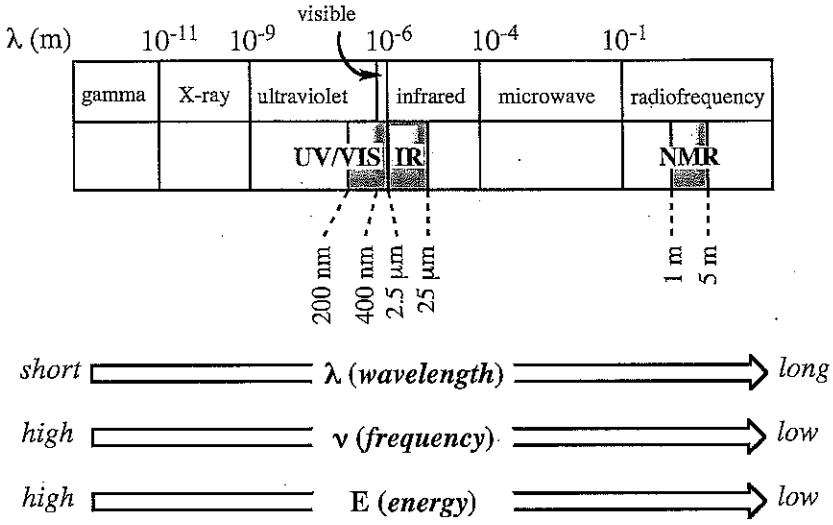
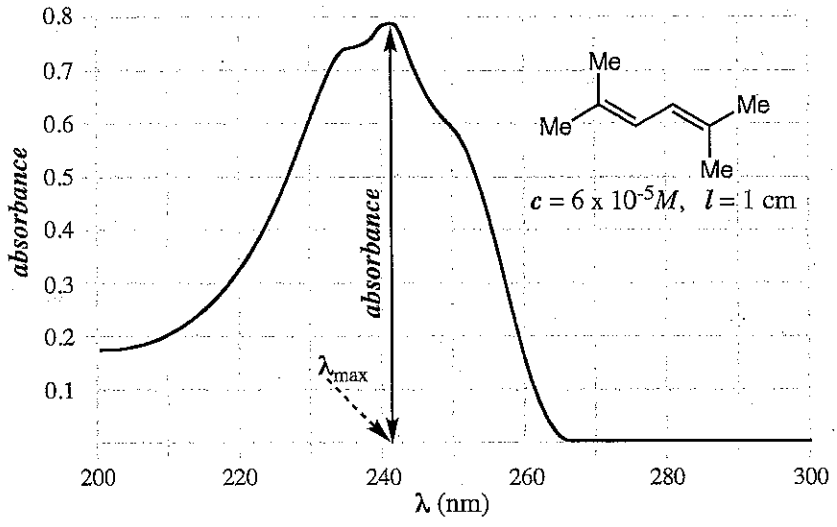
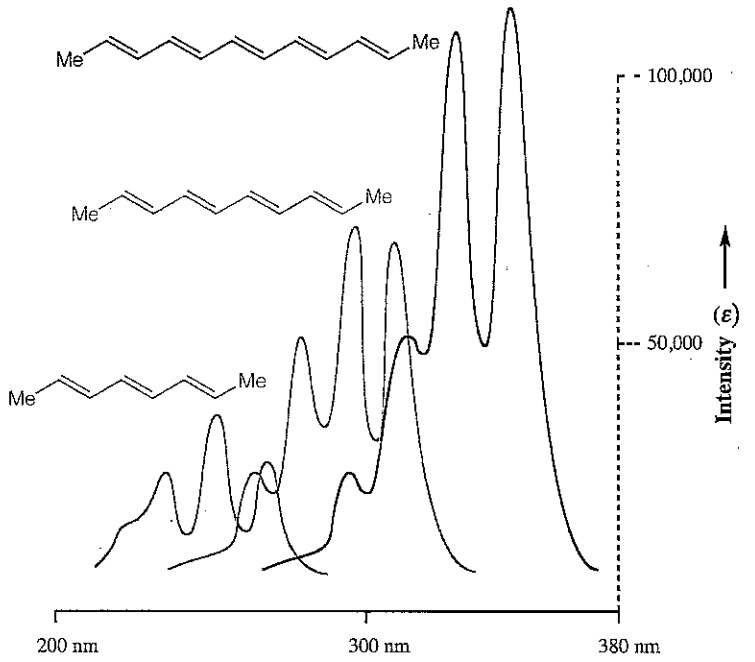
Spectroscopy and the Electromagnetic Spectrum

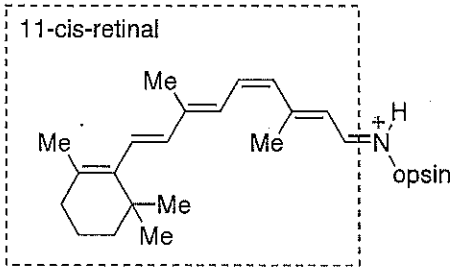


- A typical UV absorption spectrum:

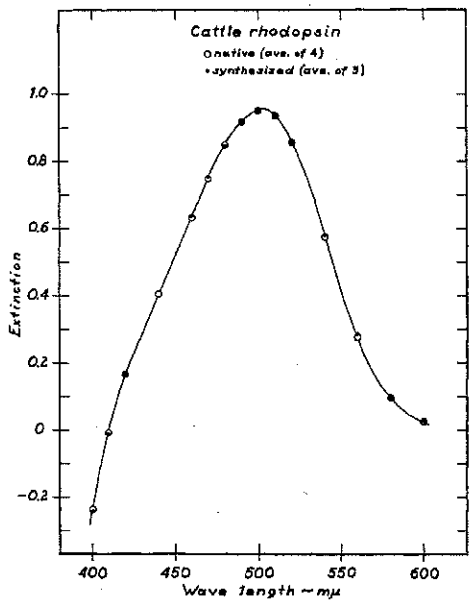




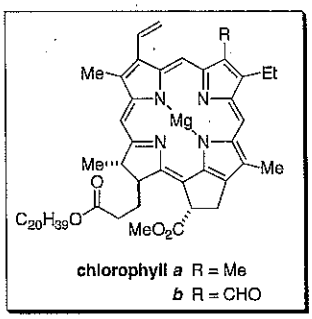
Used as a fingerprint for highly conjugated molecules:



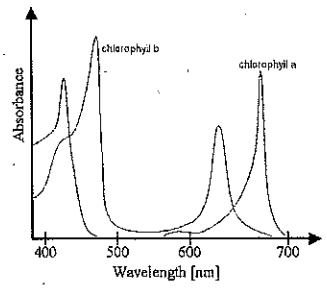
Rhodopsin

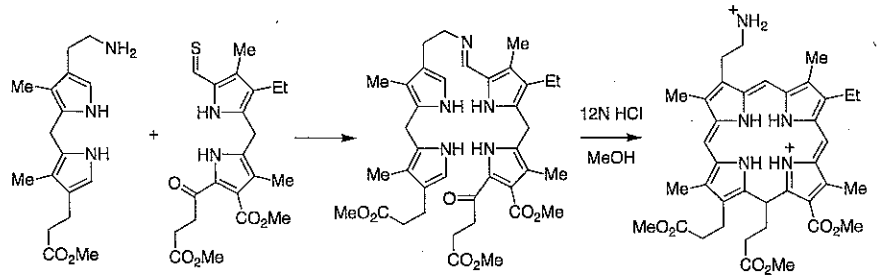


from Hubbard and Wald, *J. Gen. Phys.*, **1952,** *36(2)*, 269.



chlorophyll ***a*** R = Me
b R = CHO

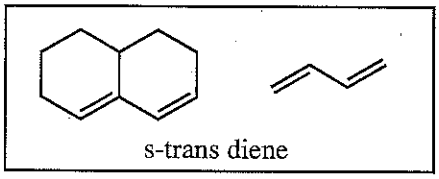




total synthesis: R.B. Woodward *et al*, *J. Am. Chem. Soc.* **1960,** *82,* 3800.

functional group	transition	λ_{max}	ε
alkene	π-π*	103	15000
		174	5500
alkyne	π-π*	178	10000
		196	2000
		223	160
thioether R-S-R	n-σ*	235	180
bromide	n-σ*	208	300
iodide	n-σ*	259	400
aldehyde/ketone	π-π*	189	900
	n-π*	270	20
ester/acid/amide	n-π*	200-210	50-200
butadiene ***	π-π*	217	23000
enone/enal ***	π-π*	227	18000
	n-π*	320	20

- Woodward-Fieser empirical rules:


s-trans diene

214 nm


s-cis diene

253 nm

substituent	bathochromic shift
additional double bond	+ 30 nm
"exocyclic" double bond	+5
alkyl group	+5
oxygen	+6
nitrogen	+60
sulfur	+30
halogen	+5

- Fieser-Kuhn empirical rules:

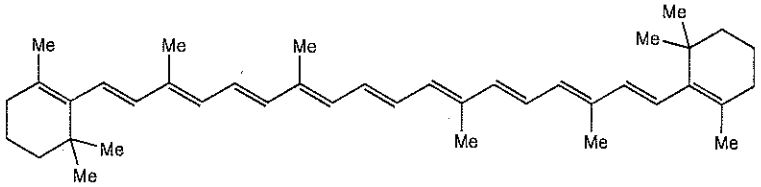
$$\lambda_{max} = 114 + 5M + n(48.0 - 1.7n) - 16.5\ R_{endo} - 10\ R_{exo}$$

n = # of conjugated double bonds

M = # of alkyl substituents

R_{endo} = # of rings with "endocyclic" double bond

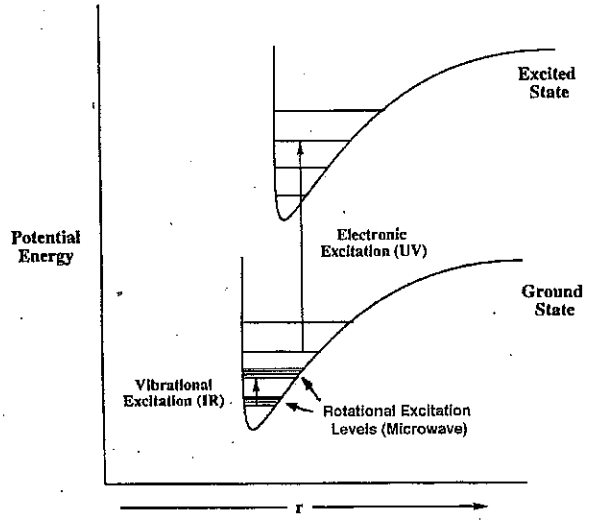
R_{exo} = # of rings with "exocyclic" double bond



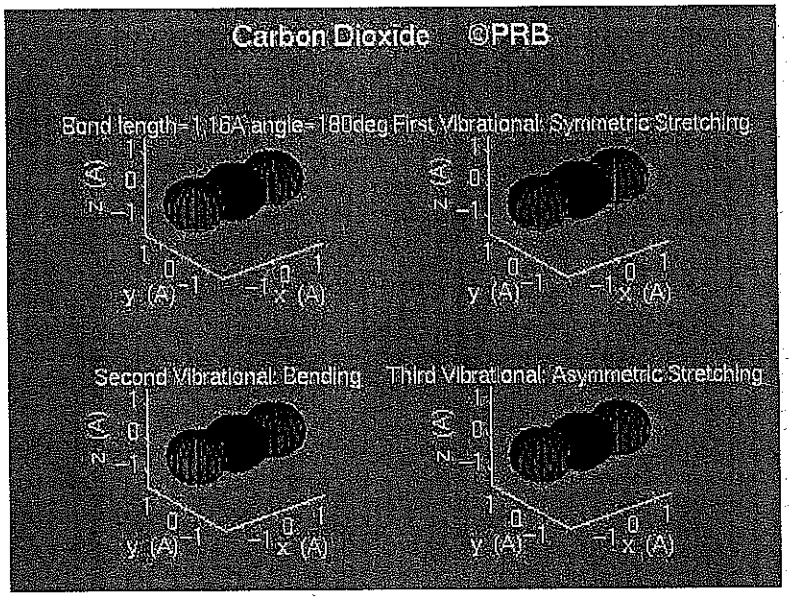
β-carotene
Predicted (Fieser-Kuhn rules) : 453 nm
observed : 452 nm

Ultraviolet Spectroscopy

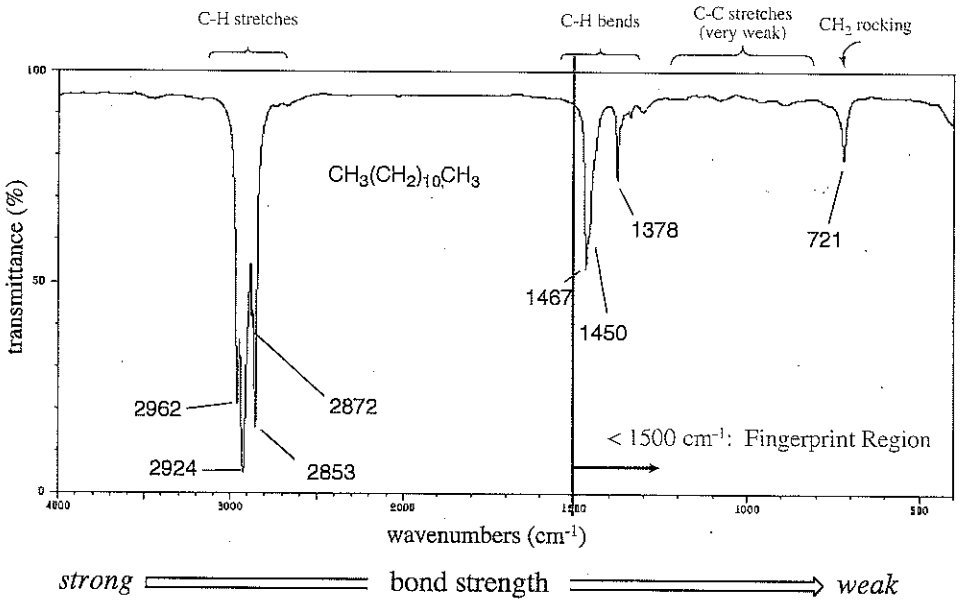
- Diagram of energy vs. bond length for a simple diatomic molecule



Vibrational Modes in CO_2

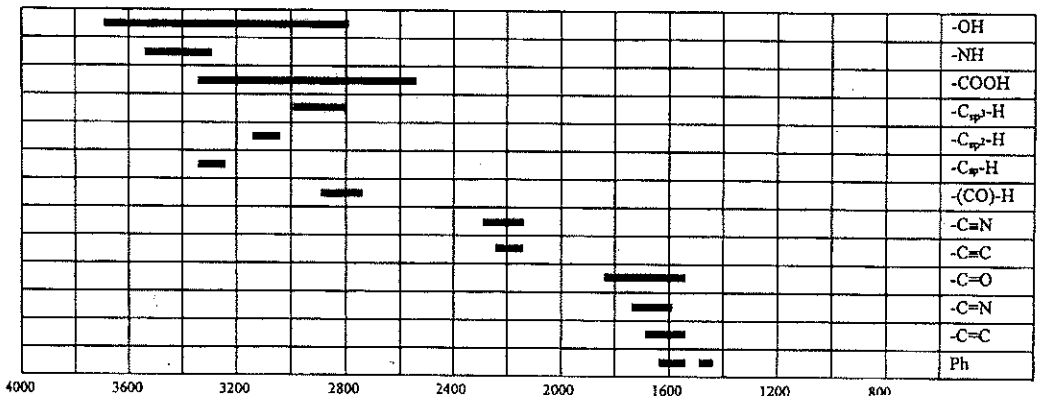


- IR spectrum of dodecane:



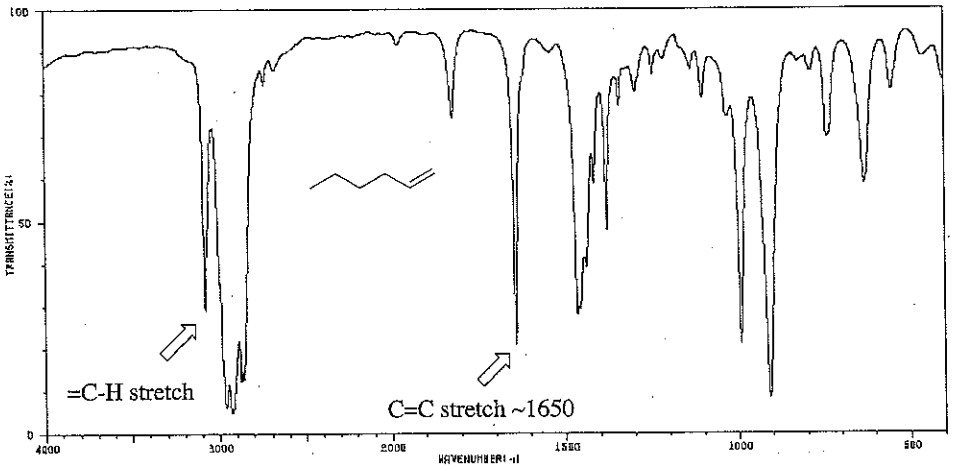
strong ⟸ bond strength ⟹ *weak*

- Diagnostic IR absorption of common functional groups:



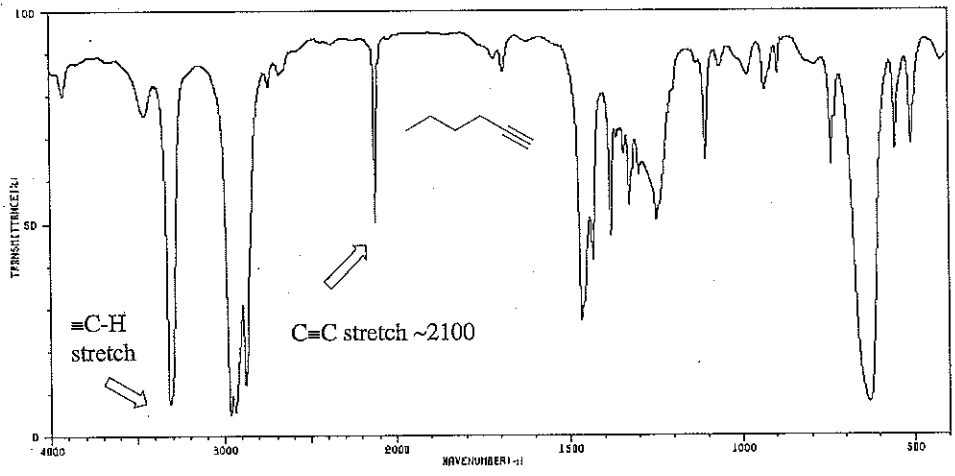
adapted from Crews, Rodriguez and Jaspars, Organic Structure Analysis, Oxford 1998

- alkenes:



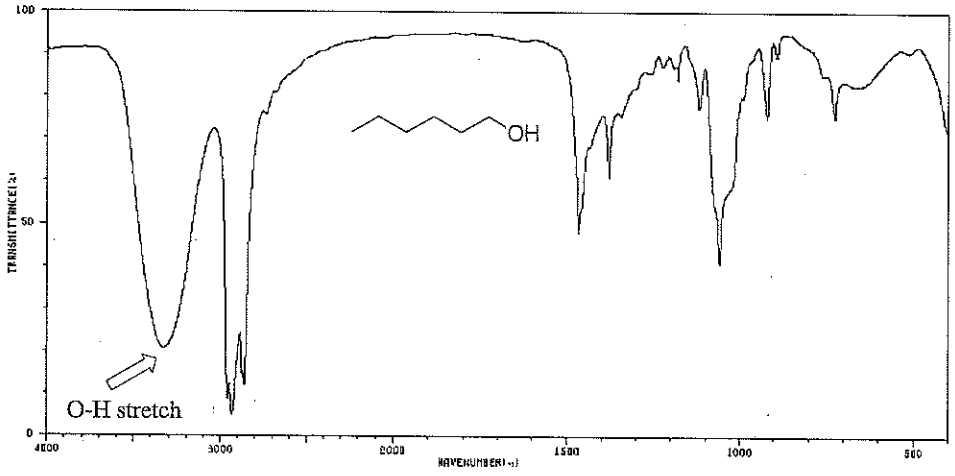
- aromatic C-H and C=C stretches are similar to alkene, but the C-H often does not appear separate from the aliphatic (sp^3) C-H peaks

- alkynes:

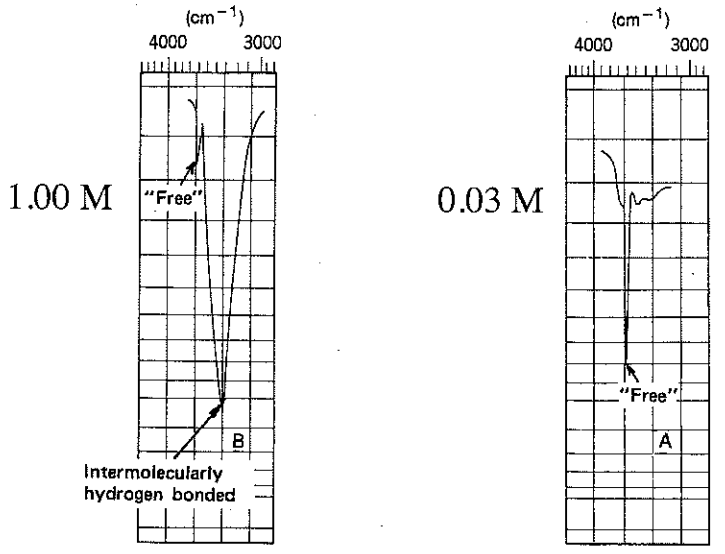


- C≡N and C=C=C (allene) stretches are also in this 2100 cm^{-1} region

- alcohols:



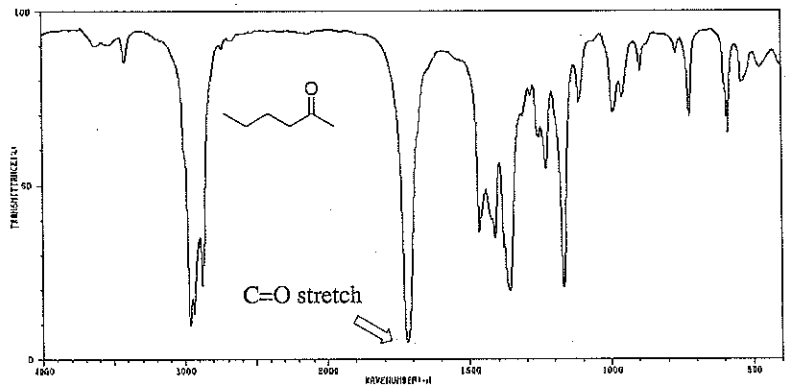
- alcohols - hydrogen bonding



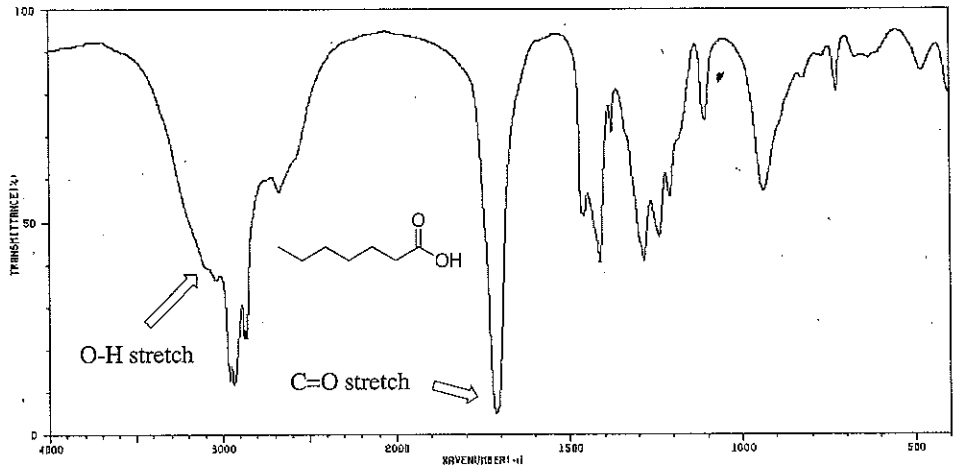
from Silverstein and Webster, Spectrometric Identification... Wiley 1998

- carbonyl compounds:

X	ν(C=O)
F	1869
Cl	1815-1785
Br	1812
OH (monomer)	1760
OR	1750-1735
OH (dimer)	1720-1709
H (aldehyde)	1720-1740
R (ketone)	**1715**
SR	1720-1690
NHR	1695-1650



- carboxylic acids:



- amines: