

Spectroscopy: Engel Chapter 18

Vibrational Spectroscopy (Typically IR and Raman)

Born-Oppenheimer approx. separate electron-nuclear

Assume elect-nuclear motion separate, full wave fct.

$\psi(r, R) = \chi_v(R) \phi_{el}(r, R)$ -- product fct. solves sum H

Electronic Schrödinger Equation

$$H_{el} \phi_{el}(r, R) = U_{el}(R) \phi_e(r, R)$$

eigen value $\rightarrow U_{el}(R)$ parametric depend on R

(*resolve electronic problem each molecular geometry*)

$U_{el}(R)$ is potential energy for nuclear motion (see below)

Nuclear Schrödinger Equation

$$H_n \chi(R) = E_v \chi_v(R)$$

$$H_n \chi(R) = -\left[\sum_{\alpha} \frac{\hbar^2}{2M_{\alpha}} \nabla_{\alpha}^2 + V_n(R) \right] \chi(R) = E_v \chi_v(R)$$

$$\text{Focus: } V_n(R) = U_{el}(R) + \sum_{\alpha, \beta} Z_{\alpha} Z_{\beta} e^2 / R_{\alpha\beta}$$

Solving this is **3N dimensional** – N atom, each has x,y,z

Simplify \rightarrow Remove (a) Center of Mass (Translate)

(b) Orientation of molecule (Rotate)

Results in **(3N – 6)** coordinates - called internal coord.

– motion of nuclei w/r/t each other

a) Translation — like atoms – no impact on spectra
since *continuous* (no potential – plane wave)

b) Rotation — also no potential but have
angular momentum—can be *quantized*

kinetic energy associated with rotation – quantized

- no potential, but angular momentum restricted

little impact biology, not solve, ident. particle on sphere

1. Diatomics (linear) solution $Y_{JM}(\theta, \phi)$

same form as H-atom angular part

$$E_{JM} = \hbar^2 J(J+1)/2I$$

$$I = \sum_{\alpha} M_{\alpha} R_{\alpha}^2$$

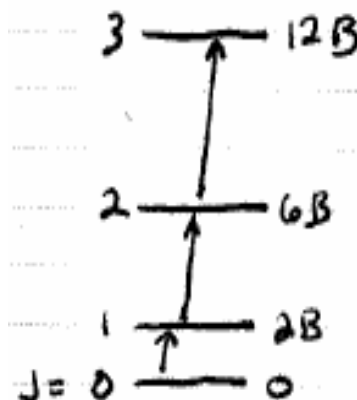
(diatomic $I = \mu R_e^2$)

selection rules: $\Delta J = \pm 1, \Delta M_J = 0, \pm 1$

transitions: $\Delta E_+ = (J + 1) \hbar^2/I$

- levels spread $\sim J^2$, difference $\sim J$

Note: 2-D problem, no momentum for rotation on z



2. Polyatomics – add coordinate (ω -orientation internal)

and quantum number (K) for its angular momentum

– previously refer J, M_J to a lab axis, now complex

(this K is projection of angular momentum onto

molecular axis, so internal orientation of molecule)

Rotational Spectra (aside – little impact on Biology)

Diatomic: $E_{JM}^{rot} = J(J+1)\hbar^2/2I$ $I = \mu R_e$ $\mu = M_A M_B / M_A + M_B$

if $B_e = h/(8\pi^2 I_c)$

or

$$E_{JM} = J(J+1) B_e \text{ in cm}^{-1}$$

$$E_{JM}^{rot} = (hc) J(J+1) B_e \text{ in Joules}$$

Note: levels increase separation as J^2 & transitions as J

Transitions allowed by absorption (far-IR or μ -wave)

Also seen in Raman scattering: $\nu_S = \nu_0 - \nu_{rot}$

(typical $B_e < 10 \text{ cm}^{-1}$, from $I_c \sim \mu$, light molecule \rightarrow highest)

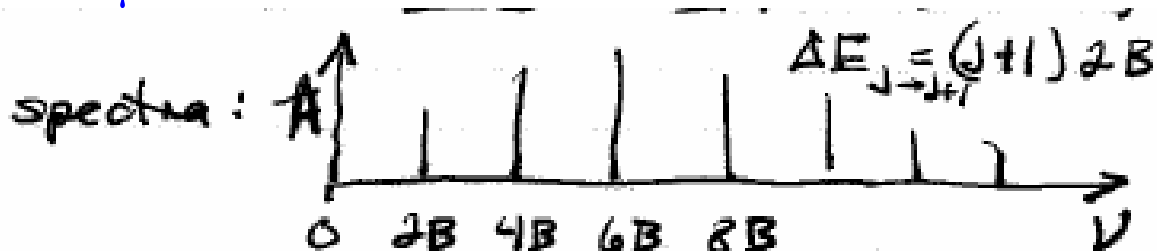
Diatomic (linear) Selection rules:

$$\Delta J = \pm 1 \quad \Delta M = 0, \pm 1 \quad \Delta E_{J \rightarrow J+1} = (J+1)2B$$

(IR, μ -wave absorb $\Delta J = +1$, Raman $\Delta J = 0, \pm 2$)

poly atomic add: $\Delta K = 0$ (or ± 1 - vary with Geometry)

IR or μ -wave – all $\Delta J = +1$



regularly spaced lines, intensity reflect

rise \rightarrow degeneracy ($\delta_J \sim 2J+1$) inc. with J (linear)

fall \rightarrow exponential depopulation \rightarrow fall with J (exp.)

$$\text{Boltzmann: } n_J = \delta_J n_0 \exp[-J(J+1)B/kT]$$

Pure Rotational Far-IR spectrum of CO

-- note 1st transition (23 cm^{-1}) is for $J=6 \rightarrow J=7$ (I think)

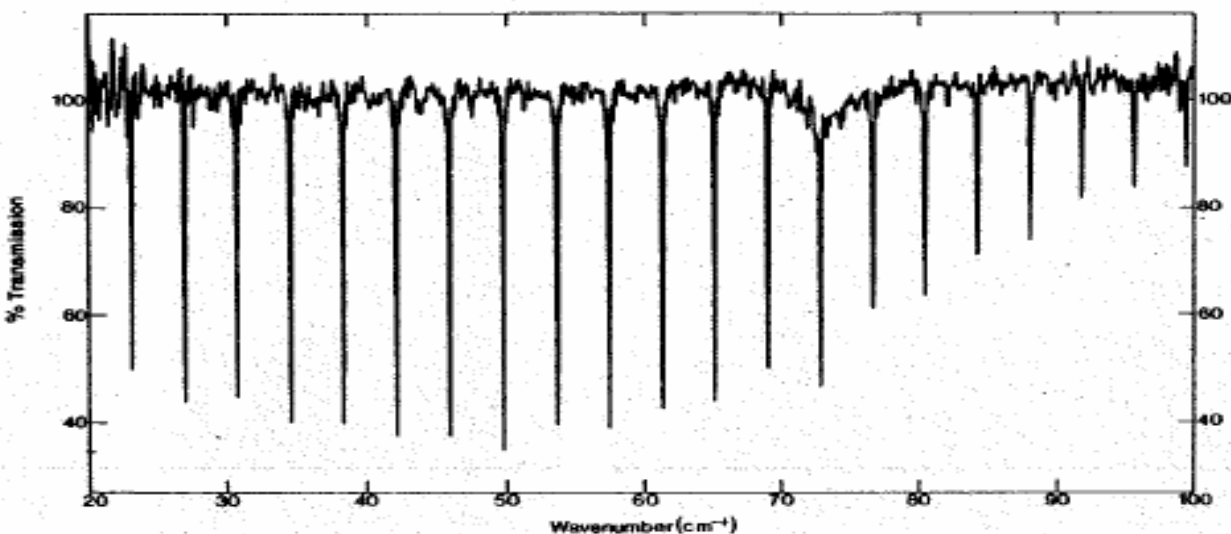
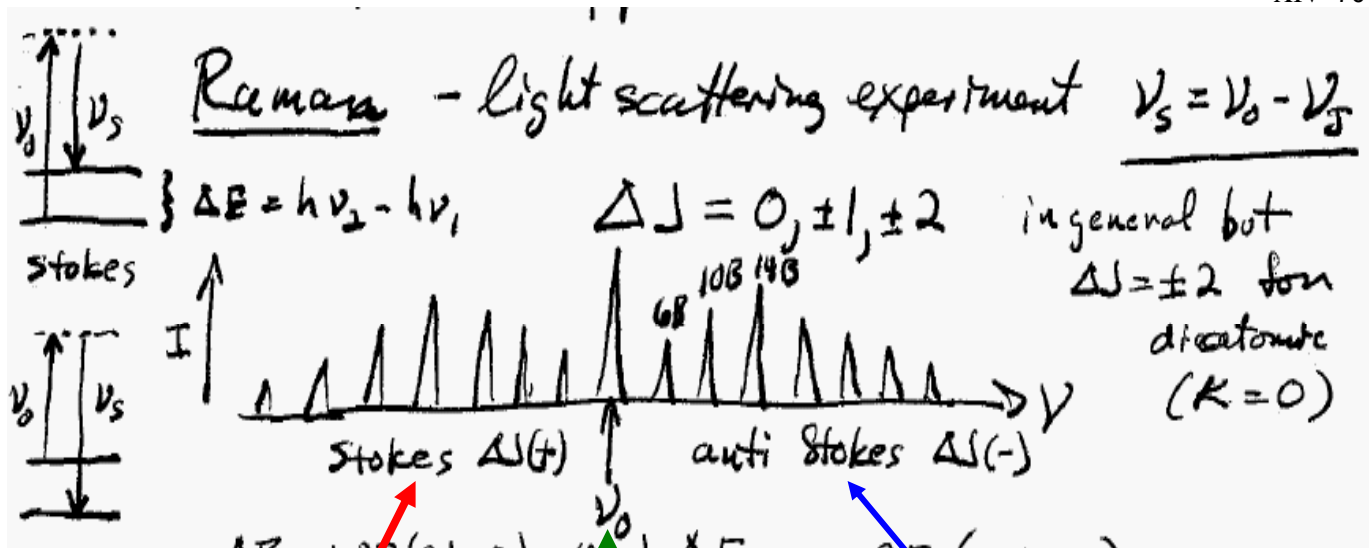


Figure 8.8. Pure rotational spectrum of CO, reproduced with permission from *Modern Aspects of Microwave Spectroscopy*, ed. G. W. Chantry, Academic Press,



Stokes = $\Delta E = -2B(2J + 3)$ (laser) $\Delta E = +2B(2J + 3)$ = AntiStokes

Raman – light scattering experiment $\nu_s = \nu_0 - \nu_J$
 $\Delta J = 0, \pm 1, \pm 2$ (Stokes +, anti-Stokes -) in general but
 $\Delta J = \pm 2$ diatomic ($K = 0$) (or linear) and spacing $\sim 4B$

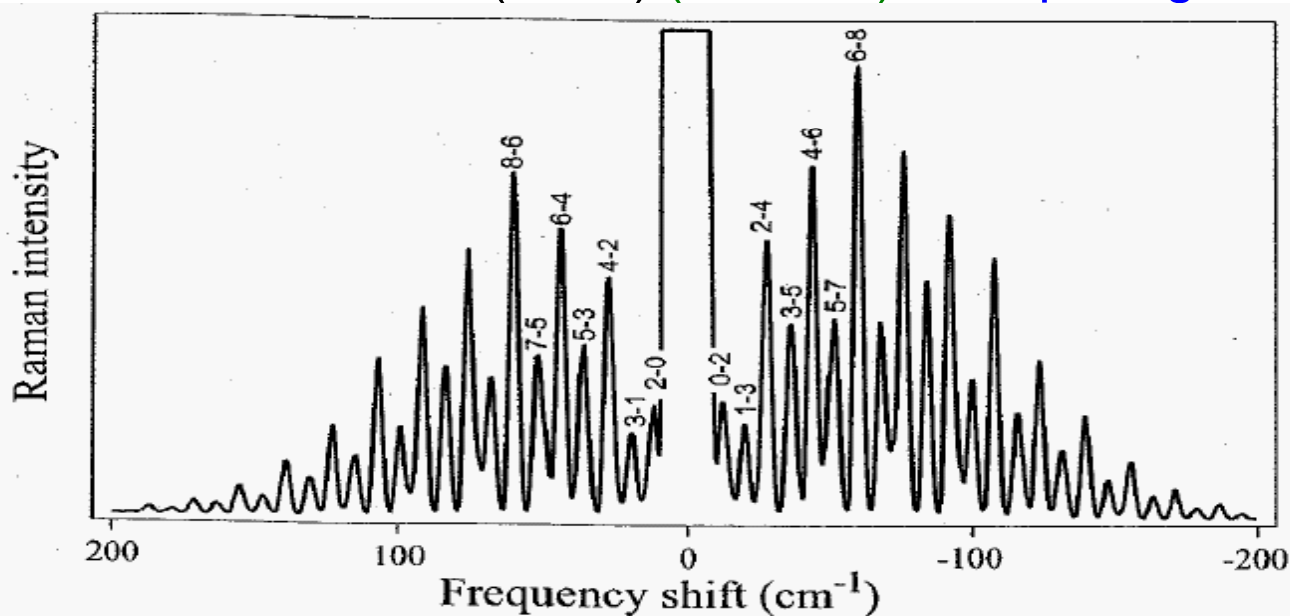


Figure 8.9. Rotational Raman spectrum of N₂, courtesy of Bryan Brooks, Department of Chemistry, University of Idaho.

Rotational Raman spect. of N₂ (alternate intensity-isotope)
 (left) anti-Stokes: $\Delta J = -2$ (right) Stokes: $\Delta J = 2$

Condensed phase – these motions wash out (bio-case)
 (still happen –no longer free translation or rotation \Rightarrow
 phonon and libron in bulk crystal or solution)

Vibration: Internal coordinates – solve
 —problem $V(R)$ not separable – $3N - 6$ coordinates

$$H(R) = -\sum_{\alpha} (\hbar^2/2M_{\alpha}) \nabla_{\alpha}^2 + V(R)$$

$V(R)$ has all electrons attract all nuclei, in principle
 could separate, but all nuclei repel, which is **coupled** - $R_{\alpha\beta}$

Harmonic Approximation – *Taylor series expansion:*

$$V(R) = V(R_e) + \sum_{\alpha} \frac{\partial V}{\partial R_{\alpha}} \Big|_{R_e} (R_{\alpha} - R_e) +$$

$$\frac{1}{2} \sum_{\alpha} \frac{\partial^2 V}{\partial R_{\alpha} \partial R_{\beta}} \Big|_{R_e} (R_{\alpha} - R_e)(R_{\beta} - R_e) + \dots$$

Expansion in Taylor Series

1st term – constant \Rightarrow just add to energy

2nd term – zero at minimum

3rd term – 1st non-zero / non-constant term
 harmonic – potential has form of $\frac{1}{2} kx^2$

Problem – R_{α}, R_{β} mixed $\Rightarrow H_n$ not separate

Solution \rightarrow New coordinates “Normal coordinates”

$$Q_j = \sum_i c_{ij} q_i \quad \text{where} \quad q_i = x_{i\alpha}/(M_{\alpha})^{1/2}, y_{i\alpha}/(M_{\alpha})^{1/2}, z_{i\alpha}/(M_{\alpha})^{1/2}$$

normal coordinates

mass weighted Cartesian

set up **separated harmonic oscillator** problem, actual a little different:

$$H = \sum_j -\hbar^2/2 \partial^2/\partial Q_j^2 + 1/2 \sum_j k_{Q_j} Q_j^2 = \sum_j h_j(Q_j)$$

See this is **summed H** →

$$\text{product } \chi = \prod_j \chi_j(Q_j)$$

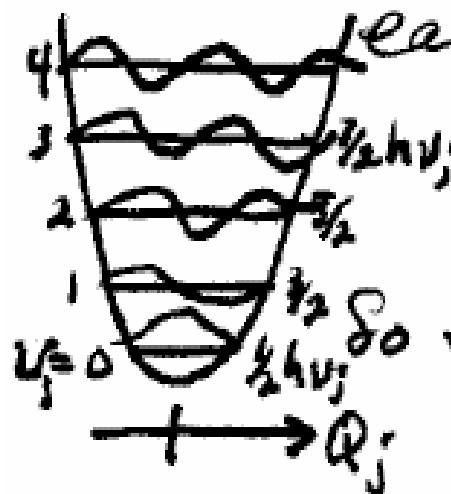
$$\text{summed } E = \sum_j E_j$$

each one is harmonic oscillator

(already know solution):

$$h_i \chi(Q_i) = E_i \chi(Q_i)$$

$$H = \sum_j h_j(Q_j) \quad E_j = (\nu_j + 1/2) h\nu_j$$



So for $3N - 6$ dimensions – see regular set E_j levels

$\nu_j = 0, 1, 2, \dots \infty$ but for each $3N-6$ coordinate j

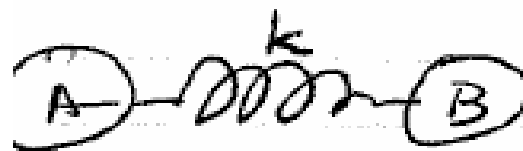
Interpret

go back to diatomic $N = 2$

$3N = 6$ coordinates

remove translation → 3 coordinates left

remove rotation (just θ, ϕ) → 1 coord. vibration bond



model of harmonic oscillator works

$$E = (\nu + 1/2) h\nu \quad \nu = (1/2\pi) \sqrt{k/\mu} \quad k - \text{force constant}$$

$$\mu = M_A M_B / (M_A + M_B)$$

heavier molecules → bigger μ - lower frequency

H ₂	~4000 cm ⁻¹	F ₂	892 cm ⁻¹
HCl	~2988 cm ⁻¹	Cl ₂	564 cm ⁻¹
HF	~4141 cm ⁻¹	I-I	~214 cm ⁻¹
C-H	~2900 cm ⁻¹	I-Cl	~384 cm ⁻¹
C-D	~2100 cm ⁻¹		

stronger bonds – higher k - higher frequency

C≡C	~2200 cm ⁻¹	O=O	1555 cm ⁻¹
C=C	~1600 cm ⁻¹	N≡O	1876 cm ⁻¹
C-C	~1000 cm ⁻¹	N≡N	2358 cm ⁻¹
		C≡O	2169 cm ⁻¹

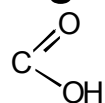
This is key to structural use of IR →
 frequency depends on mass (atom type)
bond strength (type)

Thus frequencies characteristic of structural elements

Called group frequencies:

Typical frequencies for given functional groups

e.g.



C-OH

C-X

C=O

C-NH



$$\psi_1 = \sqrt{2} \left(\frac{\alpha}{\pi}\right)^{1/4} \alpha^{1/2} x e^{-\alpha x^2/2}$$

$$\psi_2 = \frac{1}{\sqrt{2}} \left(\frac{\alpha}{\pi}\right)^{1/4} (2\alpha x^2 - 1) e^{-\alpha x^2/2}$$

$$\psi_3 = \sqrt{3} \left(\frac{\alpha}{\pi}\right)^{1/4} \left(\frac{2\alpha^{3/2} x^3}{3} - \alpha^{1/2} x\right) e^{-\alpha x^2/2}$$

$$\psi_4 = \frac{1}{\sqrt{6}} \left(\frac{\alpha}{\pi}\right)^{1/4} \left(2\alpha^2 x^4 - 6\alpha x^2 + \frac{3}{2}\right) e^{-\alpha x^2/2}$$

$$\psi_5 = \frac{1}{\sqrt{15}} \left(\frac{\alpha}{\pi}\right)^{1/4} \left(2\alpha^{5/2} x^5 - 10\alpha^{3/2} x^3 + \frac{15\alpha^{1/2} x}{2}\right) e^{-\alpha x^2/2}$$

$$\psi_v = \left(\frac{1}{2^v v!}\right)^{1/2} \left(\frac{\alpha}{\pi}\right)^{1/4} H_v(\alpha^{1/2} x) e^{-\alpha x^2/2}, \quad \alpha = \mu\omega/\hbar$$

selection rule $\Delta v = \pm 1$

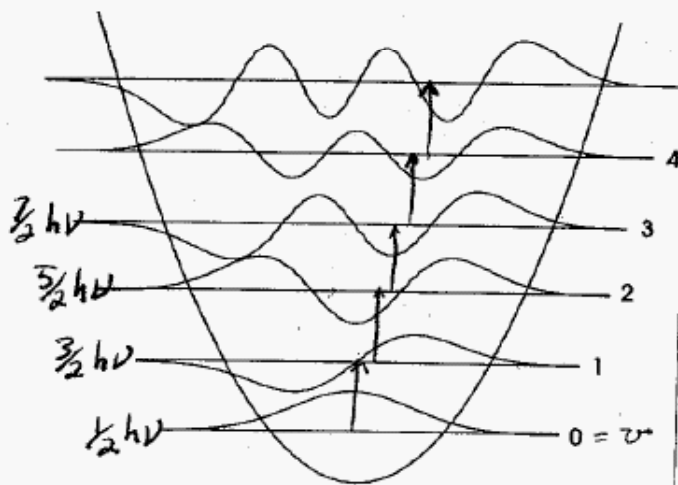
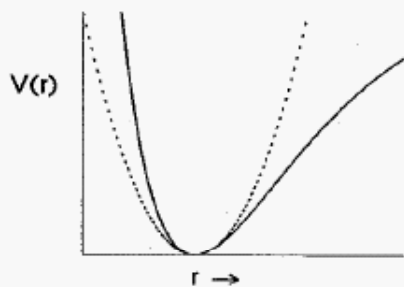
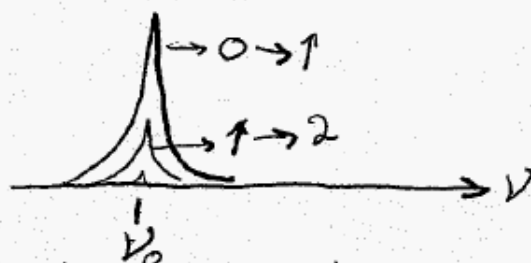


Figure 7.3. The harmonic oscillator wavefunctions.

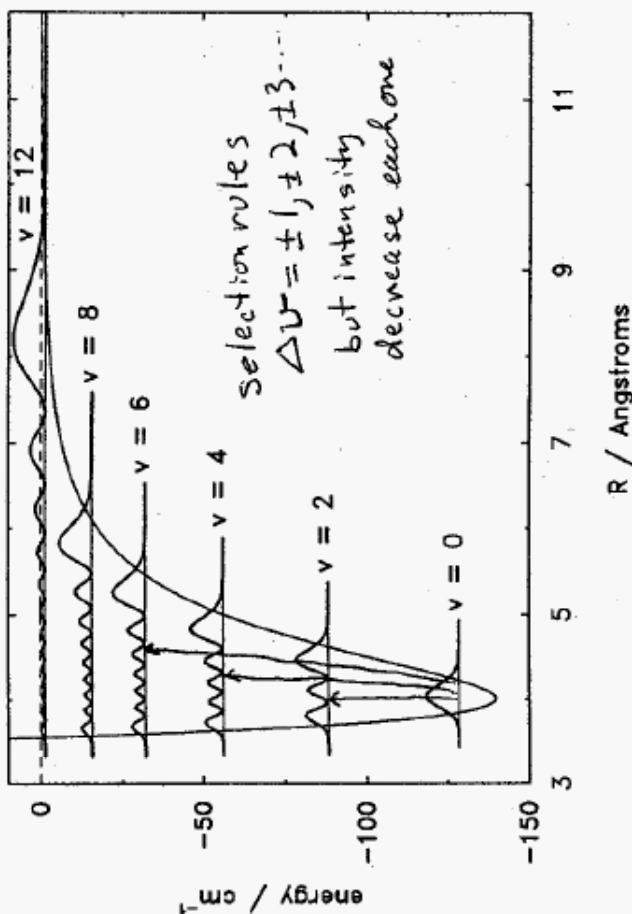
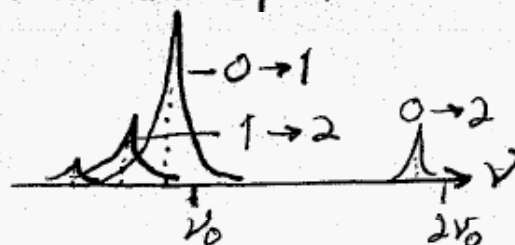


harmonic oscillator potential (dots) as compared to a real (solid).

harmonic spectra



anharmonic spectra



106

INFRA-RED SPECTROSCOPY

TABLE 3.4: Characteristic Stretching Frequencies of some Molecular Groups

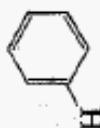
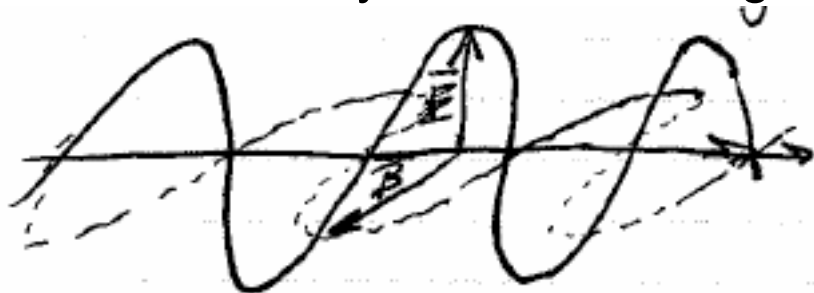
Group	Approximate Frequency (cm ⁻¹)	Group	Approximate Frequency (cm ⁻¹)
—OH	3600	>C=O	1750-1600
—NH ₂	3400	>C=C<	1650
≡CH	3300	>C=N<	1600
	3060	>C—C<	1200-1000
≡CH ₂	3030	>C—N<	
		>C—O<	
—CH ₃	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform.) 1375 (sym. deform.)	>C=S	1100
—CH ₂ —	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)	>C—F	1050
—SH	2580	>C—Cl	725
—C≡N	2250	>C—Br	650
—C=C—	2220	>C—I	550

Table 7.5 Infrared group wavenumber table

Group	v/cm ⁻¹	Group	v/cm ⁻¹
≡C—H	3300	—O—H	3600
=C—H	3020	>N—H	3360
>C—H	2960	>P=O	1296
—C≡C—	2060	>S=O	1310
>C=C<	1660	≡C—H	700
>C—C<	900	≡C—H	700
—S—H	2600	≡C—H	1100
—N=N—	1600		
>C=O	1700		
—C≡N	2100		
>C—F	1100		
>C—Cl	660		
>C—Br	660		
>C—I	600		
		C≡C—C	300

Transitions → spectra measure energy level change caused by interaction of light & molecule



E – electric field
B – magnetic field
 --in phase and \perp

E interacts with charges in molecules - like radio antenna if frequency of light = frequency of vibration (correspond to $\Delta E = h\nu = E_i - E_j$) then oscillating field drives the transition → leads to absorption or emission

Probability of induce transition - result of time-varying field

$$P_{i \rightarrow j} \sim \left| \int \psi_i^* \mu \psi_j d\tau \right|^2 \quad \text{where } \mu \text{ is electric dipole op.}$$

$$\mu = \sum_{\alpha} \sum_i [(Z_{\alpha} e) R_{\alpha} + e r_i] = \sum_j q_j r_j \rightarrow \text{sum over all charges}$$

Depends on position operator r , $R \rightarrow$ electron & nuclei

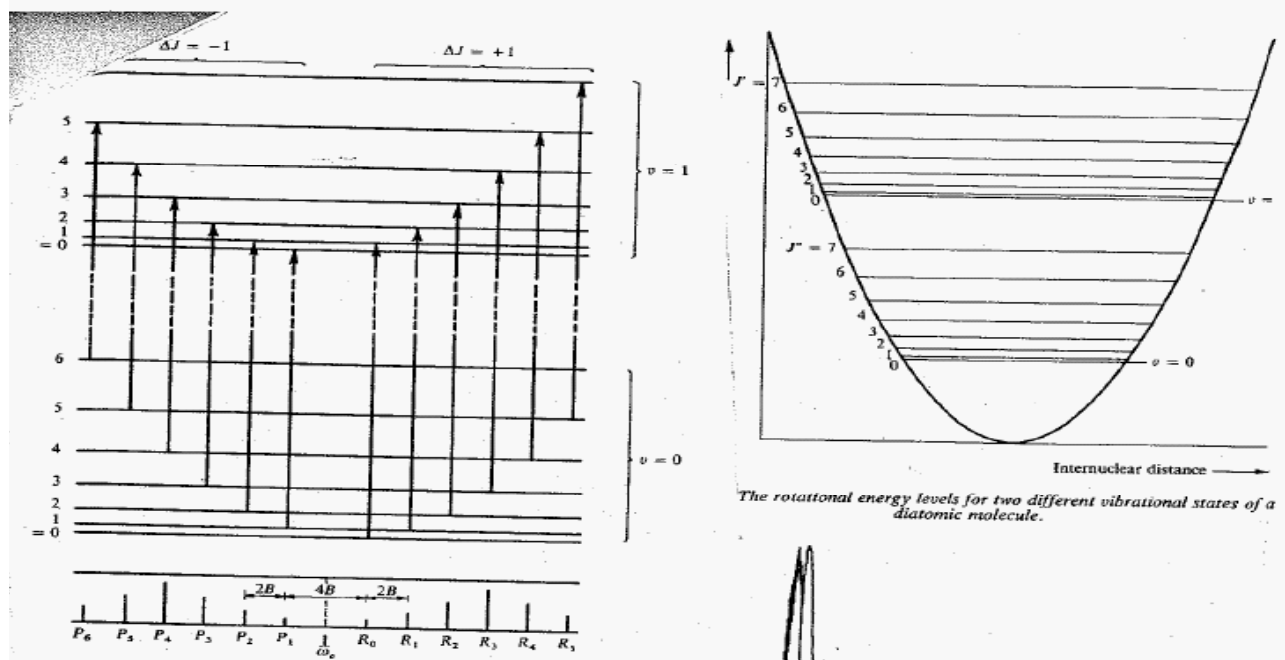
Harmonic oscillator: transform $\mu = \mu(Q_j)$ (norm. coord.)

$$\int \chi_{\nu_\ell}^*(Q_j) \mu_j \chi_{\nu_k}(Q_j) dQ_j \neq 0 \quad \text{if } \nu_k = \nu_\ell \pm 1$$

$$\text{in addition: } \partial \mu / \partial Q_j \neq 0 \quad \text{i.e. } \Delta \nu = \pm 1$$

Normal mode must change dipole moment to have dipole transition → occur in IR

Most observations are Absorption: $\nu = 0 \rightarrow \nu = 1$
 population $n_j = n_i e^{-(E_j - E_i)/kT}$ Boltzmann



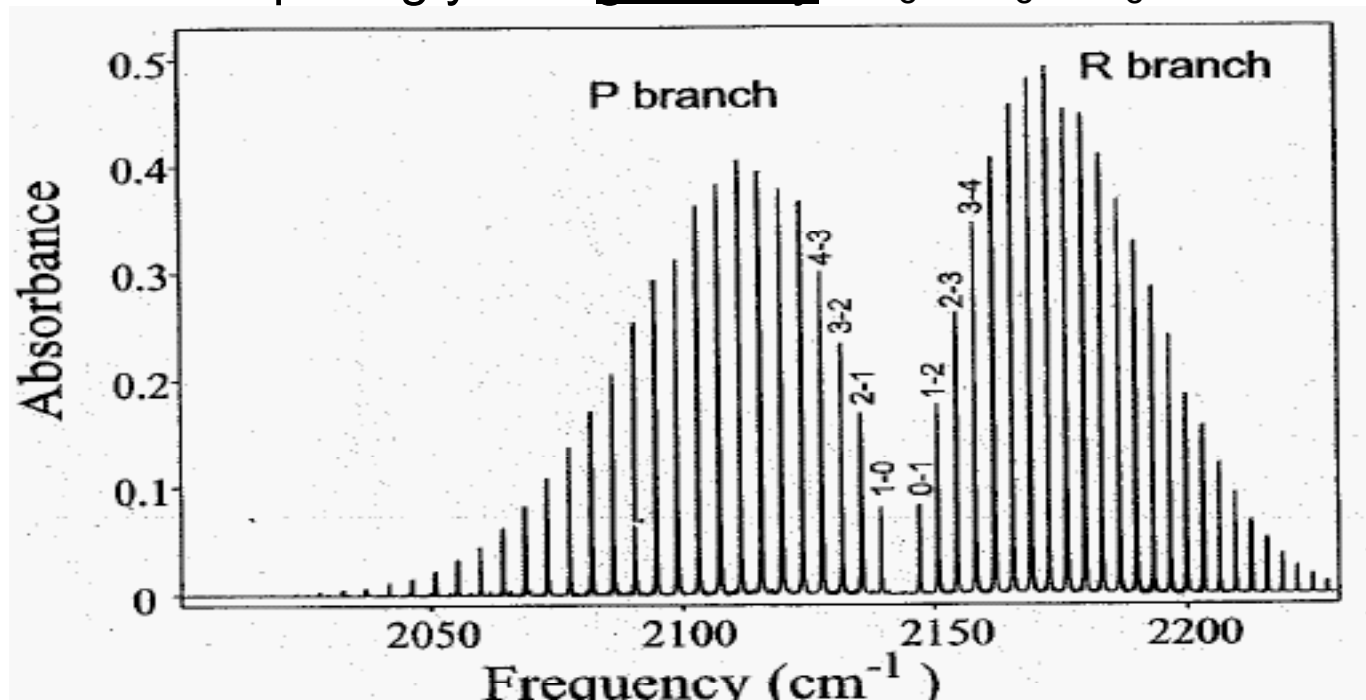
Allowed transitions

Diatomic: **IR:** $\Delta v = \pm 1$ $\Delta J = \pm 1$ (i.e. rotate-gas phase)

$\partial\mu/\partial R \neq 0 \Rightarrow$ hetero atomic

observe profiles – series of narrow lines **separate $2B$**

– spacing yields geometry: $B_e \rightarrow I_e \rightarrow R_e$



Raman: $\Delta v = \pm 1$ $\Delta J = 0, \pm 2$
 $(\partial\alpha/\partial R) \neq 0 \Rightarrow$ all molec. change polarizability

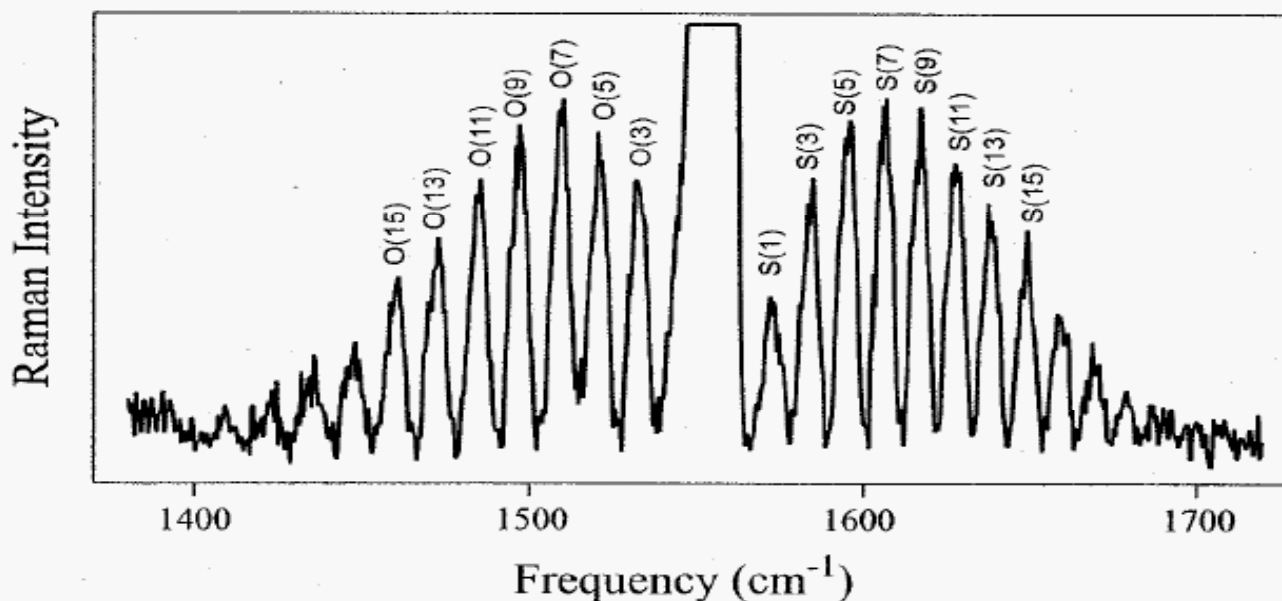


Figure 9.7. Vibration-rotation Raman spectrum of O_2 in air at atmospheric pressure. The initial quantum numbers of the O and S branch lines are indicated, & the Q branch is off scale.

Diatomic { must be hetero }
 so have dipole

Most common
 $v=0 \rightarrow v=1$
 $\Delta E = \frac{3}{2}h\nu_0 - \frac{1}{2}h\nu_0$
 $= h\nu$

if harmonic $v=1 \rightarrow v=2$ also $\Delta E = h\nu$

if anharmonic $v=1 \rightarrow v=2$ lower freq
 $v=2 \rightarrow v=3$ even lower
 get series of weaker transition - lower ν

Also - $\Delta v = \pm 1, \pm 2, \pm 3 \dots$ possible

Diatomic - must be hetero so have dipole

Most common: $v = 0 \rightarrow v = 1 \rightarrow \Delta E = h\nu$

if harmonic

$$\nu = 1 \rightarrow \nu = 2$$

$$\text{also } \Delta E = h\nu$$

if anharmonic.

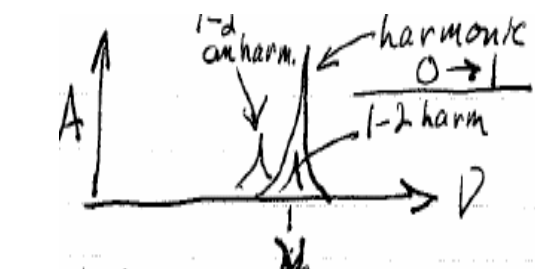
$$\nu = 1 \rightarrow \nu = 2 \quad \text{lower freq.}$$

$$\nu = 2 \rightarrow \nu = 3 \quad \text{even lower}$$

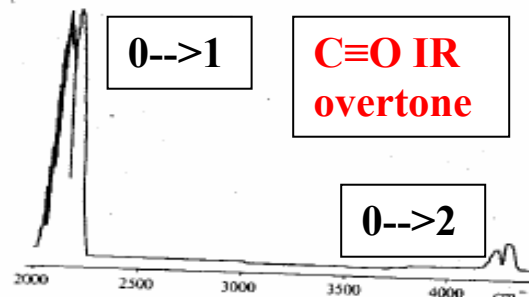
get series of weaker transition

– lower ν

Also – $\Delta n = \pm 1, \pm 2, \pm 3, \dots$
possible \rightarrow overtones



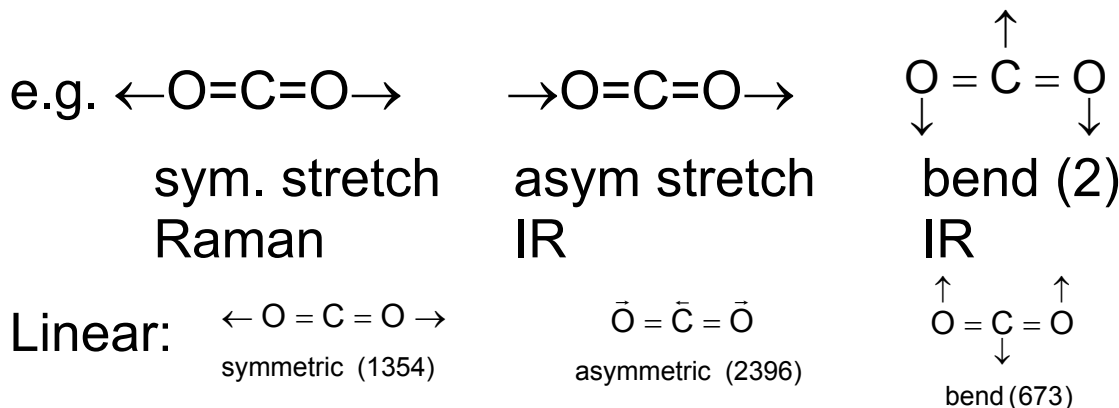
The rotational energy levels for two different vibrational states of diatomic molecule.



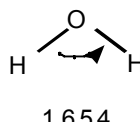
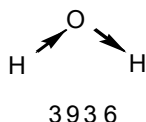
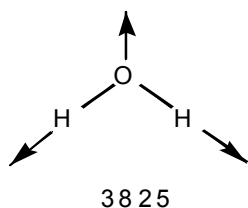
3.7(a): The fundamental absorption (centred at about 2143 cm^{-1}), first overtone (centred at about 4260 cm^{-1}) of carbon monoxide; the centre of the P branch in the fundamental.

Polyatomics –same rules: $\Delta \nu = \pm 1$ $\Delta J = \pm 1$

But include $\Delta J = 0$ for non-linear vibrations (molec.)



non-linear



(IR and Raman)

Bends normally $\sim \frac{1}{2} \nu_e$ of stretches

If 2 coupled modes, then there can be a big difference

eg. CO ₂	symm: 1354	asym: 2396	bend: 673
H ₂ O	symm: 3825	asym: 3936	bend: 1654

Selection rules Harmonic $\Delta v_i = \pm 1$, $\Delta v_j = 0$ $i \neq j$
Anharmonic $\Delta v_i = \pm 2, \pm 3, \dots$ overtones
 $\Delta v_j = \pm 1$ $\Delta v_i = \pm 1$ combination band

IR – $(\partial\mu/\partial Q_j) \neq 0 \rightarrow$ must change dipole in norm.coord.
 \Rightarrow dislocate charge

Raman – $(\partial\alpha/\partial Q_j) \neq 0 \rightarrow$ charge polarizability
 \Rightarrow typical expand electrical charge

Rotation: $\Delta J = \pm 1$ (linear vibration) \rightarrow P & R branches
 $\Delta J = 0, \pm 1$ bent or bend linear molec. \rightarrow Q-band

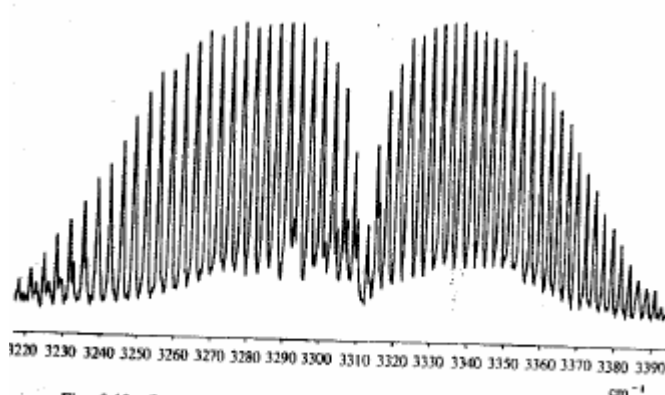


Fig. 3.12: Spectrum of the symmetric stretching vibration of the HCN molecule showing the P and R branch lines

HCN linear stretch (no Q)

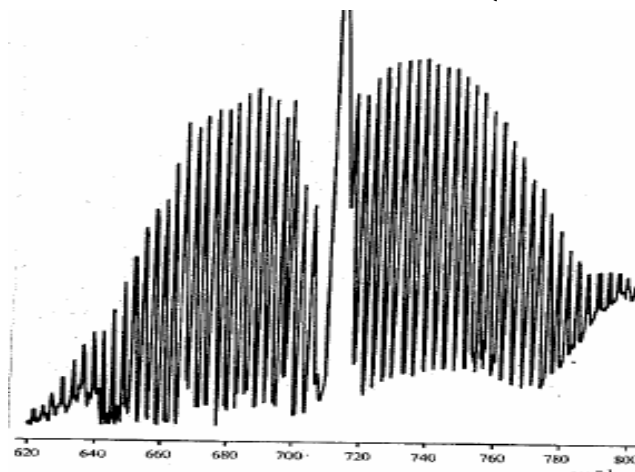


Fig. 3.14: Spectrum of the bending mode of the HCN molecule showing its PQR structure. The broad absorption centred at 800 cm⁻¹ is due to a

HCN bend mode (Q-band)

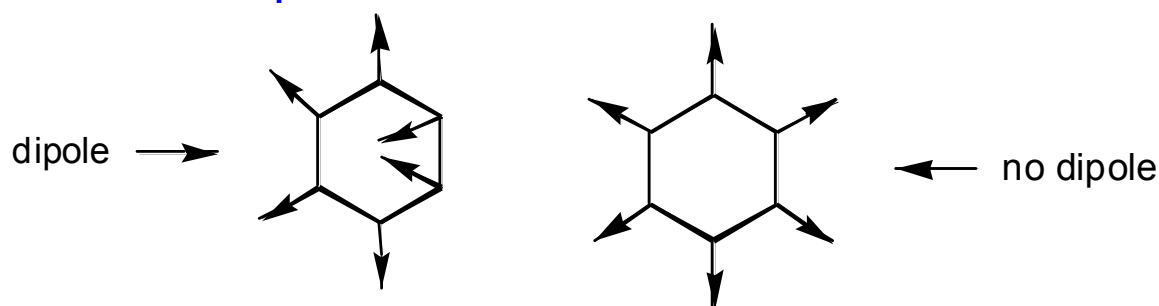
Polyatomic – $\chi = \prod_{j=1}^{3N-6} \chi_{v_0}(Q_j)$

Due to orthogonality – only one Q_j can change v_j
 $\Delta v_j = \pm 1$ $\Delta v_i = 0$ $i \neq j$ $(\partial\mu/\partial Q_j) \neq 0$

Dipole selects out certain modes

Allow \rightarrow molecules with symmetry often distort to dipole

Benzene example:



e.g.

IR Intensity \rightarrow most intense if move charge

e.g. O-H \gg C-H

C-O \gg C-C, etc.

In bio systems: -COOH, -COO⁻, amide C=O, -PO₂⁻

Raman – light scattering $\rightarrow \nu_s = \nu_0 - \nu_{\text{vib}}$

caused by polarizability

$$\Delta\nu = \pm 1$$

these tend to complement IR

$$\partial\alpha/\partial Q_j \neq 0$$

– homo nuclear diatomic

– symmetrical modes

-- aromatics, -S-S-, large groups -- most intense

C-H modes separate from lower freq.

202

Symmetry and spectroscopy

Table 3-31. Characteristic Stretching Frequencies

Bond	Type of Compound	Frequency (cm ⁻¹)	Intensity
C-H	alkane	2800-3000	strong
=C-H	alkene or arene	3000-3100	medium
≡C-H	alkyne	3300	strong
C=C	alkene	1620-1680	variable
C≡C	alkyne	2100-2260	variable
C≡N	nitrile	2200-2300	variable
C=O	ketones, aldehydes acids, esters	1700-1750	strong
O-H	alcohols	3590-3650	variable, sharp
	H-bonded alcohols	3200-3400	strong, broad
	H-bonded acids	2500-3000	variable, broad
N-H	amines	3300-3500	medium

Vibrational spectroscopy

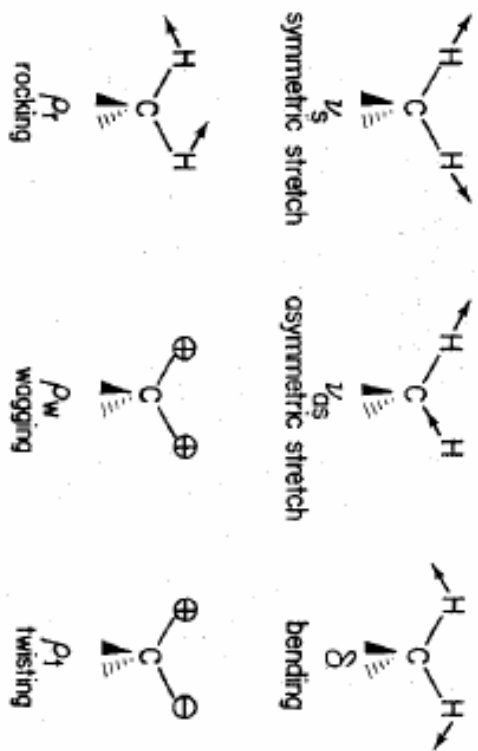
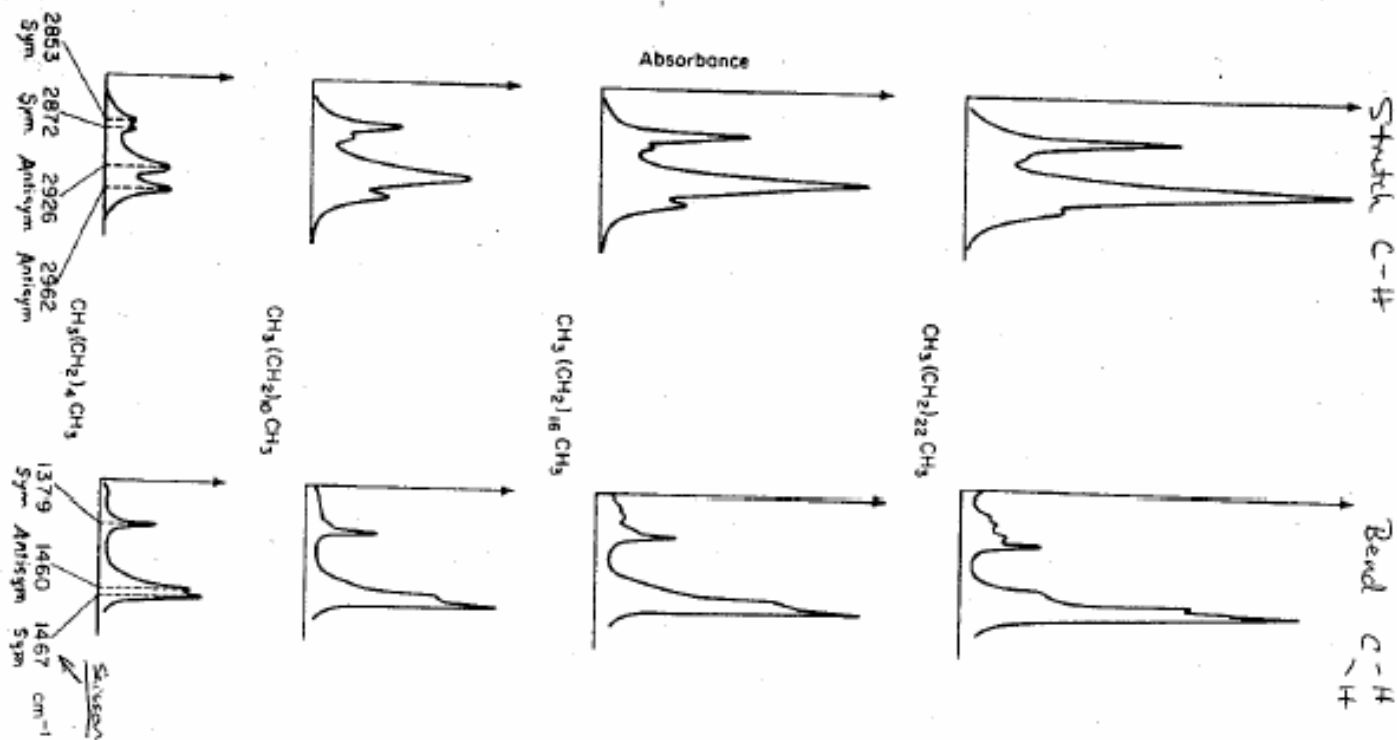
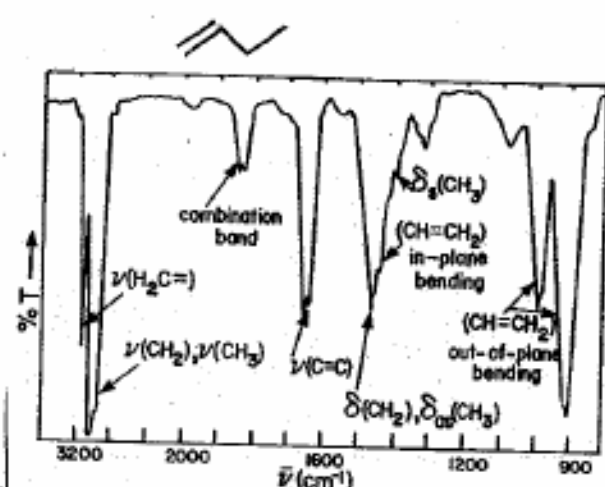
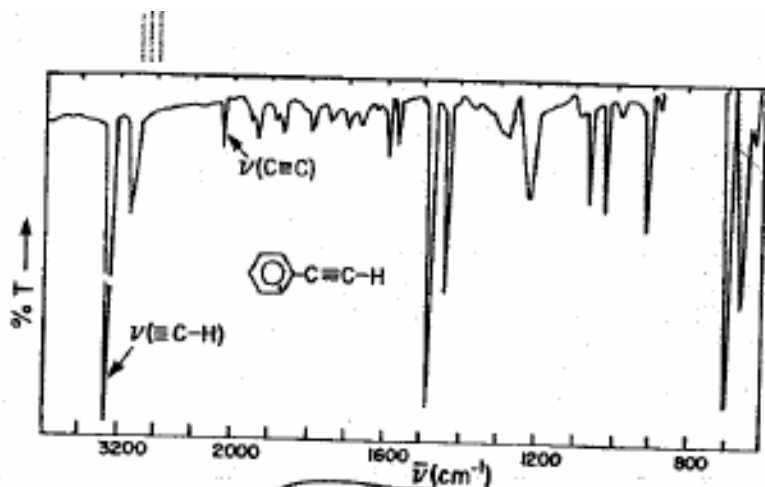


Fig. 3-75. Vibrations of a methylene group.





Infrared spectrum of phenylacetylene in CCl_4 solution. From M.C. Caserio, *Basic Principles of Organic Chemistry*, W.A. Benjamin, N.Y., 1964.

Infrared spectrum of 1-butene. From J.D. Roberts and M.C. Caserio, *Basic Principles of Organic Chemistry*, W.A. Benjamin, N.Y., 1964.

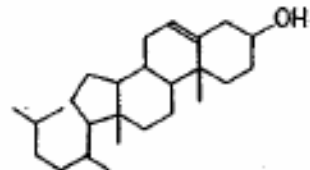
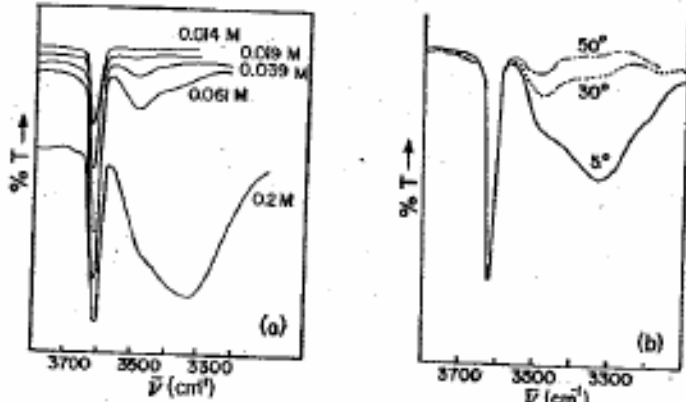
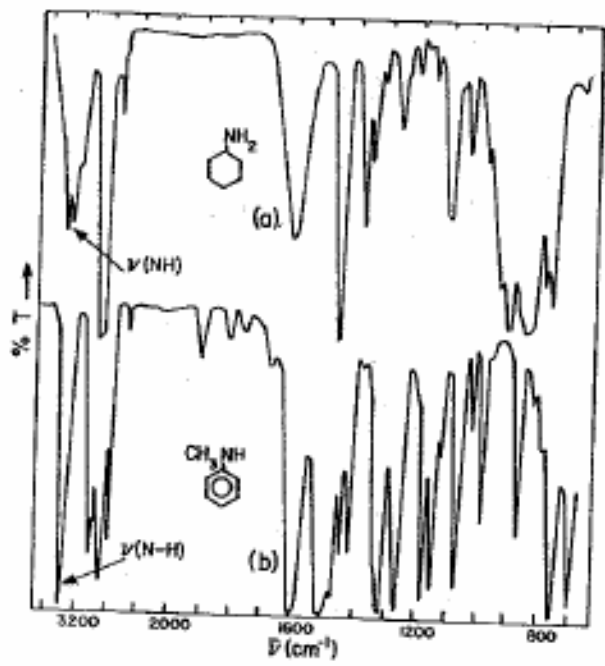


Fig. 3-83. Infrared spectrum of cholesterol as a function of (a) concentration and (b) temperature in CCl_4 solution. The sharp band near 3620 cm^{-1} is assigned to monomeric species while broad bands near 3500 and 3350 cm^{-1} are assigned to dimers and trimers, respectively. Reproduced from F.S. Parker and M.C. Caserio, *Biochem.*, 7, 1286 (1968).

Infrared spectra of (a) cyclohexylamine and (b) methanilamine. From M.C. Caserio, *Basic Principles of Organic Chemistry*, W.A. Benjamin, N.Y., 1964.

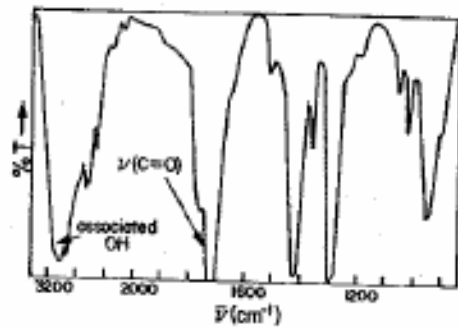
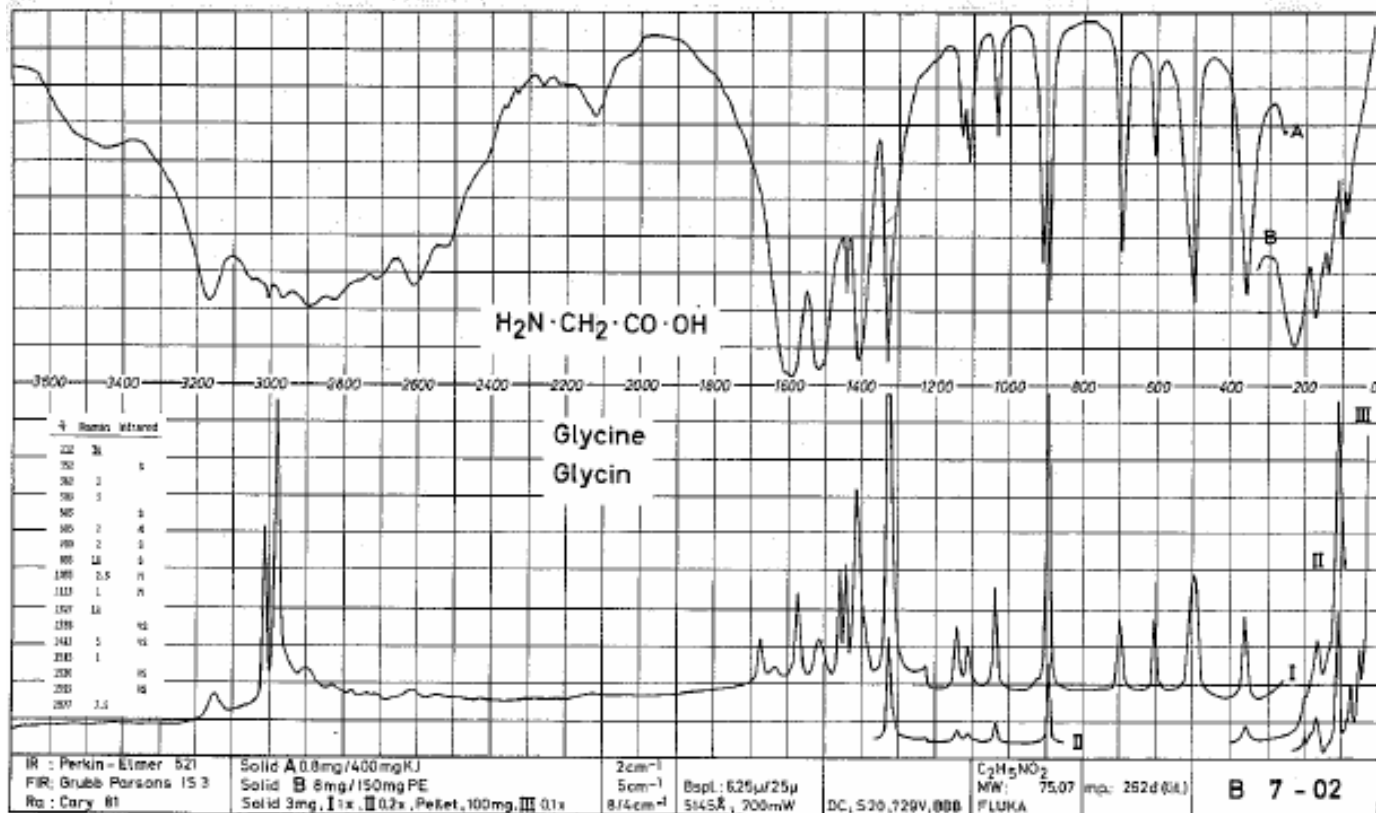
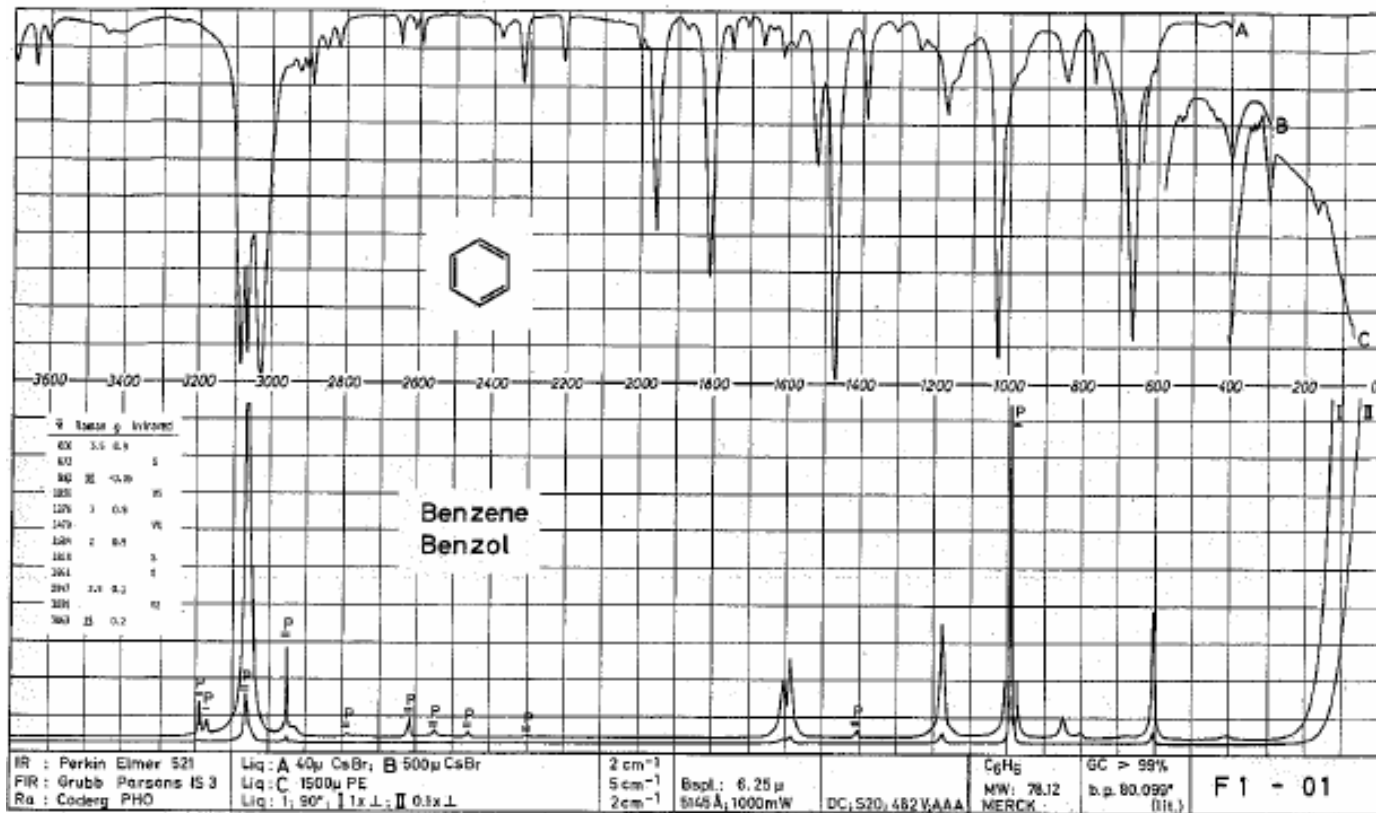
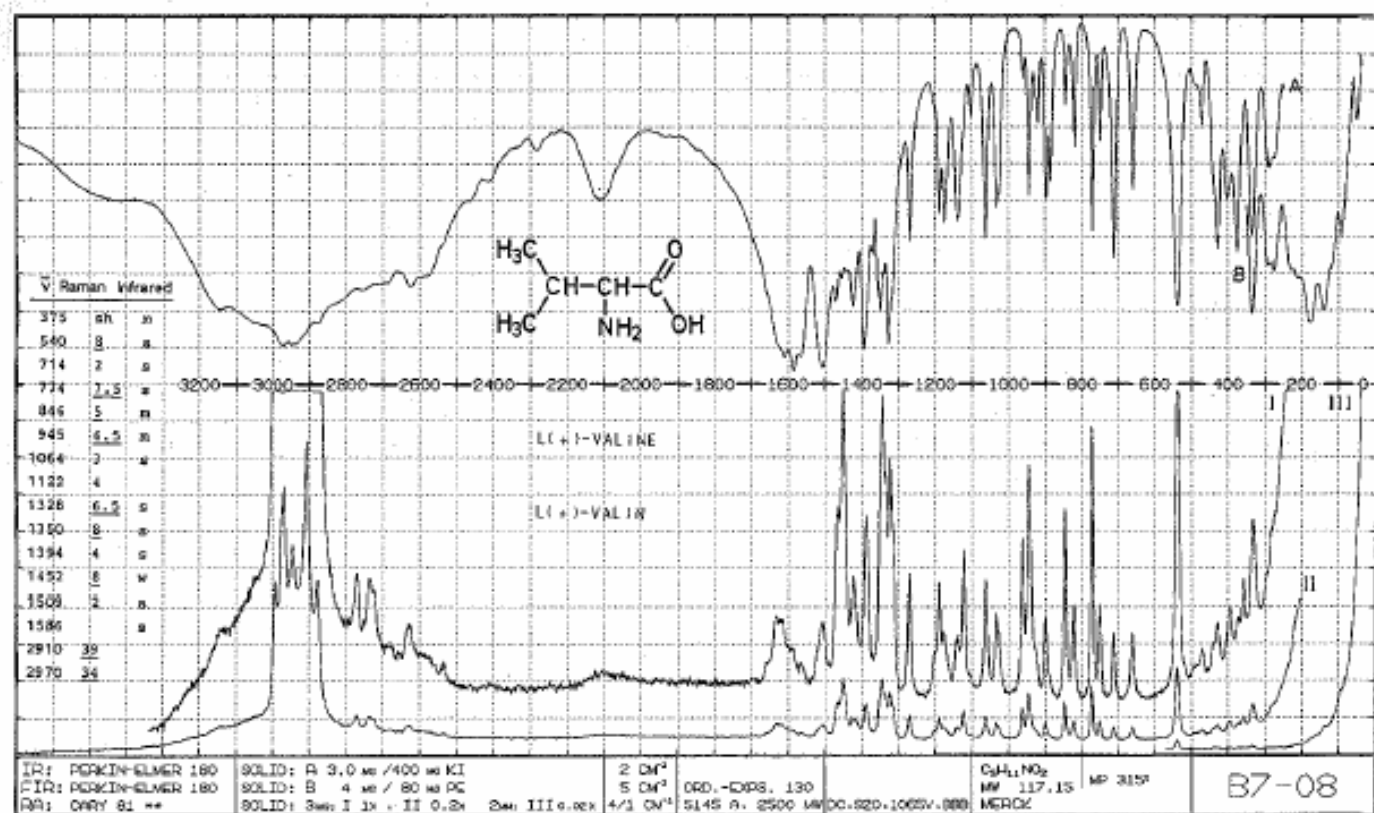
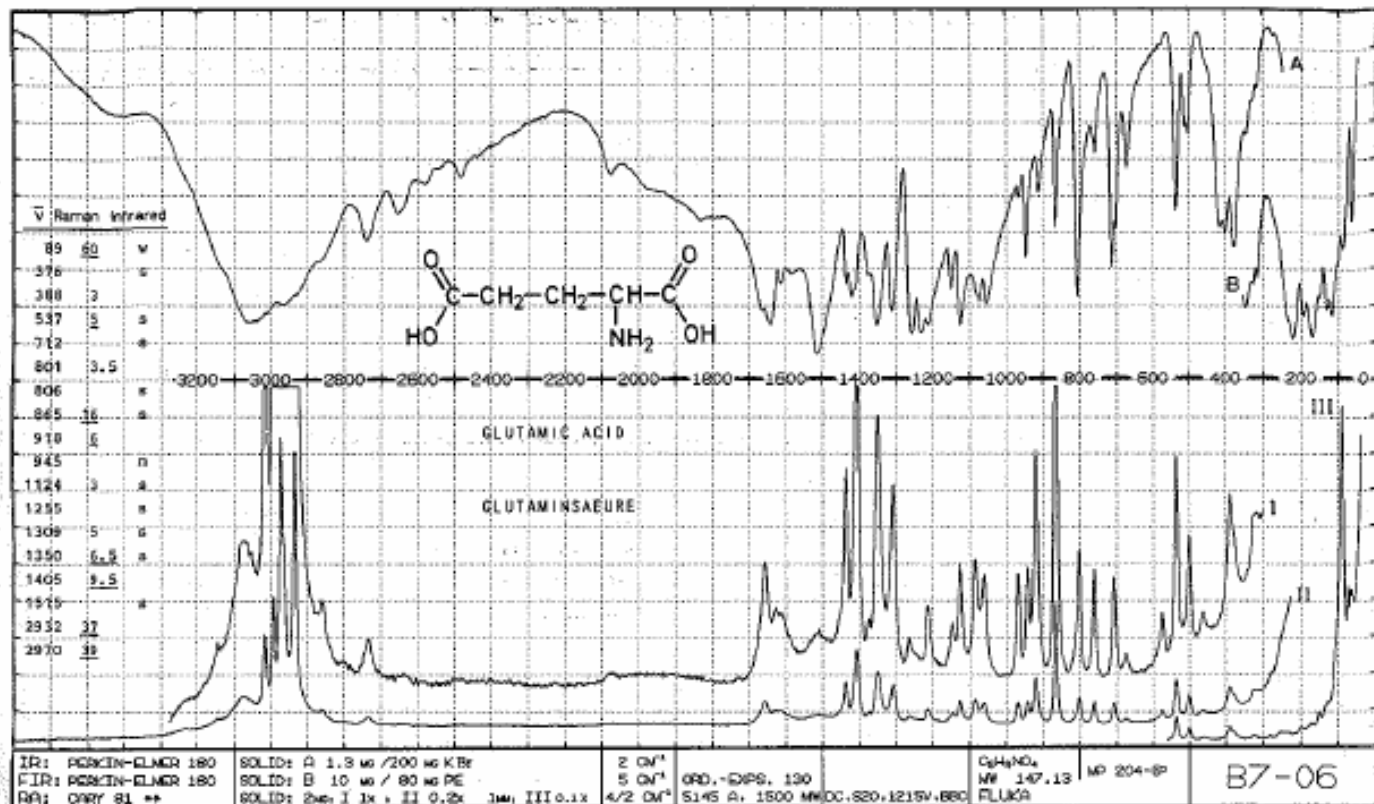
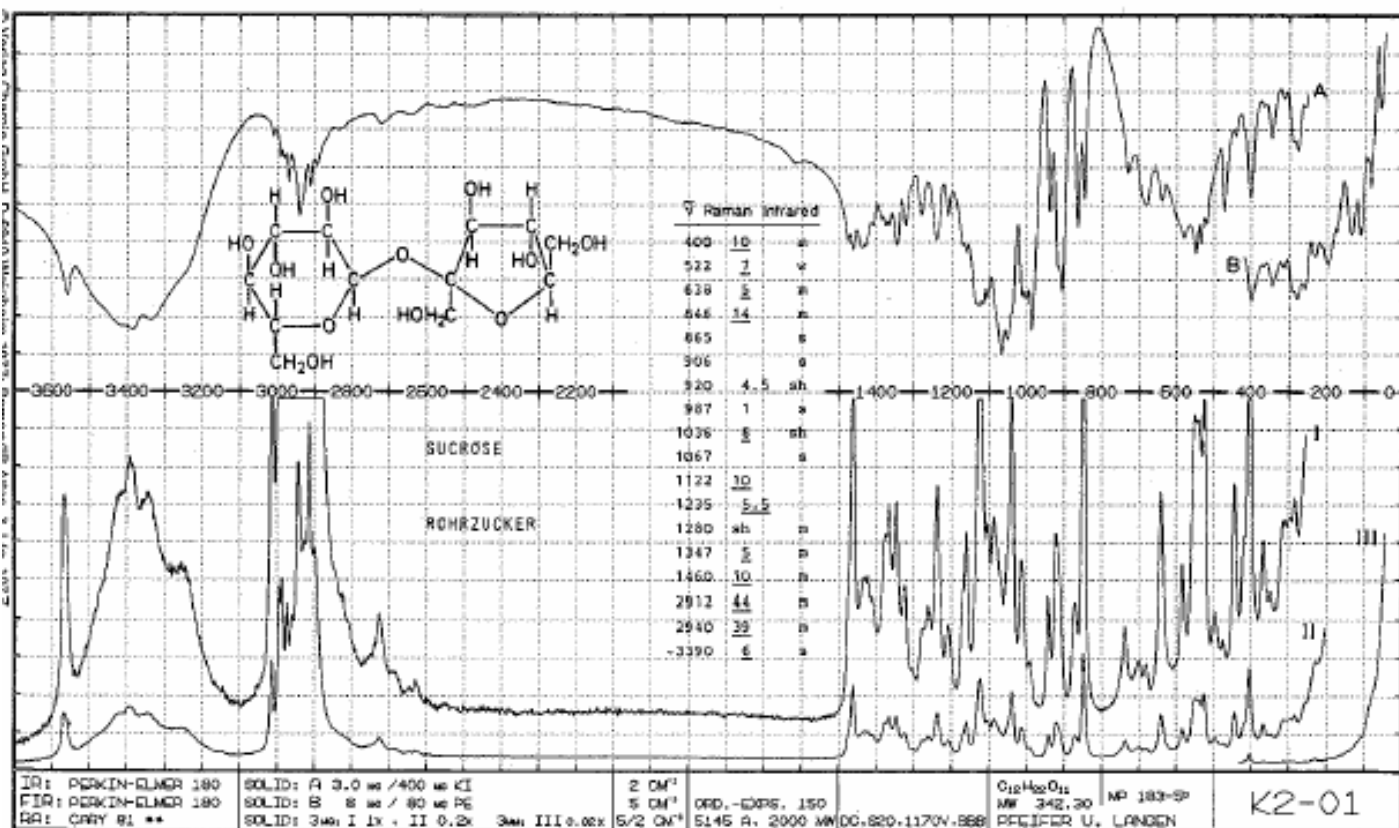
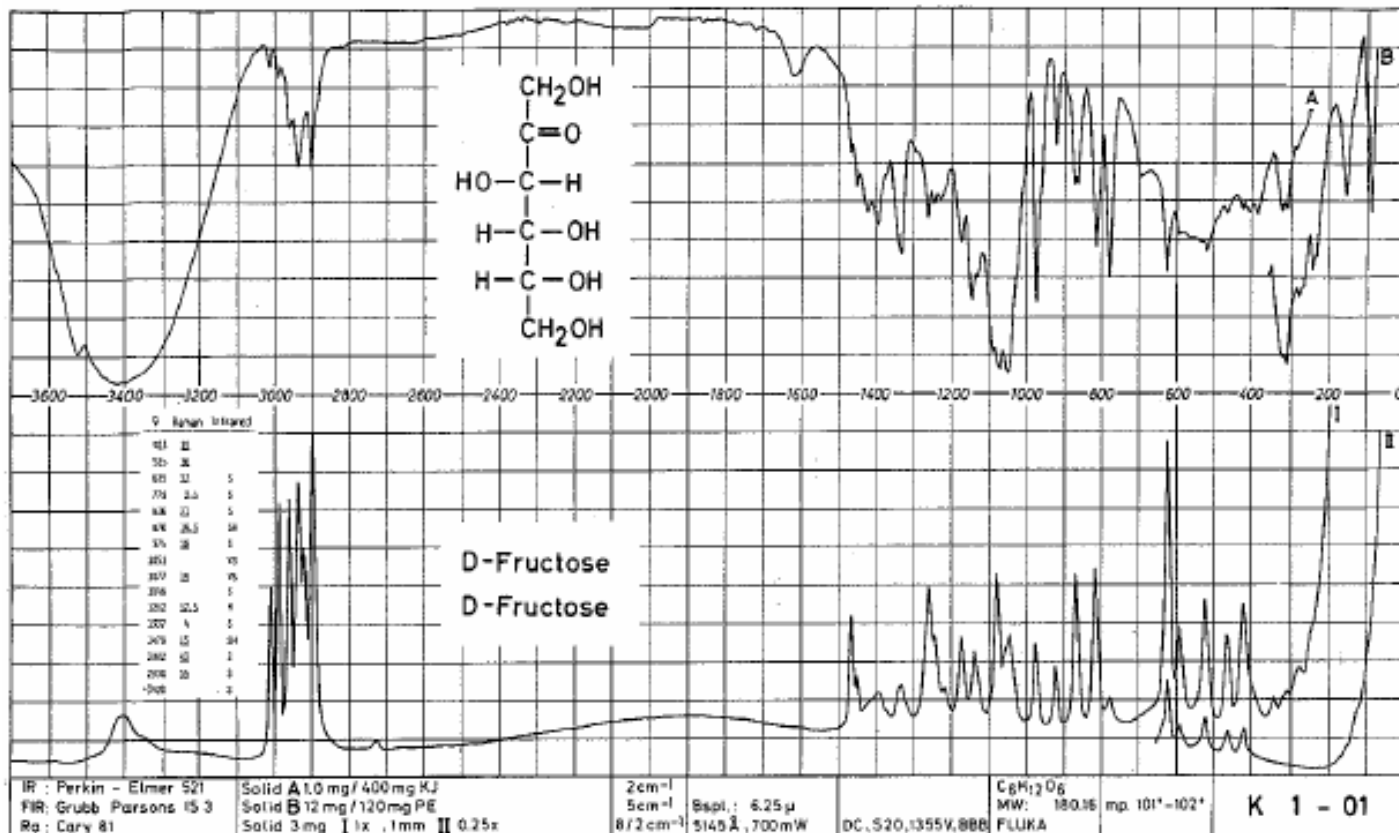


Fig. 3-84. Infrared spectrum of acetic acid. From J.D. Roberts and M.C. Caserio, *Basic Principles of Organic Chemistry*, W.A. Benjamin, N.Y., 1964.





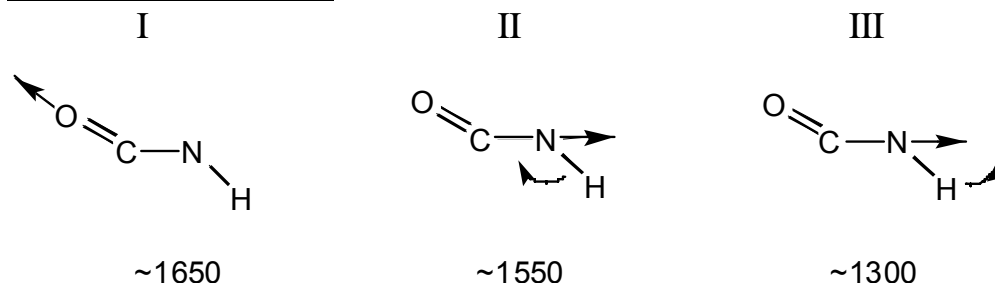


Bio-Applications of Vibrational Spectroscopy

Biggest field – proteins and peptides

a) Secondary structure

Amide modes



IR – coupling changes with conform (typ. protein freq.)

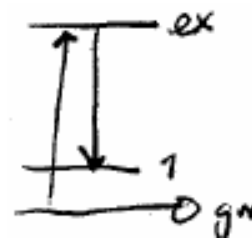
	I	II
helix	$\sim 1650^+$	1550
sheet	$\sim 1630^-$	1530
coil	$\sim 1640-50$	1520-60

Raman -see I, III – III has characteristic mix with $C_{\alpha}H$
Depends on ψ angle, characterize 2nd struct.

b) Active sites - structurally characterize, selective

i) difference spectra – e.g. flash before / after - kinetic
amides – COO^- / $COOH$ – functional group

ii) Resonance Raman – intensify modes
coupled to chromophore (e.g. heme)



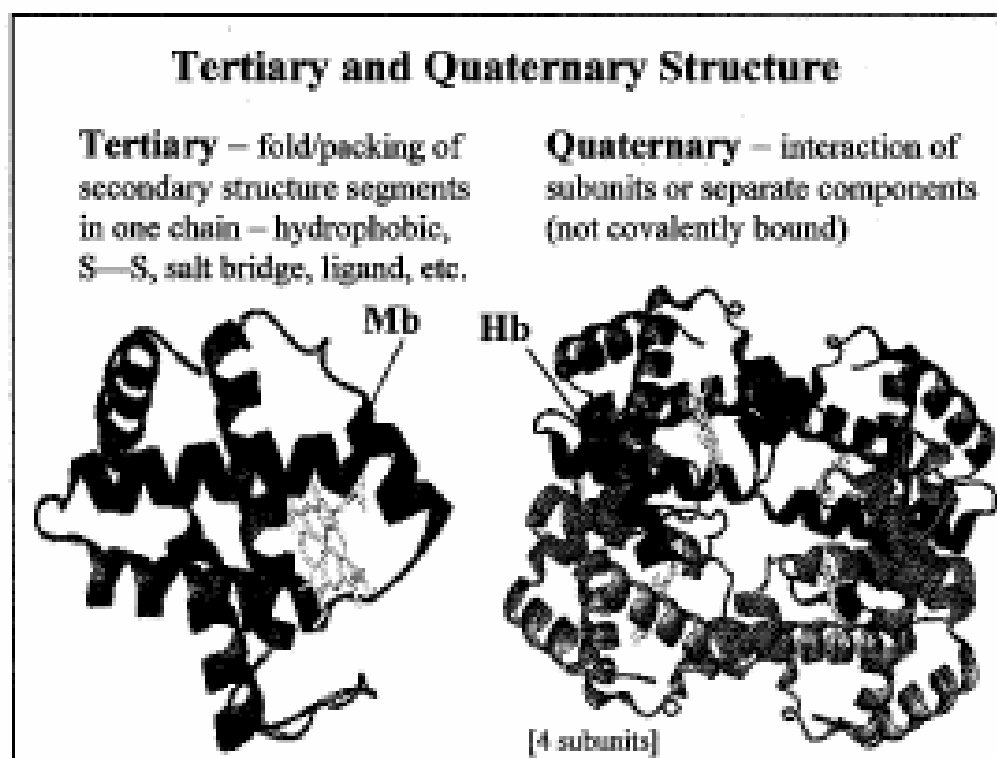
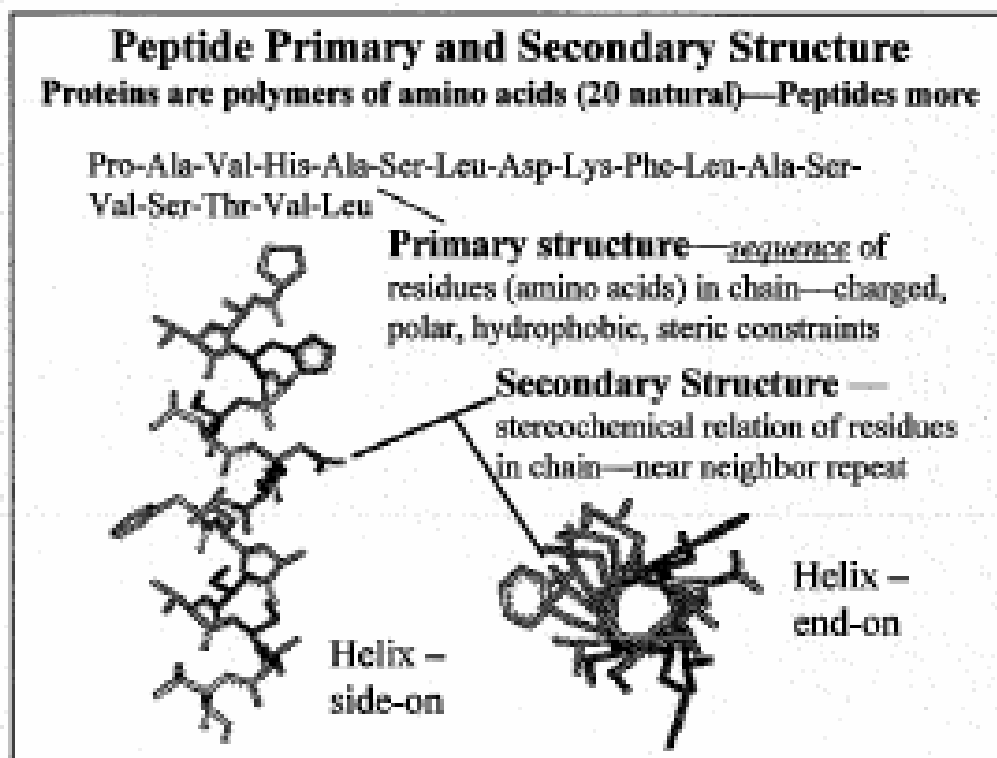
Nucleic Acids – less

a) – monitor ribose conformation

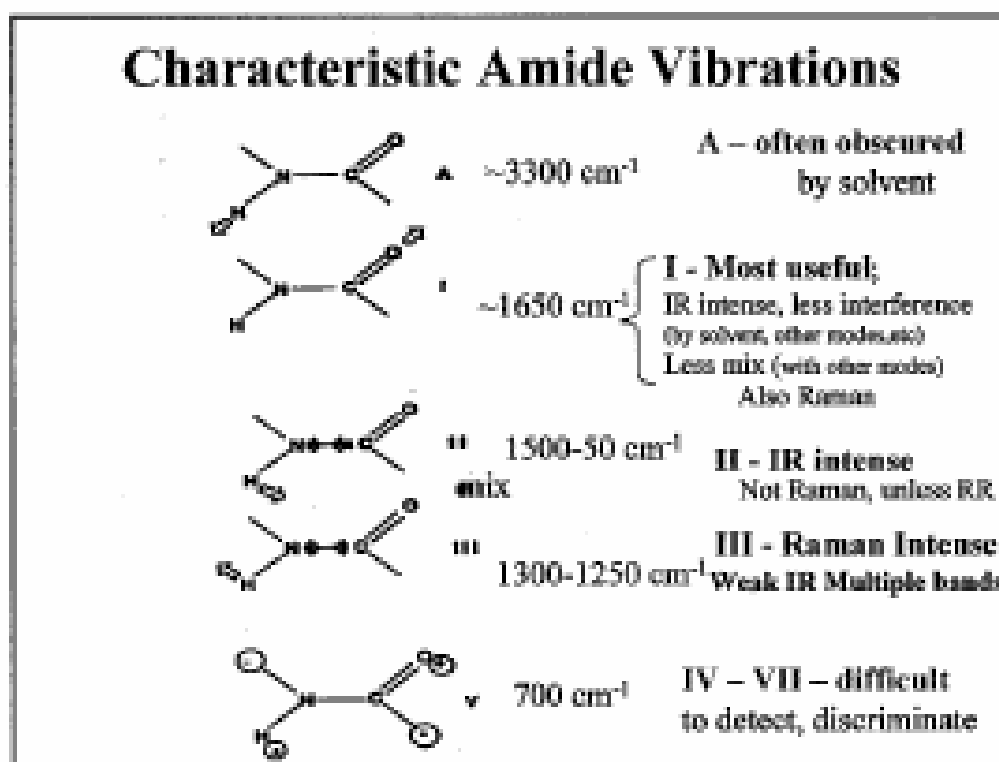
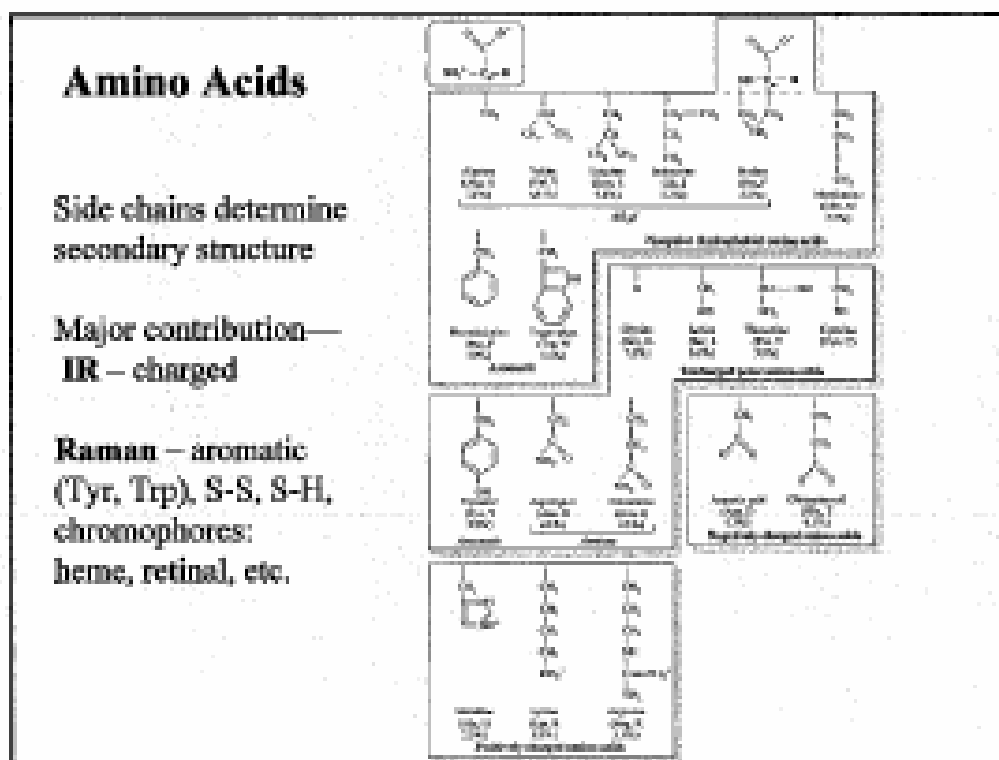
b) – single / duplex / triplex / quad – H-bond

Sugars – little done, spectra broad, some branch appl.

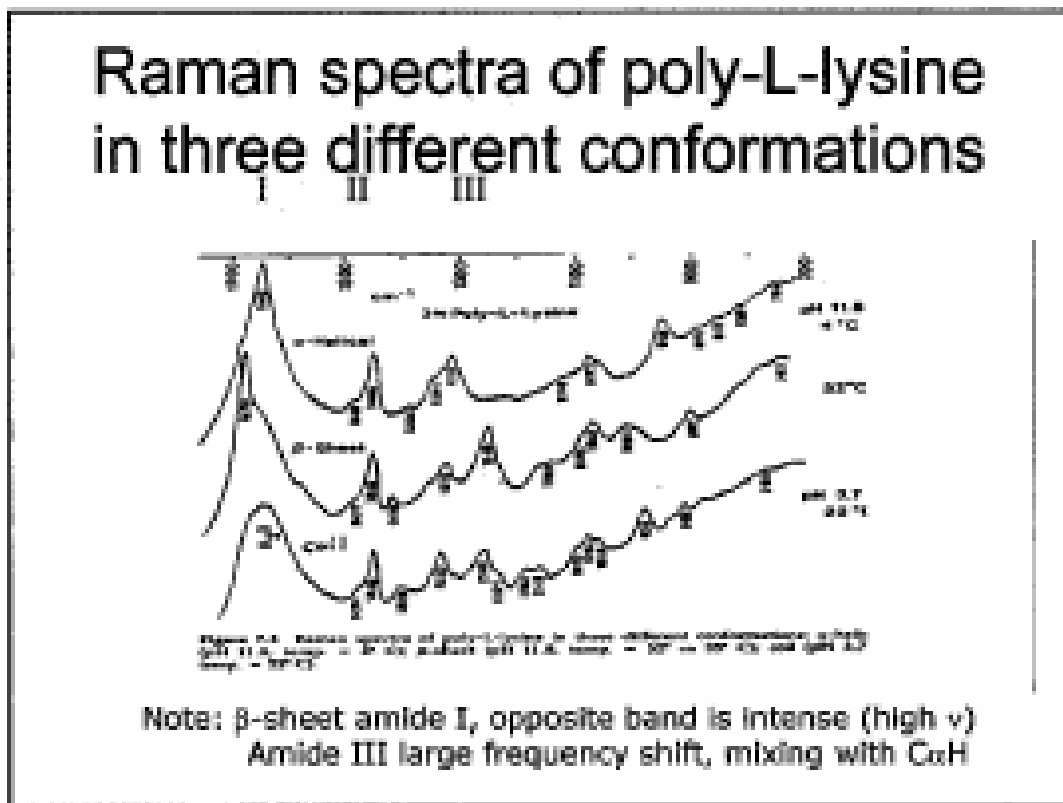
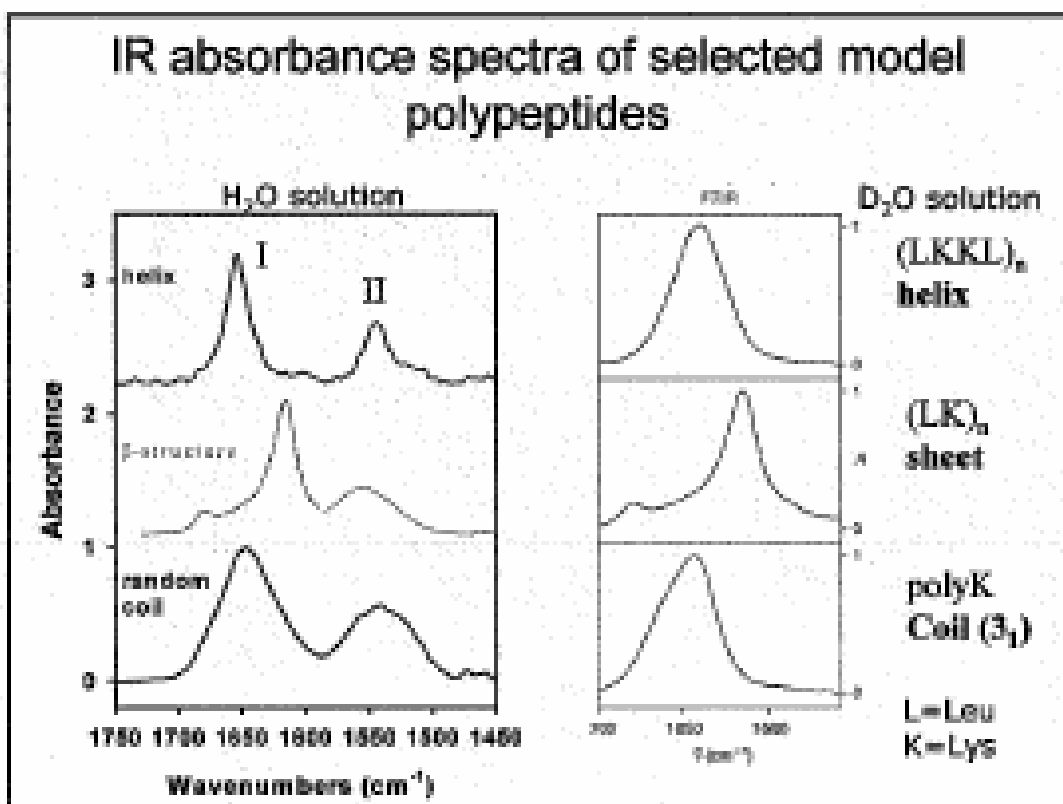
Lipids – monitor order – self assemble - polarization



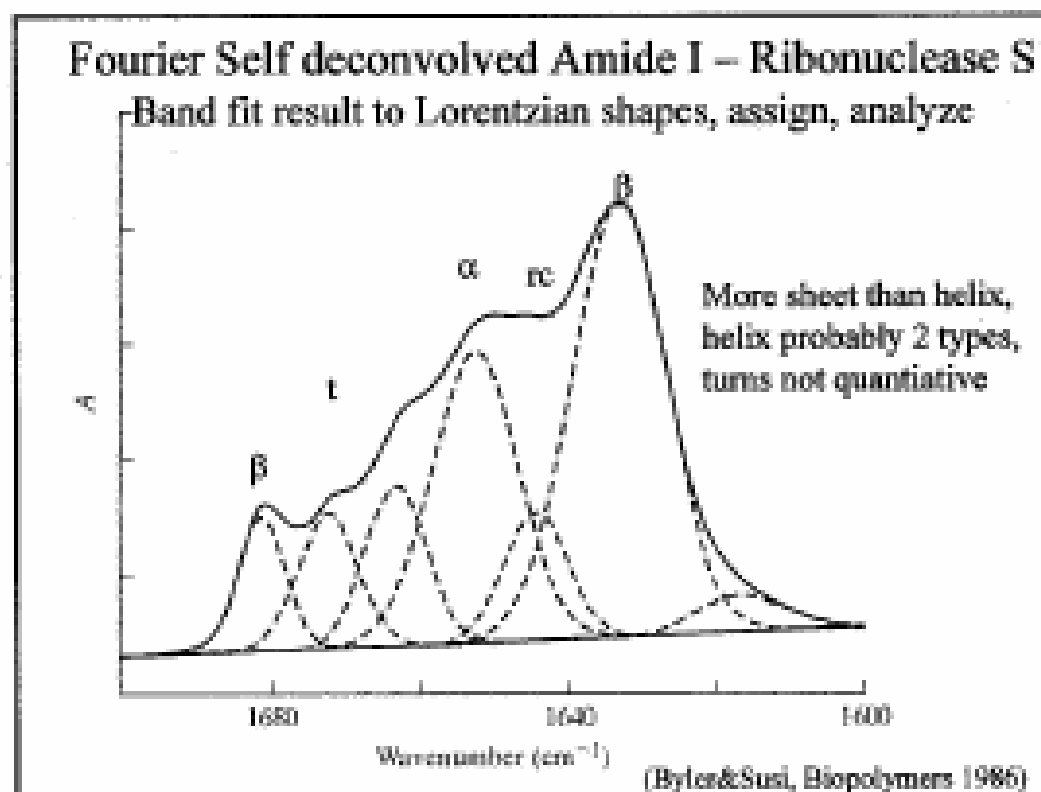
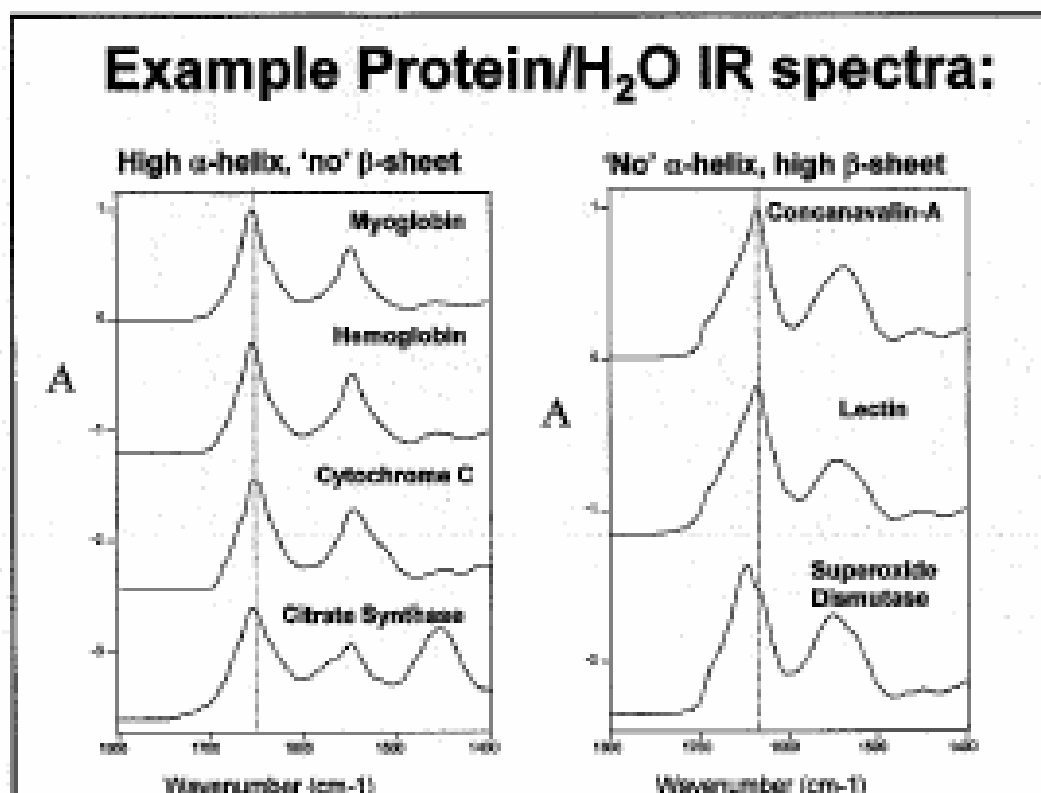
Peptide Primary, Secondary, Tertiary, Quaternary Structure diagrams (full page)



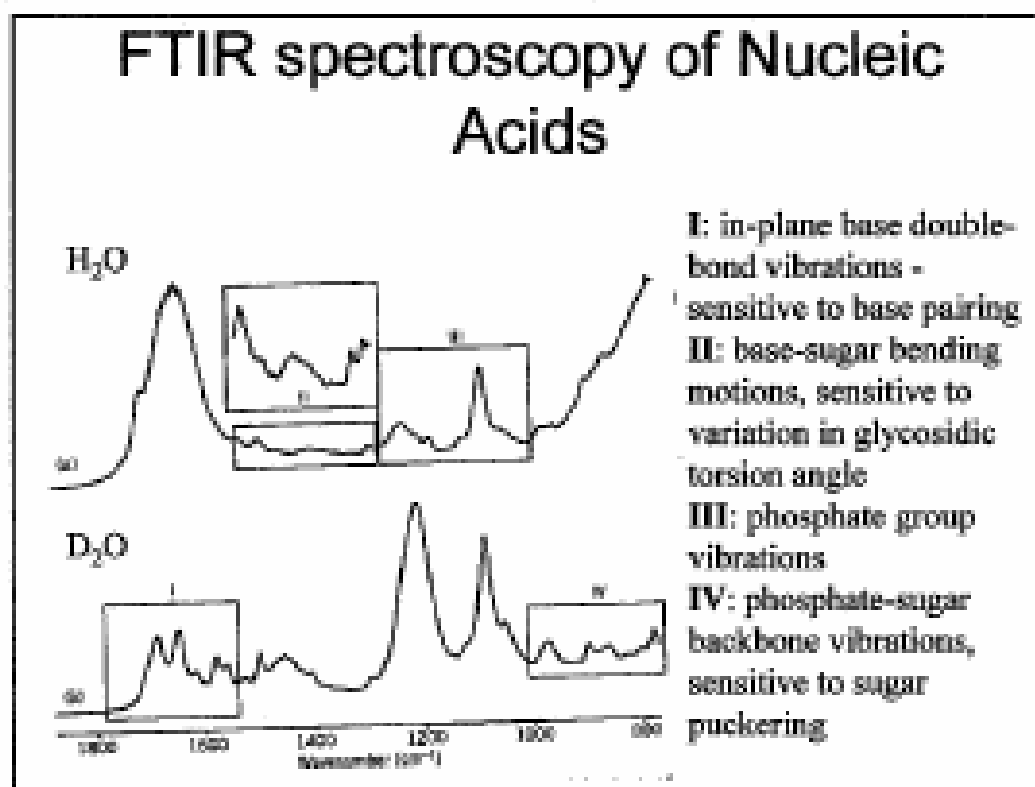
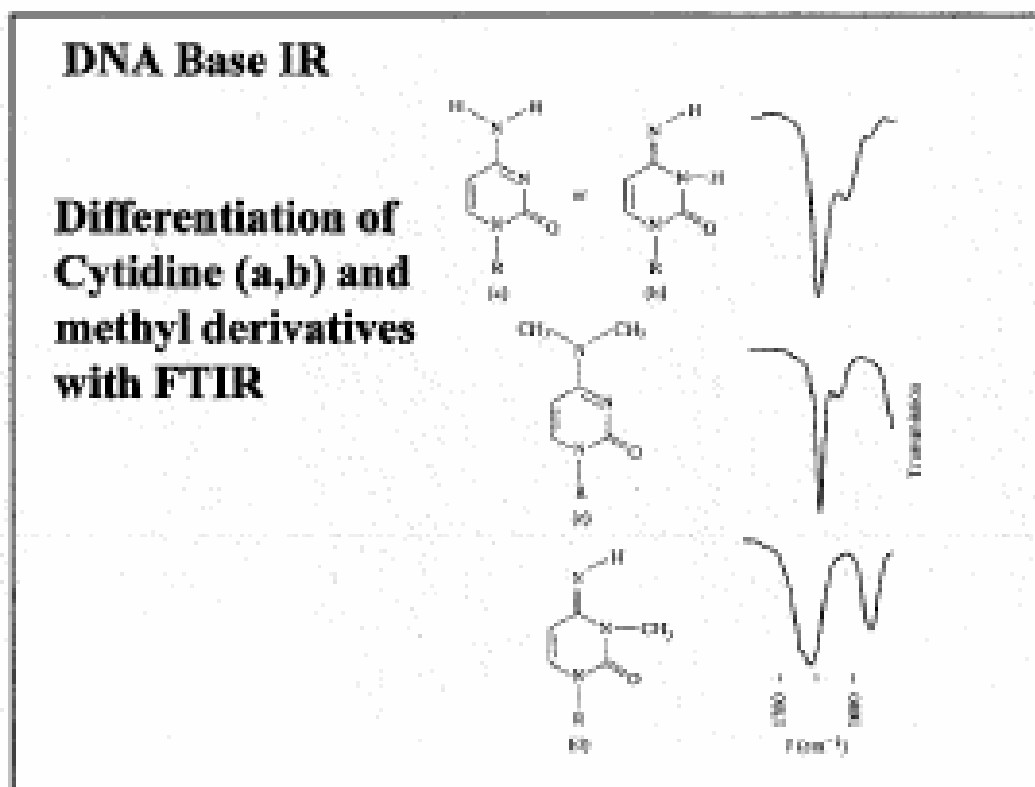
Amino Acids and Characteristic Amide Vibrations diagrams (full page)



IR absorbance and Raman spectra (full page)

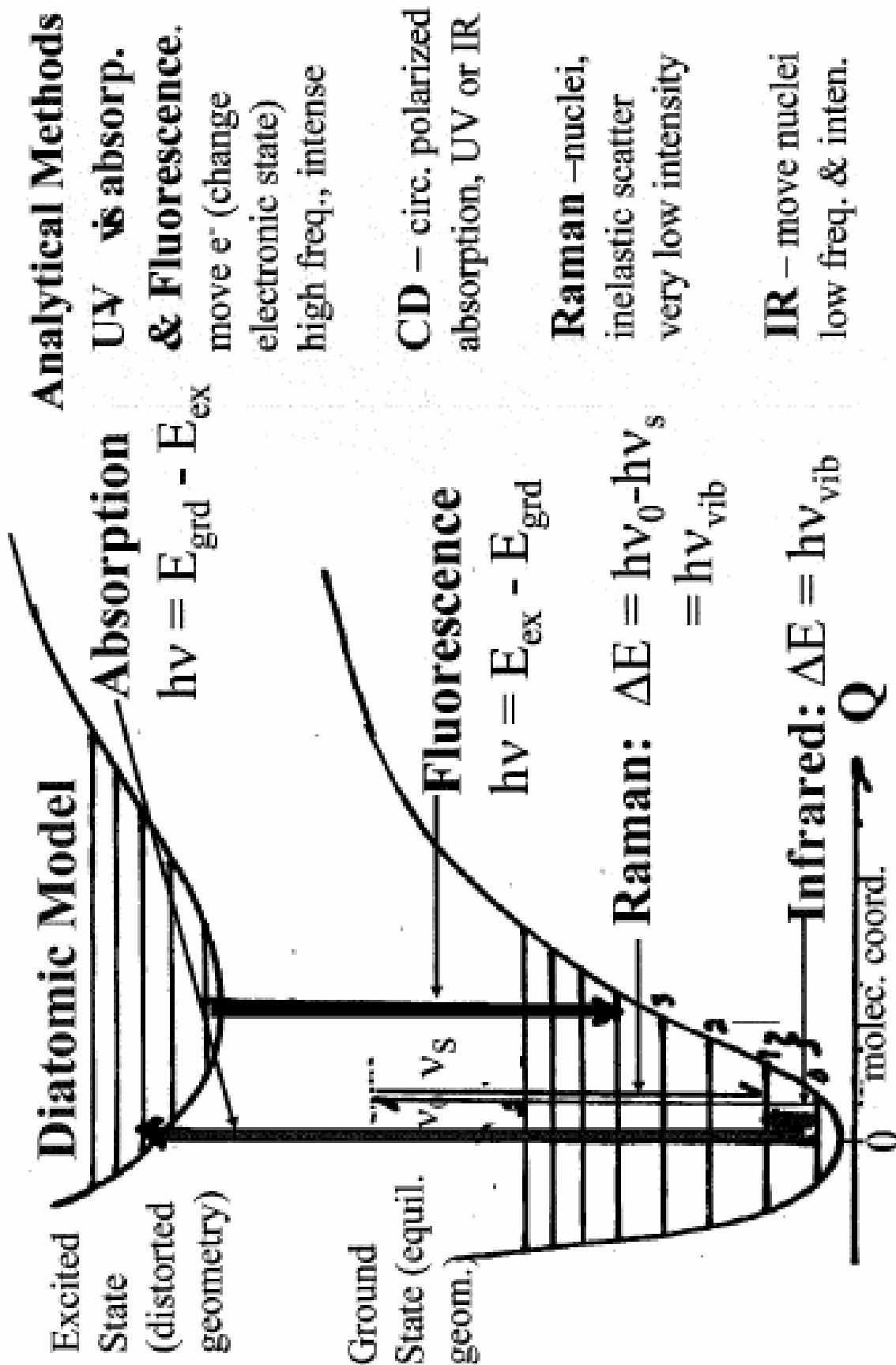


Protein/H₂O IR spectra examples (full page)



DNA Base IR and FTIR Spectroscopy of nucleic acids examples (full page)

Optical Spectroscopy - Processes Monitored UV/ Fluorescence/ IR/ Raman/ Circular Dichroism



Analytical Methods

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.

Optical Spectroscopy Processes example (full page)

Review:

Discussed Diatomic Vibrations at length
Polyatomics

a) expand $V(q) = V(q_e) + \sum_i (\partial V / \partial q_i) q_i + \sum_{i,j} (\partial^2 V / \partial q_i \partial q_j) q_i q_j$

b) diagonalize $V(q) \rightarrow V(Q)$

$$Q_i = \sum_{j} c_{ij} q_j \quad \text{linear combination x y z}$$

on each atom; $\alpha, \beta \dots$

Normal coordinates

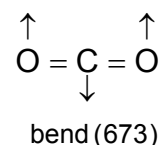
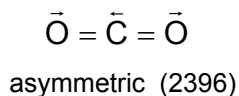
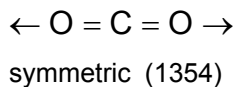
6 – Translations, rotations \rightarrow no potential E

\rightarrow eigen value “0” {diagonalize potential

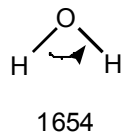
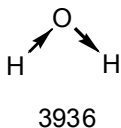
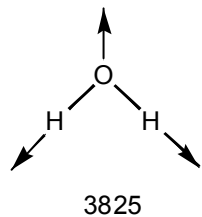
$(3N - 6)$ – vibrations \rightarrow internal nuclear motion

examples: Triatomics

linear



bent



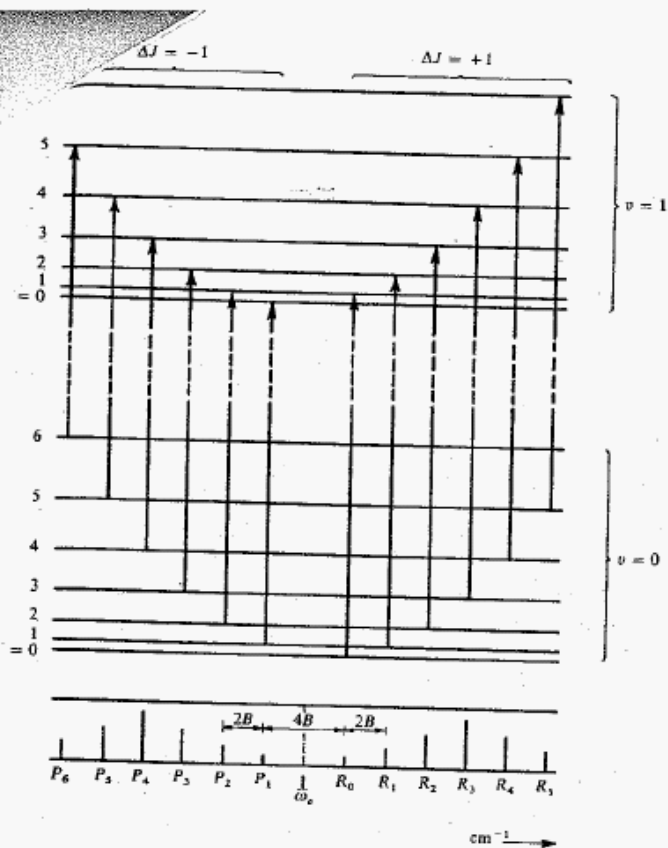
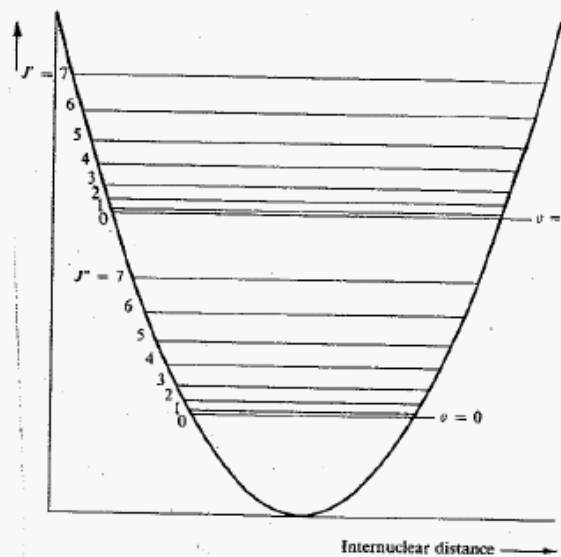


Fig. 3.6: Some transitions between the rotational-vibrational energy levels of a diatomic molecule together with the spectrum arising from them.



The rotational energy levels for two different vibrational states of a diatomic molecule.

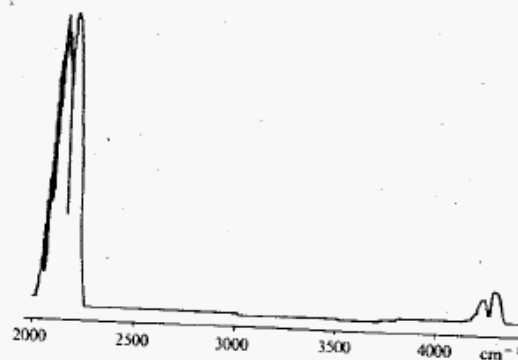


Fig. 3.7(a): The fundamental absorption (centred at about 2143 cm^{-1}), the first overtone (centred at about 4260 cm^{-1}) of carbon monoxide; the J structure of the P branch in the fundamental is partially resolved. (C pressure 650 mm Hg in a 10 cm cell.)

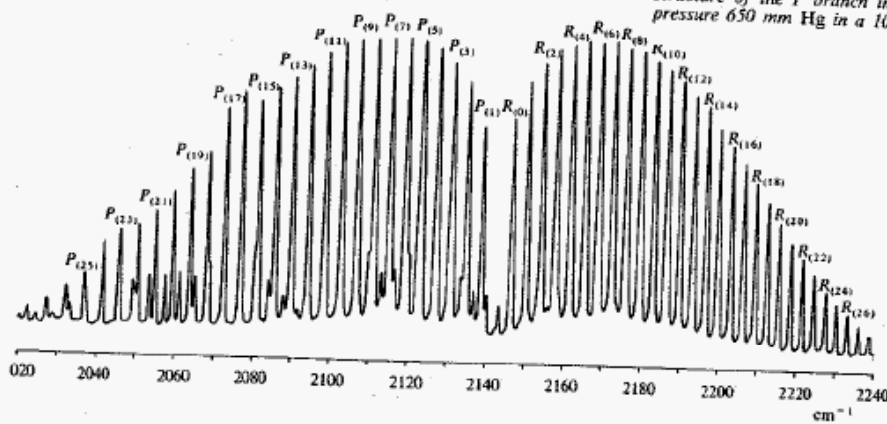


Fig. 3.7(b): The centre of the fundamental band of carbon monoxide under higher resolution than in (a). (Gas pressure 100 mm Hg in a 10 cm cell.) The lines are labelled according to their J values. The P branch is complicated by the presence of a band centred at about 2100 cm^{-1} due to the 1% of ^{13}CO in the sample; some of the rotational lines from this band appear between P branch lines, others are overlapped by a P branch line and give it an enhanced intensity to ν lines P.

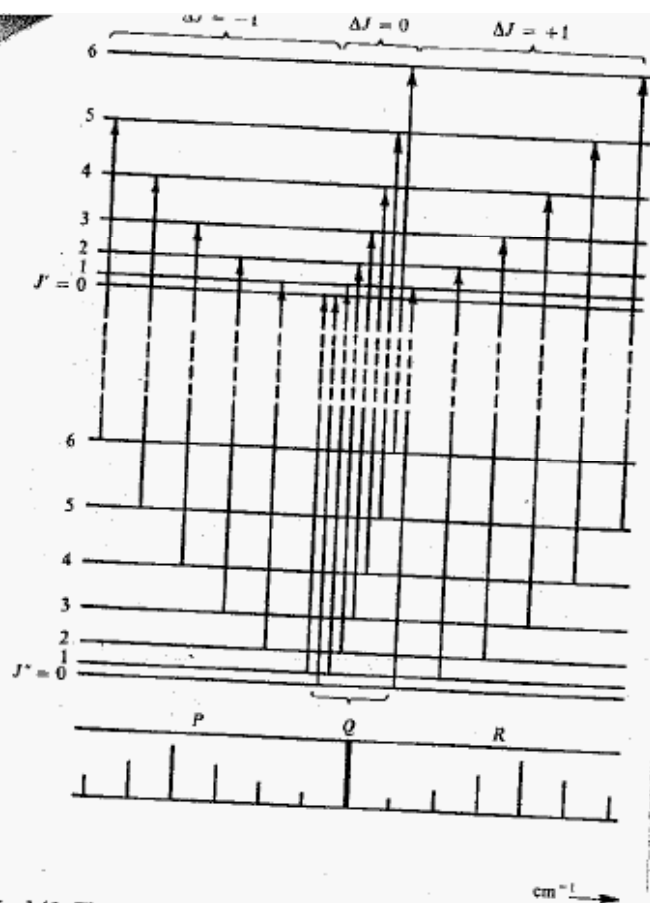


Fig. 3.13: The rotational energy levels for two vibrational states showing the effect on the spectrum of transitions for which $\Delta J=0$.

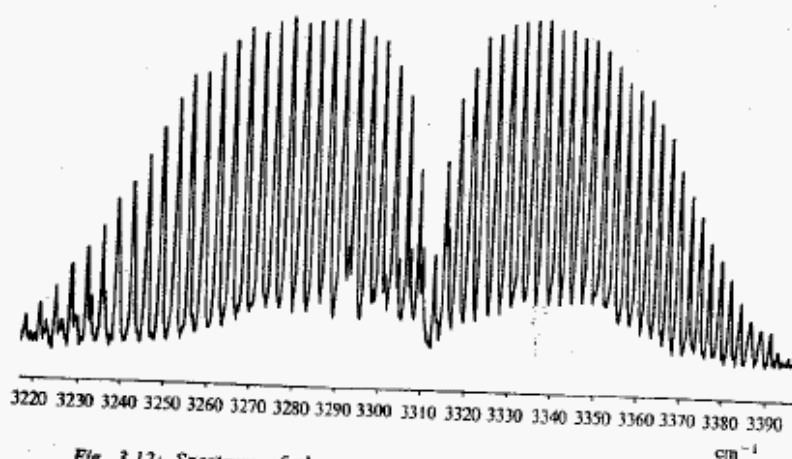


Fig. 3.12: Spectrum of the symmetric stretching vibration of the HCN molecule showing the P and R branch lines.

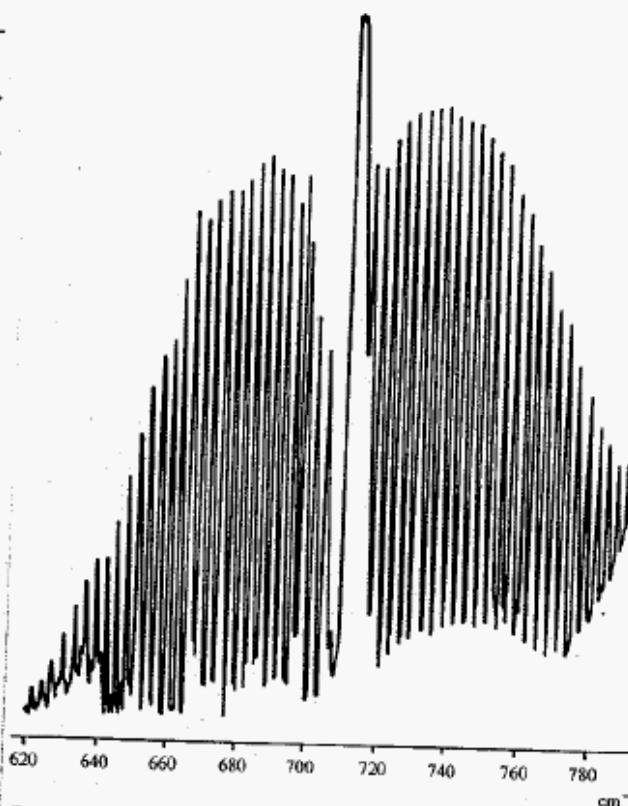


Fig. 3.14: Spectrum of the bending mode of the HCN molecule showing PQR structure. The broad absorption centered at 800 cm^{-1} is due to impurity.

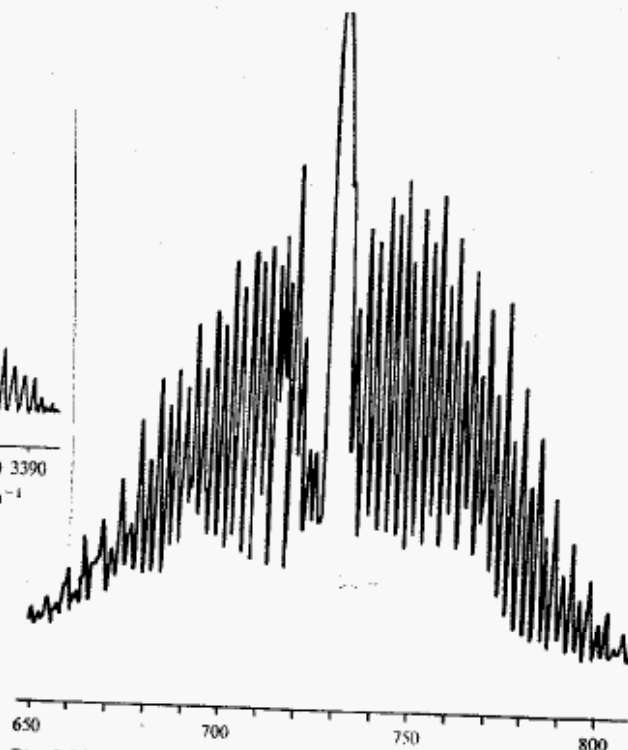


Fig. 3.16: The spectrum of a bending mode of acetylene, $\text{HC}\equiv\text{CH}$, showing the strong, weak, strong, weak, ... intensity alternation in the rotation structure due to the nuclear spin of the hydrogen atoms.