

<http://www.k2.phys.waseda.ac.jp/Movies.html>

Moves **clockwise** if ATP **synthesized** from free energy of H^+ $pH5 \rightarrow pH7$
Moves **counter-clockwise** if ATP being **used** and **pumping** H^+ $pH7 \rightarrow pH5$

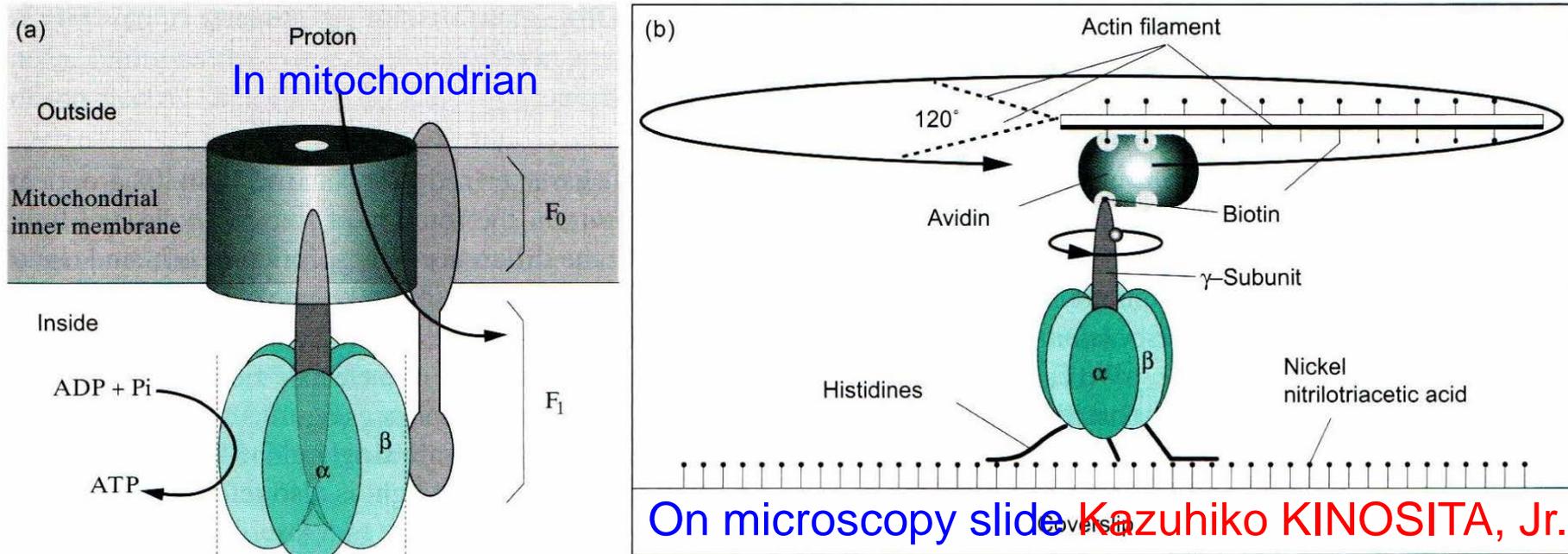


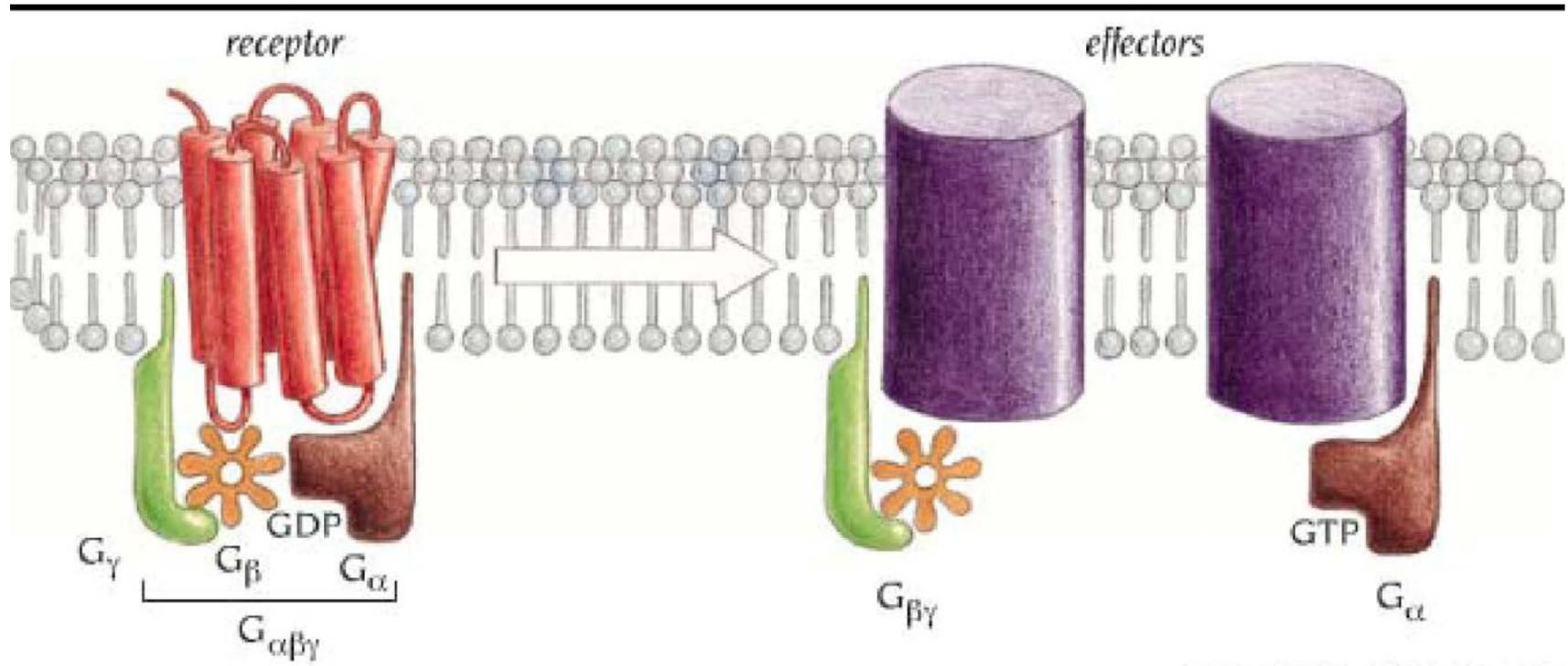
FIGURE 13.27 Single-molecule studies of F_1 -ATPase. (a) The F_0F_1 -ATPase is shown schematically. The F_0 subunit is embedded in the membrane and is a proton pump. The F_1 -ATPase is a rotary motor that synthesizes ATP from ADP and inorganic phosphate. (b) In the experiment, the F_1 subunit was attached to a glass coverslip through nickel-histidine linkages, and a fluorescent actin filament was attached to the gamma subunit. The rotation of a single actin filament could be observed by fluorescence microscopy. (Reprinted from Cell, 93 (1), F1-ATPase: A Rotary Motor Made of a Single Molecule, pp. 21, Copyright © 1998, with permission from Elsevier.)

- **G-Protein-Coupled receptors** have emerged over the last 30 years as a MAJOR biological signaling motif--constituting perhaps 10% of the human genome, and the target of 60% of commercial drug research .

- Examples:

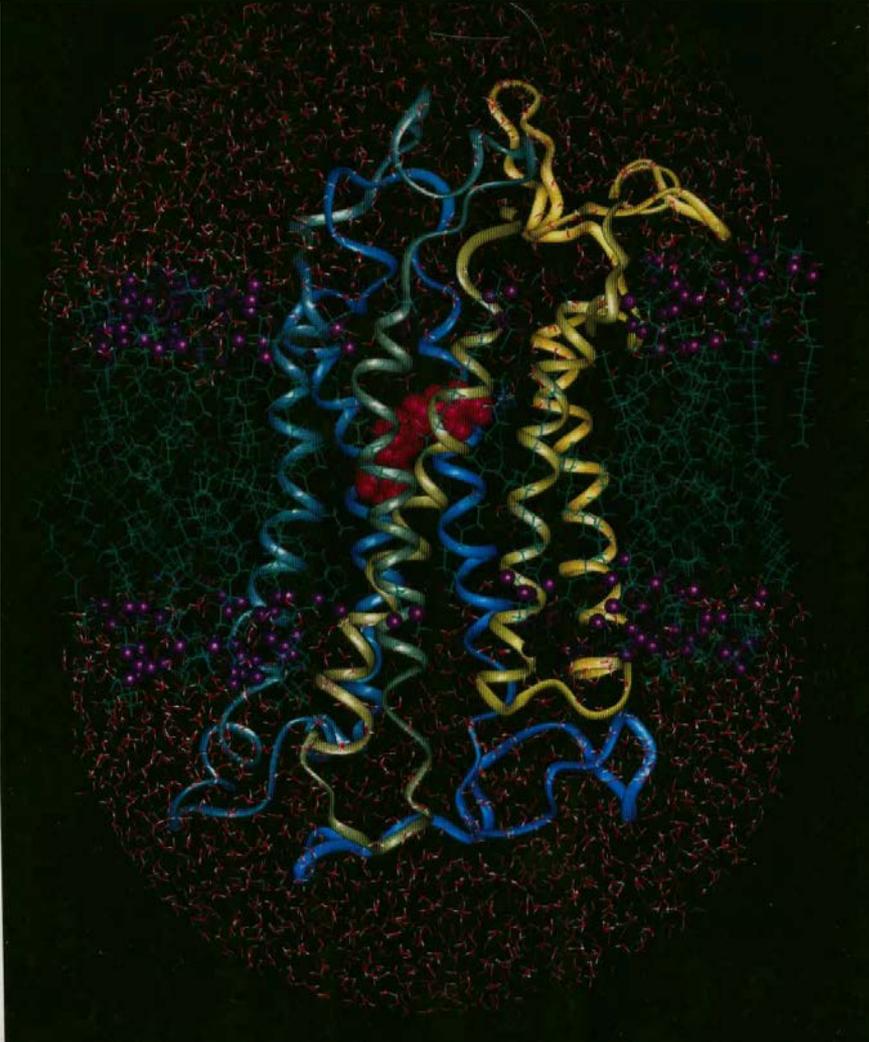
| <u>Receptor</u> | <u>Mediates</u> | <u>Drug/Hormone (ligand)</u> |
|-------------------|-----------------|------------------------------|
| Adrenergic | hypertension | beta blockers/adrenaline |
| Cannabinoid | lots of things | marijuana |
| dozens more | | |

Rhodopsin **vision** **retinal Schiff base + light**



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Rhodopsin, harboring the visual pigment retinal (pink) is a member of the large class of signal transducing proteins called G-protein coupled receptors.



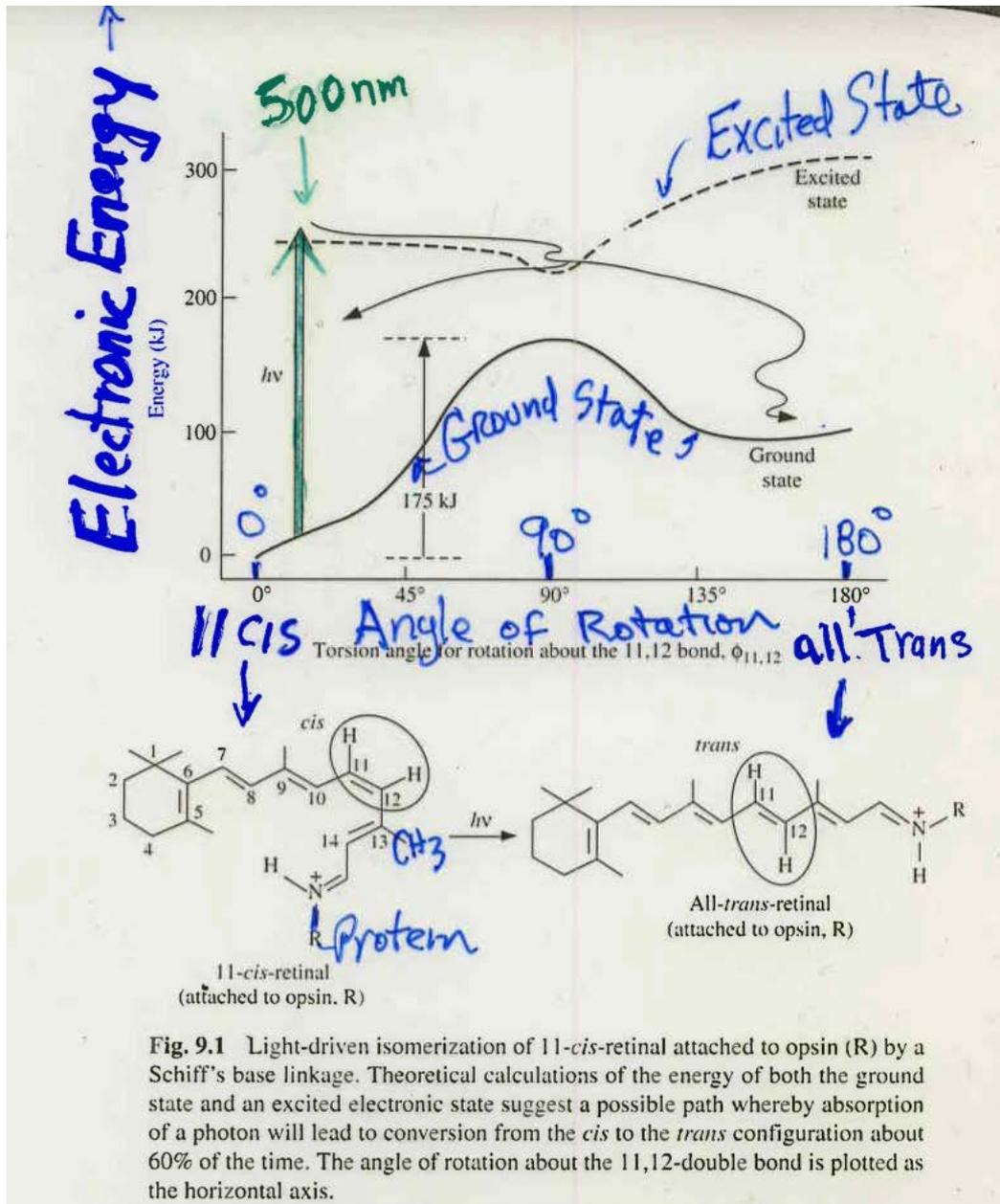
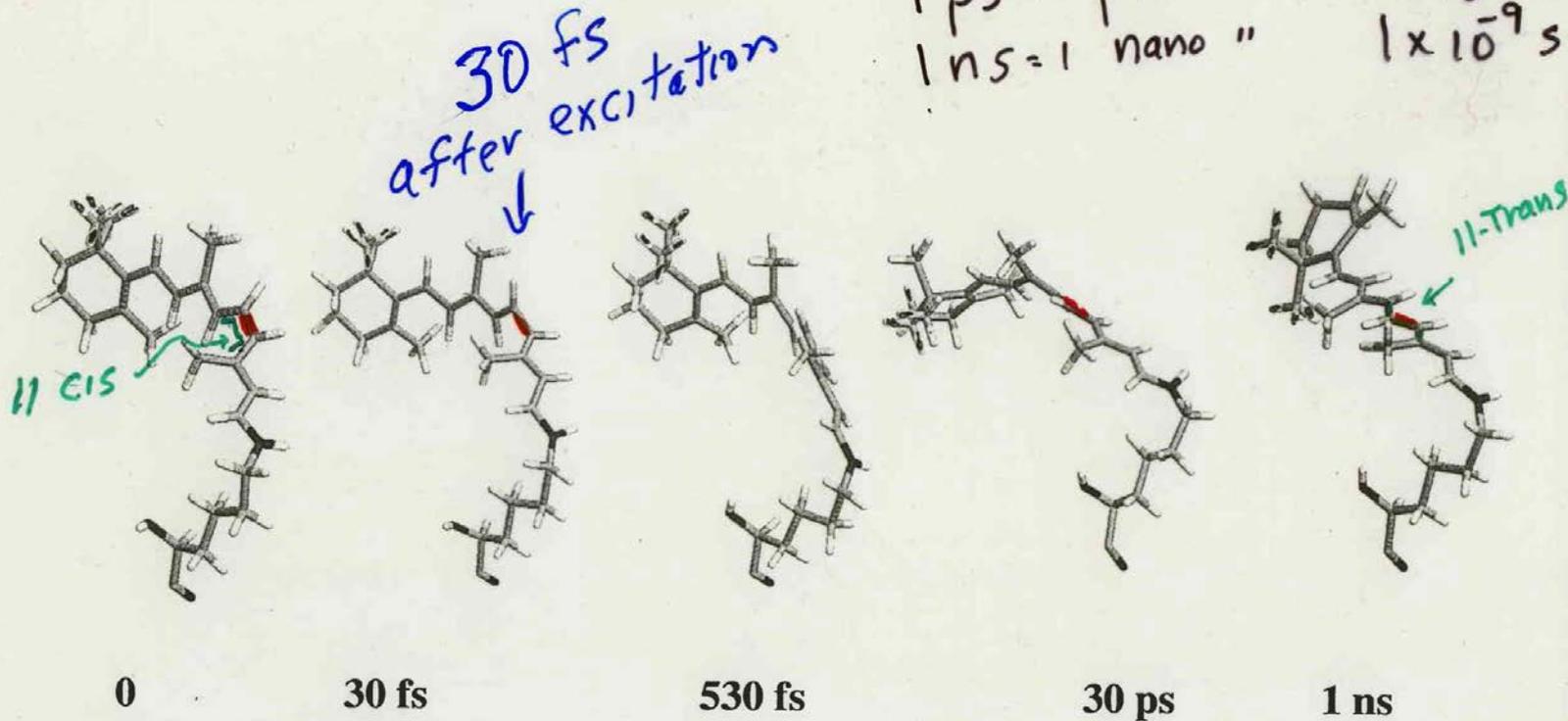


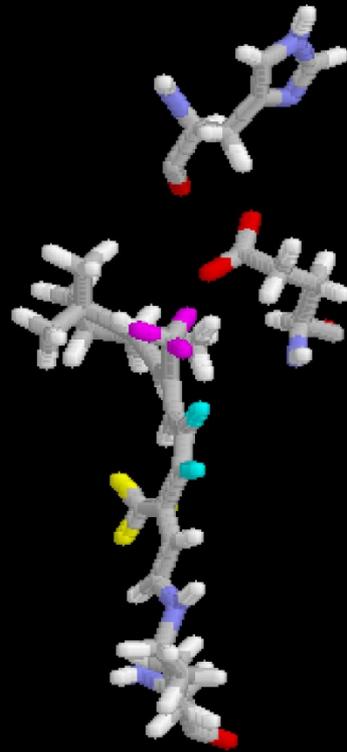
Figure 11.3
page 410

$1 \text{ fs} = 1 \text{ femtosecond} = 1 \times 10^{-15} \text{ s}$
 $1 \text{ ps} = 1 \text{ pico " } = 1 \times 10^{-12} \text{ s}$
 $1 \text{ ns} = 1 \text{ nano " } = 1 \times 10^{-9} \text{ s}$

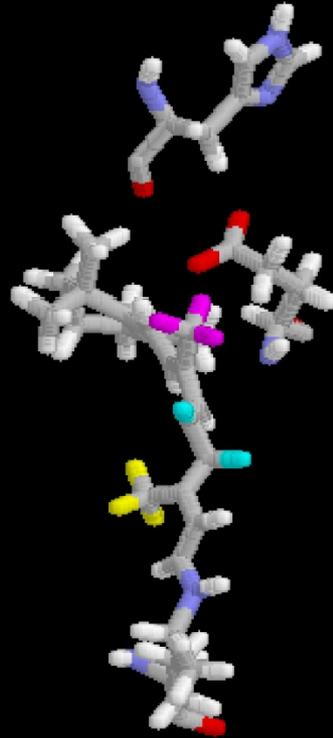


Snapshots of simulated isomerization of retinal Schiff base of rhodopsin (1hzx)

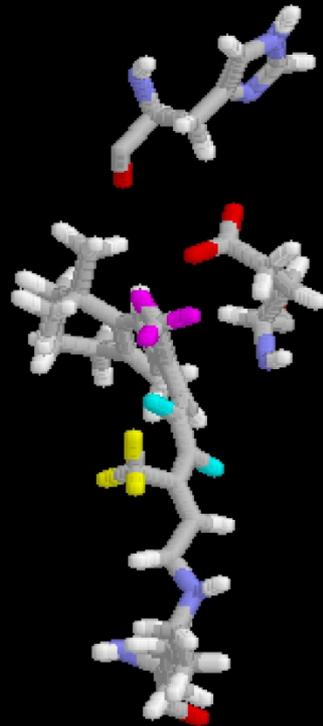
Retinal: 11-cis



excited state



all-trans



Optical Rotary Dispersion (ORD) and Circular Dichroism (CD) of Nucleic Acids

Very useful when biopolymers absorb light strongly and have **chirality**

A **chiral molecule** is a type of molecule that has a non-superimposable mirror image.

A chiral molecule will rotate the plane of LINEARLY polarized light.

Every photon of **linearly polarized** light shakes electrons back and forth in same direction.

Photons of **unpolarized** light have **random** polarization directions.

The polarization of **circularly polarized** light photons depends on time and position in a sinusoidal manner.

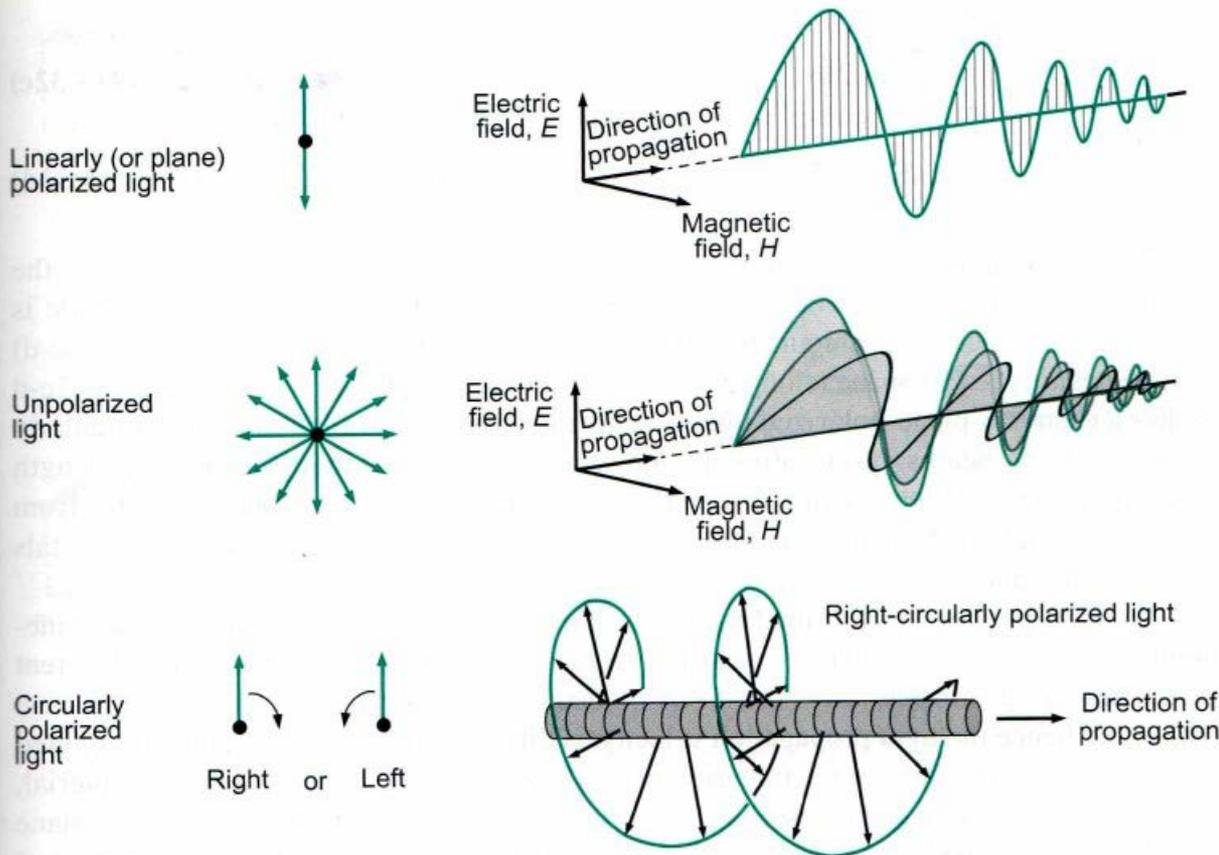


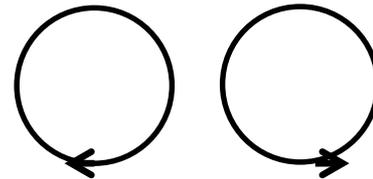
FIGURE 13.28 Different types of polarized light. In the middle column, the arrows represent the electric vector of the light as seen by an observer moving with the light (or equivalently viewing the light down the direction of propagation). The light is moving into the page.

What is CIRCULARLY polarized light?

With LINEARLY polarized light the electric field shake electrons back and forth in straight line.



CIRCULARLY polarized light the field continually direction rotates in a **circle**
Electrons move around in a small circle



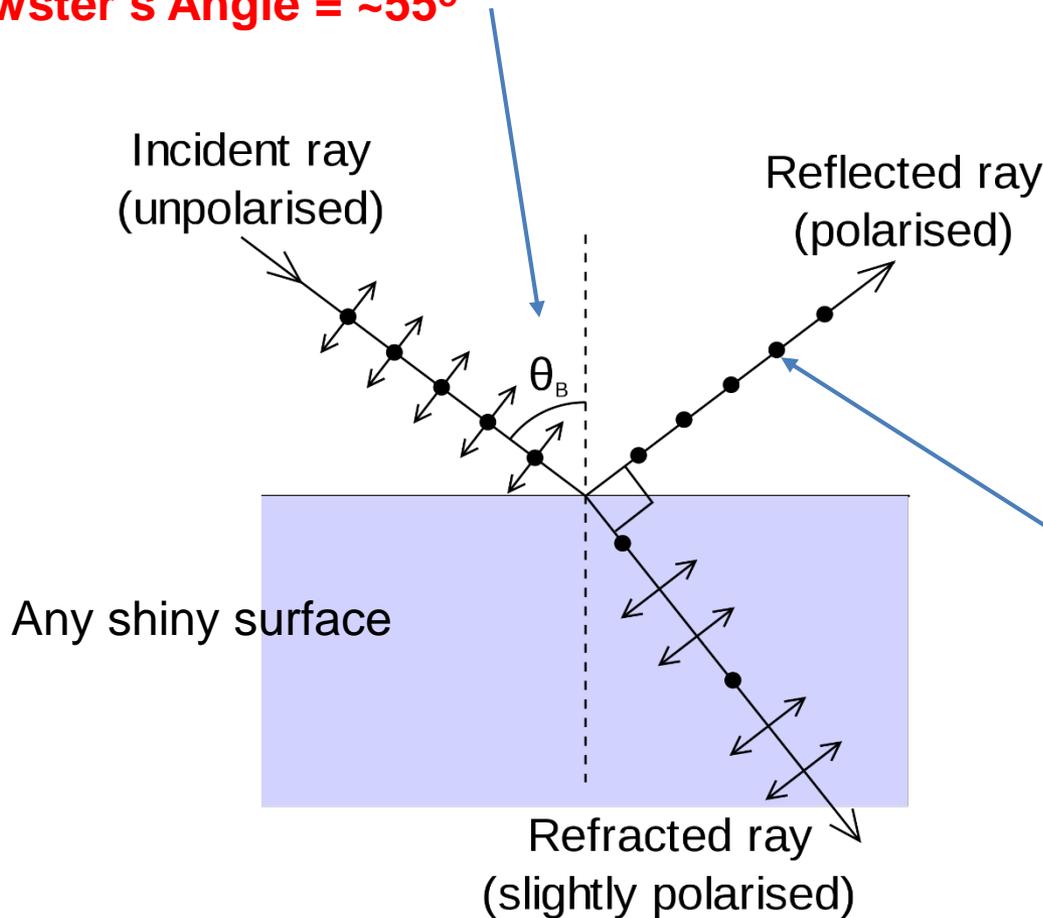
Circular Dichroism

$$\text{CD signal} = \epsilon_{\text{Left}} - \epsilon_{\text{Right}}$$

i.e., the **difference** of UV absorbance using **left** and **right** CIRCULARLY polarized light.

Suppose you are in a store to buy polaroid sunglasses: How to check whether sun glasses are polaroid or not

Brewster's Angle = $\sim 55^\circ$



Rotate the glasses while view a reflection off the floor at about 50 degree angle.

The reflected light is almost ALL HORIZONTALLY POLARIZED, which does not pass through the sunglasses in the normal orientation

[Brewster's angle - Wikipedia](#)

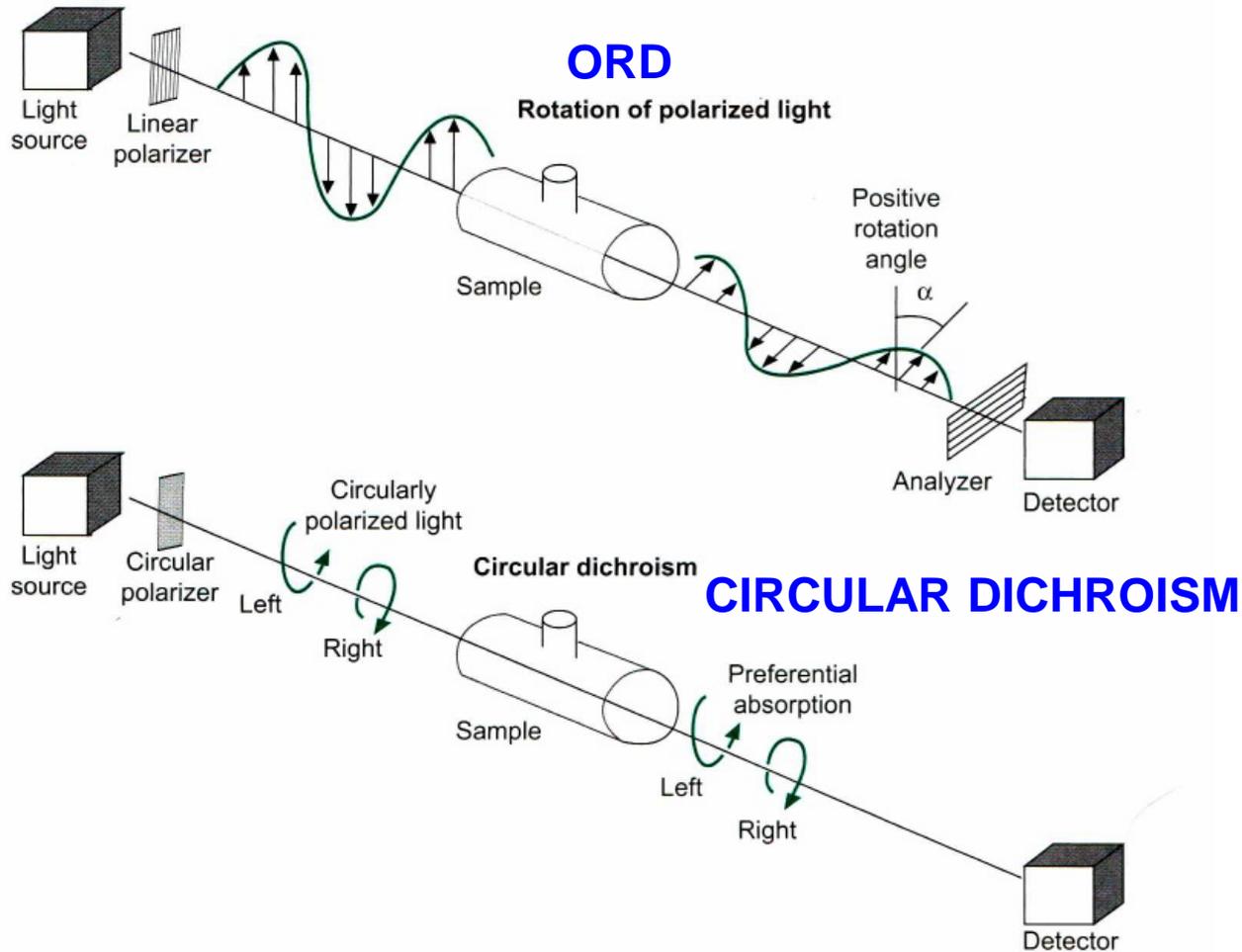


FIGURE 13.29 (top) Measurement of the rotation of linearly polarized light. If the sample in the top cell has significant absorbance, the transmitted light will be elliptically polarized (figure 13.30). (bottom) Measurement of circular dichroism, the preferential absorption of circularly polarized light. The detector measures the difference in absorbance of the right- and left-circularly polarized light.

RNA and DNA easily distinguished with CD

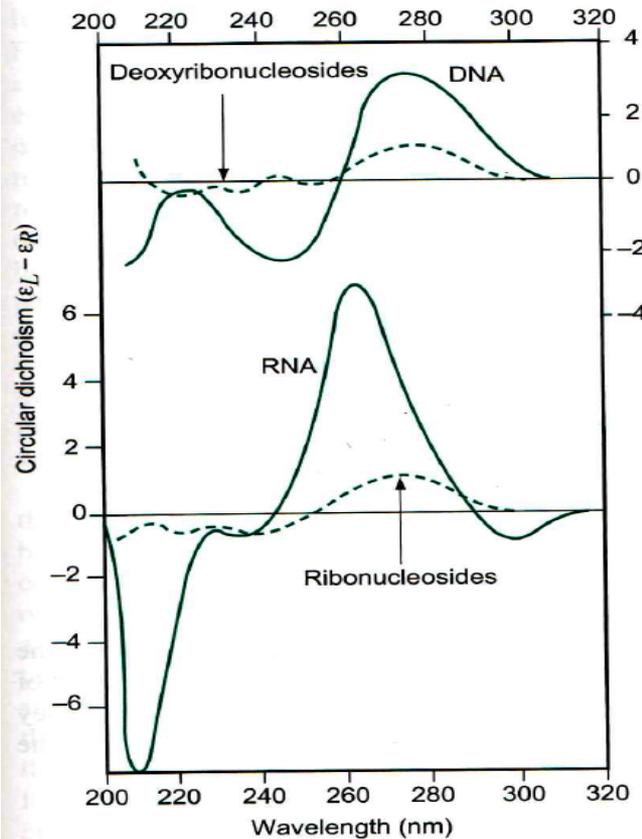


FIGURE 13.31 Circular dichroism of double-stranded DNA and RNA compared with their component mononucleosides. (*M. lysodeikticus* DNA data from F. Allen et al., 1972, *Biopolymers* 11:853. Rice dwarf virus RNA data from T. Samejima et al., 1968, *J. Mol. Biol.* 34:39. Nucleoside spectra calculated from the base composition (72% G + C for the DNA; 44% G + C for the RNA) and CD data of C. R. Cantor et al., 1970, *Biopolymers* 9:1059, 1079.) (From V. A. Bloomfield, D. M. Crothers, and I. Tinoco, Jr., 1974, *Physical Chemistry of Nucleic Acids* (New York: Harper & Row), 134.)

3 forms of DNA easily distinguished with CD

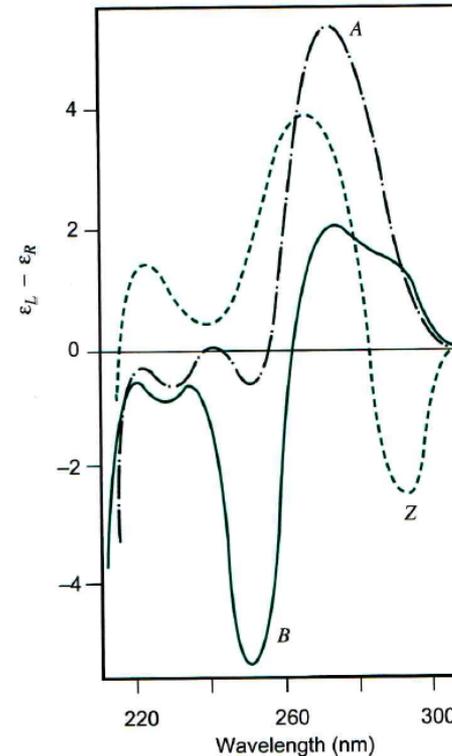


FIGURE 13.32 Circular dichroism of the synthetic polynucleotide poly(dG-dC). (poly(dG-dC) in different conformations. The polynucleotide is a double-stranded helix; each strand has a sequence of alternating deoxyguanylic acid (dG) and deoxycytidilic acid (dC). Different conformations are obtained by changing the solvent. The B form is obtained in 0 to 40% ethanol or 10^{-3} M to 2 M NaCl; it is a right-handed helix with about 10 base pairs per turn of the double helix. The Z form is obtained in 56% ethanol or 3.9 M NaCl; it is a left-handed helix. The A form is obtained in 80% ethanol; it is a right-handed helix with about 11 base pairs per turn. (Reprinted by permission from Macmillan Publishers Ltd: *Nature*, Polymorphism of a synthetic DNA in solution, by F. M. Pohl, vol. 260, p. 365, copyright © 1976. (<http://www.nature.com/nature/journal/v260/n5549/pdf/260365a0.pdf>))

Vibrational Spectroscopy and Light Scattering

Fig. 13.26

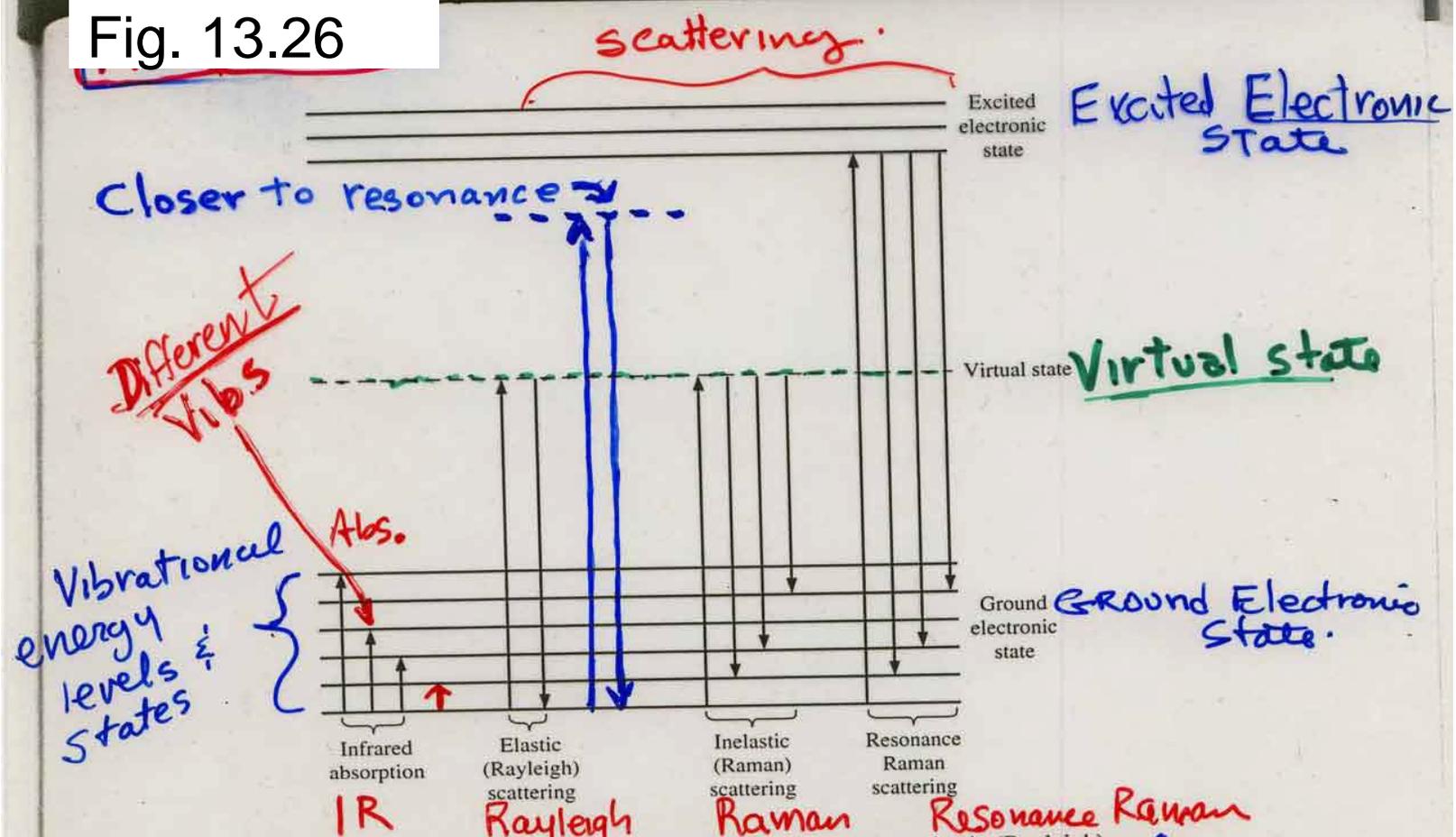


Fig. 10.41 Energy-level diagram for infrared absorption, elastic (Rayleigh) scattering, and inelastic (Raman) scattering. Transitions between vibrational energy levels of the ground electronic state absorb infrared radiation; not all transitions are allowed. For elastic scattering the frequency of the incident light is equal to the frequency of the scattered light. For inelastic scattering the frequency of the scattered light is different from that of the incident light. The virtual state shown can have any energy; the scattering of light occurs in any region of the spectrum.

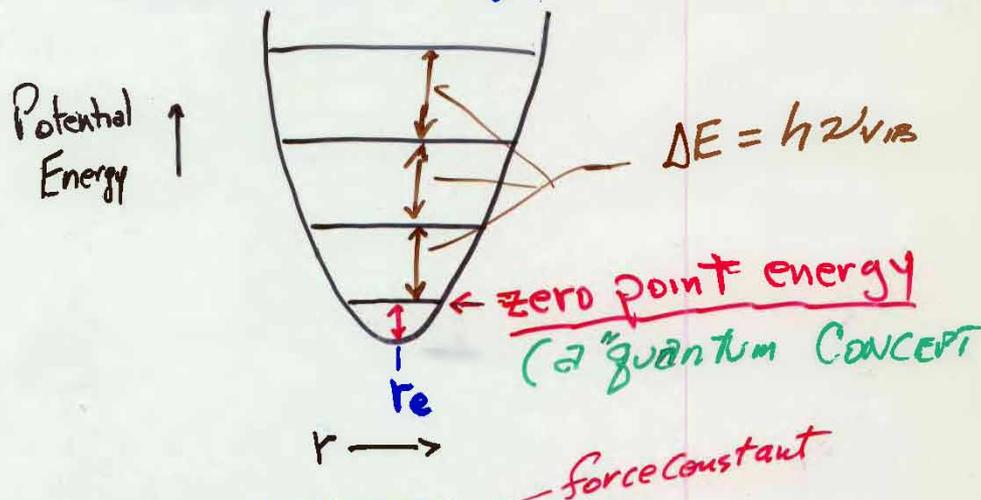
Resonance Raman
 ~ 1000 times enhanced.

Chemical Bond \cong Hooke's Law Spring

$$\text{Potential Energy} = \frac{1}{2} k (r - r_e)^2$$

↑ force constant

where r_e = equilibrium bond length



$$\nu_{\text{vib}} = \frac{1}{2\pi} \sqrt{\frac{k}{\text{mass}}}$$

↑ force constant

IF $^{12}\text{C}-\text{H}$ has $\nu_{\text{vib}} = 3000 \text{ cm}^{-1}$

then $^{13}\text{C}-\text{H}$ " " = $\sqrt{\frac{12}{13}} \times 3000 \text{ cm}^{-1}$
 = 2882 cm^{-1}

FOR C-D $\nu_{\text{vib}} = \sqrt{\frac{1}{2}} \times 3000 = 2121 \text{ cm}^{-1}$

Vibrational Signatures

$$\nu_{\text{VIB}} = \frac{1}{2\pi} \sqrt{\frac{k}{\text{mass}}}$$

High Freq. from ξ large force constant (K) (strong bond)
 Small mass $\text{H-H} = 4400 \text{ cm}^{-1}$
 $\text{N}\equiv\text{N} = 2300 \text{ cm}^{-1}$

Low Freq. from ξ small force const. (weak bond)
 large mass. $\text{I-I} \sim 200 \text{ cm}^{-1}$

Stretching:
 Bond $\frac{1}{\lambda} \text{ cm}^{-1}$

O-H 3600

>C-H 3000

$\text{-C}\equiv\text{C-}$ 2100

>C=O 1700

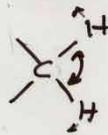
-C=C- 1600

>C-C< 900

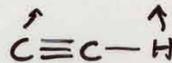
>C-I 500

I-I 200

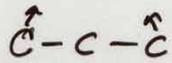
Bending:



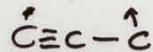
1450 cm^{-1}



700

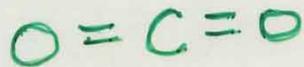


~ 500



300

What if two identical bonds
 strongly coupled?



Normal Mode
 Demo.

NORMAL MODES OF BENZENE

C-H stretches

3061 cm^{-1}
1158 cm^{-1}

$3N-6 = 30$ vibrat
mod
N = number of atoms

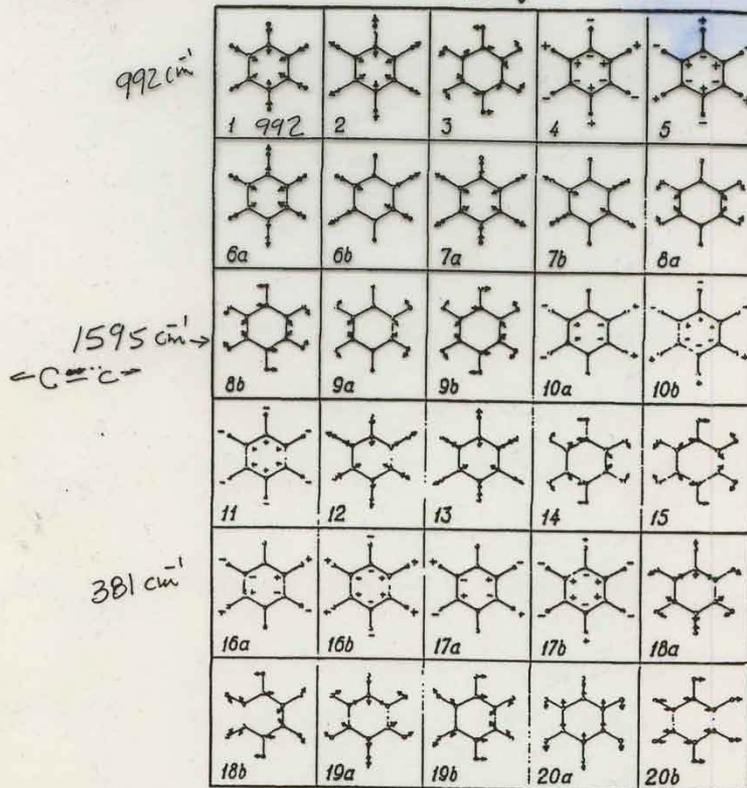


Figure 4

Group Modes

In many instances, functional groups (-OH, -C=O, COOH, NO₂) of organic/ inorganic molecules are not related via symmetry to other parts of the molecule. Under those circumstances, their internal motions are largely isolated from the delocalized normal coordinates of the parent molecule and thus appear in vibrational spectra at energies characteristic of the given functional group. Table 2 lists some of the more common of these group modes. The spread in energies for group modes largely reflects the influence of the rest of the molecule on the local bond strengths of the functional group. In many respects the localized vibrational behavior of functional groups mimics that of isolated small molecules. For instance, the Raman and IR intensities of group modes reflect the