Absorption or Emission Spectroscopy

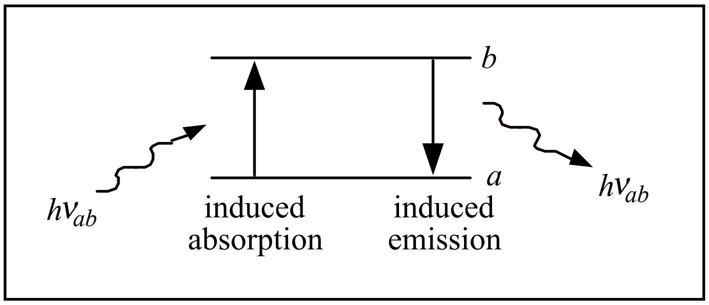


Figure 11-1

$$B_{ab} = B_{ba} = \left(\frac{2}{3}\right)\left(\frac{\pi}{\hbar^2}\right)\left|\int \phi_b^* \vec{\mu}\, \phi_a\, d\vec{r}\right|^2$$

where $\vec{\mu} = -|e|\,\vec{r}$ for an electron

or $\vec{\mu} = \sum_i q_i \vec{x}_i = \sum_i z_i |e| \vec{x}_i$ for a molecule

or $\int \rho(\vec{x})\,\vec{x}\,dv$

The above result is from time-dependent quantum mechanics.

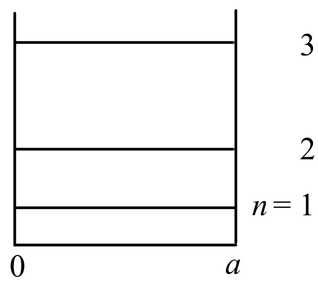
The integral $\int \phi_b^* \vec{\mu}\, \phi_a\, dv$ is called the transition dipole.

$= \mu_{ab}$ or μ_{ba} for short

This is an important concept or quantity, because unless $\mu_{ba} \neq 0$, there is no transition induced by $\vec{E}$ of light, or no <u>electric dipole</u> transition.

Selection Rules for Simple Situations

a) Particle in a Box (1D)



$$\phi_n(x) = \frac{\sqrt{2}}{\sqrt{a}} \sin\frac{n\pi x}{a}$$

$$W_n = \frac{n^2 h^2}{8ma^2} \qquad (n = \text{ integer})$$

Figure 11-2

$$\mu_{n\to m} = \mu_{nm} = \int_0^a \phi_m^*(x)\,\mu\,\phi_n(x)dx$$

$$= -|e|\left(\sqrt{\frac{2}{a}}\right)^2 \int_0^a \sin\frac{m\pi x}{a} \cdot x \cdot \sin\frac{n\pi x}{a}\,dx$$

The integral vanishes unless $m = n \pm 1,\ n \pm 3,\ n \pm 5, \ldots\ldots$

It follows from the symmetry of the problem that:

x is an odd function if reflected about $x = a/2$ (middle of box); i.e., it changes sign.

$\phi_n(x)$ is an even function for n odd (antisymmetric function).

$\phi_n(x)$ is an odd function for n even (symmetric function).

$\phi_m^*(x)\,\phi_n(x)$ is an odd function for $m = n \pm 1,\ n \pm 3,\ n \pm 5, \ldots\ldots$; it is an even function otherwise.

For the integral not to vanish,

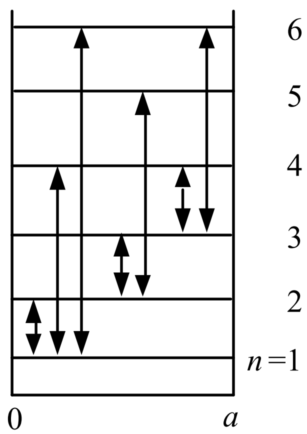
integral $\phi_m^*(x)\cdot x\cdot\phi_n(x)$ must be an even function upon reflection about $x = a/2$,

or $\phi_m^*(x)\,\phi_n(x)$ must be an odd function to compensate for x being an odd function

or $m = n \pm 1,\ n \pm 3,\ n \pm 5,\ \ldots\ldots$

$\Uparrow$

Selection rule for electric dipole transitions for a particle in a box.



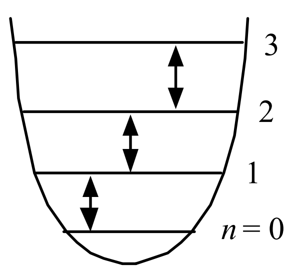
$\Delta n = \pm 1$ strongest

$\Delta n = \pm 3$ weaker, i.e., μ_{nm} smaller

$\Delta n = \pm 5$ weaker yet

Figure 11-3

(b) e^- In a Harmonic Potential or Harmonic Oscillator



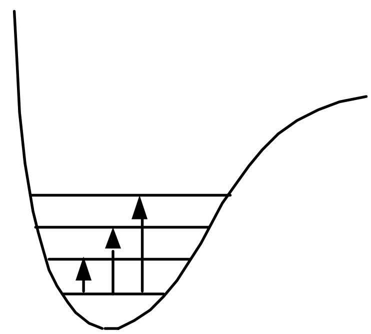
$$W_n = h\nu_0\left(n + \frac{1}{2}\right)$$

Figure 11-4

Selection rules for electric dipole transitions: $\Delta n = \pm 1$ only.

Note $\Delta n \pm 3,\ \pm 5$ transitions are allowed by symmetry, but the integrals all turn out to vanish.

(c) Anharmonic Oscillator with Cubic Anharmonicity



no longer a symmetry restriction

Selection rules:

$\Delta n = \pm 1$ strongest

$\Delta n = \pm 2$ allowed, but weak

$\Delta n = \pm 3$

Figure 11-5

$0 \rightarrow 1$ transition usually called "fundamental"

$0 \rightarrow 2$ transition usually called "1st overture"

$1 \rightarrow 2$ transition usually called "1st hot band"

(d) Anharmonic Oscillator with Quartic Anharmonicity

The problem again has symmetry.

Selection rules for electric dipole transitions: $\Delta n = \pm 1,\ \pm 3,\ \pm 5$ etc. as for a particle in a box.

(e) Hydrogen-like Atom

Quantum states are identified by quantum number n, l, m_l.

Selection rules for electric dipole transitions:

$\Delta n = \pm 1,\ \pm 2,$ K K no restriction

$\Delta l = \pm 1$ only $s \leftrightarrow p,\ \ p \leftrightarrow d,\ \ d \leftrightarrow f$ transitions only

$\Delta m_l = \pm 1,\ 0$

A More Complex Situation: Formaldehyde

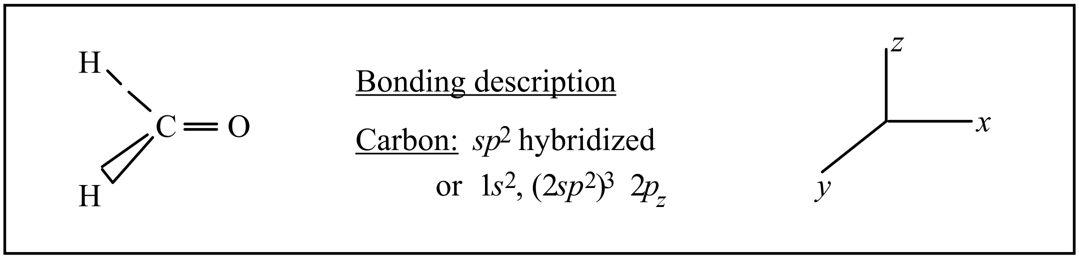


Figure 11-6

2 C—H bonds are formed by carbon hybrid sp^2 orbital overlapping with hydrogen 1*s*. The third sp^2 orbital of carbon overlaps with O $2p_x$ orbital to form C—O sigma bond. C $2p_z$ and O $2p_z$ orbitals form π-bond (π-MO with 2 e^-'s), and remaining two oxygen electrons are in 2 p_y orbital of the oxygen.

HOMO and LUMO's

HOMO — highest occupied MO's

LUMO — lowest unoccupied MO's

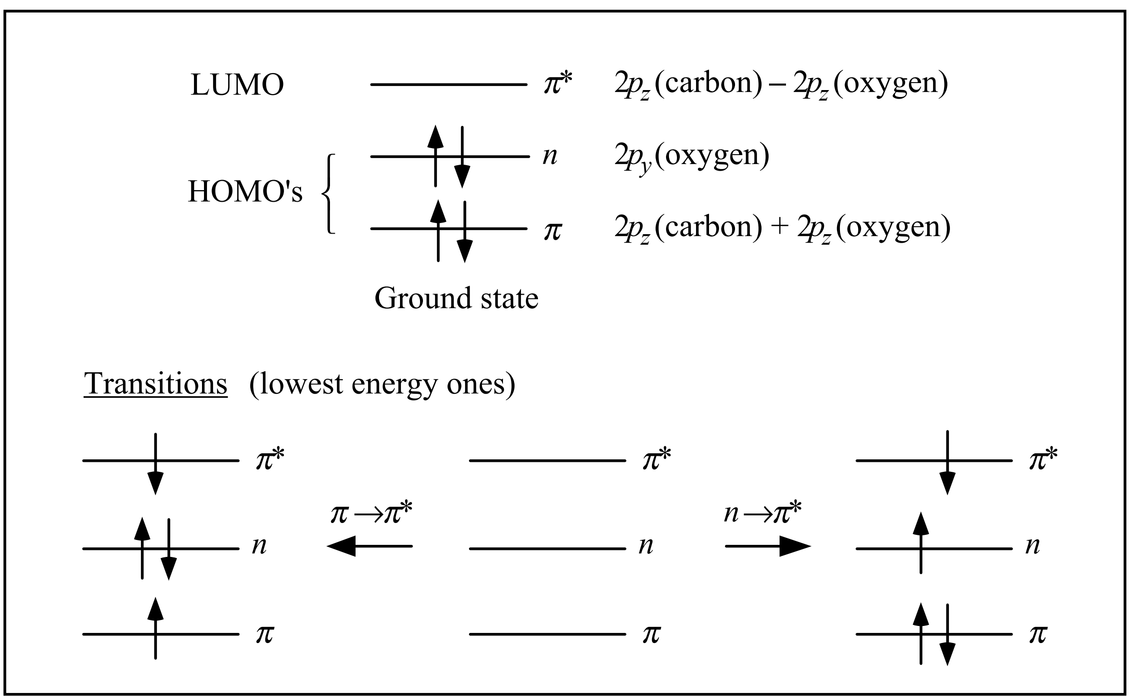


Figure 11-7

$\pi \rightarrow \pi^*$ Transition

$$\int \phi_{\pi^*}^{*} \vec{\mu} \, \phi_{\pi} \, d\vec{r} = \vec{i} \int \phi_{\pi^*}^{*} \mu_x \, \phi_{\pi} \, d\vec{r} + \vec{j} \int \phi_{\pi^*}^{*} \mu_y \, \phi_{\pi} \, d\vec{r} + \vec{k} \int \phi_{\pi^*}^{*} \mu_z \, \phi_{\pi} \, d\vec{r}$$

Only $\int \phi_{\pi^*}^{*} \mu_x \; \phi_{\pi} \, d\vec{r}$ is nonzero; the others vanish by symmetry.

The result is a transition dipole along the $C=O$ bond or intense absorption can only occur when $\vec{E}^*$ of the light wave is parallel to the $C=O$ bond; i.e., the transition is polarized along the $C=O$ bond.

$n \rightarrow \pi^*$ Transition

$$\int \phi_{\pi^*}^{*} \vec{\mu} \, \phi_{n} \, d\vec{r} = 0 \quad \text{for} \quad \mu_x, \mu_y, \text{ and } \mu_z$$

$n \rightarrow \pi^*$ transition is symmetry forbidden; in practice it can be observable, but is extremely weak. Typically, $n \rightarrow \pi^*$ absorption has an intensity ~1% of the $\pi \rightarrow \pi^*$ transition.

Absorption Spectrum of Acetone

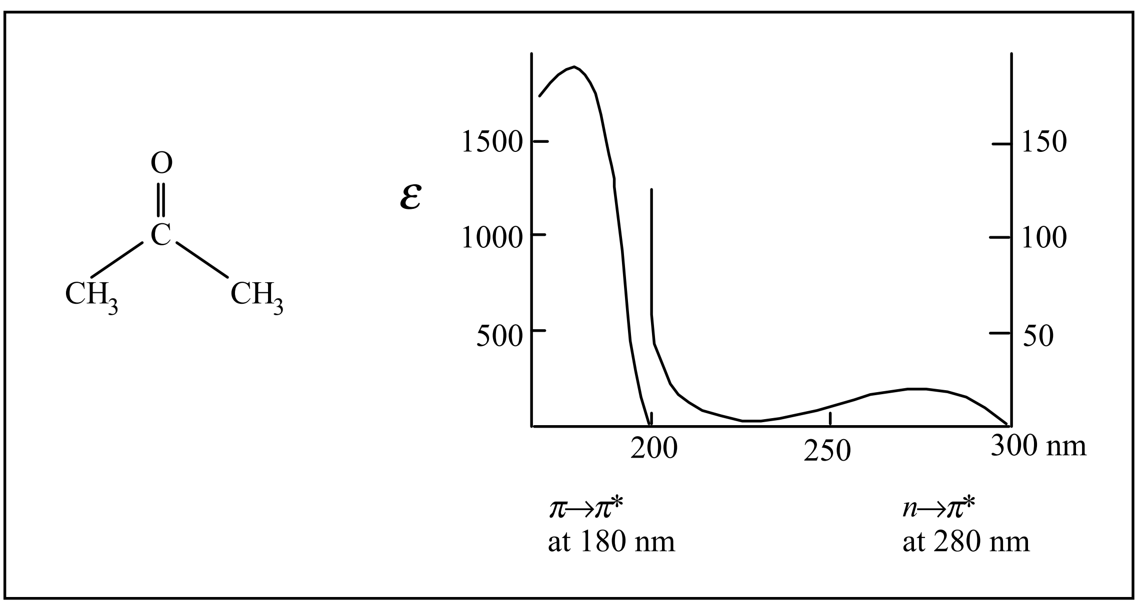


Figure 11-8

Biological Chromophores

Protein Chromophores

peptide bond

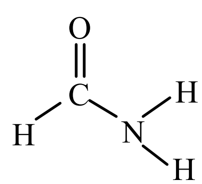
amino acid side chains (trp, tyr, phe)

prosthetic groups (hemes, flavins, blue coppers)

Nucleic Acid Chromophores — bases

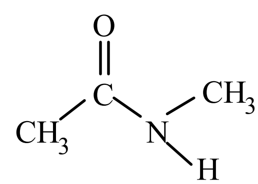
Peptide Bond

Typical models:



formamide

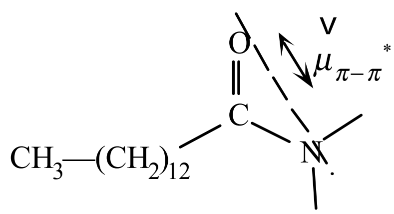
or



N-methyl acetamide

Peptide bond

$n \rightarrow \pi^*$ absorption	210-220 nm	$\varepsilon_{max} \sim 100$ weak
$\pi \rightarrow \pi^*$	190 nm	$\varepsilon_{max} \sim 7000$



myristamide

$\vec{\mu}_{\pi-\pi^*}$ not along C═O but along a line between O and N in plane of peptide bond — determined by polarized absorption of single crystals

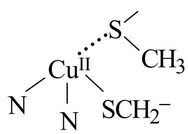
Amino Acid Side Chains

Table 11-1. Absorption of Amino Acid Side Chains

Trp (tryptophan); not present in large amounts in proteins	240-290 nm	most intense	absorption complex (3 transitions of indole ring)
Tyr (tyrosine)	274 nm	$\pi-\pi^*$ ($\varepsilon_{max} \sim 1400$)	analogous to 271 nm absorption in phenol
Phe (phenylalanine)	250 nm	weak $\pi-\pi^*$ symmetry forbidden	analagous to 256 nm absorption in benzene

Prosthetic Groups

Table 11-2. Absorption of Prosthetic Groups

Protein	Prosthetic Group	Longest λ Absorption		2nd Longest λ Absorption	
		λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$
Amino acid oxidase (rat kidney)	FMN	455	1.27	358	1.07
Azurin, P. fluorescene, plastocyanin, spinach stellacyanin	 *	781	0.32	625**	0.35
Ceruloplasmin (human)	8 coppers type 1, 2, 3	794	2.2	610	1.13
Cytochrome *c* (reduced) (human)	Fe^{II}-heme	550	2.77		
Ferrodoxin	$2Fe^{III}$-$2S^{-}$cluster	421	0.98	330	1.33
Flavodoxin (C. pasteurianium)	FMN	443	0.91	372	0.79
pyruvate dehydrog-enase (E. coli)	FAD	460	1.27	438	1.46
Rhodopsin (bovine)	retinal-lys	498	4.2	350	1.1
Reubredoxin (M. aerogenes)	(Fe^{III},4 Cys) tetrahedra	570	0.35	490	0.76
Xanthine oxidase	Fe, Mo	550	2.2		
Threonine deaminase (E. coli)	4 pyridoxal phosphates	415	2.6		

*blue copper

** $Cu^{II} \leftarrow S^{-}$ charge transfer

Other Protein Chromophores

retinal in bacteriorhodopsin

chlorophylls in reaction centers of cyanobacteria PS I and II

hemes and coppers in cytochrome oxidase (heme λ_{max} 420-600 nm; Cu λ_{max} 830 nm)

Nucleic Acid Bases

In DNA and RNA, absorption is dominated by nucleic acid bases (A, G, T/U, C).

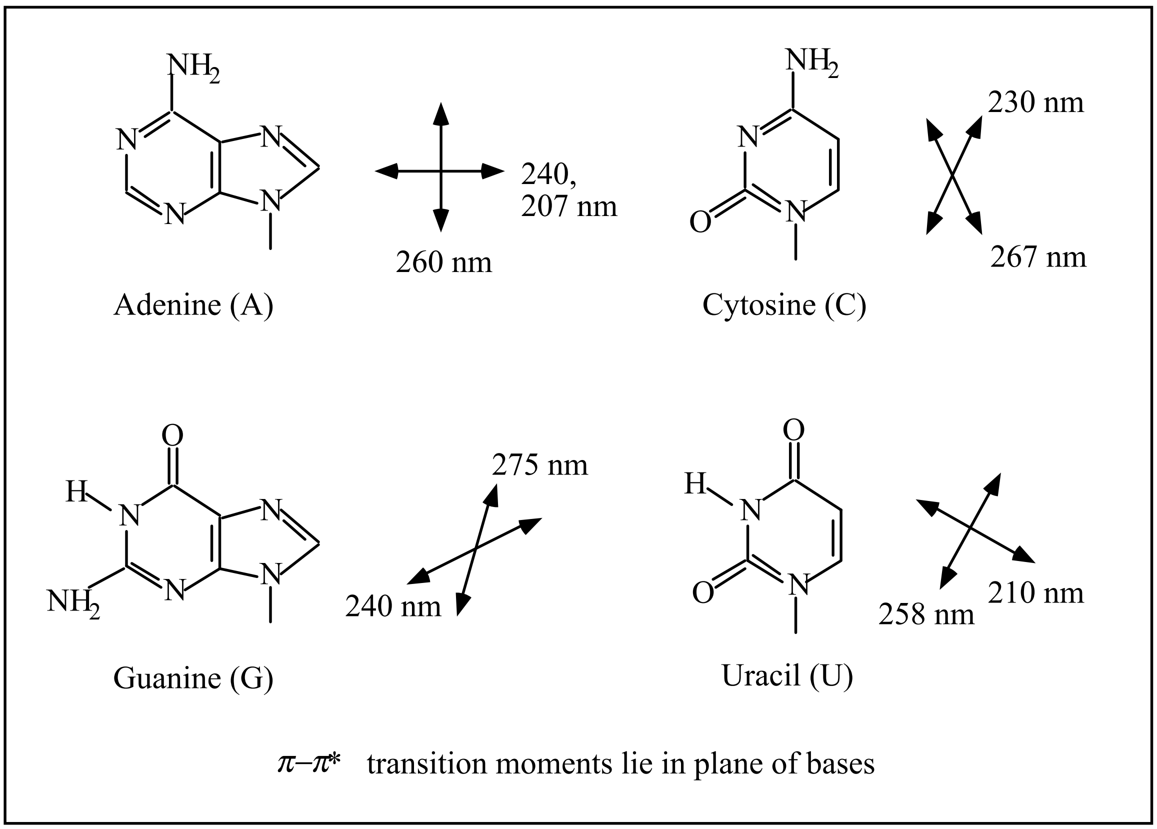


Figure 11-9

Vibrational Spectroscopy / Rotational Spectroscopy

Absorption arises from the interaction of the dipole moment of a molecule with $\vec{E}^{*}$ of the light wave.

$$\text{dipole moment of molecule} = \vec{\mu}\left(\underset{\sim}{R}\right)$$

$$= \vec{\mu}\left(\underset{\sim}{R_0}\right) + \sum_i \left(\frac{\partial \vec{\mu}}{\partial R_i}\right)_{R_0^i} \left(R_i - R_0^i\right) + \ldots$$

where $\vec{\mu}\left(\underset{\sim}{R_0}\right) =$ permanent dipole moment, responsible for <u>pure</u> rotational spectroscopy

$\sum_i \left(\frac{\partial \vec{\mu}}{\partial R_i}\right)_{R_0^i} \left(R_i - R_0^i\right) =$ dipole derivative, responsible for

(a) vibrational-rotational spectroscopy of gases

(b) vibrational spectroscopy of liquids

For a Diatomioc Molecule

(a) Rotational Spectroscopy

No absorption unless $\vec{\mu}\left(\underset{\sim}{R_0}\right) =$ permanent dipole moment $\neq 0$

<u>Selection rule</u>: $\Delta J = \pm 1$

$\left.\begin{matrix} H_2 \\ N_2 \\ F_2 \end{matrix}\right\}$ no rotational absorption spectrum

$\left.\begin{matrix} HCl \\ HF \end{matrix}\right\}$ rotational absorption spectrum

(b) Vibrational Spectroscopy

No vibrational excitation unless $\left(\frac{\partial \mu}{\partial R}\right)_{R_0} \neq 0$ (dipole derivative) e.g., H_2

<u>Selection rule</u>: $\underset{\text{strong}}{\Delta n = \pm 1}$, $\underset{\text{weak}}{(\pm 2, \ldots)}$

For a Linear Triatomic Molecule

CO_2 No $\overset{\vee}{\mu}\left(\underset{\sim}{R_0}\right)$ or permanent dipole moment.

Vibrations:

4 normal modes (normal coordinates Q_i)

symmetric stretch $\leftarrow O{=}C{=}O \rightarrow$ $\left(\dfrac{\partial \mu}{\partial Q_i}\right)_0 = 0$

asymmetric stretch $\overrightarrow{O}{=}\overleftarrow{C}{=}O \rightarrow$ $\left(\dfrac{\partial \mu}{\partial Q_i}\right)_0 \neq 0$

bending

- $\underset{\downarrow}{O}{=}\overset{\uparrow}{C}{=}\underset{\downarrow}{O}$ $\left(\dfrac{\partial \mu}{\partial Q_i}\right)_0 \neq 0$
- $\overset{\oplus}{O}{=}\overset{\ominus}{C}{=}\overset{\oplus}{O}$ $\left(\dfrac{\partial \mu}{\partial Q_i}\right)_0 \neq 0$

Accordingly,

symmetric stretch	infrared inactive
asymmetric stretch, bending	infrared active

For a Peptide Group

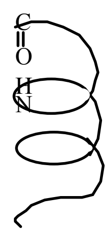
Table 11-3. Characteristics of Principal Infrared Absorption Bands

Vibration	$\left(\frac{\partial \mu}{\partial Q}\right)$	Hydrogen-bonded Forms* α-Helix Frequency	α-Helix Dichroism	β-Sheet Frequency	β-Sheet Dichroism	Non-hydrogen Bonded Forms Frequency
N—H stretch	←N—H→ ↔ †	3290-3300 cm^{-1}	‖	3280-3300 cm^{-1}	⊥	~3400 cm^{-1}
Amide I C=O stretch	←O═C→ ↔ †	1650-1660 cm^{-1}	‖	1630 cm^{-1}	⊥	1680-1700 cm^{-1}
Amide II**	H↑ | ←C—N→ ↓↙ †	1540-1550 cm^{-1}	⊥	1520-1525 cm^{-1}	‖	<1520 cm^{-1}

* <u>α-helix</u>:

N—H ----- O═C   hydrogen bonds ‖ helix axis

⟶ α-helix axis

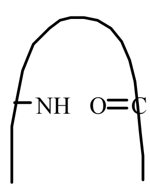


↑ α-helix axis

<u>β-sheet</u>:

N—H ----- O═C

↑ long axis of extended peptide chain



** polarized near C—N bond or ⊥ N—H bond

† polarization vector