

Basics-6

Electronic Spectroscopy

Born–Oppenheimer Approximation

Molecules are collections of electrons and nuclei:

$$H\psi(\mathbf{r}, \mathbf{R}) = E\psi(\mathbf{r}, \mathbf{R})$$

$$H = T_e(\dot{\mathbf{r}}) + T_n(\dot{\mathbf{R}}) + V_{en}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r}) + V_{nn}(\mathbf{R})$$

$$H_e = T_e(\dot{\mathbf{r}}) + V_{en}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r})$$

... Nuclei move so slowly compared to electrons, so electrons adjust instantaneously to any nuclear motion.

$$\psi(\mathbf{r}, \mathbf{R}) = \psi_e(\mathbf{r}; \mathbf{R})\psi_n(\mathbf{R})$$

Electronic S – eqn: $H_e\psi_e(\mathbf{r}; \mathbf{R}) = E_e(\mathbf{R})\psi_e(\mathbf{r}; \mathbf{R})$

$$H_n\psi_n(\mathbf{R}) = (T_n + V_{nn}(\mathbf{R}) + E_e(\mathbf{R}))\psi_n(\mathbf{R}) = E_n\psi_n(\mathbf{R})$$

$$\therefore E_{tot} = E_e + E_n; \quad \psi_{tot} = \psi_{el}\psi_{nuc} \quad " | \epsilon v > "$$

* Electronic Schrödinger equation of many electron molecules

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}} + \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

– *Approximate Solutions of $\hat{H}_{el}\psi_{el} = E_{el}\psi_{el}$:*

molecular orbital (i.e. one electron wavefunction)

$$\phi_i = \sum_j \sum_A C_{ij} \phi_j^A \quad (\text{LCAO}) \leftarrow \phi_j^A : \text{atomic orbital}$$

total electronic wavefunction $\psi_{el} = \psi_{orbital} \psi_{spin}$

"antisymmetric wrt exchange \rightarrow Slater determinant"

$$\psi_{el} = |\phi_1(1)\bar{\phi}_1(1)\dots| = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \bar{\phi}_2(1) & \phi_3(1) & \bar{\phi}_4(1) & \dots \\ \phi_1(2) & \bar{\phi}_2(2) & \phi_3(2) & \bar{\phi}_4(2) & \dots \\ \dots & \dots & \dots & \dots & \dots \\ \phi_1(N) & \bar{\phi}_2(N) & \phi_3(N) & \bar{\phi}_4(N) & \dots \end{vmatrix}$$

Hartree – Fock approximation for closed shell molecules

Fock operator \hat{f} "one – electron hamiltonian"

$$\hat{f} = \hat{h} + \sum_j \{2J_j - K_j\}$$

$$\leftarrow \hat{h} = -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}}; J_j = \text{"coulomb operator"}; K_j = \text{"exchange operator"}$$

molecular orbital $\phi = \sum_{\nu} c_{\nu} b_{\nu}$ "LCAO"

$$\hat{f}\phi = \varepsilon\phi \rightarrow \sum_{\nu} \hat{f}b_{\nu}c_{\nu} = \varepsilon \sum_{\nu} b_{\nu}c_{\nu} \rightarrow \sum_{\nu} (f_{\mu\nu} - \varepsilon S_{\mu\nu})c_{\nu} = 0$$

$$\dots \rightarrow |f - \varepsilon S| = 0, f_{\mu\nu} = h_{\mu\nu} + 2J_{\mu\nu} - K_{\mu\nu}$$

$$\leftarrow h_{\mu\nu} = \langle b_{\mu} | -\frac{1}{2}\nabla^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{i\alpha}} | b_{\nu} \rangle, J_{\mu\nu} = \sum_j \sum_{\sigma\lambda} \langle b_{\mu}(1)b_{\sigma}(2) | \frac{1}{r_{12}} | b_{\nu}(1)b_{\lambda}(2) \rangle c_{j\lambda}c_{j\sigma}$$

$$K_{\mu\nu} = \sum_j \sum_{\sigma\lambda} \langle b_{\mu}(1)b_{\sigma}(2) | \frac{1}{r_{12}} | b_{\lambda}(1)b_{\nu}(2) \rangle c_{j\lambda}c_{j\sigma}$$

"solve iteratively and self-consistently using variational principle"

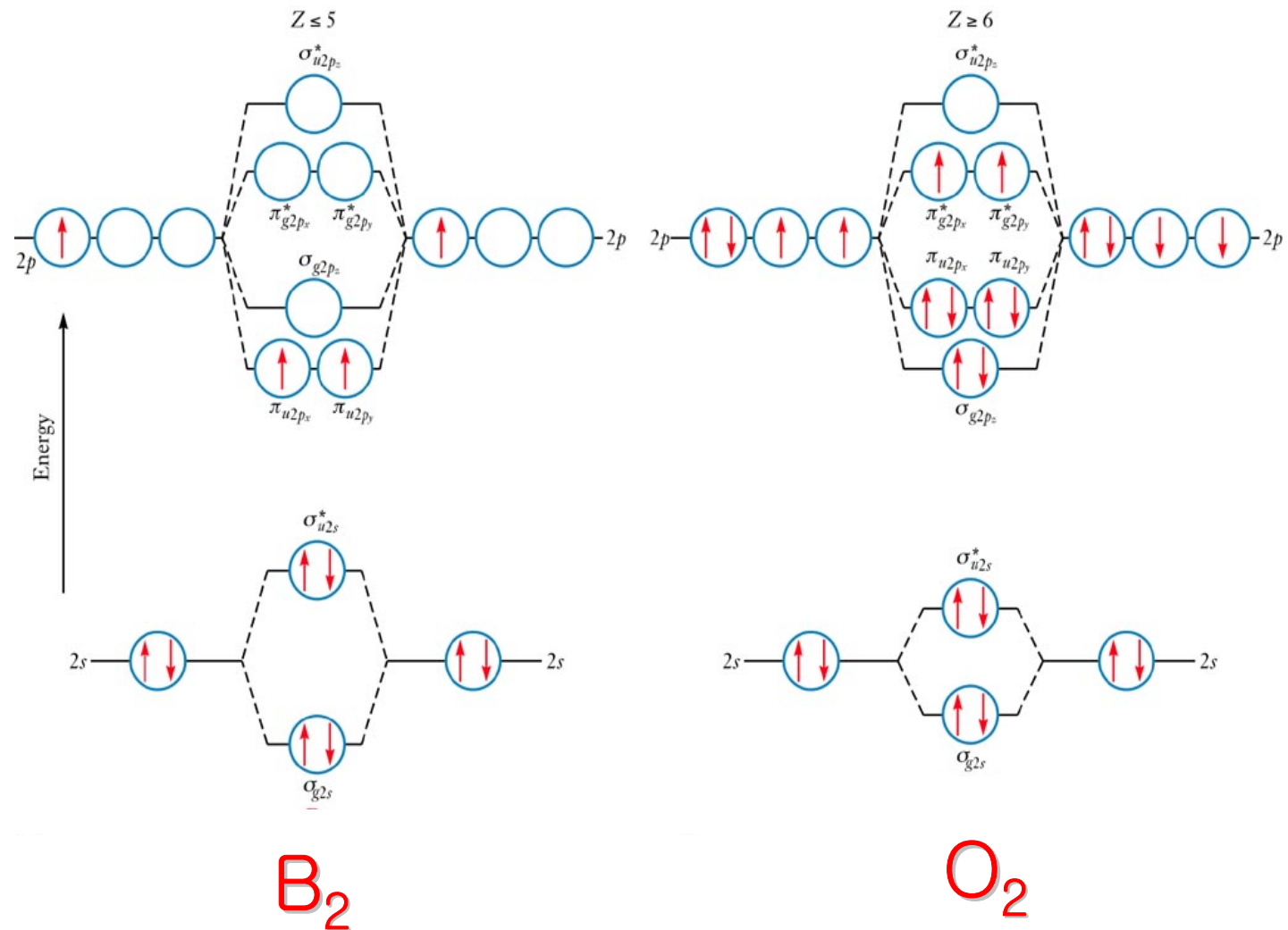
first guess orbital coefficients $c_{j\lambda}, c_{j\sigma}$, etc

→ solve Fock matrix → new coefficients → ...until convergence

"Ab initio methods"

Spectra of Diatomic Molecules

– molecular orbital diagram (Oxtoby)



- Symbols of molecular orbitals (diatomic case: $C_{\infty v}$, $D_{\infty h}$)

$$\hat{l}_z \phi = m_l \hbar \phi$$

“types of molecular orbital”

$$\lambda = |m_l| = 0(\sigma), 1(\pi), 2(\delta), \dots, l$$

$$l = 0 \quad s \rightarrow |m_l| = 0(\sigma)$$

$$l = 1 \quad p \rightarrow |m_l| = 0(\sigma), 1(\pi)$$

$$l = 2 \quad d \rightarrow |m_l| = 0(\sigma), 1(\pi), 2(\delta)$$

- Ground state total electronic configuration (O_2 case):



– Total electronic state (use character table):

$$\pi_g \otimes \pi_g = \overset{\text{symmetric}}{\Sigma_g^+} \oplus [\overset{\text{antisymmetric wrt inversion (E* n LFC)}}{\Sigma_g^-}] \oplus \Delta_g$$

*on electronic wavefunction
(σ_v in MFC)*

– Pauli principle:

$\psi_{el} \psi_{spin}$: *antisymmetric by electron exchange (fermion)*
($C_2(y)$ in MFC)

Σ_g^+, Δ_g : *symmetric ψ_{el}*

→ *antisymmetric ψ_{spin} ($S = 0$): $\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$*

Σ_g^- : *antisymmetric ψ_{el}*

→ *symmetric ψ_{spin} ($S = 1$): $\alpha\alpha, \beta\beta, \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha)$*

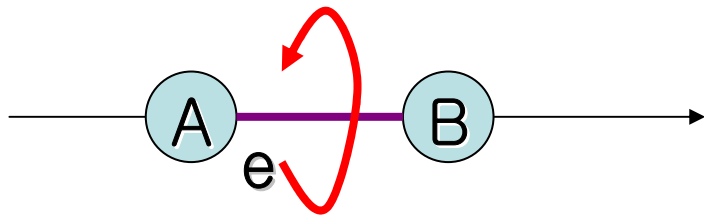
∴ (O_2 case) $^1\Sigma_g^+, ^1\Delta_g, \textcircled{^3\Sigma_g^-}$
lowest in energy

– Angular momentum coupling:

Electron:	orbital AM (L) spin AM (S)
Nuclei:	rotational AM (R) spin AM (I) vibrational AM (V)

→ Total AM $J = L + S + R + I + V$

Important coupling !



*“cylindrical symmetry
along molecular axis”*

cf. spherical symmetry for atoms

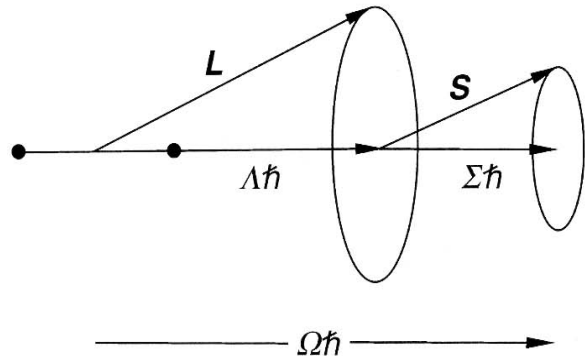
electron motions couple to bond axis

by electric field of nuclei → generate magnetic fields

→ spin (S)–orbit (L) coupling occur

Hund's case (a): weak spin-orbit coupling

e.g. molecules w/ light atoms



L, S couple to bond axis

→ “precession” occurs

→ L : not good quantum number

∴ projection QN: $\Lambda, \Sigma =$ good QN

$\Lambda = 0, 1, 2, \dots; \Sigma = S, S-1, \dots -S$

total electron AM $\Omega = |\Lambda + \Sigma|$

total AM $J = \Omega + R$ (rotation)

$$|n\Lambda S \Sigma\rangle |v\rangle |\Omega J M_J\rangle$$

“Molecular term symbol”

$${}^{2S+1}\Lambda_{\Omega}$$

$$\leftrightarrow {}^{2S+1}L_J(\text{atom})$$

$\Lambda = 0$ (Σ), 1 (Π), 2 (Δ), 3 (Φ), 4 (Γ), ...

“Energy splittings”

$$\Delta E = A \Sigma \Lambda$$

A : positive (normal) → lower Ω : lower energy

A : negative (inverted) → higher Ω : lower energy

Hund's case (b): medium spin-orbit coupling

“Only L couples to bond axis → only Λ defined”

$$N = \Lambda + R(\text{rotation})$$

$$\text{total AM } J = N + S(\text{spin})$$

$$2S+1 \Lambda$$

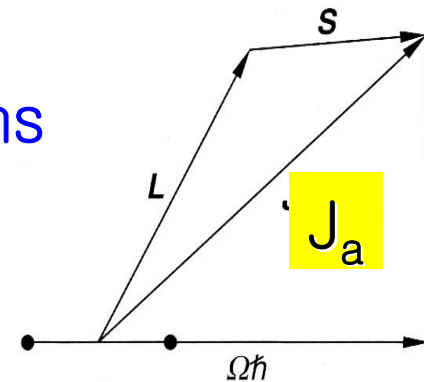
Hund's case (c): strong spin-orbit coupling

e.g. molecules w/ heavy atoms

“L, S strongly couple: $J_a = L + S$ ”

→ J_a couple to bond axis: Ω

→ total AM $J = \Omega + R$ (rotation)



$$2S+1 J_{\Omega}$$

– Symmetry of energy levels: Parity

$$[\hat{H}, \hat{O}_s] = 0 \rightarrow \hat{H}\psi_{\pm} = E_{\pm}\psi_{\pm}, \hat{O}_s\psi_{\pm} = \pm\psi_{\pm}$$

Total parity (+/-): symmetry wrt inversion (E^*) in lab coordinate

$$\hat{E}^* \psi(X_i, Y_i, Z_i) = \psi(-X_i, -Y_i, -Z_i) = \pm \psi(X_i, Y_i, Z_i)$$

$$(Hougen) \hat{E}^*(lab) = \hat{\sigma}_v(mol)$$

$$e.g. \hat{E}^* \mu(\text{dipole moment}) = -\mu$$

$$\therefore \text{dipole transition} : + \leftrightarrow -$$

$$cf. \hat{\sigma}_v \psi_{orbital} = \pm \psi_{orbital} : \Sigma^{\pm} \text{ (not total parity)}$$

Rotationless parity (e/f):

$$\psi = \psi_{el} \psi_{vib} \psi_{rot}, \hat{E}^* \psi_{vib} = \psi_{vib}; \hat{E}^* \psi_{rot} = (-1)^J \psi_{rot}$$

$$e : \hat{E}^* \psi = +(-1)^J \psi; \quad f : \hat{E}^* \psi = -(-1)^J \psi$$

gerade/ungerade(*g/u*) parity: symmetry wrt inversion
in MFC

“only for homonuclear diatomics and
electronic orbital wavefunctions”

$$\hat{i}\psi_{el}(x_i, y_i, z_i) = \psi_{el}(-x_i, -y_i, -z_i) = \pm\psi_{el}(x_i, y_i, z_i)$$

+ *gerade* / - *ungerade*

(*electric dipole transition*) $g \leftrightarrow u$

s/a parity : symmetry wrt permutation in LFC

“only for molecules w/ identical nuclei”

$$\hat{P}_{12}(\psi\psi_{nspin}) = \pm\psi\psi_{nspin} (+ : \textit{boson} / - : \textit{fermion})$$

$$\hat{P}_{12}(\textit{lab}) = \hat{\sigma}_v \hat{i}(\textit{mol}) = \hat{C}_2(\textit{y})(\textit{mol})$$

$$s : \hat{P}_{12}\psi = +\psi; a : \hat{P}_{12}\psi = -\psi$$

– Electronic selection rules:

$$\Delta\Lambda = 0, \pm 1 \text{ (e.g. } \Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Sigma, \Delta \leftrightarrow \Pi \dots)$$

$$\Delta S = 0, \Delta\Sigma = 0$$

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

Parity : total parity + \leftrightarrow -; g \leftrightarrow u

$$\Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^- \text{ (: } \mu_z \text{ : } \Sigma_u^+)$$

– Labeling of electronic states:

(Diatomics) ground state : X (e.g. $X \ ^3\Sigma_g^-$)

excited states w/ same spins as GS : A, B, C, \dots

(e.g. $A \ ^3\Sigma_u^+, B \ ^3\Sigma_u^-, \dots$)

excited states w/ different spins as GS : a, b, c, \dots

(e.g. $a \ ^1\Delta_g, b \ ^1\Sigma_g^+, \dots$)

(Polyatomics) : $\tilde{X}, \tilde{A}, \tilde{B}, \dots, \tilde{a}, \tilde{b}, \dots$

* Vibrational structures in electronic spectra

– Potential energy curves: C₂ case

GSEC : $(\sigma_g 1s)^2 (\sigma_u^* 1s)^2 (\sigma_g 2s)^2 (\sigma_u^* 2s)^2 (\pi_u 2p)^4$ "closed" $X^1\Sigma_g^+$

ESEC : $\dots (\pi_u 2p)^3 (\sigma_g 2p)^1$; $A^1\Pi_u, a^3\Pi_u$

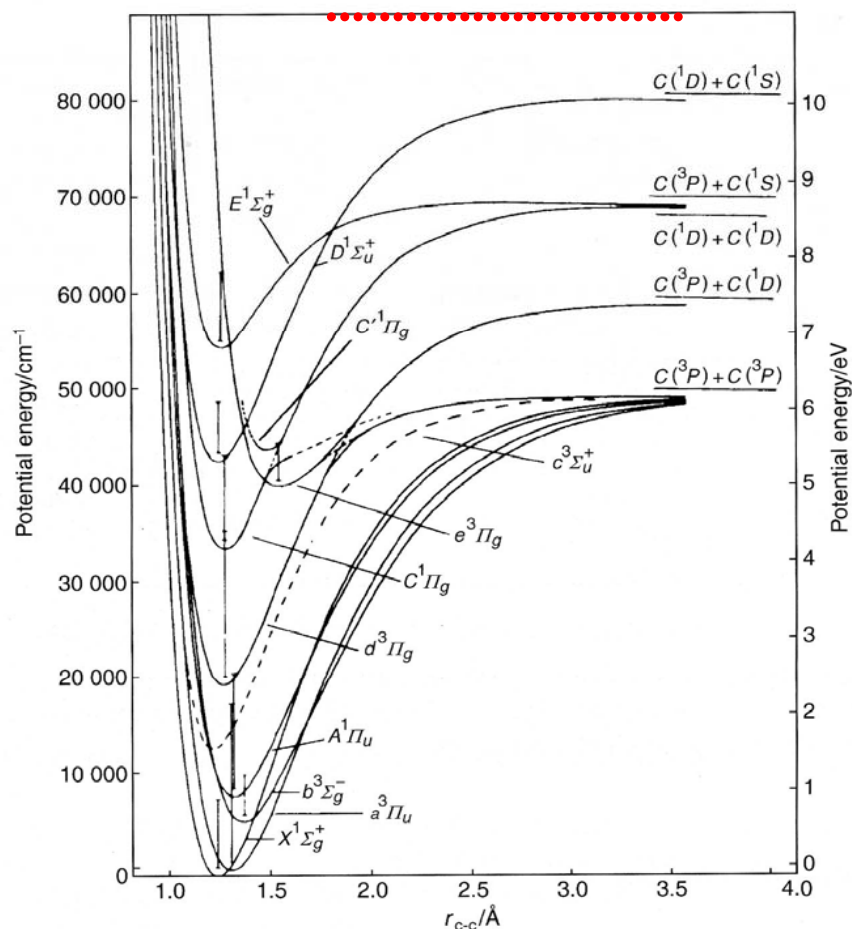
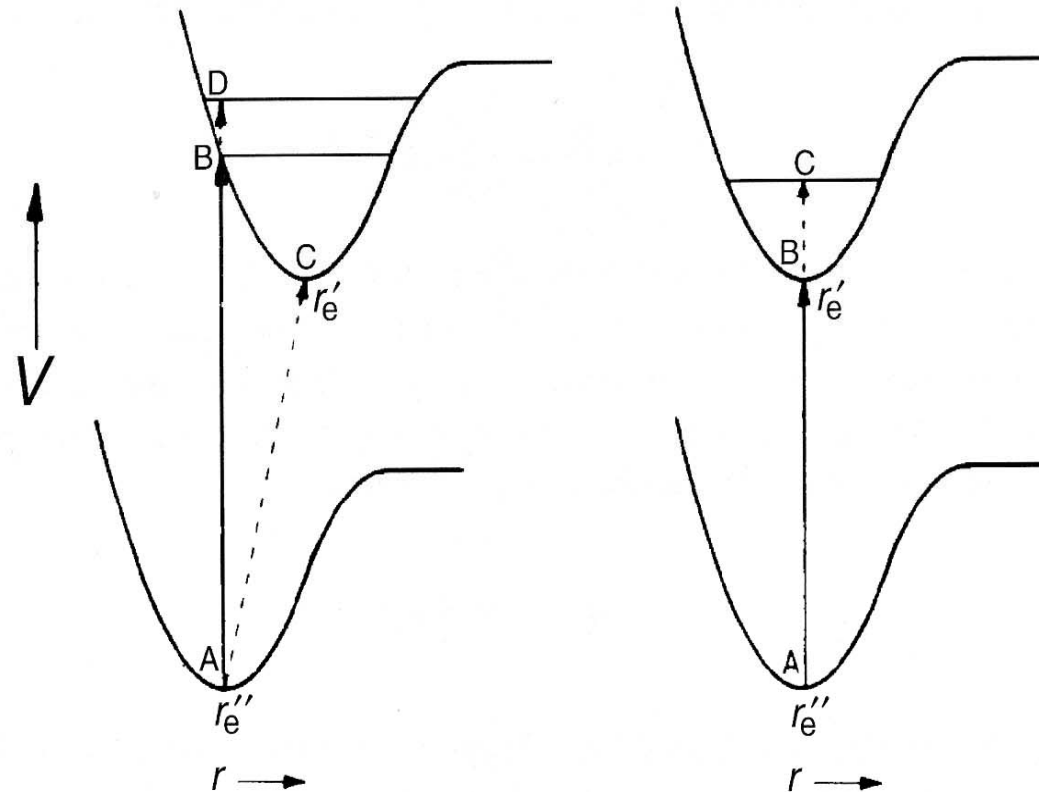


Table 7.6 Electronic transitions observed in C₂

Transition	Names associated	Special region/nm	Source of spectrum
$b^3\Sigma_g^- \rightarrow a^3\Pi_u$	Ballik–Ramsay	2700–1100	King furnace
$A^1\Pi_g \rightleftharpoons X^1\Sigma_g^+$	Phillips	1549–672	Discharges
$d^3\Pi_g \rightleftharpoons a^3\Pi_u$	Swan	785–340	Numerous, including carbon arc
$C^1\Pi_g \rightarrow A^1\Pi_u$	Deslandres–d’Azambuja	411–339	Discharges, flames
$e^3\Pi_g \rightarrow a^3\Pi_u$	Fox–Herzberg	329–237	Discharges
$D^1\Sigma_u^+ \rightleftharpoons X^1\Sigma_g^+$	Mulliken	242–231	Discharges, flames
$E^1\Sigma_g^+ \rightarrow A^1\Pi_u$	Freymark	222–207	Discharge in acetylene
$f^3\Sigma_g^- \leftarrow a^3\Pi_u$	—	143–137	Flash photolysis of mixture of a hydrocarbon and an inert gas
$g^3\Delta_g \leftarrow a^3\Pi_u$	—	140–137	
$F^1\Pi_u \leftarrow X^1\Sigma_g^+$	—	135–131	

– Franck–Condon principle:

“...electronic transition occurs within a stationary nuclear framework \leftrightarrow vertical transition in PES picture”



A–B transition is dominant!

Transition dipole moment ($|\varepsilon'v'\rangle \leftarrow |\varepsilon''v''\rangle$)

BO approxi : $|\varepsilon v\rangle = \psi_\varepsilon(\mathbf{r};\mathbf{R})\psi_v(\mathbf{R})$

$$\therefore M_{\varepsilon'v',\varepsilon''v''} = \langle \varepsilon'v' | \mu | \varepsilon''v'' \rangle \leftarrow \mu = -e \sum_i r_i + e \sum_A Z_A R_A = \mu_e + \mu_N$$

$$= \int_r \int_R \psi_{\varepsilon'}^*(\mathbf{r};\mathbf{R}) \psi_{v'}^*(\mathbf{R}) \{ \mu_e + \mu_N \} \psi_{\varepsilon''}(\mathbf{r};\mathbf{R}) \psi_{v''}(\mathbf{R}) d\mathbf{r} d\mathbf{R}$$

$$= \int_R \psi_{v'}^*(\mathbf{R}) \left\{ \int_r \psi_{\varepsilon'}^*(\mathbf{r};\mathbf{R}) \mu_e \psi_{\varepsilon''}(\mathbf{r};\mathbf{R}) d\mathbf{r} \right\} \psi_{v''}(\mathbf{R}) d\mathbf{R} \quad M_{\varepsilon'\varepsilon''}(\mathbf{R})$$

$$+ \int_R \psi_{v'}^*(\mathbf{R}) \mu_N \left\{ \int_r \psi_{\varepsilon'}^*(\mathbf{r};\mathbf{R}) \psi_{\varepsilon''}(\mathbf{r};\mathbf{R}) d\mathbf{r} \right\} \psi_{v''}(\mathbf{R}) d\mathbf{R} \quad \delta_{\varepsilon'\varepsilon''}$$

$$= \langle v' | M_{\varepsilon'\varepsilon''}(\mathbf{R}) | v'' \rangle + \langle v' | \mu_N | v'' \rangle \delta_{\varepsilon'\varepsilon''} \quad \text{Pure vibrational transitions}$$

if $M_{\varepsilon'\varepsilon''}(\mathbf{R}) \approx M_{\varepsilon'\varepsilon''}(\mathbf{R}_{eq})$,

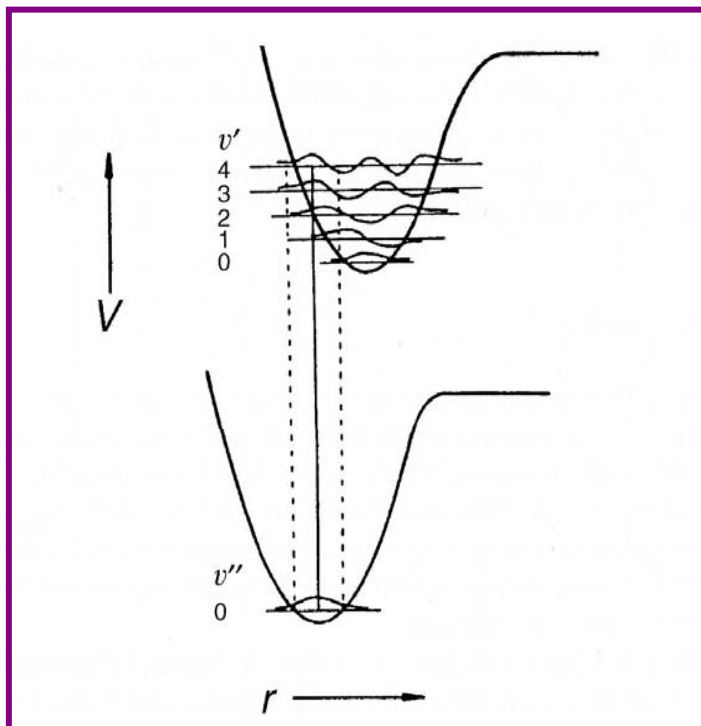
$$\therefore M_{\varepsilon'v',\varepsilon''v''} = M_{\varepsilon'\varepsilon''}(\mathbf{R}_{eq}) \langle v' | v'' \rangle$$

$$= M_{\varepsilon'\varepsilon''}(\mathbf{R}_{eq}) S(v',v'') \leftarrow S : \text{overlap integral}$$

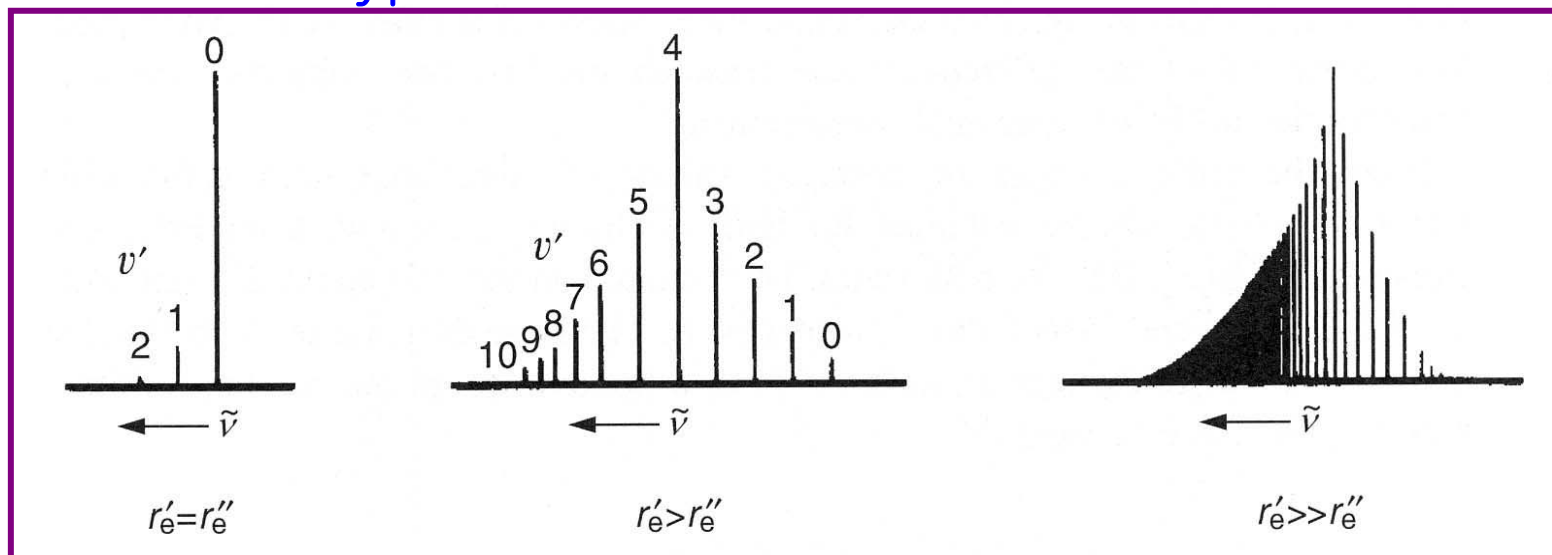
$$\text{Intensity } I_{\varepsilon'v',\varepsilon''v''} \propto |M_{\varepsilon'v',\varepsilon''v''}|^2 = |M_{\varepsilon'\varepsilon''}(\mathbf{R}_{eq})|^2 |S(v',v'')|^2$$

Franck-Condon factor

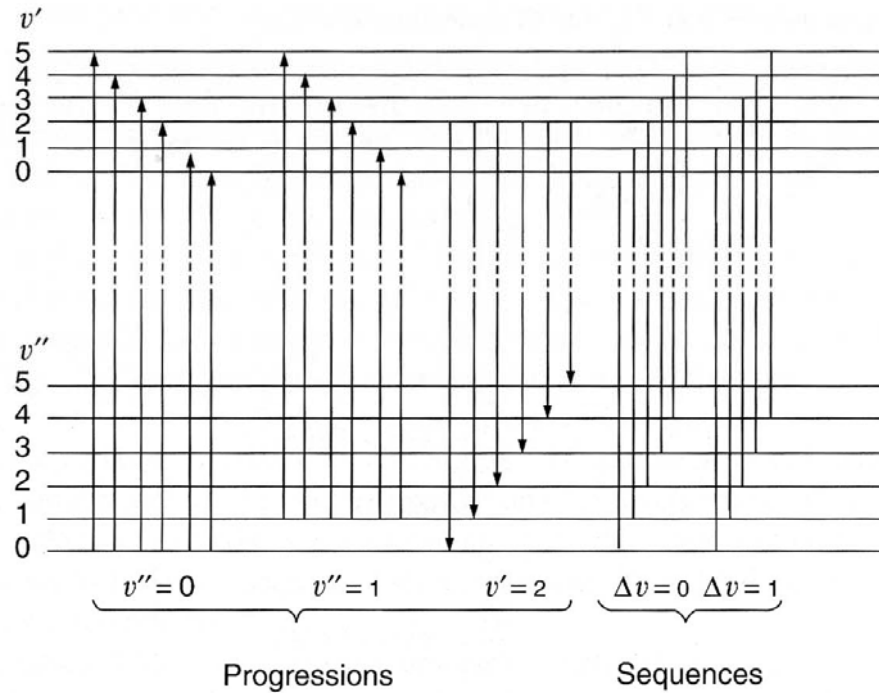
Example of Vibronic transitions



Typical Vibrational Structures



– Vibrational progressions: $\Delta v = \pm(\text{any integers})$



$$\frac{N_{v''}}{N_0} = e^{-(E_{v''}-E_0)/kT}$$

Vibrational progressions!

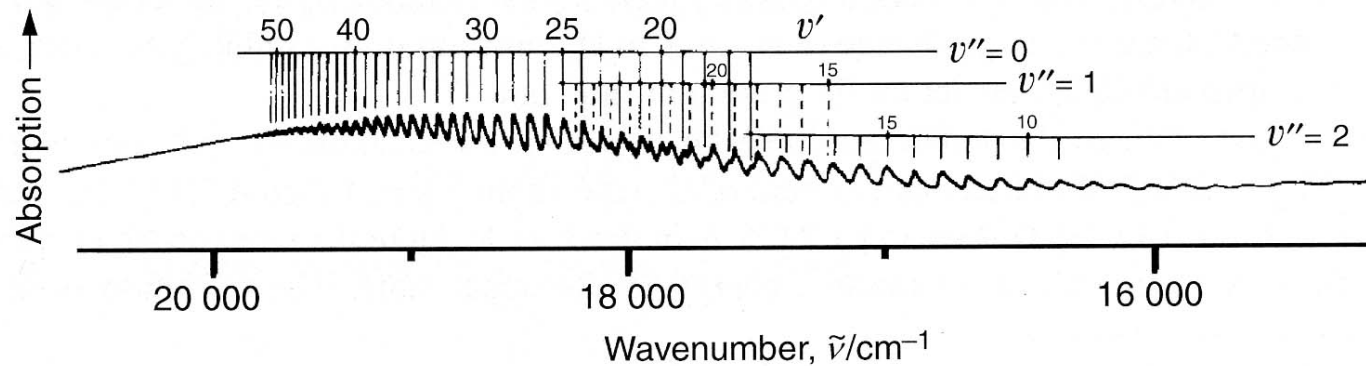


Figure 7.19 Progressions with $v'' = 0, 1$ and 2 in the $B^3\Pi_{0u^+} - X^1\Sigma_g^+$ system of I_2

– Deslandres table:

Table 7.7 Deslandres table for the $A^1\Pi - X^1\Sigma^+$ system of carbon monoxide^a

v'	$v''=0$		$v''=1$		$v''=2$		$v''=3$		$v''=4$		$v''=5$		$v''=6$	
0	64 758	(2145)	62 613	(2117)	60 496	(2092)	58 404	(2063)	56 341	(2037)	54 304			—
	(1476)		(1485)					(1487)		(1486)		(1487)		
1	66 234	(2136)	64 098		—		59 891	(2064)	57 827	(2036)	55 791	(2010)	53 781	
	(1448)		(1441)				(1444)				(1443)		(1443)	
2	67 682	(2143)	65 539	(2115)	63 424	(2089)	61 335		—		57 234	(2010)	55 224	
	(1407)		(1413)		(1414)								(1410)	
3	69 089	(2137)	66 952	(2114)	64 838		—		60 683	(2039)	58 644		—	
	(1378)		(1382)		(1370)					(1379)				
4	70 467	(2133)	68 334	(2126)	66 208	(2085)	64 123	(2061)	62 062		—		58 011	
	(1341)		(1338)		(1350)		(1343)						(1340)	
5	71 808	(2136)	69 672	(2114)	67 558	(2092)	65 466		—		61 365	(2014)	59 351	
	(1307)		(1305)		(1303)		(1299)				(1307)		—	
6	73 115	(2138)	70 977	(2116)	68 861	(2096)	66 765	(2053)	64 712	(2040)	62 672		—	

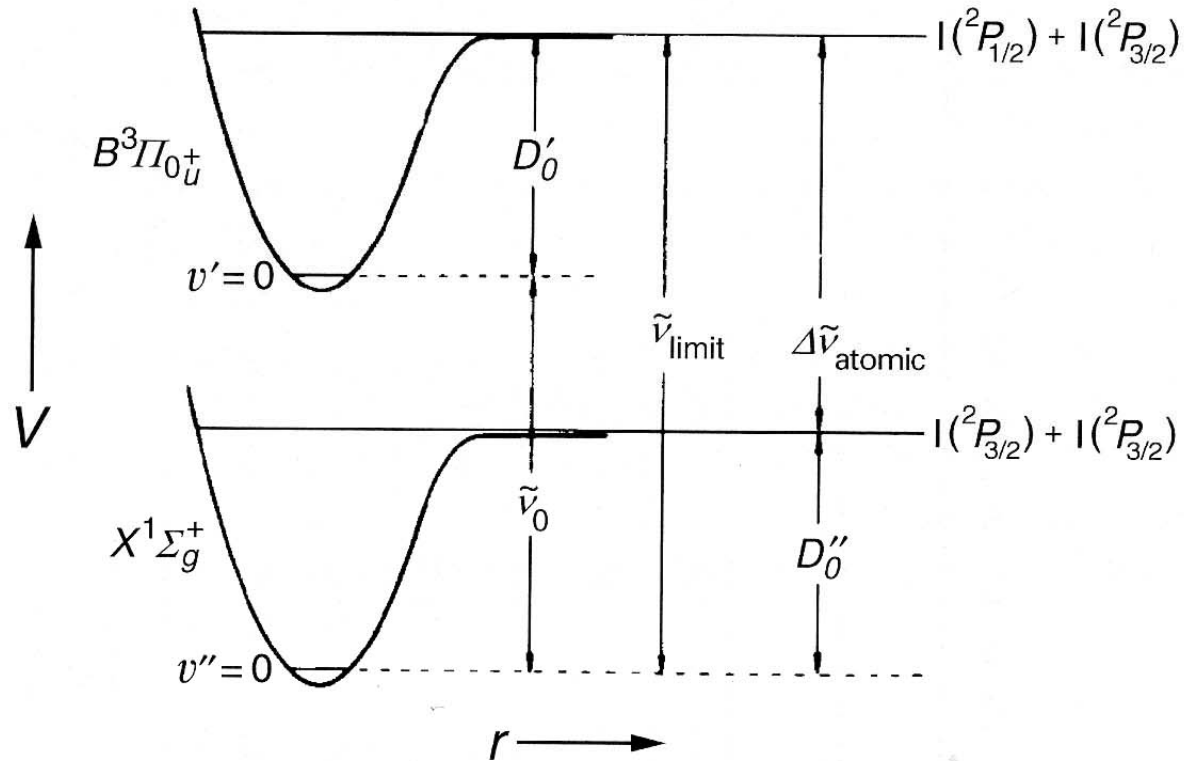
^a Units are cm^{-1} throughout. Measurements are of band heads, formed by the rotational structure, not band origins. Figures in parentheses are differences; variations in differences (e.g. between the first two columns) are a result of uncertainties in experimental measurements.

*Vibrational spacing
in excited electronic state*

*Vibrational spacing
in ground electronic state*

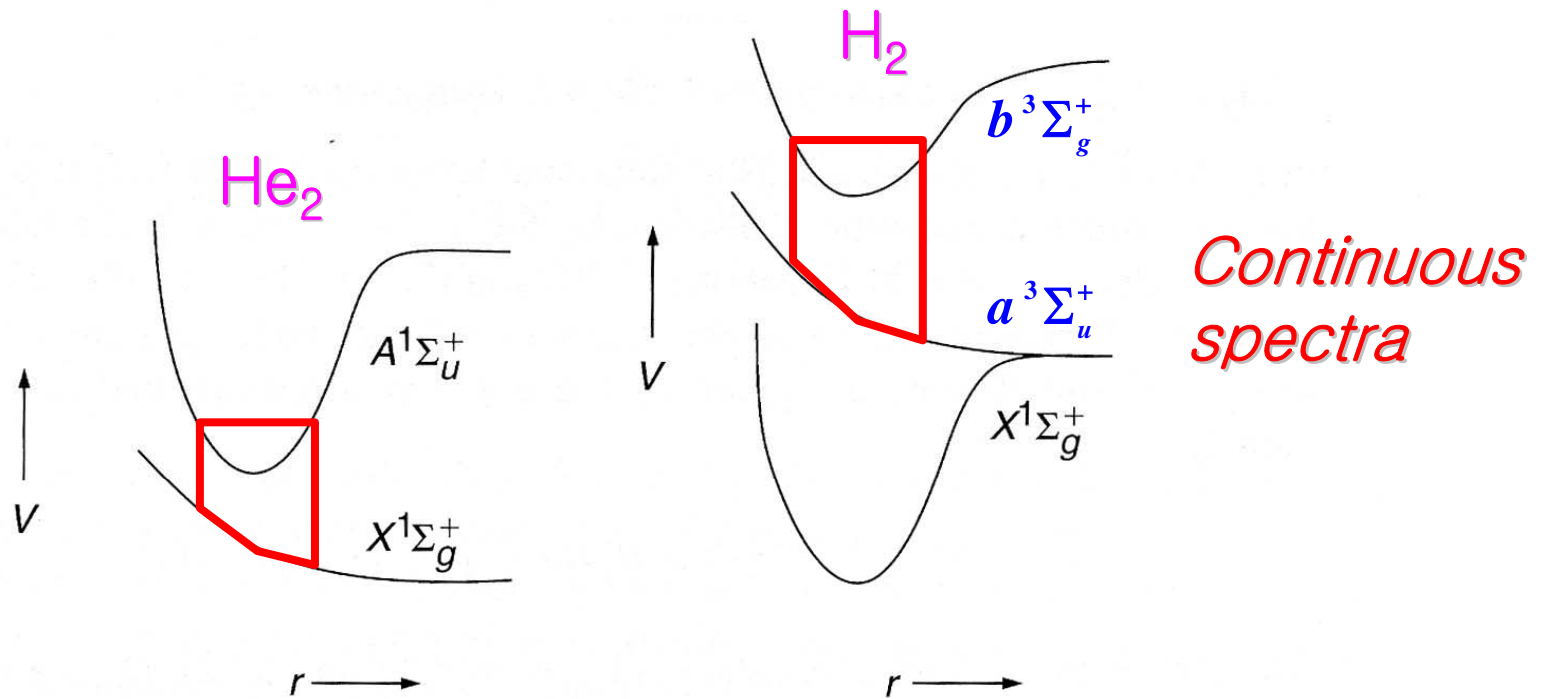
– Determination of dissociation energies:

use of Birge–Sponer extrapolation



$$\tilde{\nu}_{\text{limit}} = D'_0 + \tilde{\nu}_0 = D''_0 + \Delta\tilde{\nu}_{\text{atomic}}$$

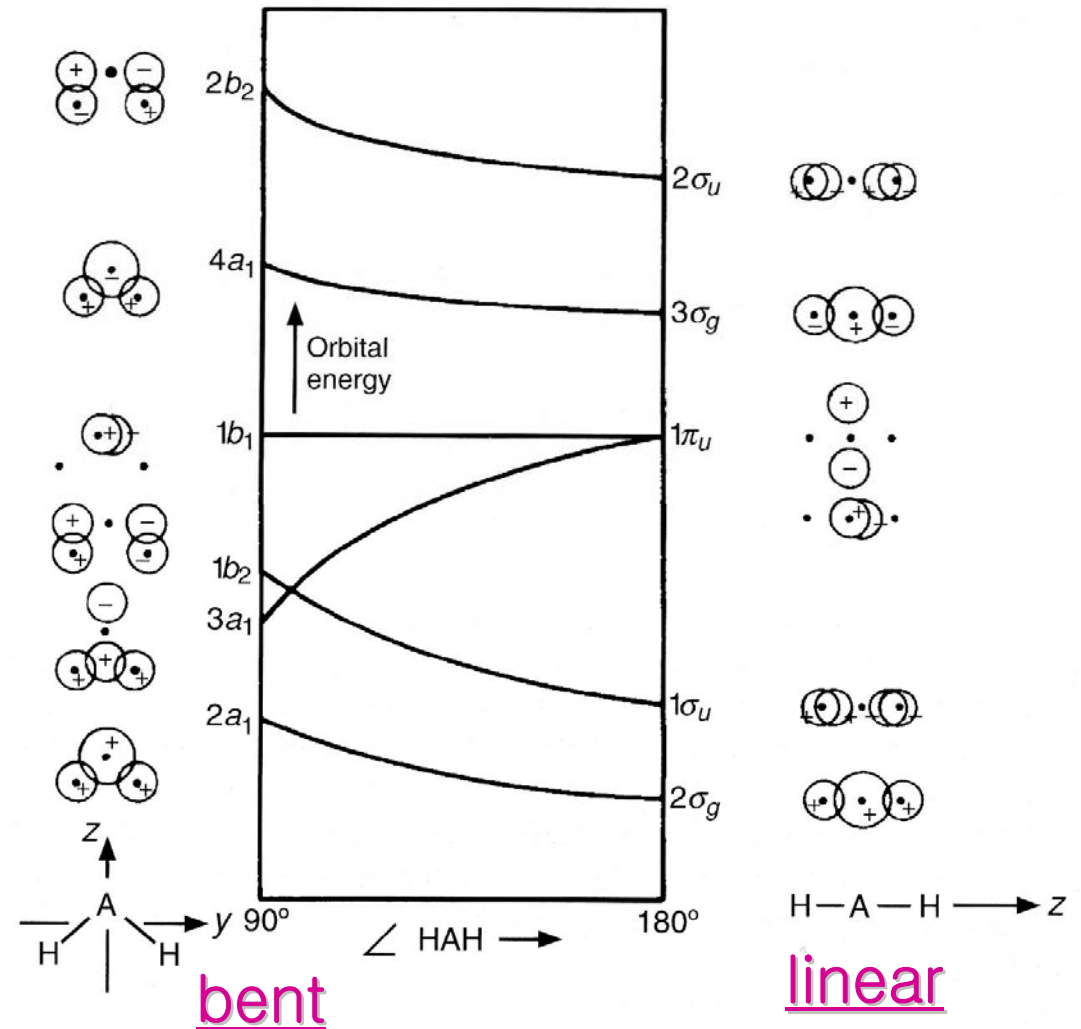
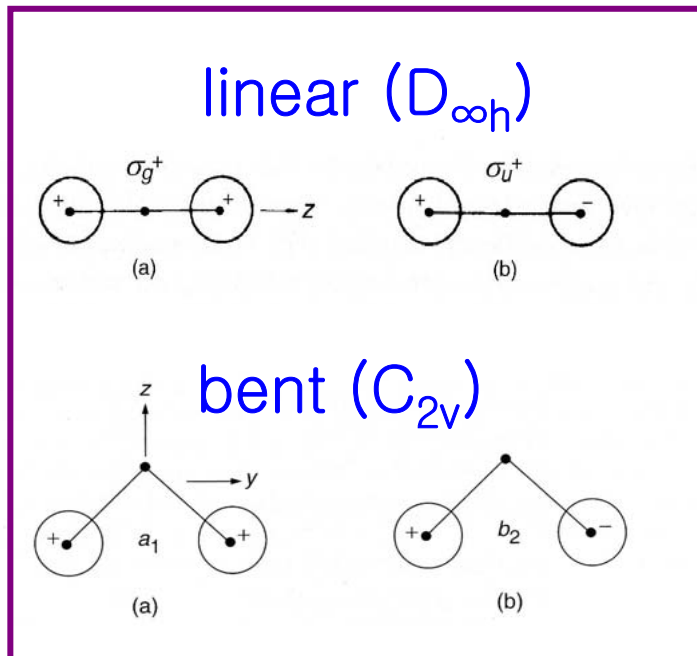
– Repulsive states and continuous spectra:



Spectra of Polyatomic Molecules

* Triatomic molecules AH_2 : $1s + (2s, 2p_x, 2p_y, 2p_z) + 1s$

Walsh diagram



Labelling of Polyatomics: $\tilde{X}, \tilde{A}, \tilde{B}, \dots, \tilde{a}, \tilde{b}, \dots$

e.g. $\tilde{X}^1A_1, \tilde{a}^3B_1, \dots$

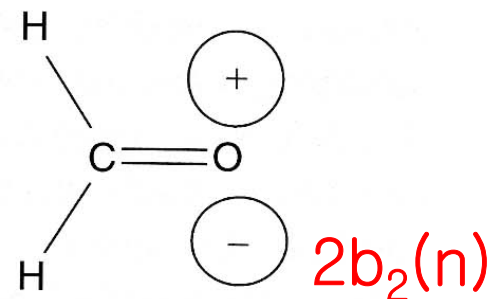
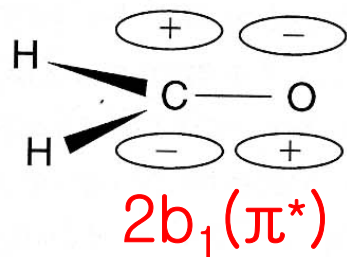
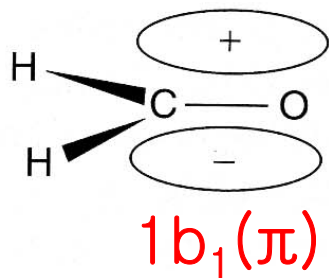
Table 7.8 Ground and excited configurations of some AH₂ molecules

Molecule	Configuration	State	\angle HAH
LiH ₂ ^a	$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^1$	$\tilde{X}^2\Sigma_u^+$	180°(?)
	$(1a_1)^2(2a_1)^2(3a_1)^1$	\tilde{A}^2A_1	< 180°(?)
BeH ₂ ^a	$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$	$\tilde{X}^1\Sigma_g^+$	180°(?)
	$(1a_1)^2(2a_1)^2(1b_2)^1(3a_1)^1$	\tilde{a}^3B_2	< 180°(?)
		\tilde{A}^1B_2	< 180°(?)
BH ₂	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1$	\tilde{X}^2A_1	131°
	$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2(1\pi_u)^1$	$\tilde{A}^2\Pi_u$	180°
CH ₂	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$	\tilde{a}^1A_1	102.4°
	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$	\tilde{X}^3B_1	134°
		\tilde{b}^1B_1	140°
NH ₂ (H ₂ O ⁺)	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$	\tilde{X}^2B_1	103.4° (110.5°)
	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$	\tilde{A}^2A_1	144° (180°)
H ₂ O	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$	\tilde{X}^1A_1	104.5°

^a The question marks indicate uncertainty, as the molecule is an unknown species.

* H₂CO case:

“12 valence electrons, three σ -bonds, 1 π -bond”



ground state : $\tilde{X}^1A_1 \leftarrow \dots(1b_1)^2(2b_2)^2$

excited state : $\tilde{A}^1A_2, \tilde{a}^3A_2 \leftarrow \dots(1b_1)^2(2b_2)^1(2b_1)^1$

$\tilde{A} - \tilde{X}$ transition : *n-to- π^* transition*

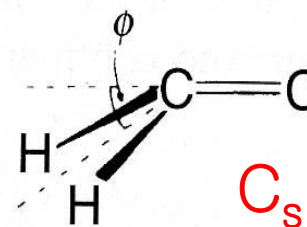
(weak transition \because forbidden by symmetry)

; blue-shifted by hydrogen bonding

(2b₁)¹ π^* electron favor bent geometry :

\tilde{A} state : $\phi = 38^\circ$

\tilde{a} state : $\phi = 43^\circ$



* Conjugated molecules:

– Hückel MO theory:

$\hat{H}_{el} = \hat{H}_{\sigma} + \hat{H}_{\pi}$, $\psi_{el} = \psi_{\sigma}\psi_{\pi}$ ← assume $\sigma - \pi$ separability
for π – electrons only

$\hat{H}_{\pi} = \sum_{k=1}^n \hat{H}^{eff}(k)$ ← one – electron picture

$\hat{H}^{eff} \phi = E \phi$, $\phi_i = \sum_{j=1}^n C_{ij} \chi_j$ ← χ_j : p_z – orbital on atom j

$$\sum_{j=1}^n C_{ij} \hat{H}^{eff} \chi_j - \sum_{j=1}^n C_{ij} E \chi_j = \mathbf{0} \rightarrow \sum_{j=1}^n C_{ij} \langle \chi_i | \hat{H}^{eff} | \chi_j \rangle - \sum_{j=1}^n C_{ij} E \langle \chi_i | \chi_j \rangle = \mathbf{0}$$

$$\sum_{j=1}^n \{ \langle \chi_i | \hat{H}^{eff} | \chi_j \rangle - E \langle \chi_i | \chi_j \rangle \} C_{ij} = \mathbf{0} \rightarrow \therefore \sum_{j=1}^n \{ \hat{H}_{ij}^{eff} - ES_{ij} \} C_{ij} = \mathbf{0}$$

(matrix form) $(\hat{\underline{\underline{H}}}^{eff} - \underline{\underline{E}}\underline{\underline{S}})\underline{\underline{C}} = \mathbf{0} \rightarrow$ secular determinant: $|\hat{\underline{\underline{H}}}^{eff} - \underline{\underline{E}}\underline{\underline{S}}| = \mathbf{0}$

(Hückel theory) $\hat{H}_{ii}^{eff} = \alpha$ (Coulomb integral), $S_{ij} = \delta_{ij}$

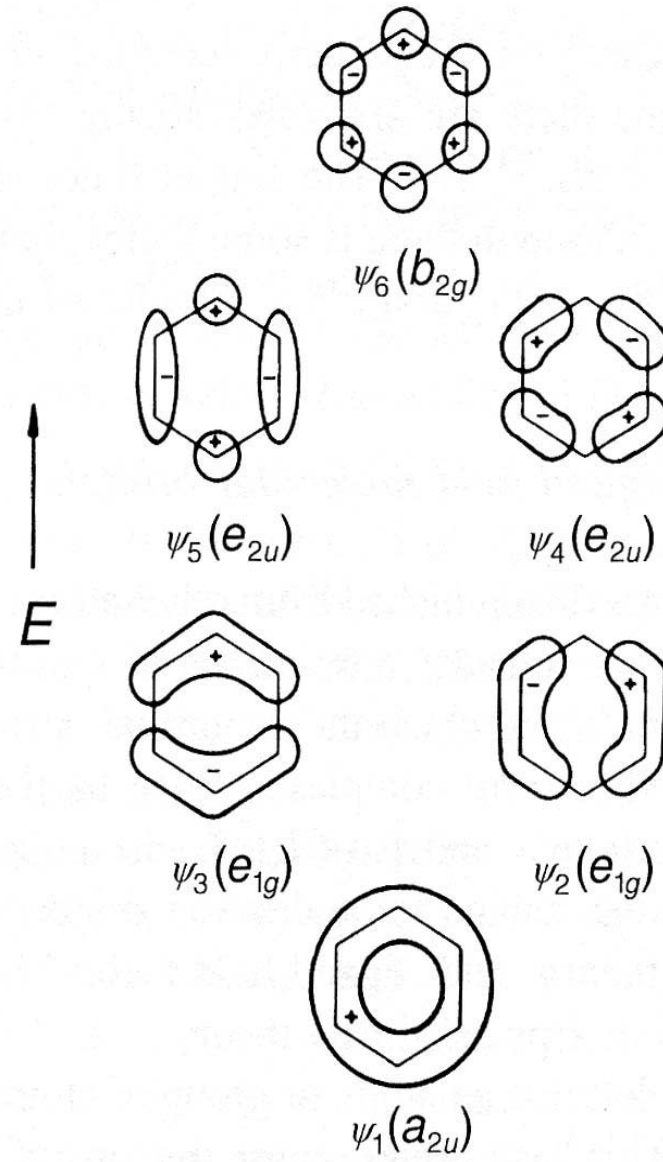
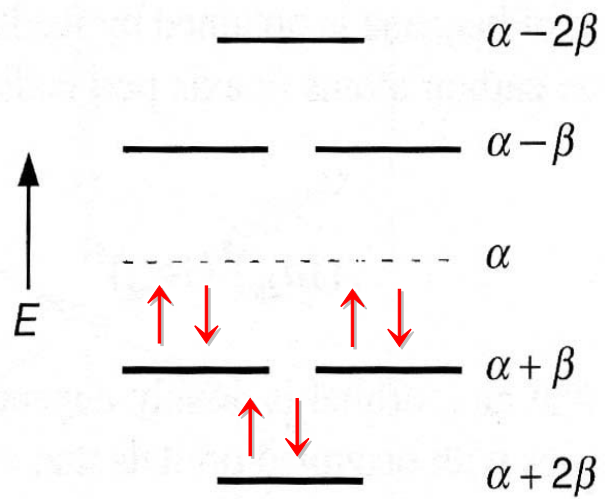
$\hat{H}_{ij}^{eff} = \beta$ (adjacent) or 0 (others) (resonance integral)

Benzene Case:

$$|\hat{H} - ES| = \begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

$$\therefore E = \alpha \pm \beta, \alpha \pm \beta, \alpha \pm 2\beta$$

*Eigenfunctions : Use SALC (symmetry – adapted linear combination)
of 6p_z orbitals*



Hückel molecular orbitals in benzene

$$GSEC : \dots(1a_{2u})^2(1e_{1g})^4; \tilde{X}^1A_{1g}$$

$$ESEC : \dots(1a_{2u})^2(1e_{1g})^3(1e_{2u})^1; e_{1g} \otimes e_{2u} = b_{1u} \oplus b_{2u} \oplus e_{1u}$$

$$\therefore \tilde{A}^1B_{2u}, \tilde{a}^3B_{1u}, \tilde{B}^1B_{1u}, \tilde{b}^3E_{1u}, \tilde{C}^1E_{1u}, \tilde{c}^3B_{2u}$$

Electronic selection rule :

$$\Delta S = 0,$$

$$\langle \psi_f | \mu | \psi_i \rangle \neq 0 \Leftrightarrow \Gamma(\psi_f) \otimes \Gamma(\mu_{x,y,z}) \otimes \Gamma(\psi_i) \supset A_1$$

$$\text{Benzene} : \Gamma(\mu_{x,y}) = E_{1u}; \Gamma(\mu_z) = A_{2u}$$

$$\tilde{X}^1A_{1g} \rightarrow \tilde{A}^1B_{2u} : \text{forbidden } (\sim 260\text{nm}) \text{ but relaxed}$$

$$\tilde{X}^1A_{1g} \rightarrow \tilde{B}^1B_{1u} : \text{forbidden } (\sim 200\text{nm}) \text{ but relaxed}$$

$$\tilde{X}^1A_{1g} \rightarrow \tilde{C}^1E_{1u} : \text{allowed } (\sim 185\text{nm})$$

Vibronic coupling :

∴ breakdown of Born – Oppenheimer approxim.

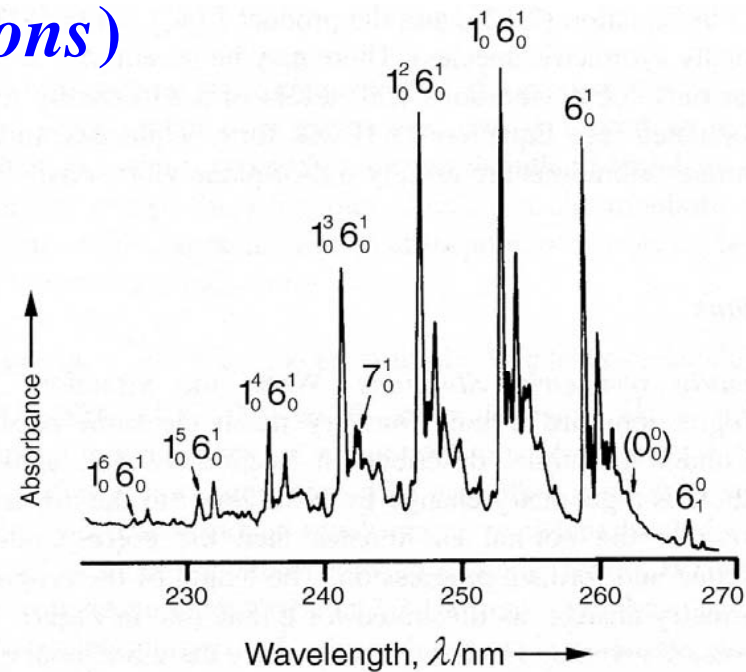
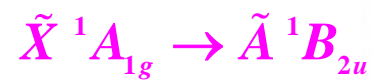
$$\rightarrow \Gamma^{\text{vibronic}}(\psi) = \Gamma(\psi_e) \otimes \Gamma(\psi_v)$$

e.g. $\tilde{X}^1A_{1g} \rightarrow \tilde{A}^1B_{2u}$, if $\Gamma(\psi_v) = e_{2g}(v_6 = 1)$

$$A_{1g} \otimes B_{2u} \otimes E_{2g} = E_{1u} \text{ (same as } \tilde{C} \text{ state)}$$

∴ relaxed ($1_0^n 6_0^1$ progressions)

Benzene



** Jahn – Teller, Herzberg – Teller, Renner-Teller effect*

- Organic Chromophores: $\pi^* \leftarrow n$ transition
- $\pi^* \leftarrow \pi$ transition

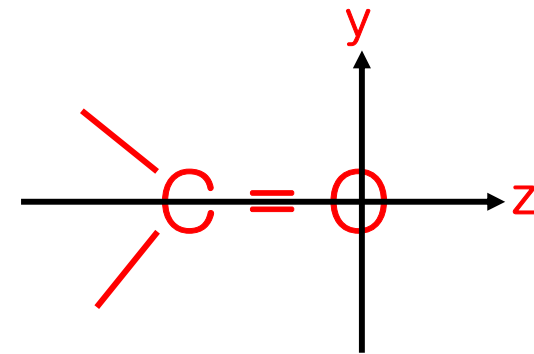
e.g. Carbonyl $\pi^ \leftarrow n$ transition :*

$$\phi_{nb} \sim O_{p_y}$$

$$\phi_{\pi^*} \sim \phi(C_{p_x}, O_{p_x})$$

$$\rightarrow \langle \pi^*(x) | \mu_{x,y,z} | nb(y) \rangle = 0$$

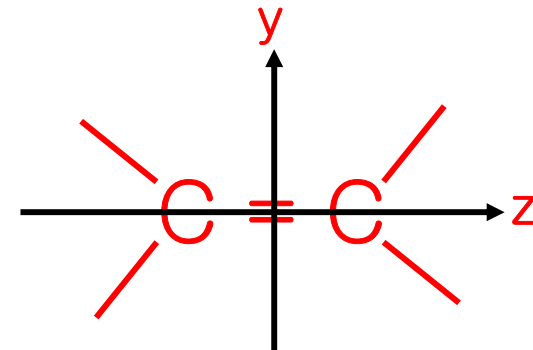
→ forbidden but relaxed by VB



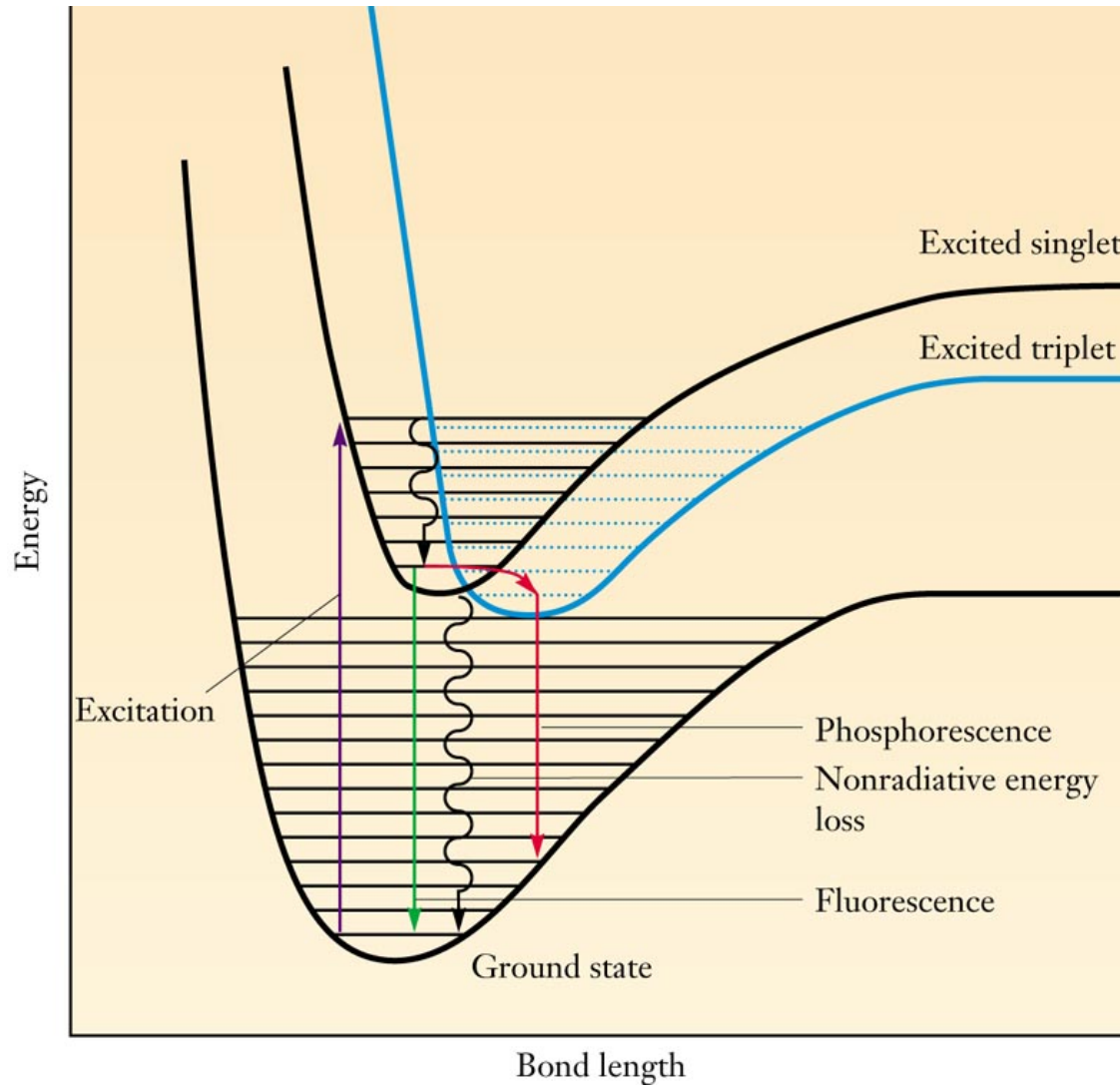
Ethylene $\pi^ \leftarrow \pi$ transition :*

$$M_{\pi^*\pi} \propto \hat{z} \text{ (bond axis)} \quad \therefore \text{allowed}$$

$(\pi)^1 (\pi^)^1$: two CH_2 's perpendicular*



– Decay behaviors of excited states:



$$\Delta\tilde{\nu}(cm^{-1}) = \frac{1}{2\pi c} \left(\frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \right)$$

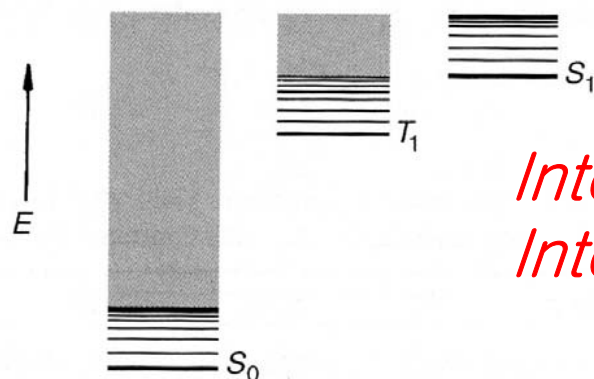
$$= \frac{k_r + k_{nr}}{2\pi c}$$

← τ_r, τ_{nr} : *lifetimes*

k_r, k_{nr} : *rate constants*

(*radiative, nonradiative*)

Coupling w/ pseudo-continuum of S_0 , T_1 :



Internal conversion ($S_1 \rightarrow S_0$)
Intersystem crossing ($S_1 \rightarrow T_1$)

Fluorescence quantum yield:

$$\Phi_F = \frac{\text{no. of fluorescence photons}}{\text{no. of absorbed photons}} = \frac{k_r}{k_r + k_{nr}}$$

$$\text{Fluorescence lifetime } \tau_F = \frac{1}{k_r + k_{nr}}$$

Table 7.11 Fluorescence quantum yield Φ_F , fluorescence lifetime τ_F , radiative, k_r , and non-radiative, k_{nr} , rate constants for the S_1 state of benzene

Vibronic level	Φ_F	τ_F/ns	k_r/s^{-1}	k_{nr}/s^{-1}
0^0	0.22	90	2.4×10^{-6}	8.7×10^{-6}
6^1	0.27	80	3.4×10^{-6}	9.1×10^{-6}
$1^1 6^1$	0.25	68	3.7×10^{-6}	11.0×10^{-6}