CHEM 524 -- Course Outline (Part 13)—Molecular Spectroscopy –2013
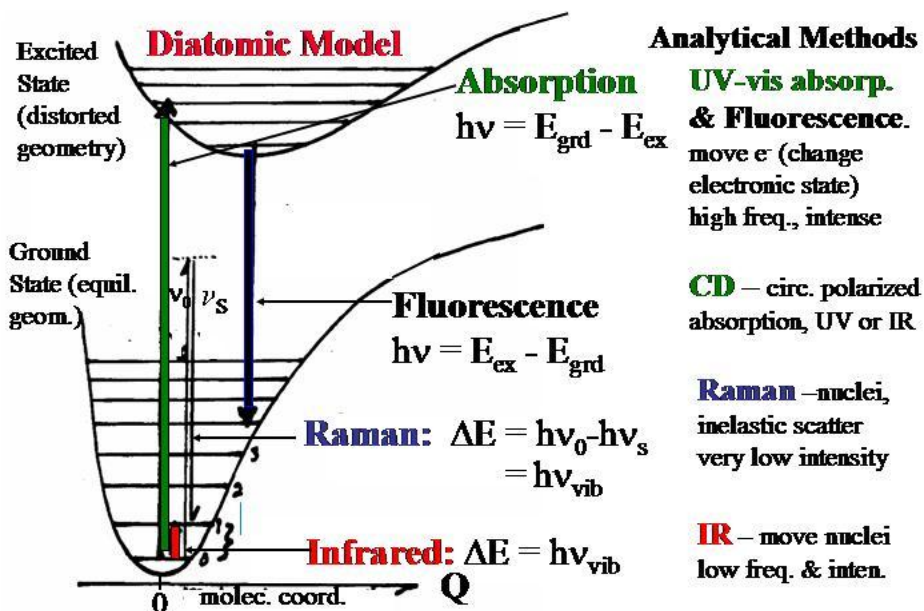
For HTML version of 2005 notes – click here

IX.   Molecular Spectroscopy (Chap. 12 -- read) – look at set of general slides linked here

Spectroscopic regions, vary with wavelength/frequency – different molecular motions

Typical wavelength (cm)	Approximate energy (kcal mole-1)	Spectroscopic region	Techniques and Applications
10^{11}	3×10^{8}	γ-ray	Mössbauer
10^{8}	3×10^{5}	X-ray	x-ray diffraction, scattering
10^{5}	3×10^{2}	Vacuum UV	Electronic Spectra
3×10^{-5}	10^{2}	Near UV	Electronic Spectra
6×10^{-5}	5×10^{3}	Visible	Electronic Spectra
10^{3}	3×10^{0}	IR	Vibrational Spectra
10^{2}	3×10^{1}	Far IR	Vibrational Spectra
10^{1}	3×10^{2}	Microwave	Rotational Spectra
10^{0}	3×10^{3}	Microwave	Electron paramagnetic resonance
10	3×10^{4}	Radio frequency	Nuclear magnetic resonance

A.   Transitions between molecular states -- characterized by nuclear and electronic motion
(two main sources of state energies and distributions)

Optical Spectroscopy - Processes Monitored
UV/ Fluorescence/ IR/ Raman/ Circ. Dichroism

Diatomic Model

Excited State (distorted geometry)

Ground State (equil. geom.)

Analytical Methods

Absorption $h\nu = E_{grd} - E_{ex}$

Fluorescence $h\nu = E_{ex} - E_{grd}$

Raman: $\Delta E = h\nu_0 - h\nu_s$ $= h\nu_{vib}$

Infrared: $\Delta E = h\nu_{vib}$

UV-vis absorp. & Fluorescence. move e⁻ (change electronic state) high freq., intense

CD – circ. polarized absorption, UV or IR

Raman –nuclei, inelastic scatter very low intensity

IR – move nuclei low freq. & inten.

molec. coord. Q

Degrees of freedom—N-nucleii, n-electrons
→(3N+3n), describe by state eqn.

Transition: $\Delta E = h\nu = E_i - E_j$

     where *i,j* designate real (lifetime) states
Potential surfaces → constraint on nuclear
motion (PE), reflect bond stability (energy),
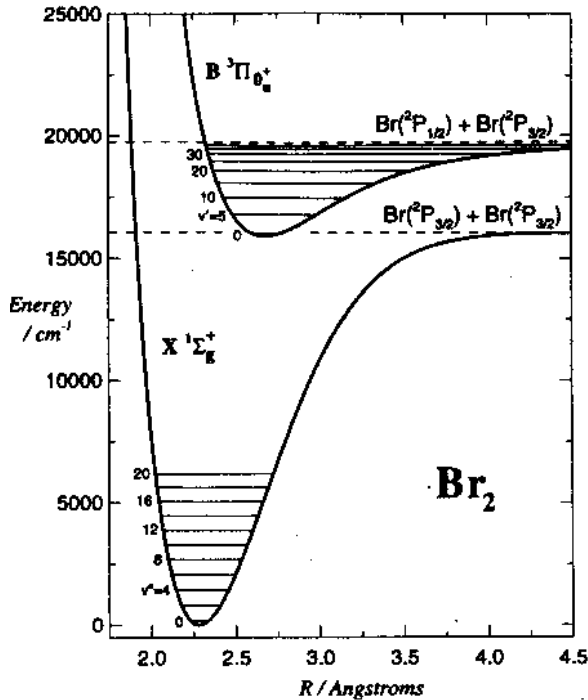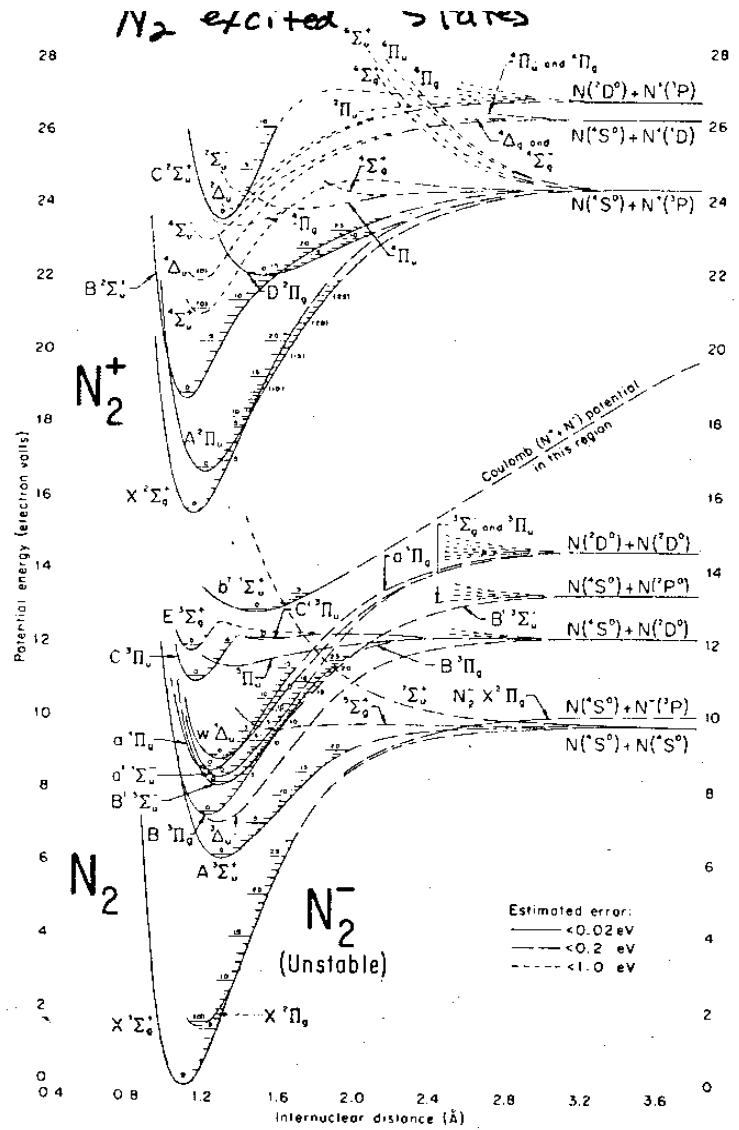normally excited state shallower (weaker),
minimum shifted to longer bond

ure 9.9. The Br, $B^3\Pi_{o+}$ and $X^1\Sigma_g^+$ potential energy curv

N_2 excited states

Potential-energy curves for N_2^- (unstable), N_2 and N_2^+

B.   Types of motion - leads to differentiation of spectroscopy types

Translation not quantized—continuous distribution of energies

1. *Rotation* (motion of whole molecule) – sharp transitions, low energy (μ-wave)

--quantized angular momentum (conserved)
   $Y_{JM}(\theta,\phi)$ where J=0,1,2,3. . , M = 0,±1,±2. . ±J
   $E_J = BJ(J+1) \, [+ K^2(A\text{-}B) \,]$ $B = (h/8\pi^2 c) / I$
   linear + *top*   moment: $I = \Sigma \, mr_i^2$
-- bigger heavier molecules, *lower B and ΔE_J*
   selection rules: IR ΔJ = ±1, 0, + *top* [ΔK = ±1, 0]   Raman, ΔJ = ±2, ±1, 0
Thermally many levels populated: $P_J \sim (2J+1)\exp[-BJ(J+1)/kT]$

pure rotation spectra -- not analytically useful —transitions weak, require long paths, etc.
but impact all states— in vapor phase analysis see contributions
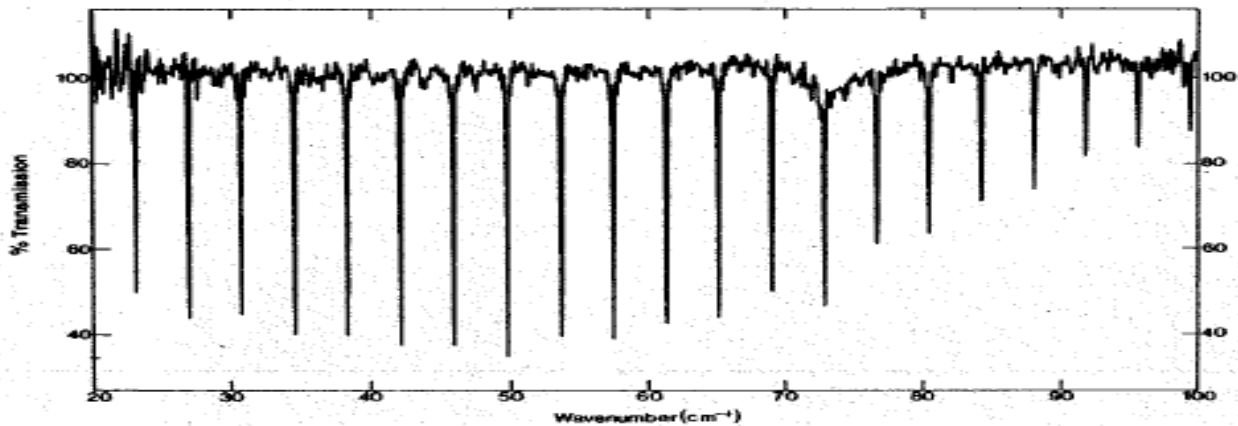
Pure Rotational *Far-IR spectrum* of CO – spacing is 2B
-- note 1st transition (23 cm^{-1}) is for J=5 → J=6 (I think)
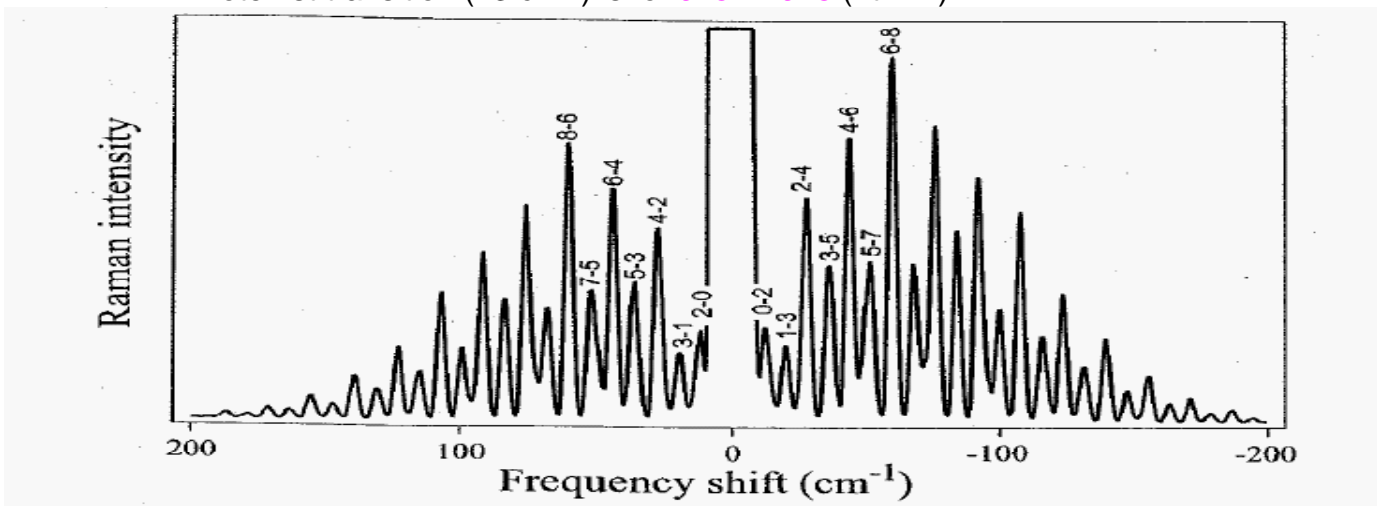
Rotational Raman spectrum of N_2 (alternating intensity-due to isotope) – spacing is 4B
(left) anti-Stokes: $\Delta J = -2$ (right) Stokes: $\Delta J = 2$ n (shifts relative to laser ν_0)

2. **Vibration** - internal motion (nucleii move to each other on a potential surface resulting from electron energy variation with nuclear position)

    – see slides on states, transitions, IR/Raman
- *Web Page has links to above notes*
- *also IR developments links*

-- absorption spectra, ΔE_{01} = hν_{vib} measure in *infrared - light freq match vibration frequency*

-- or with Raman scattering, $\nu_s = \nu_0 \pm \nu_{vib}$ - any region

--states describe motion in nuclear degrees of freedom: (3N-6) unless linear (3N-5)
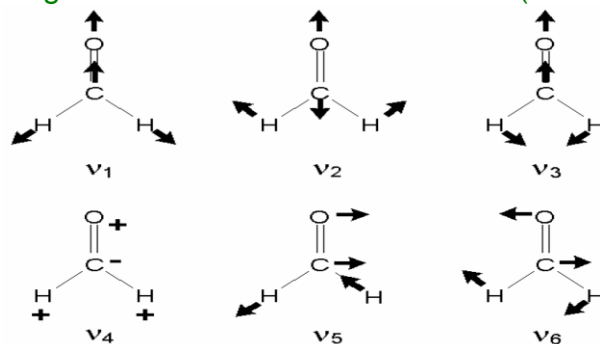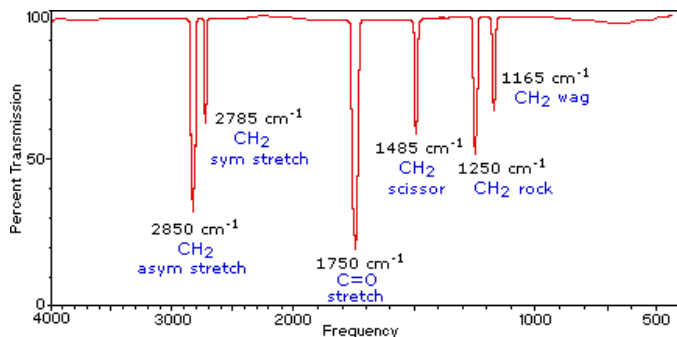   Multidimensional for polyatomics, many states, most spectra lowest transition: 0→1

    a. *Characteristic frequencies* -- property of atoms/bonds –ex. diatomic: $\nu = (2\pi)^{-1}(k/\mu)^{1/2}$
        k → curvature of potential surface - $\partial^2 E/\partial Q^2$ - typically stronger bond, bigger k
        --k increase, frequency increase (eg. C=C ~1600 cm^{-1}, and C≡C ~2200 cm^{-1})
        --mass increase, frequency decrease (eg. HCl ~2800 cm^{-1}, DCl ~2100 cm^{-1})

3

Polyatomics, frequencies characteristic of structural elements, i.e. mass and bond strength
Called *group frequencies:* Book list Typical frequencies for given functional groups
e.g.– formaldehyde, below, qualitative analysis and orgo books often list them in tables (below)

ν_1 ν_2 ν_3

ν_4 ν_5 ν_6

Table 7.5 Infrared group wavenumber table

Group	ν/cm^{-1}	Group	ν/cm^{-1}
≡C—H	3300	—O—H	3600
=C‹H	3020	›N—H	3350
›C—H	2960	›P=O	1295
—C≡C—	2050		
›C=C‹	1650	›S=O	1310
›C—C‹	900	≡C—H	700
—S—H	2500		
—N=N—	1600	≡C‹H H	1100
›C=O	1700		
—C≡N	2100	—C‹H H H	1000
›C—F	1100		
›C—Cl	660	›C‹H H	1450
›C—Br	660		
›C—I	500	C=C—C	300

106   INFRA-RED SPECTROSCOPY

TABLE 3.4: Characteristic Stretching Frequencies of some Molecular Groups

Group	Approximate Frequency (cm⁻¹)	Group	Approximate Frequency (cm⁻¹)
—OH	3600	›C=O	1750–1600
—NH₂	3400	›C=C‹	1650
≡CH	3300	›C=N‹	1600
(benzene ring)—H	3060	›C—C‹ ›C—N‹ ›C—O‹	1200–1000
=CH₂	3030	›C=S	1100
—CH₃	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform.) 1375 (sym. deform.)	›C—F	1050
		›C—Cl	725
—CH₂—	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)	›C—Br	650
		›C—I	550
—SH	2580		
—C≡N	2250		
—C≡C—	2220		

b. Selection rules (result of <u>harmonic</u> oscillator properties, violated when <u>anharmonic</u>)

$$E_{vib} = \sum (\upsilon_i + \tfrac{1}{2}) h\nu_l \qquad \Delta\upsilon_i = \pm 1 \ , \ \Delta\upsilon_j = 0 \ \text{ for } i \neq j \qquad \text{so } \Delta E_i = h\nu_i$$

fundamental transitions in 100-4000 cm⁻¹ range, lightest = highest (H₂)

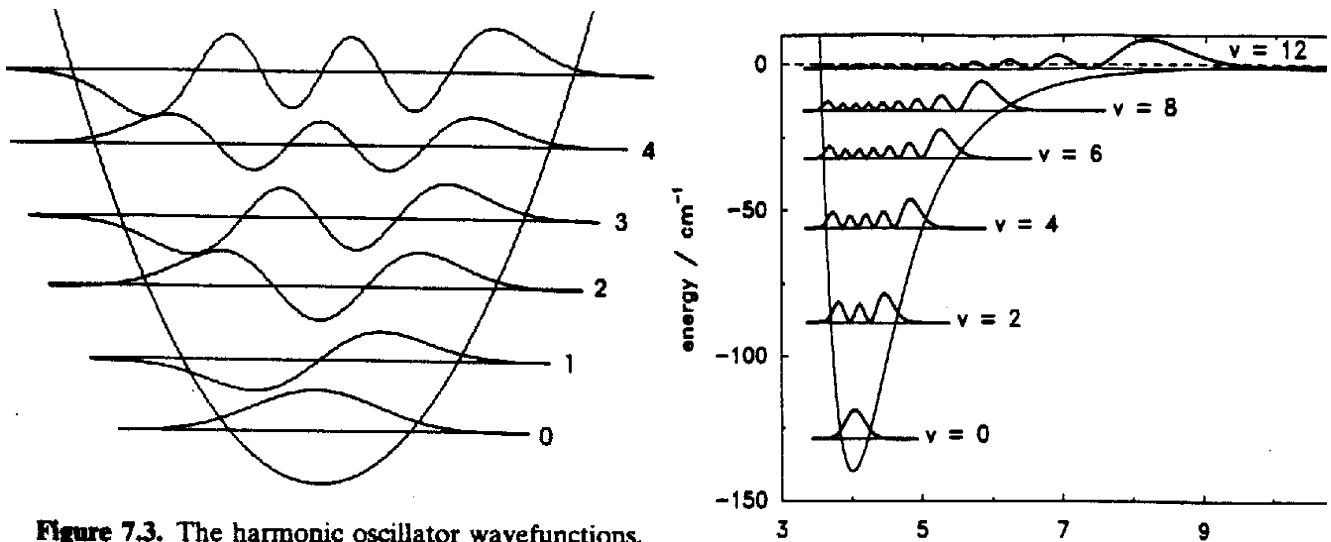**Figure 7.3.** The harmonic oscillator wavefunctions.

harmonic potential: parabola ($1/2\ kQ^2$)   **anharmonic** potential reflect dissociation (E = 0, at Q = ∞→atoms) & nuclear repulsion (E = ∞ at Q = 0)

3. *Vapor* -- rotation-vibration transitions combine (ΔJ = 0,±1), can get complex (NH$_3$)

   IR Diatomic (linear) no pure vib transition seen, many lines above, two dominant branches:
   R - adding (ΔJ=+1) or below P - subtracting (ΔJ = -1) rotational energy, result from many
   rotational states: **|JM>,** populated thermally → $n_J = n_0(2J+1)\exp[-BJ(J+1)/kT]$
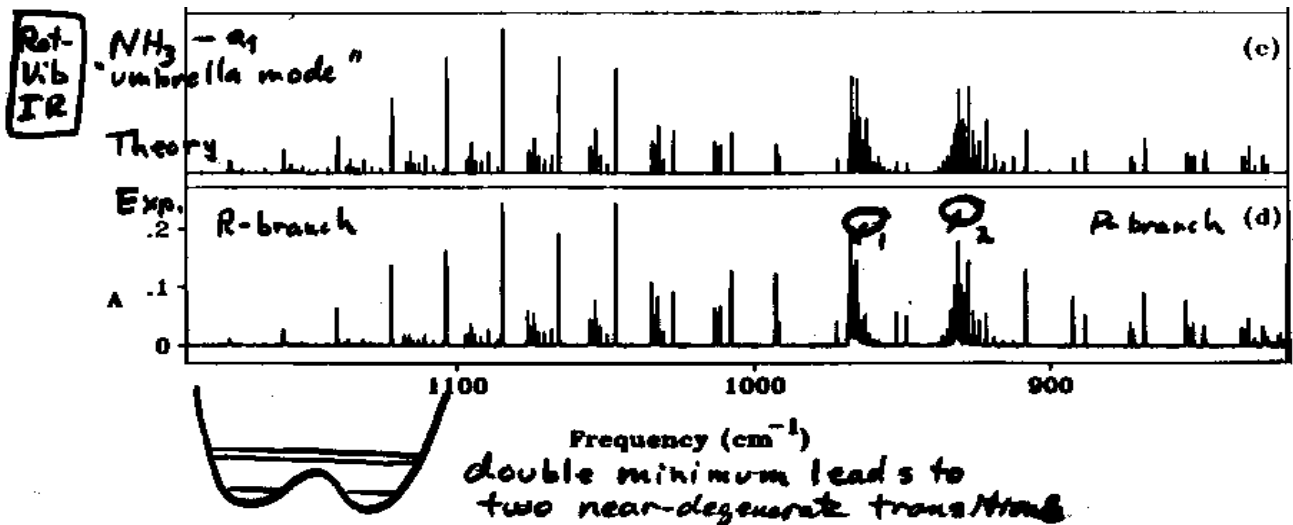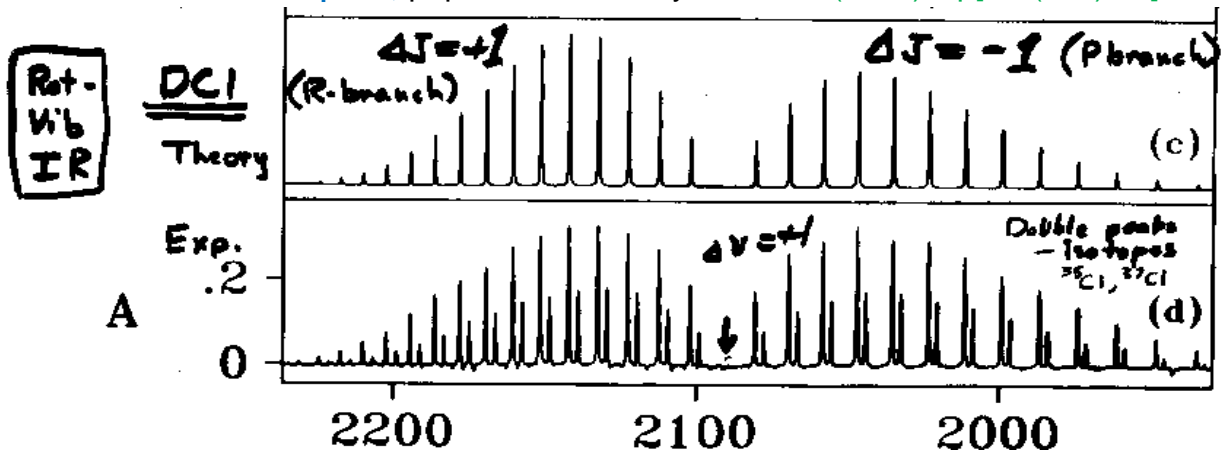
Thus frequencies characteristic of structural elements
Called *group frequencies:* Typical frequencies for given functional groups
e.g.– formaldehyde, below, and table next page and orgo books
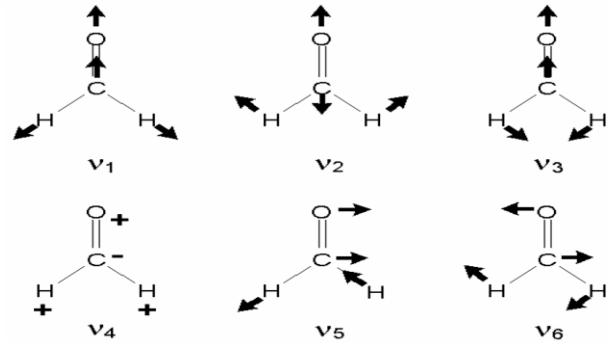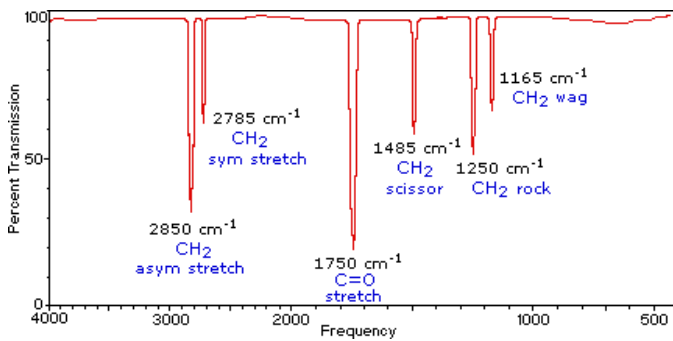
Condense phase --broaden vibrational bands (couple to matrix—libration→rotation, phonons→translation, both hindered in condensed phase, have band of energies)
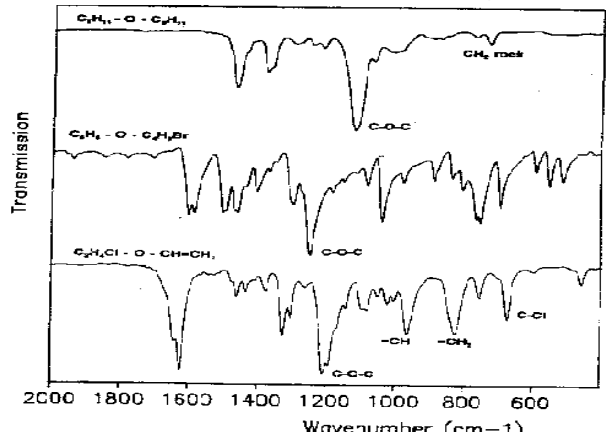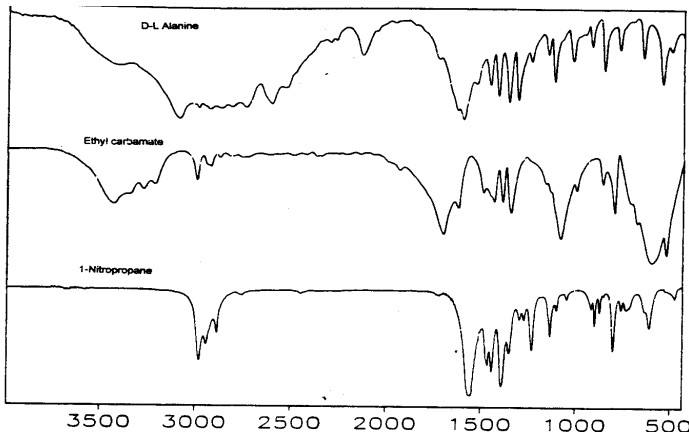

Discriminate structures: various $C_3H_7O_2N$ molecules

Various ethers – "fingerprint"

Protein and polypeptide secondary structural obtained from **vibrational** modes of amide (peptide bond) groups

Aside: Raman is similar, but different amide I, little amide II, intense amide III

What do you see?
Model peptide IR

Amide I
(1700-1600 cm^{-1})

Amide II
(1580-1480 cm^{-1})

Amide III
(1300-1230 cm^{-1})
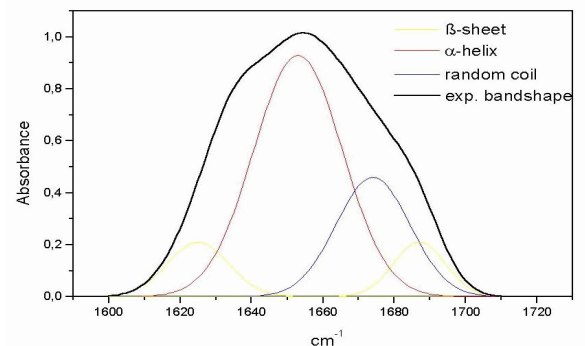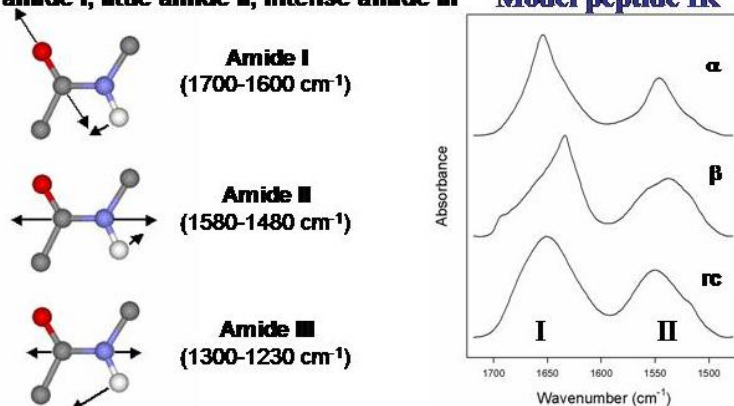
Can deconvolve shapes for mixed structures (e.g. proteins). Similar behaviors in nucleic acids, separate base and backbone structure changes

Larger molecules, polymers - bands overlap, broaden apparent spectra.
Repeating functional groups can characterize polymer (subunits) and the variation in frequencies, intensities can be used to determine structure. Very useful for sensing change especially in biopolymers, e.g. see peptide shifts with secondary structure

Benzene / Benzol

C_6H_6

Benzene
Benzol

IR : Perkin Elmer 521	Liq : A 40µ CsBr; B 500µ CsBr	2 cm⁻¹		C₆H₆	GC > 99%	
FIR : Grubb Parsons IS 3	Liq : C 1500µ PE	5 cm⁻¹	Bspl.: 6.25µ	MW: 78.12	b.p. 80.099°	F 1 - 01
Ra : Coderg PHO	Liq : I; 90°, I 1x ⊥ ; II 0.3x ⊥	2 cm⁻¹	5145 Å; 1000mW	DC; S20; 482 V,AAA	MERCK	(lit.)

Glycine / Glycin

$H_2N \cdot CH_2 \cdot CO \cdot OH$

Glycine
Glycin

IR : Perkin-Elmer 521	Solid A 0.8mg/400mg KJ	2 cm⁻¹		C₂H₅NO₂	m.p. 262 d (lit.)	
FIR; Grubb Parsons IS 3	Solid B 8mg/150mg PE	5 cm⁻¹	Bspl.: 6.25µ/25µ	MW: 75.07		B 7 - 02
Ra : Cary 81	Solid 3mg, I 1x , II 0.2x , Pellet, 100mg, III 0.1x	8/4 cm⁻¹	5145 Å, 700mW	DC, S20, 729V, BBB	FLUKA	

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4.   Analytical -- Vibrational spectra useful for qualitative discrimination (examples, nitrobenzene, ethers, Raman-IR complementary,)
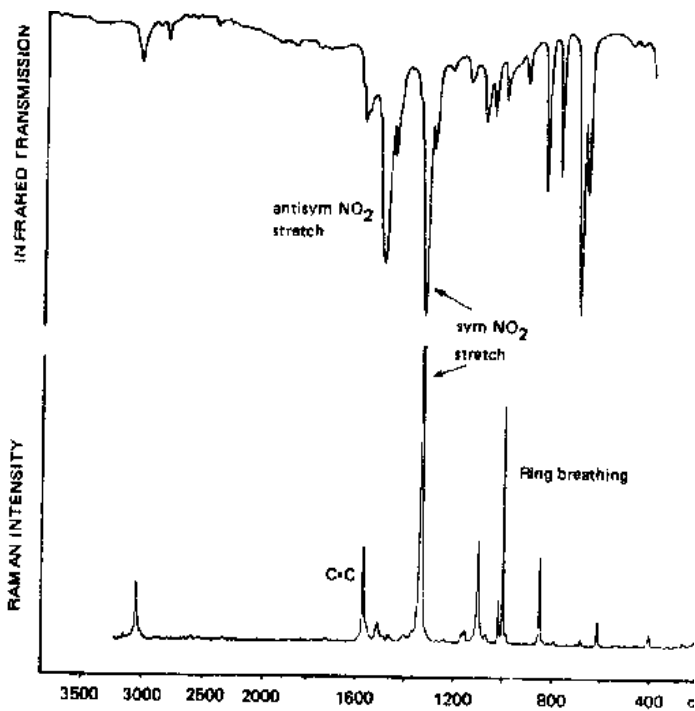

Figure 9-13 (a) Infrared and (b) Raman spectra of nitrobenzene.

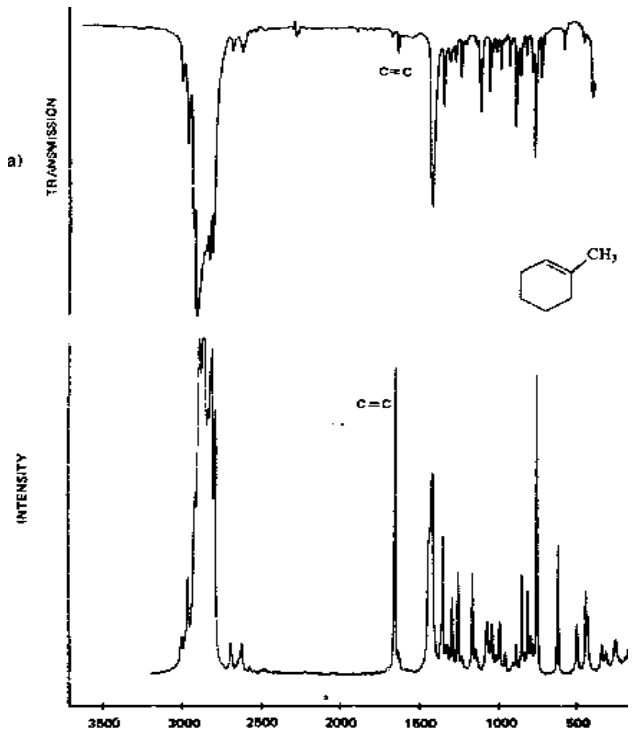Raman - polarizability / IR - dipole

Figure 9-15 (a) Infrared and (b) Raman spectra of 1-meth hexene. Complementary bands for ar

Quantitative: S/N and concentration can be limiting factors (less sensitive than uv-vis)
Raman issue -- internal standard needed, no absolute intensity

C.   Electronic Transitions

1.   To bound state -- include. rot. and vib./ transitions to unbound states poorly defined

H₂ excited state
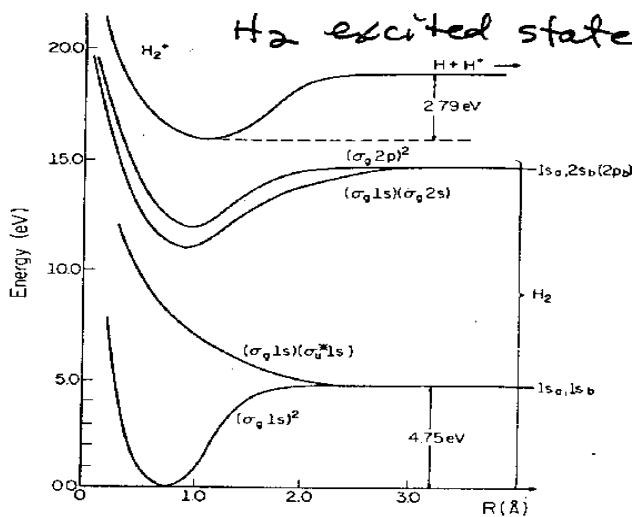
6-2 Energy level diagram showing some of the electronic states in H₂ and state of H₂⁺ obtained by ionizing H₂. Only the singlet state manifold is sh
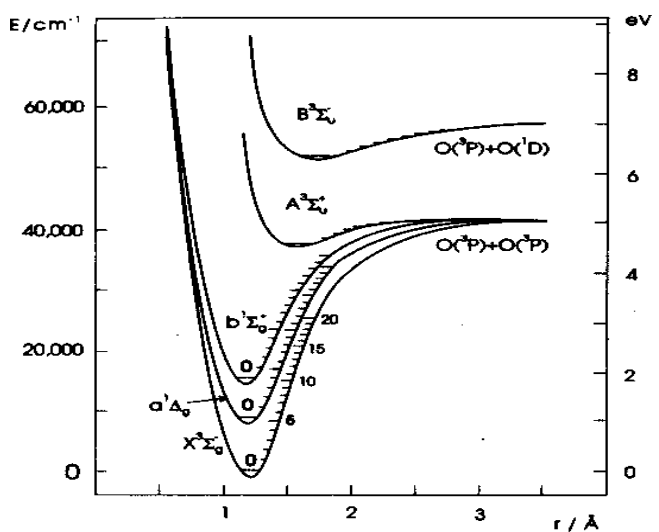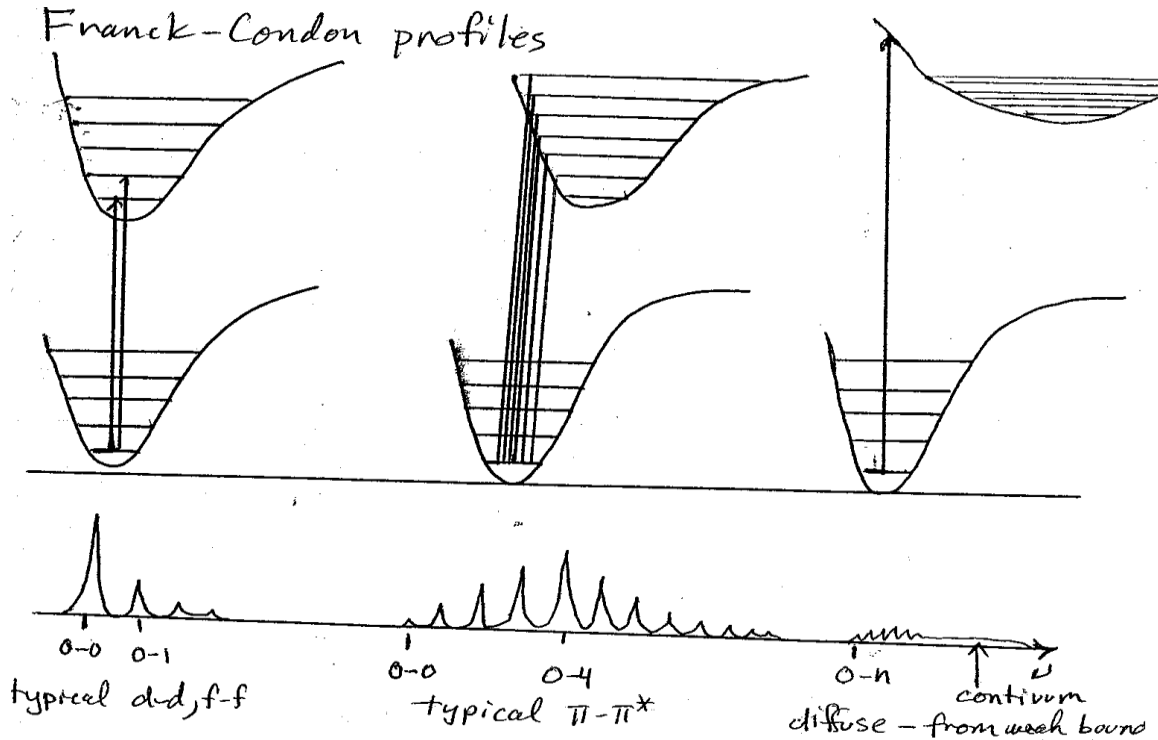
Figure 9.5. The low-lying electronic states of the O₂ molecule.

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vertical transition most intense (no nuclear geom. change) [Franck-Condon] –shape diagnostic

Franck-Condon profiles

0-0   0-1
typical d-d, f-f

0-0   0-4
typical π-π*

0-n   continuum
diffuse – from weak bond

Molecular electronic transitions also involve excitation of vibrations → band profile/info

Optical Spectroscopy – Electronic, Example Absorption and Fluorescence
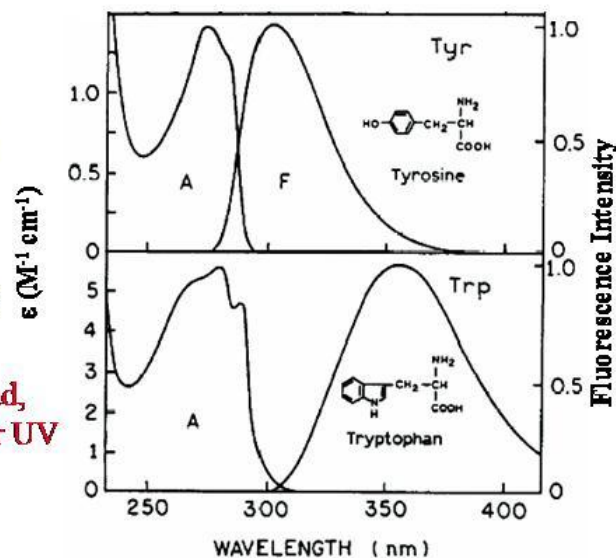
Essentially a probe technique sensing changes in the local environment of fluorophores

What do you see?
[protein example]
**Intrinsic fluorophores**

eg. Trp, Tyr

Change with tertiary structure, compactness

Amide absorption broad, Intense, featureless, far UV ~200 nm and below

Frequency shifts complex, since due to overall vibronic profile on electronic state, overlap
Fluorescence and absorbance often mirror each other from F-C transition intensity profile
        Analytically use the peak, maximum intensity, pure electronic transition between them

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2. Intensity depend on types (allowed or forbidden)
   organic -- closed shell--in VUV (radical lower Energy)
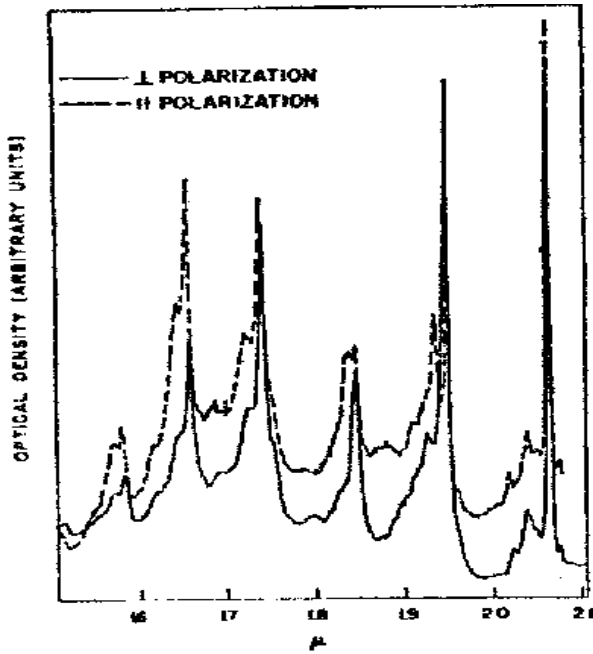   -- π-system in UV, dominant utility--arenes,
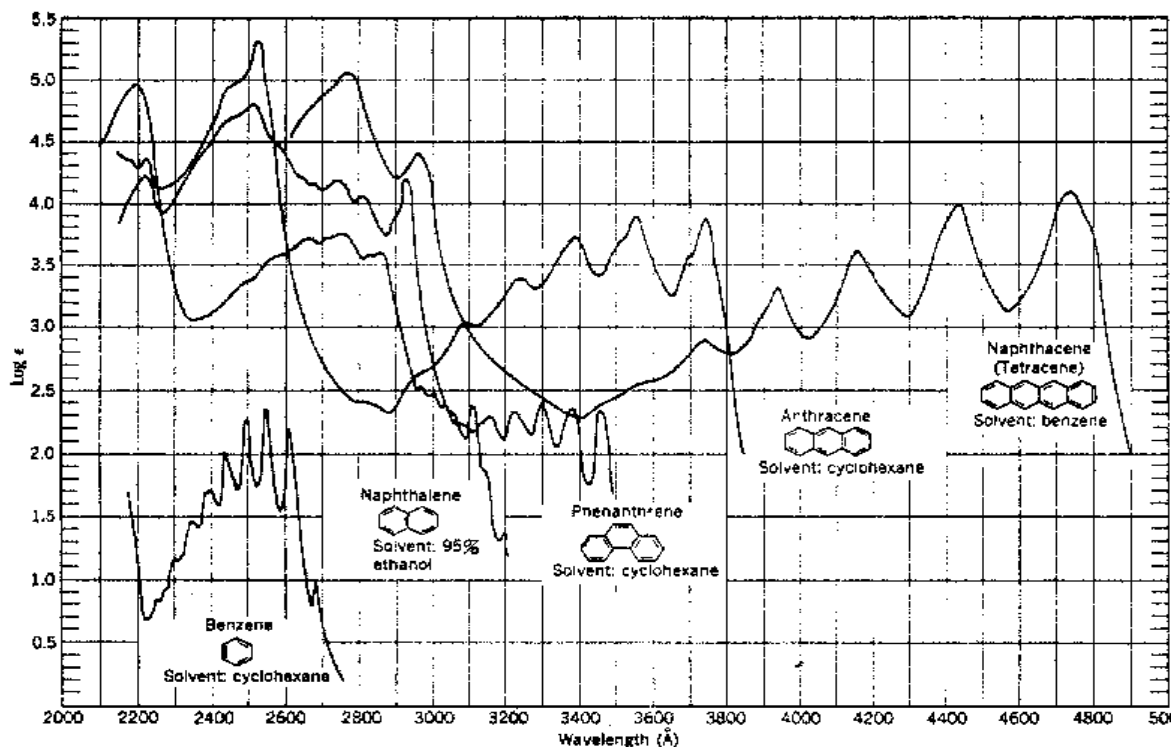
heteroaromatics, Azines -- non-bonded electron pairs, heavy hetero-atoms (lower energy)
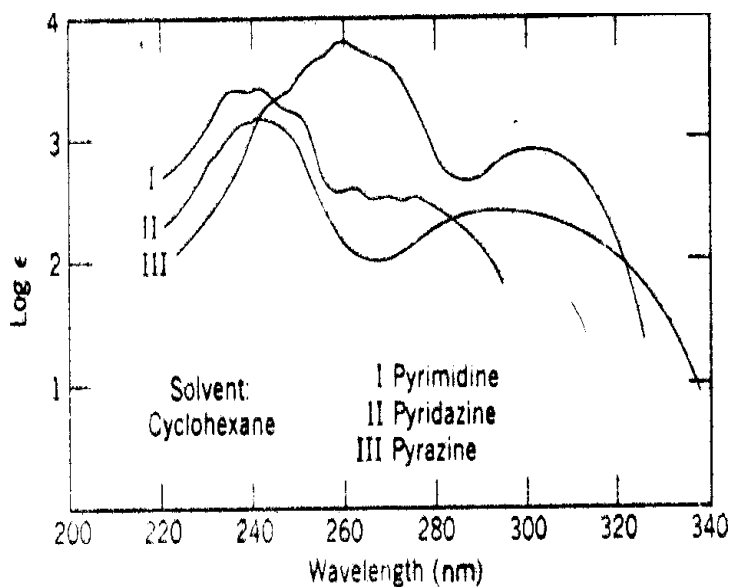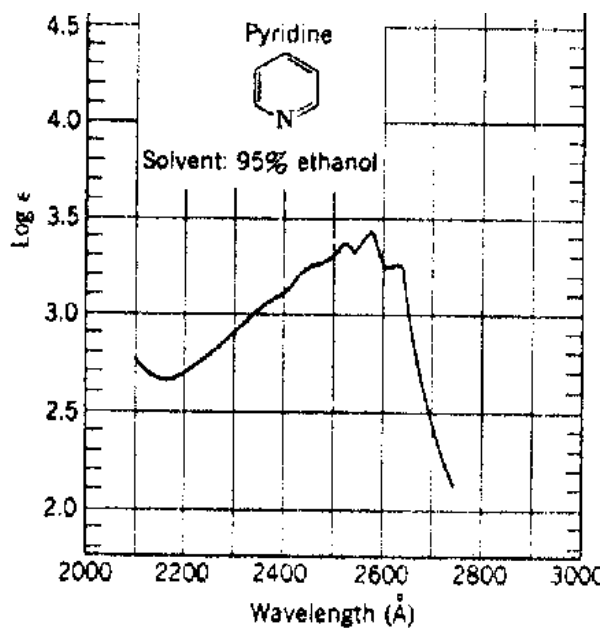
Transition metal complexes -- open shell

        d-d -- vibronic allowed (parity forbidden, $\Delta\ell = 0$)), weak but visible/characteristic
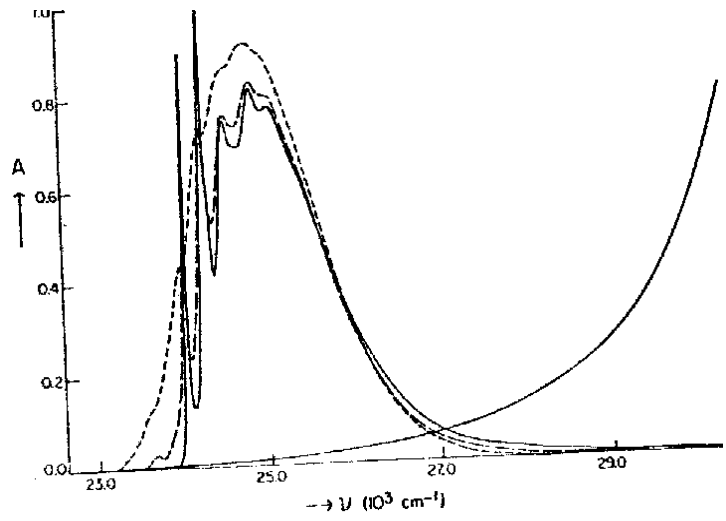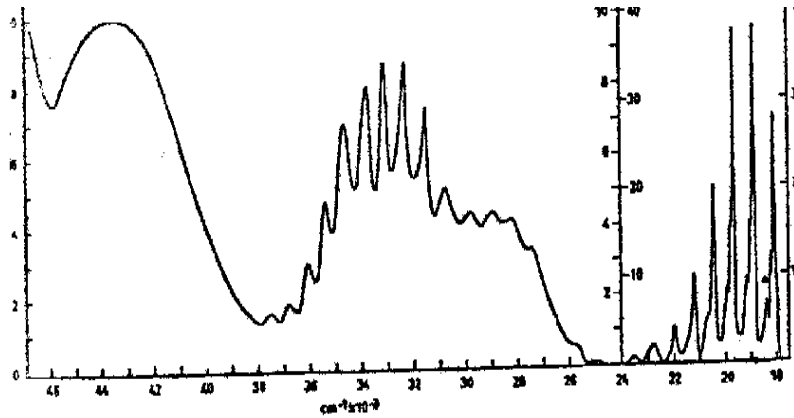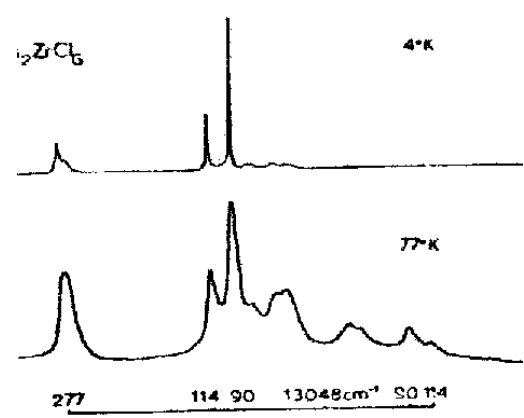

Cs_3CoCl_5 MgO: Ni^{+2}

Charge Transfer & d-p -- intense/higher energy   f-f & spin change ($\Delta S \neq 0$) -- very weak

$KMnO_4$ in $KClO_4$ U^{+4} in Cs_2ZrCl_4

D.   Measurement: (Appendix E)

    1. Beer-Lambert Law $A = \varepsilon bc$ experimental observable

        Dipole strength computed: $D = |<g|\mu_{ei}|ex>|^2 = 0.92 \times 10^{-38} \int \varepsilon/\nu\, d\nu\ (esu\text{-}cm)^2$

    2. Einstein coefficient: absorption = emission (stimulated) ~ emission (spontaneous)

            $B_{ij} = 8\pi^3 D/3h^2 g_l$ $B_{ji} = g_i/g_j\, B_{ij}$ oscillator strength: $f_{ij} = 2.5 \times 10^{-34}\, B_{ij}/\lambda m$

3. [Jablonski diagram -- follow the energy](#)
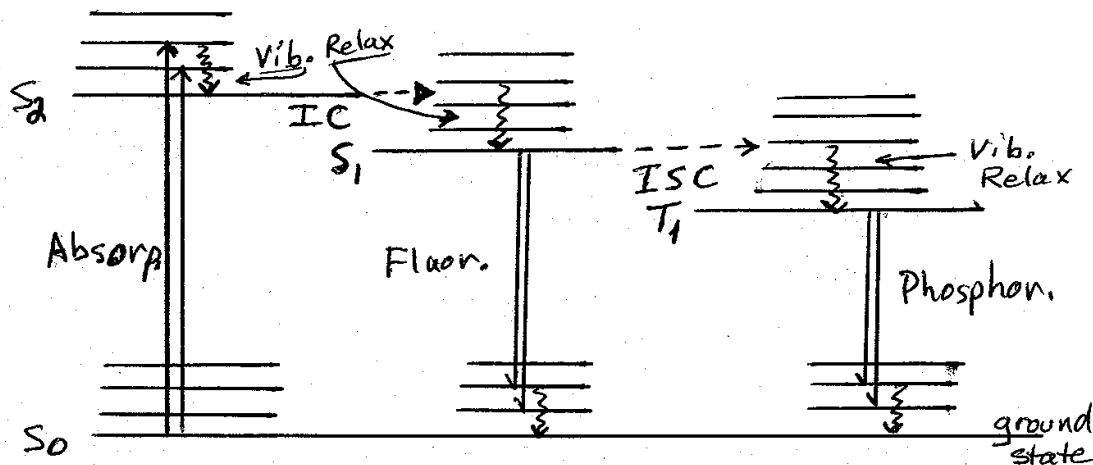
Vib, Relax, — vibrational relaxation — collision

IC - internal conversion $(\Delta S = 0)$ max, rate
when surfaces cross (degen, same struct) $\sim 10^{-12}$ s

ISC — intersystem crossing $(\Delta S \neq 0)$
slower due to spin — spin-orbit coupling enhan

Vibrational Relaxation (VR)—energy transfer from one vibrational level to another or to "heat", i.e. general K.E. of surroundings (via collision)

Non-radiative decay (NR) – energy lost outside of molecule, usually from a non-emitting state

Internal conversion - IC—move energy to another electronic state with minimal loss $(\Delta S=0)$,

Intersystem crossing - ISC—move energy to triplet manifold from singlets (or vice versa) with little loss – violates $\Delta S = 0$, so weak or slow process

Fluorescence –radiative relaxation of excited state $(\Delta S=0)$

Phosphorescence—radiative relaxation of state with spin change (typical $T_1 \rightarrow S_0$)

Quantum Yield—ratio of photons out to photons in or rates of processes: $\phi = k_F/k_F + k_{nr}$

Lifetimes and Quenching-- $k_F = 1/\tau$ if fluorescence is only process, but if add quencher, lower quantum yield, shorten lifetime, τ, because of competition with quenching

Homework

Discussion: Chap 12: #6, 11, 13

To hand in: Chap 12: # 1, 4, 9,

Links

Spectroscopy magazine, workbench columns

http://www.spectroscopymag.com/spectroscopy/article/articleList.jsp?categoryId=2942

Spectroscopy now has current happenings in various areas

http://www.spectroscopynow.com/coi/cda/list.cda?catId=2524&type=Link&sort=az&chId=7

Kaiser Optical Raman tutorial

http://www.kosi.com/raman/resources/tutorial/

Akron Organic Molecular spectroscopy unit:

http://ull.chemistry.uakron.edu/analytical/Mol_spec/

UIC's organic course IR tutorial (Paul Robert Young), UC Boulder lab course and a UK course:

http://chipo.chem.uic.edu/web1/ocol/spec/IR1.htm

http://orgchem.colorado.edu/hndbksupport/irtutor/main.html

http://www.shu.ac.uk/schools/sci/chem/tutorials/molspec/irspec1.htm

General spectroscopy comments from Korean site:

http://elchem.kaist.ac.kr/vt/chem-ed/spec/spectros.htm

Companies

Thermo molec spec—FTIR mostly

http://www.thermo.com/com/cda/category/category_lp/1,2152,312,00.html

Analytik Jena

http://www.analytik-jena.de/e/bu/as/molec/molec.html