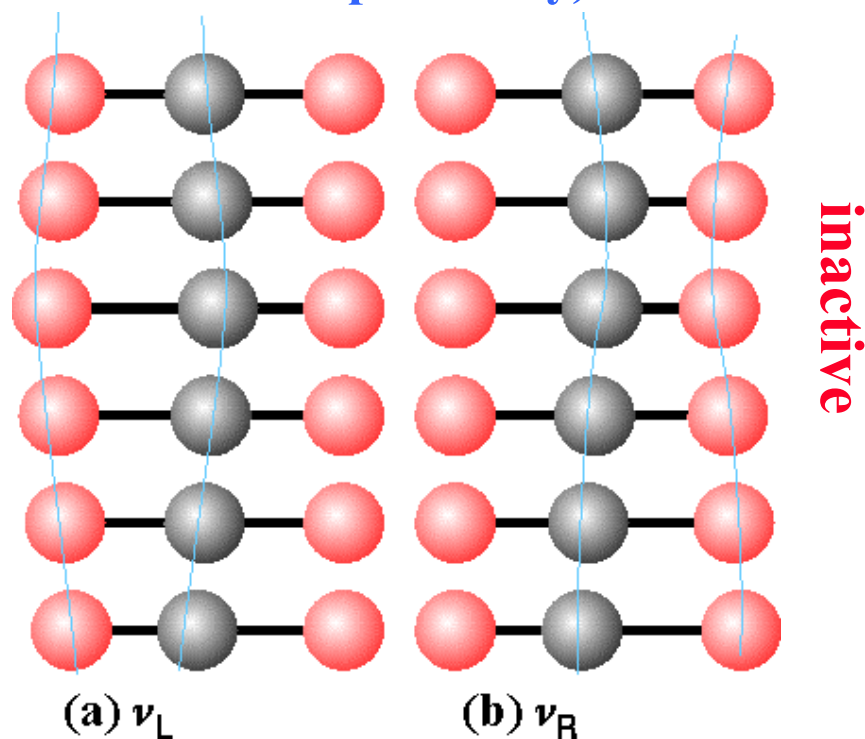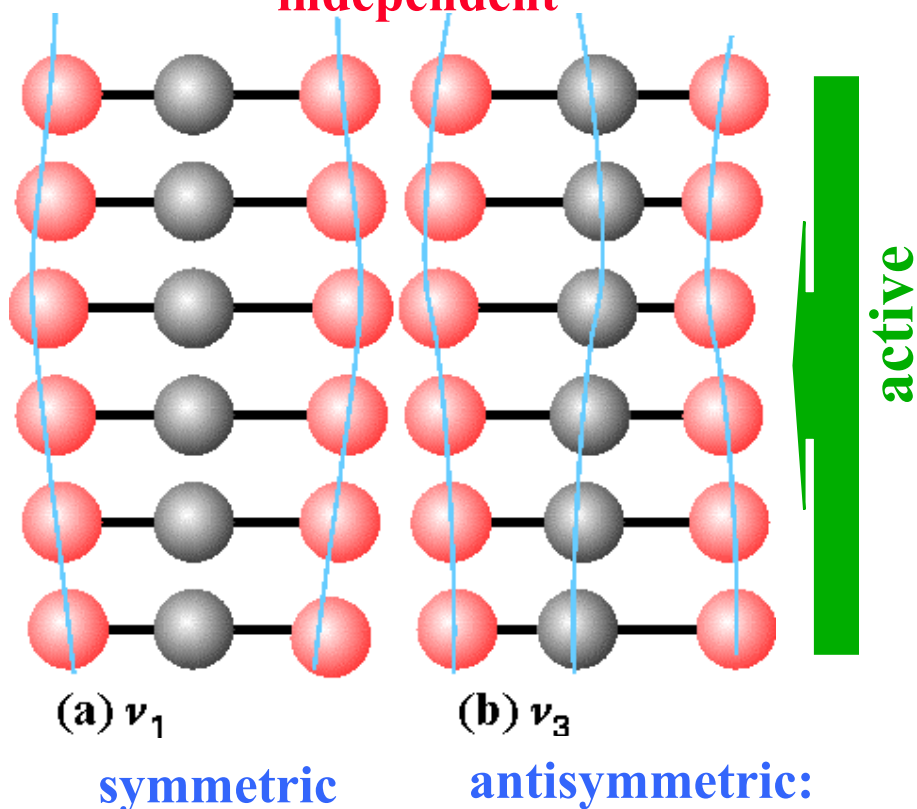# Vibrations of polyatomic molecules: How can one describe them?

CO_2: C-O stretch vibrations are **NOT** independent (cannot be excited independently)

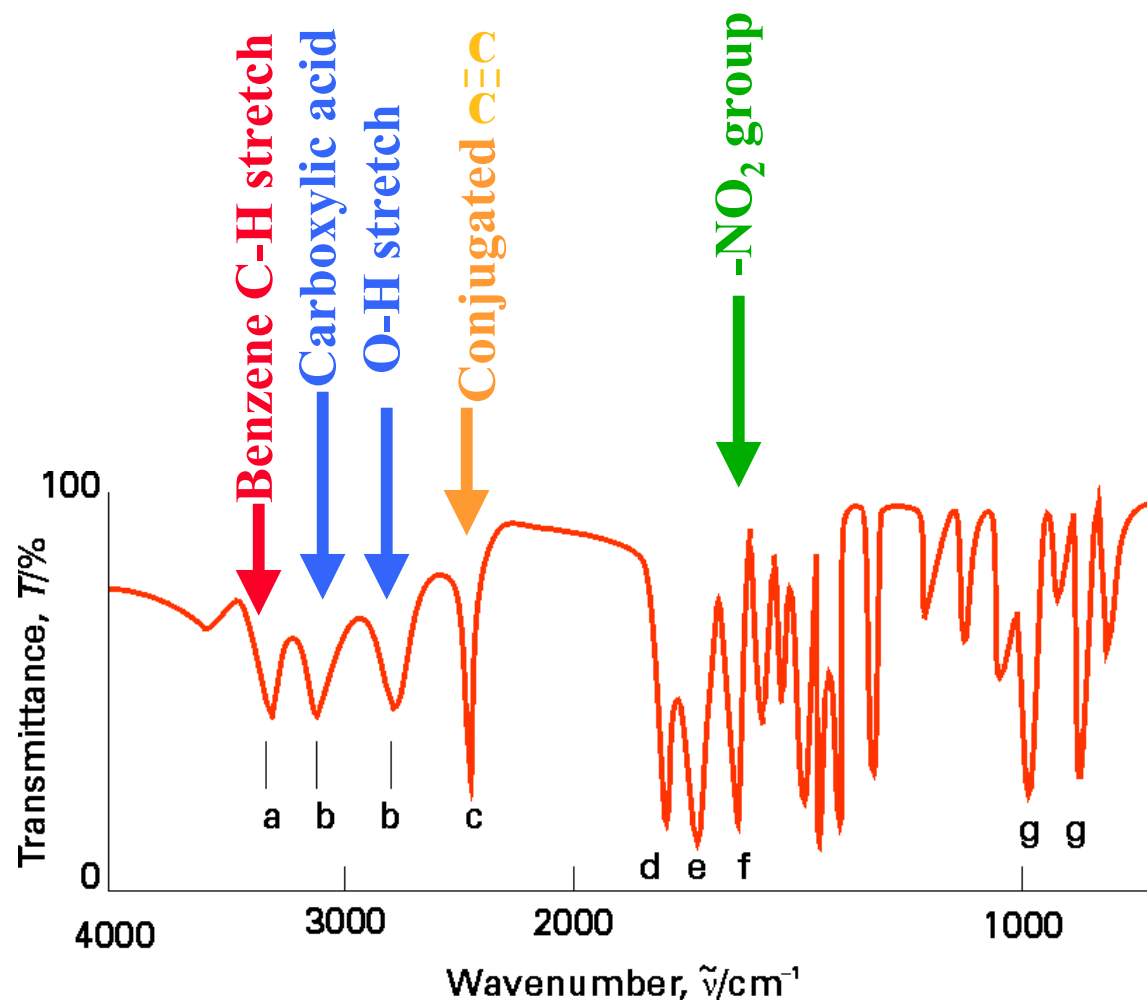Normal stretch modes (linear combinations of C-O stretches) **ARE** independent

inactive

active

(a) ν_L

(b) ν_R

(a) ν_1

(b) ν_3

symmetric

antisymmetric: CO_2 as greenhouse gas!

What is all this good for???

Wavenumbers of normal modes are the same in different chemical contexts ⇒ Tabulation!

Table 17.2 *Typical vibrational wavenumbers*

Vibration type	$\tilde{v}/cm^{-1}$
C—H stretch	2850–2960
C—H bend	1340–1465
C—C stretch, bend	700–1250
C=C stretch	1620–1680
C≡C stretch	2100–2260
O—H stretch	3590–3650
C=O stretch	1640–1780
C≡N stretch	2215–2275
N—H stretch	3200–3500
Hydrogen bonds	3200–3570

Benzene C-H stretch

Carboxylic acid

O-H stretch

Conjugated C≡C

$-NO_2$ group

Transmittance, $T/\%$

Wavenumber, $\tilde{v}/cm^{-1}$

a b b c d e f g g

Identification of organic compounds!!!

Nils Walter: Chem 260

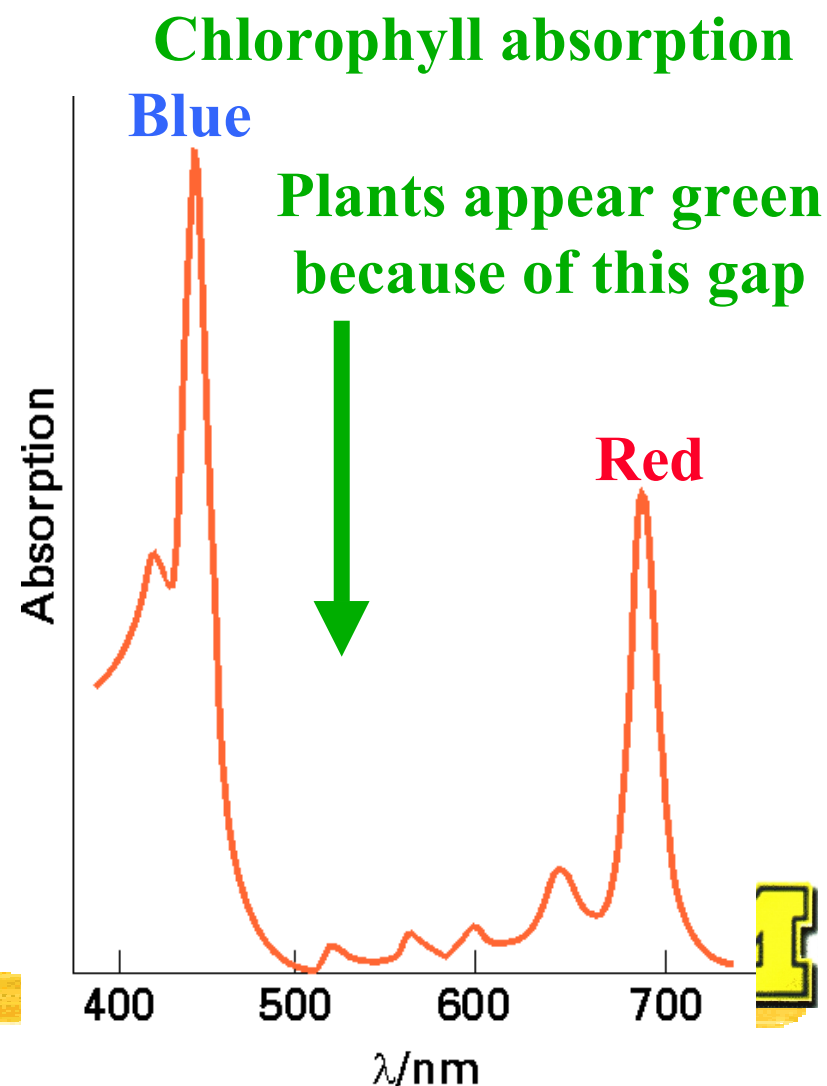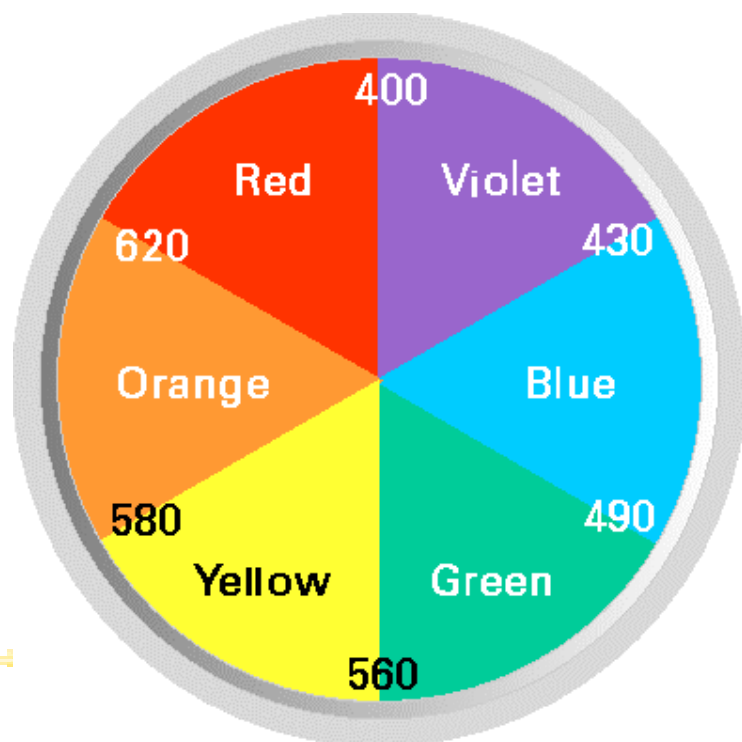# Electronic transitions: The visible electromagnetic spectrum

Atkins, Chapter 18

Red light: 14,000 cm^{-1} (171 kJ/mol)
Blue light: 21,000 cm^{-1} (254 kJ/mol)
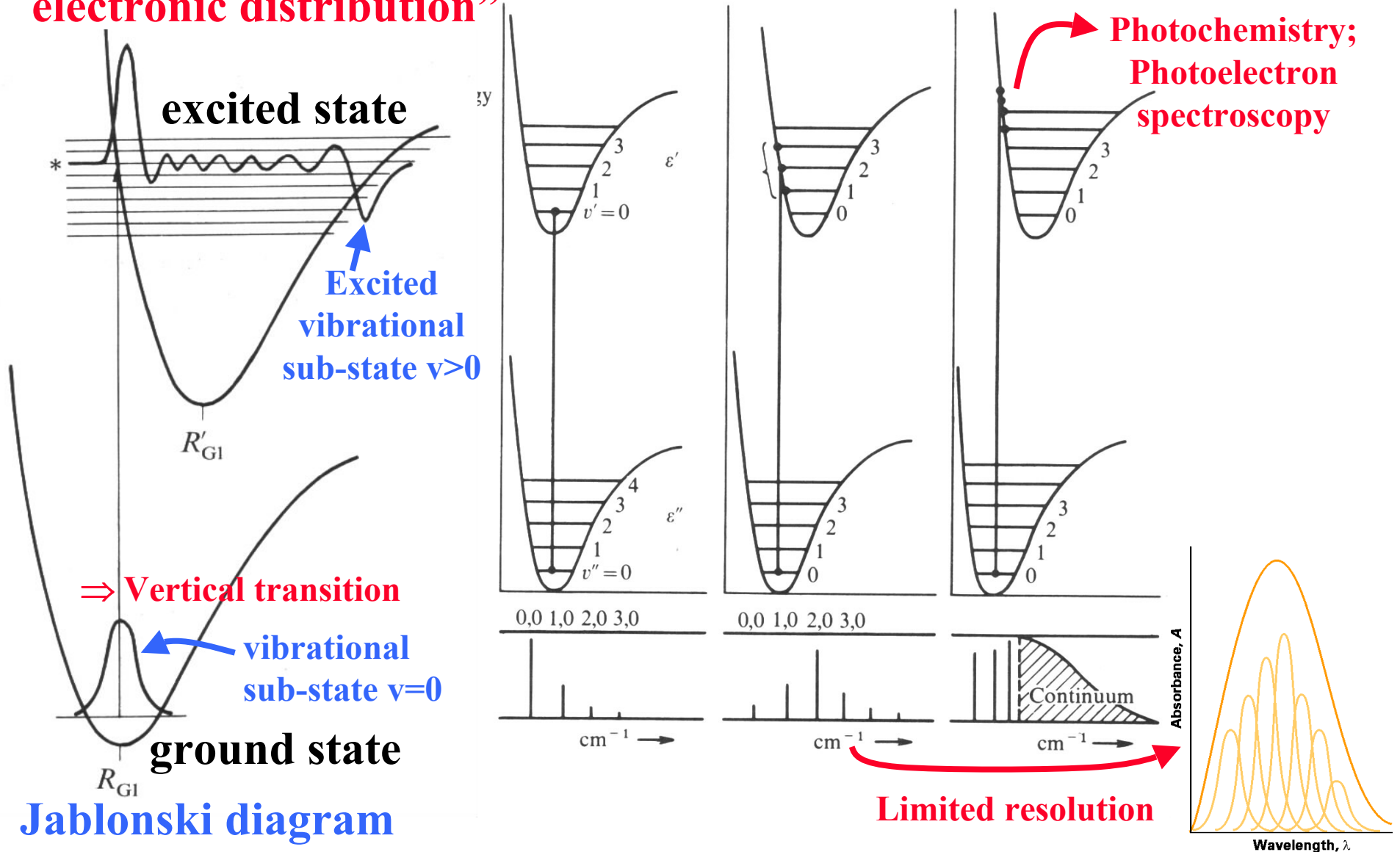Ultraviolet radiation: 50,000 cm^{-1} (598 kJ/mol)

Chlorophyll absorption
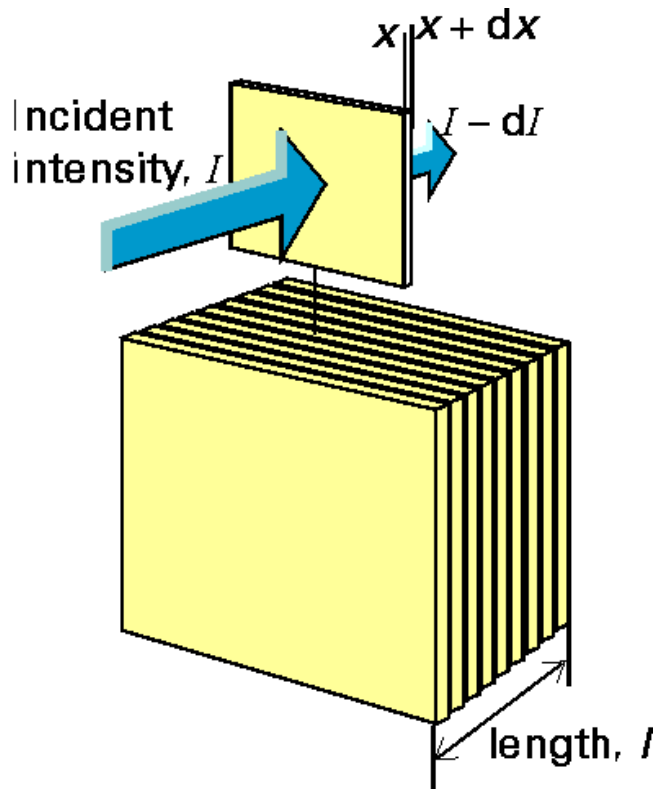
Plants appear green because of this gap

The Franck-Condon principle

"The heavy nuclei don't have time to react to fast changes in the electronic distribution"

excited state

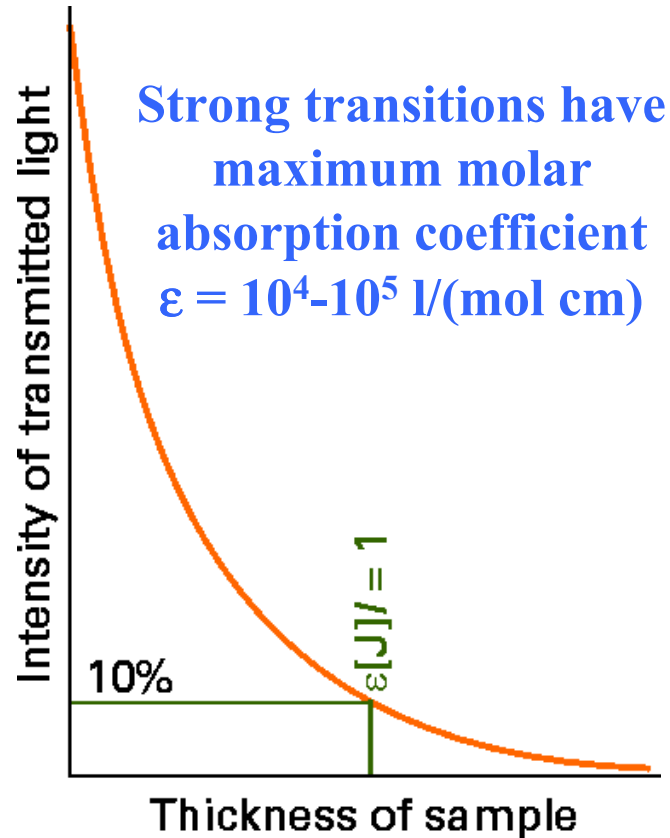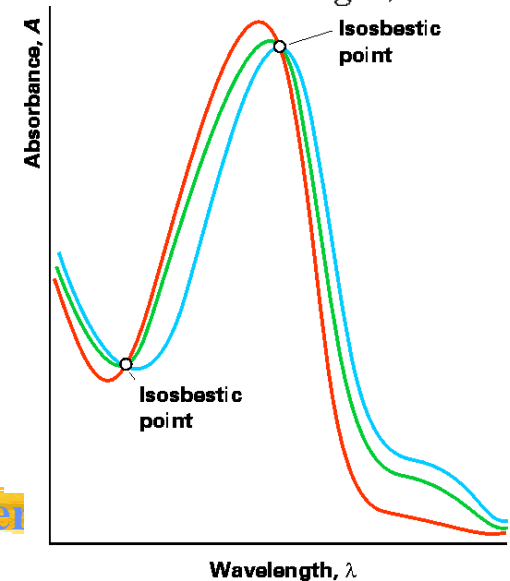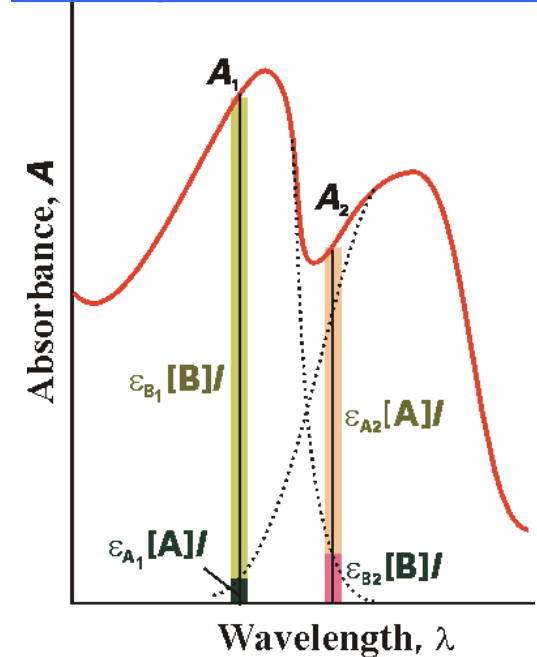**Photochemistry; Photoelectron spectroscopy**

Excited vibrational sub-state v>0

R'_{G1}

⇒ **Vertical transition**

vibrational sub-state v=0

ground state

R_{G1}

Jablonski diagram

Limited resolution

Absorption intensity

Mixing two substances:

Incident intensity, I

x | $x + dx$

$I - dI$

length, l

Intensity of transmitted light

Strong transitions have maximum molar absorption coefficient $\varepsilon = 10^4\text{-}10^5$ l/(mol cm)

$\varepsilon[J]l = 1$

10%

Thickness of sample

Absorbance, A

A_1

A_2

$\varepsilon_{B_1}[B]l$

$\varepsilon_{A_2}[A]l$

$\varepsilon_{A_1}[A]l$

$\varepsilon_{B_2}[B]l$

Wavelength, λ

Absorbance, A

Isosbestic point

Isosbestic point

Wavelength, λ

$$dI = -\varepsilon c_J I dx$$
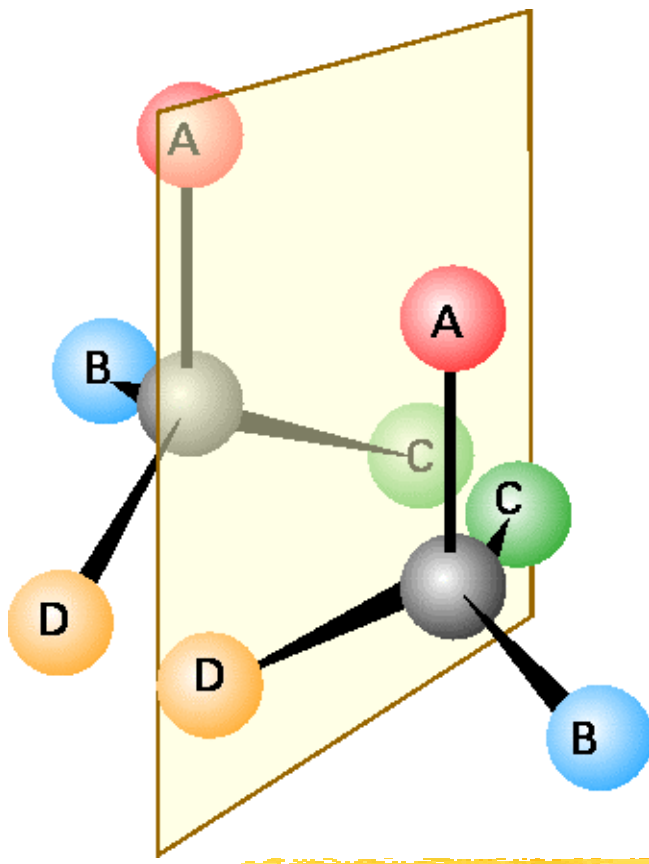
$$\frac{I}{I_0} = \exp(-\varepsilon c_J l)$$
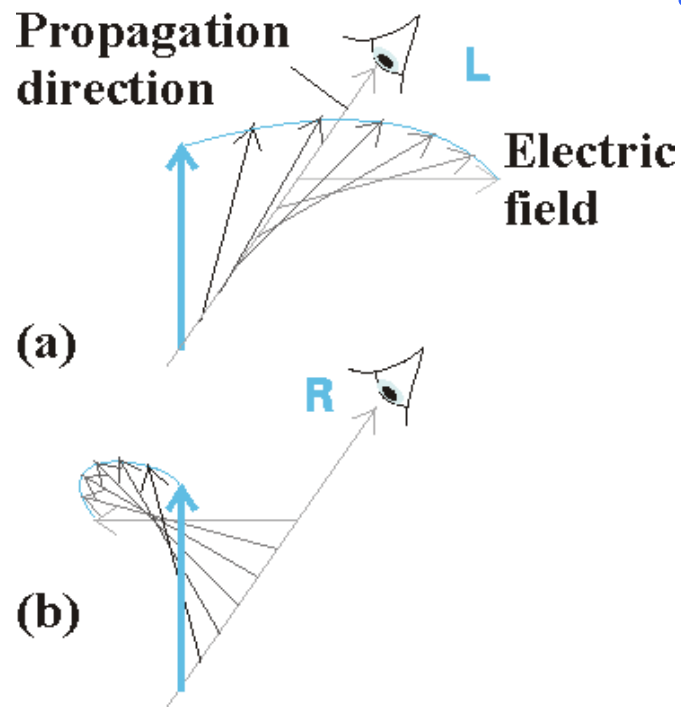
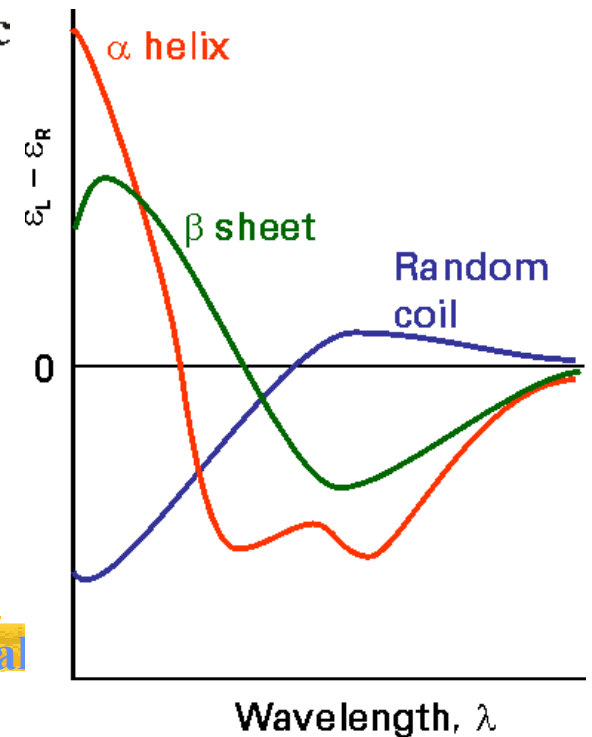**Beer-Lambert law**

Nils Walter

Circular dichroism

Chiral molecules have optical activity

Light can be left- or right-circularly polarized

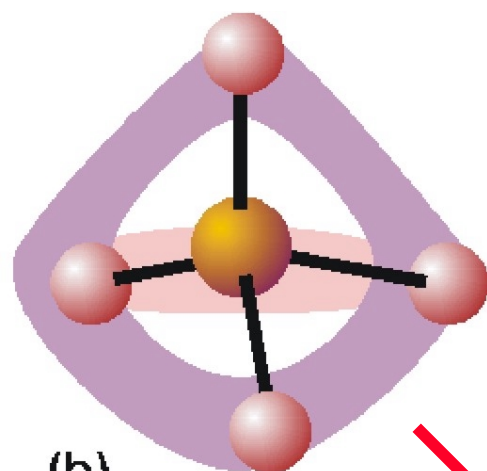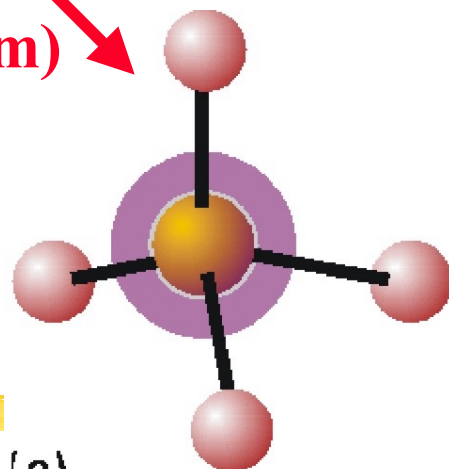**An optically active polypeptide shows differential absorption of left- and right-circularly polarized light**
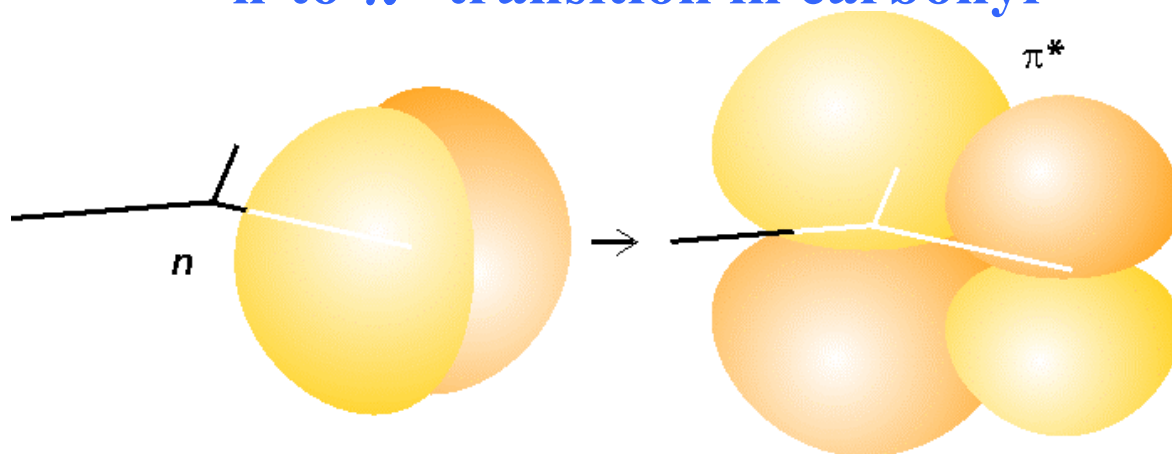
Specific transitions

Charge transfer:
Example MnO_4^-

n-to-π^* transition in carbonyl

hν (420-700 nm)

(b)

(a)

π-to-π^* in C=C double bond