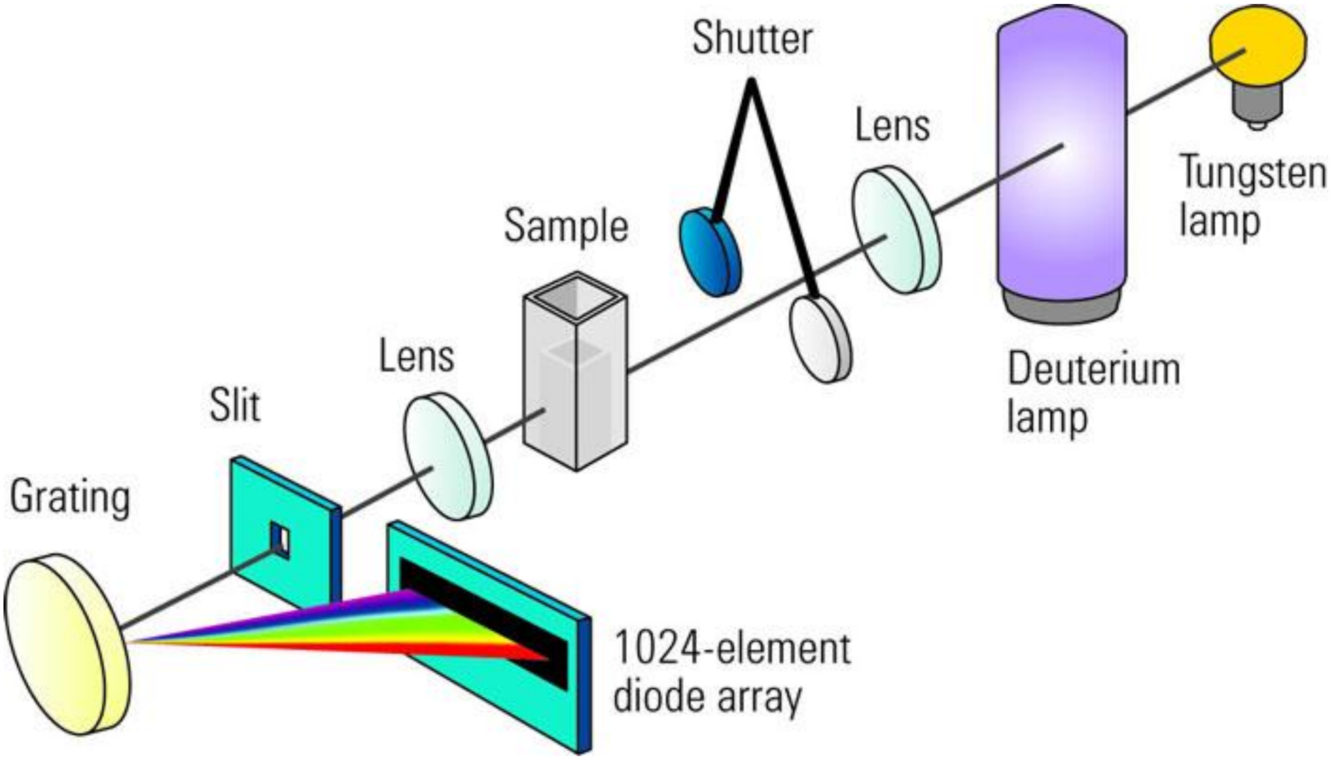


http://bouman.chem.georgetown.edu/S00/handout/spectrometer.htm

1.7. Diode array

   1.7.1. Grating disperses photons according to wavelength

   1.7.2. Each diode is dedicated to specific wavelength range



http://www.chem.agilent.com/en-US/Products/Instruments/molecularspectroscopy/uv-vis/PublishingImages/photodiode_array.jpg

2. Electronic absorption
3. Spectral range
    - 3.1. Near UV – 200-400 nm
    - 3.2. Visible – 400-800 nm
    - 3.3. Energy of photons - $E = h\nu$
        - 3.3.1. $E = \frac{28600(kcal/mol)}{\lambda(nm)}$
        - 3.3.2. 300 nm = 95.3 kcal/mol
        - 3.3.3. 600 nm = 47.7 kcal/mol
    - 3.4. Occupied to unoccupied orbital
    - 3.5. $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$, $d \rightarrow d$, $d \rightarrow \pi^*$,

3.6. virtual orbitals? compare Na and Na^+: 3s and σ^*

4. Appearance of spectra

4.1. Franck-Condon Principle

4.1.1. Electrons move faster than nuclei

4.1.2. Nuclei do not move during transition

4.1.3. Energy gap (between states) correlates with equilibrium position

4.2. Probability for transition from one electronic state to another

4.2.1. $P_n \approx \frac{4\pi^2 E_0 |\mu_{nm}|^2 t^2}{h^2}$: E_o = amplitude of photon electric field, t is time,

4.2.2. $\mu_{nm} = \int_0^t \psi_n | -\mu \bullet E | \psi_m dt$: $| -\mu \bullet E |$ is photon operator, dot product is zero for orthogonal components

4.3. determine if transition is allowed by inspection of ψ_m, ψ_n and E

4.3.1. anti-symmetric function has zero integral: sin(x) function versus x^2 or $\sin^2(x)$

4.3.2. operator for photon is anti-symmetric

4.3.3. product for wave function and photon creates new function with opposite symmetry

4.3.4. two wave functions must have opposite symmetry for non zero integral

4.4. transition probability also depends on wave functions spatial overlap

4.4.1. $P \propto \left| \int \Psi^*_{v'}(r) \Psi_{v''}(r) dr \right|^2$ = Franck-Condon factor: see figure

4.4.2. σ or n orbital in nodal plane of π^*: no overlap: forbidden

4.4.3. Out of plane bending breaks symmetry allowing transition

4.4.4. positions for excited state depends on vibrational state

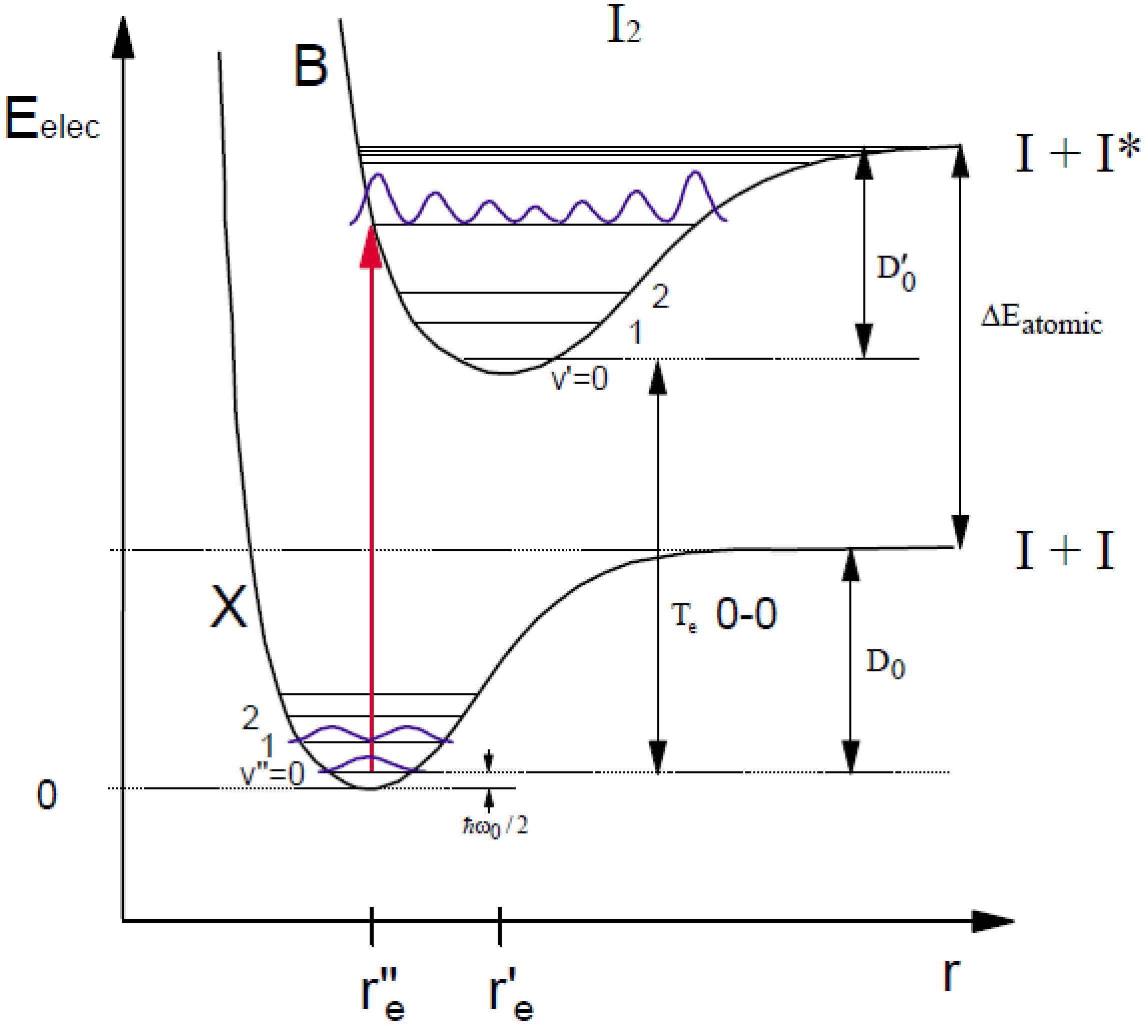
4.4.5. Note amplitude of ground state vibration is maximum at minimum energy???

4.4.6. Excited state has a very different equilibrium position, bond length is different

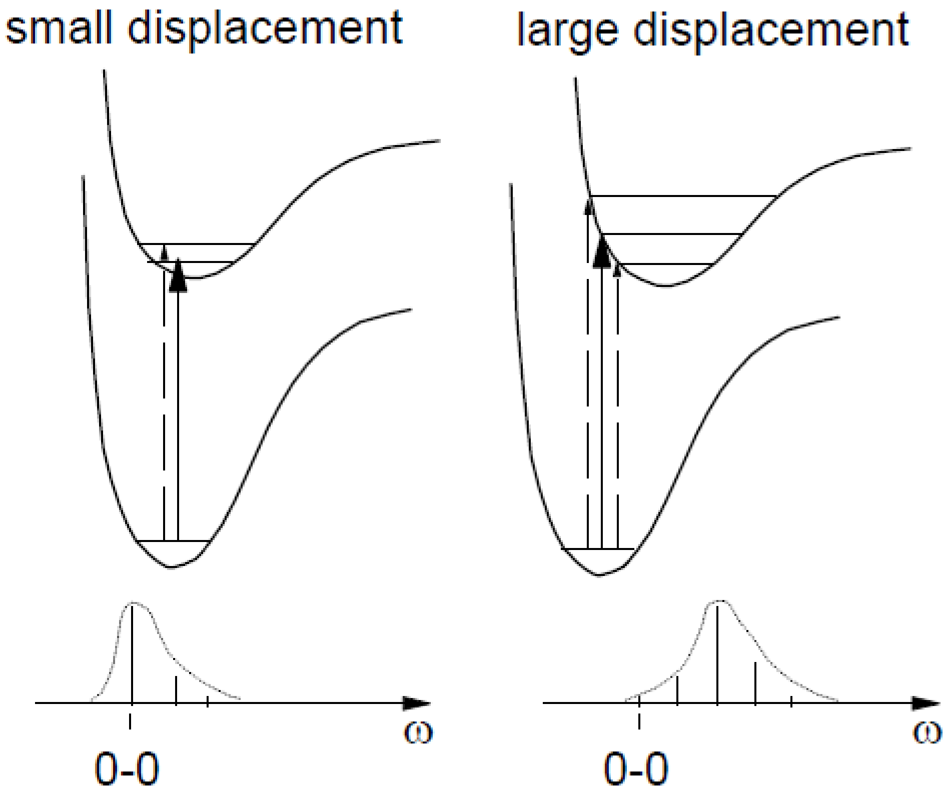
4.4.7. Where do electrons go? See 3.5 above

4.4.8. Excited state is vibrationally excited because greater probability of population higher vibration states

4.4.9. Molecule is formed in “compressed” non-equlibrium position, not enough attraction for electron distribution, repulsive position

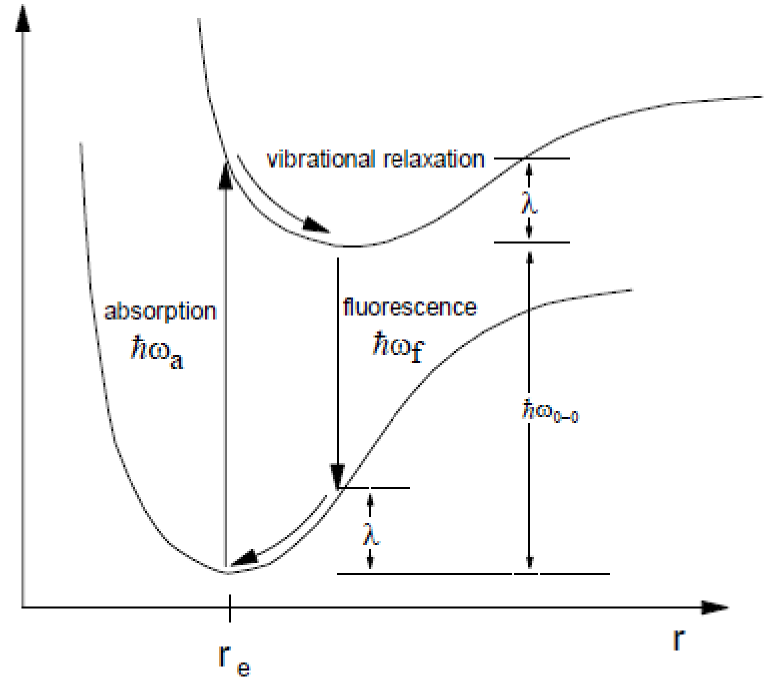


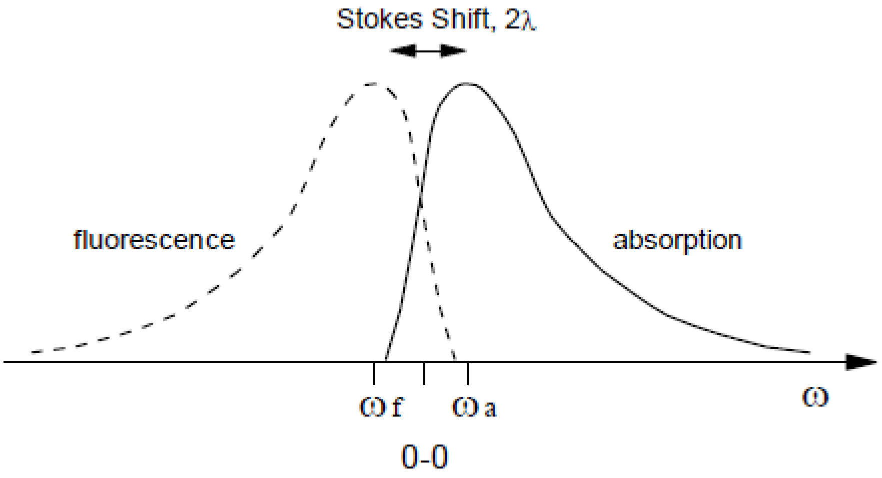
web.mit.edu/5.33/www/lec/spec6.pdf



Position of peak absorption related to displacement

5. Relaxation of excited state
    5.1. Vibrational reorganization - fast
    5.2. Collisions with environment- fast
    5.3. Fluorescence – emission of photon – energy always less than absorption
    5.4. Normally from ground vibrational state of excited state
    5.5. Same selection rules apply – energy and probability depend on vibrational states of excited and ground state



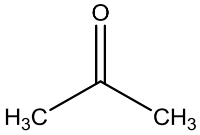
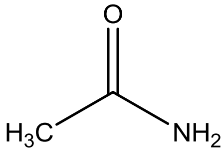
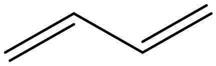
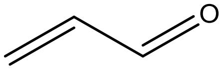
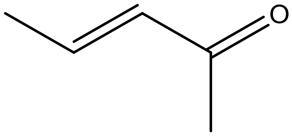


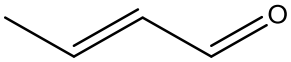
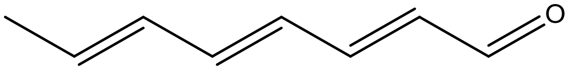
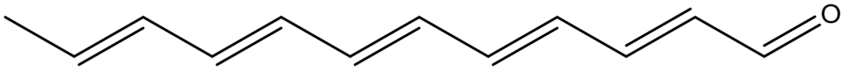
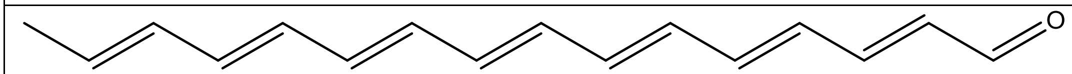
6. Structure – wavelength relationship

    6.1. Alkane transition? <190 nm

    6.2. Effect of heteroatom, type of transition?

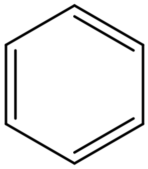
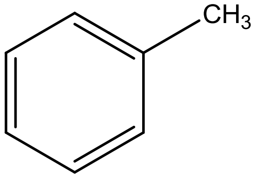
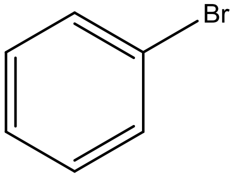
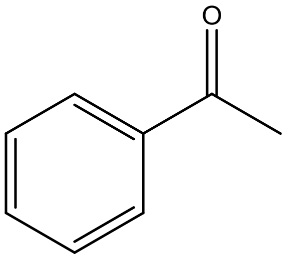
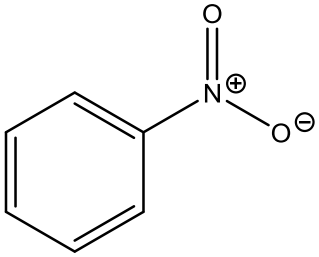
    6.3. and double bond?

chromophore	λ_{max} (nm)	ε_{max} ($cm^{-1}M^{-1}$)
CH_3OH	183	150
CH_3Cl	173	100
$(CH_3)_3N$	227	900
CH_3I	258	378
	279 189	15 900
	220 178	63 9500
	217	20,900
	218 320	18,000 30
	224 314	9,750 38

Extended conjugation	λ_{max} (nm)	ε_{max} ($cm^{-1}M^{-1}$)
	217	15,650
	312	40,000
	370	57,000
	415	63,000

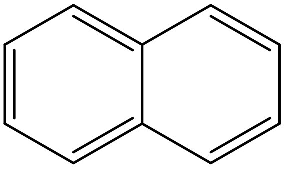
b-carotene – 11 doubles bond, 452 nm (ε_{max} = 139,000) 478 nm (122,000)

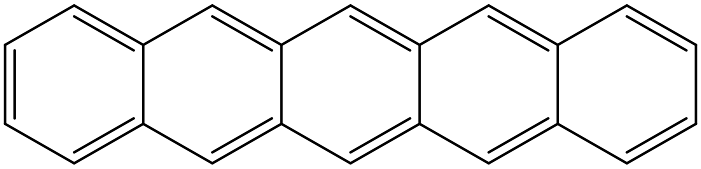
7. aromatics

chromophore	λ_{max} (nm)	ε_{max} ($cm^{-1}M^{-1}$)
	203.5 254	7400 204
	206.5 261	7,000 225
	210 261	7,900 192
	245.5	9,800
	268.5	7,800

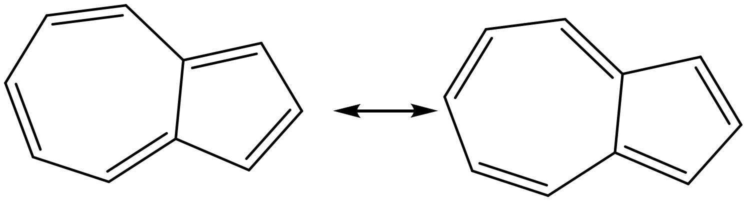
8. polyaromatics

8.1. naphthalene (colorless) v. pentacene (blue)





8.2. Azulene v. napthalene? Use SHMO



9. Beer-Lambert law

   9.1. for an increment of solution with width *dx* the change in light intensity $-dI = \alpha I c dx$

      9.1.1. α is the cross-sectional area per molecule in cm^2

      9.1.2. c is concentration of molecules per cm^3

      9.1.3. dI is independent of c only if a fraction of molecules absorb light

      9.1.4. intensity I_x after passing through distance x is related to initial intensity I_o then

$$\int_{I_0}^{I_x} -\frac{dI}{I} = \int_0^x \alpha c dx \Rightarrow -[lnI_x - lnI_0] = \alpha cx$$

      9.1.5. $ln\frac{I_o}{I_l} = \alpha cx \Rightarrow \frac{I_o}{I_l} = e^{\alpha cx} \Rightarrow I_l = I_0 e^{-\alpha cx}$

      9.1.6. molecular to molar conversion concentration: ε= molar extinction coefficient, M = molar concentration, common logarithm

      9.1.7. $\frac{I_T}{I_0} = 10^{-\varepsilon Ml}$ l = pathlength, I_T = intensity of transmitted light

      9.1.8. $log\frac{I_T}{I_0} = -\varepsilon Ml,\ \ \varepsilon Ml = A = log\frac{I_0}{I_T}$

      9.1.9. decadic response

         9.1.9.1. Abs = 1, 10% transmission, 90% absorption

         9.1.9.2. Abs = 2, 1 % transmission

         9.1.9.3. Abs = 3, 0.1 % transmission

         9.1.9.4. Abs = 0.5, 32 % transmission

         9.1.9.5. Abs = 0.25, 56 % transmission

         9.1.9.6. Abs = 0.1, 79% transmission

9.1.9.7. Abs = 0.01, 97.7% transmission

9.1.10. $I_A = I_o - I_T$ (absorbed intensity is equal to incident intensity minus transmitted)

9.1.11. $I_A = I_0 - I_0 10^{-\varepsilon M l} = I_0(1 - 10^{-\varepsilon M l})$

9.1.12. For a mixture: $log\frac{I_0}{I_T} = \varepsilon_1 M_1 l + \varepsilon_2 M_2 l + \varepsilon_3 M_3 l + \cdots$

9.2. Problem

9.2.1. dilute solution of Abs = 2 by factor of two, what fraction of light is absorbed

9.2.2. two solutions containing different components but each has Abs = 2. Dilute each with equal amount of water. (a) after mixing what fraction of light is absorbed by each solution? (b) after mixing together equal amounts of each solution what fraction of light is absorbed by components of first solution and by that of second solution?