# Lecture 5

# Electronic Spectroscopy

# Born-Oppenheimer Approximation

**Molecules are collections of electrons and nuclei:**

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

$$\psi(r,R) = \psi(r;R)\,\chi(R)$$

$$\hat{H}_{total} = \hat{T}_n + \hat{H}_e;\ \hat{H}_{total}\Psi(r,R) = W\Psi(r,R)$$

$$\rightarrow (BO)\ \Psi(r,R) = \psi(r;R)\chi(R)$$

$$(electronic\ \ part)\ \hat{H}_e\psi(r;R) = E^e(R)\psi(r;R)$$

$$\hat{H}_{total}\Psi(r,R) = (\hat{T}_n + E^e(R))\psi(r;R)\chi(R) = W\psi(r;R)\chi(R)$$

$$(nuclear\ \ part)\ (\hat{T}_n + E^e(R))\chi(R) = W\chi(R)$$

## * Electronic Schrödinger equation of many electron molecules

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_{i,A}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 r_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

*nuclear part, but included in $H_e$*

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

*molecular orbital (i.e. one electron wavefunction)*

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

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

*"antisymmetric wrt exchange* $\rightarrow$ *Slater determinant"*

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

## Hatree – Fock approximation for closed shell molecules

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

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

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

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

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

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

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

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

"solve iteratively and self-consistently using variational principle"

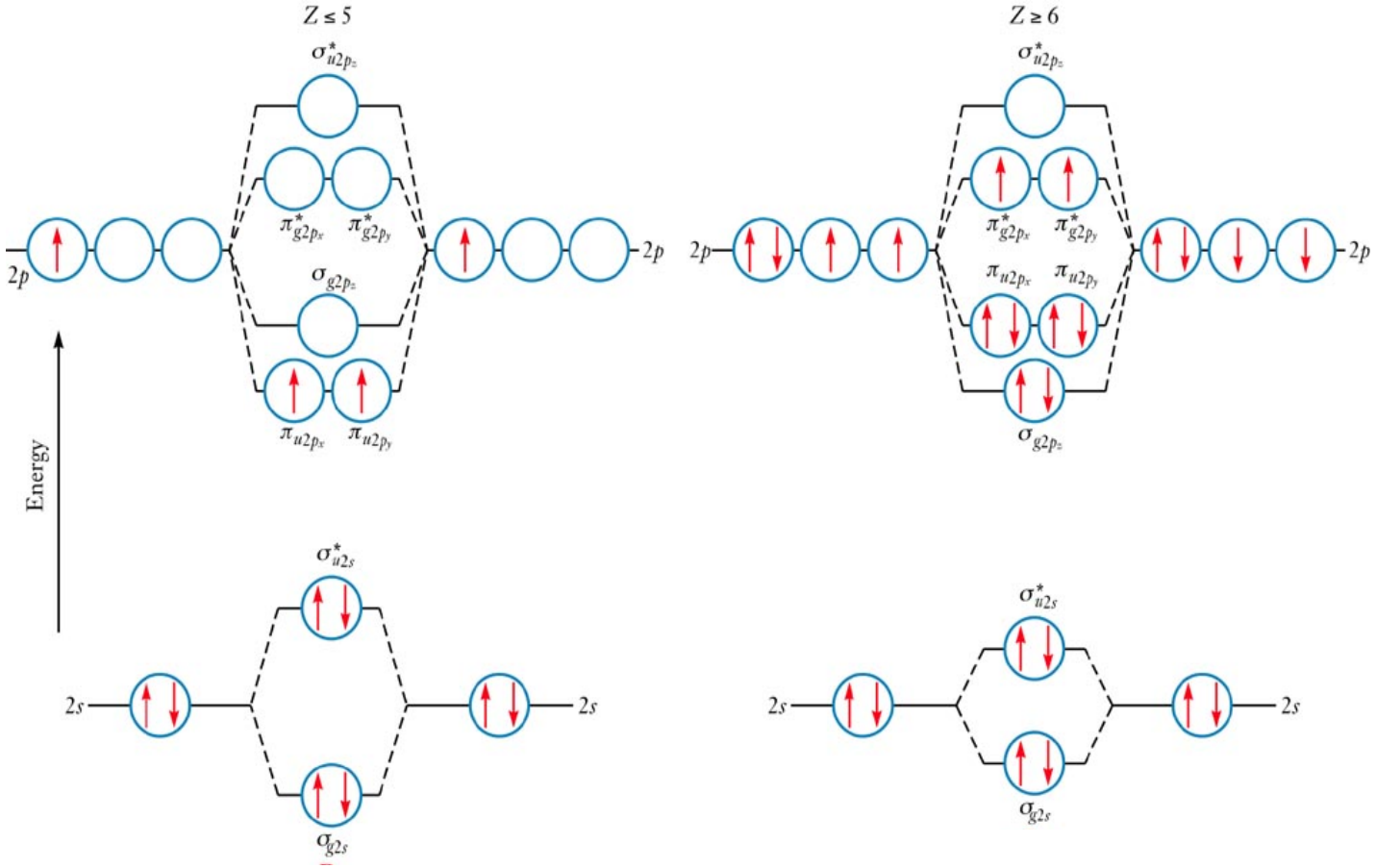
first guess orbital coefficients $c_{j\lambda}, c_{j\sigma}$, etc

$\rightarrow$ solve Fock matrix $\rightarrow$ new coefficients $\rightarrow$ ...until convergence

"Ab initio methods"

# Spectra of Diatomic Molecules

## - Molecular Orbital Diagram (Oxtoby)




$B_2$ $O_2$

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

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

*"types of molecular orbital"*

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

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

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

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

## - Ground state total electronic configuration ($O_2$ case):

$$(\sigma_{1g})^2 (\sigma_{1u}^*)^2 \ldots (\pi_g^*)^2$$

*only unpaired electrons characterize electronic states*

## - Total electronic state (use character table):

*symmetric* *antisymmetric* *wrt inversion ($E^*$ in LFC) on electronic wavefunction ( $\sigma_v$ in MFC)*

$$\pi_g \otimes \pi_g = \Sigma_g^+ \oplus [\Sigma_g^-] \oplus \Delta_g$$

## - Pauli principle:

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

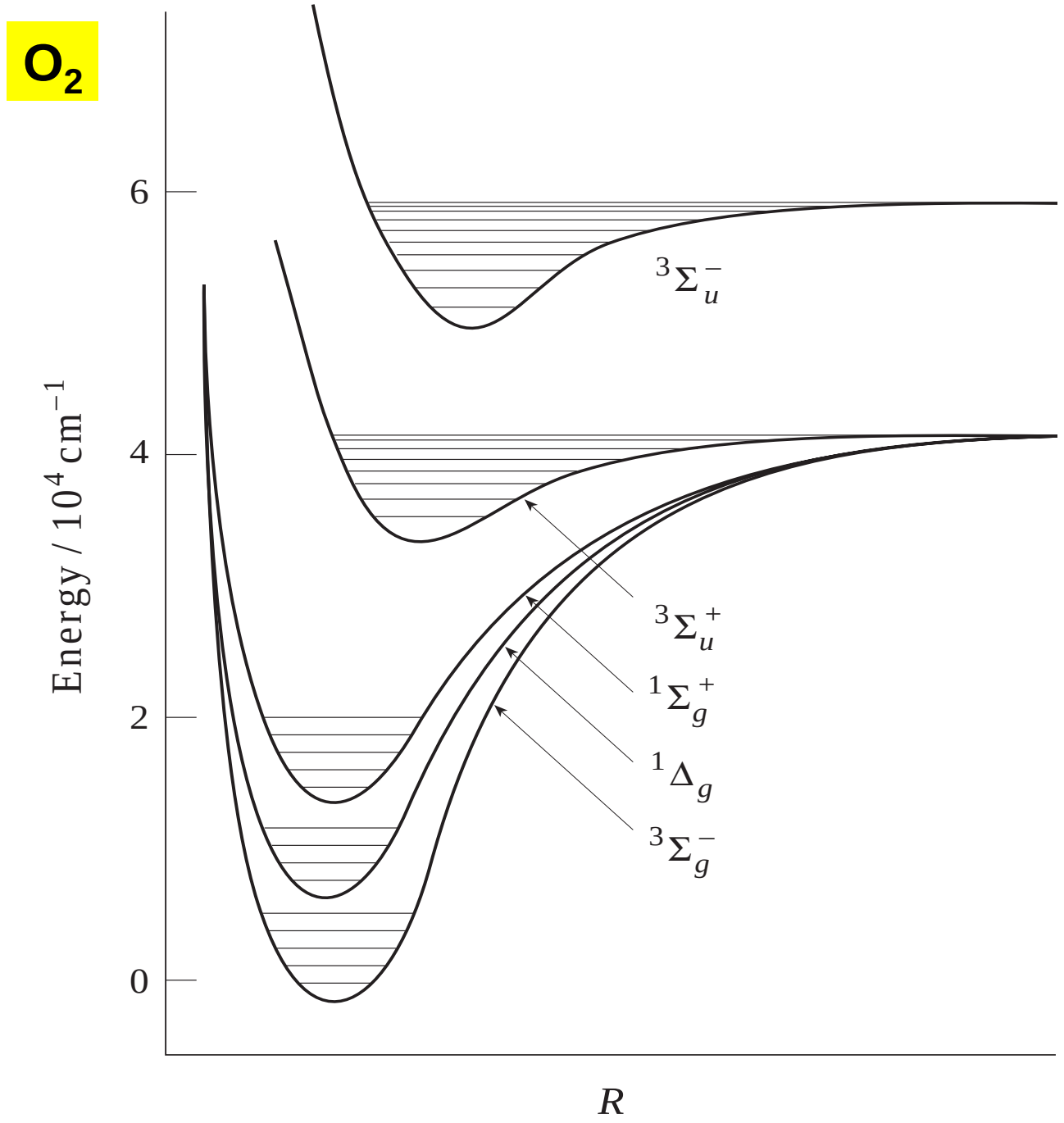
$\Sigma_g^+, \Delta_g$ : *symmetric* $\psi_{el}$

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

$\Sigma_g^-$ : *antisymmetric* $\psi_{el}$

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

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


O2
6
4
2
0
Energy / 10^4 cm^-1
R
3Σu−
3Σu+
1Σg+
1Δg
3Σg−

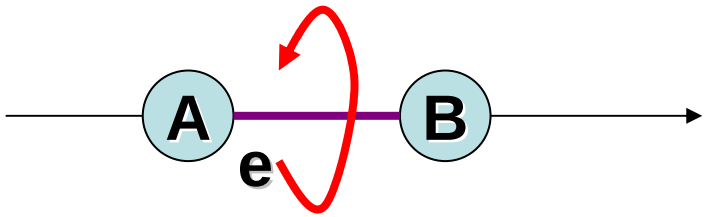
## - Angular momentum coupling:

**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 !***



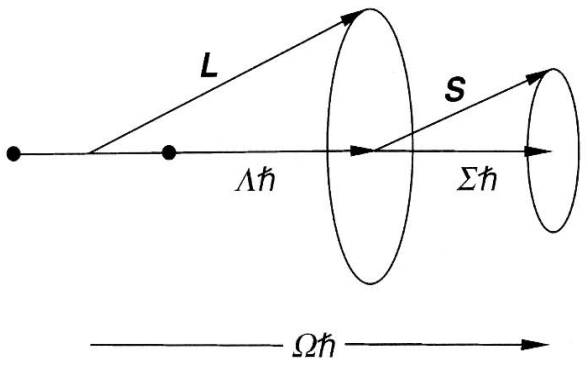

*"cylindrical symmetry along molecular axis"*

*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: Λ, Σ = good QN**
**Λ= 0, 1, 2, …; Σ= S, S-1, … -S**
**total electron AM Ω = |Λ+ Σ|**
**total AM J = Ω + R (rotation)**

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

## "Molecular term symbol"

$$\boxed{{}^{2S+1}\Lambda_{\Omega}} \quad \leftrightarrow \quad {}^{2S+1}L_J\,(atom)$$

**Λ = 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"

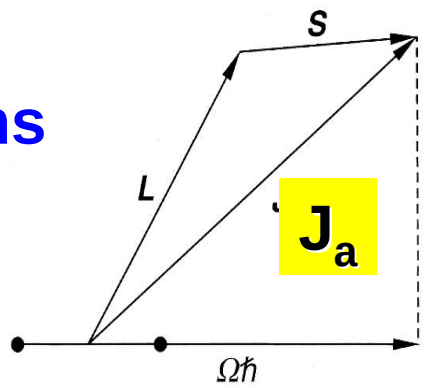
$$N = \Lambda + R(rotation)$$

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

$$^{2S+1}\Lambda$$

## 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 = Ω + 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

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

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

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

$$\therefore\ dipole\ \ transition: + \leftrightarrow -$$

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

**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"**

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

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

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

- **Electronic selection rules:**

$$\Delta\Lambda = 0, \pm 1 \; (e.g.\; \Sigma \leftrightarrow \Sigma, \Pi \leftrightarrow \Sigma,\; \Delta \leftrightarrow \Pi \ldots)$$

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

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

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

$$\Sigma^+ \leftrightarrow \Sigma^+, \Sigma^- \leftrightarrow \Sigma^- \; (\because \mu_z : \Sigma_u^+)$$

- **Labeling of electronic states:**

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

$excited \;\; states \;\; w/ \;\; same \;\; spins \;\; as \;\; GS: A, B, C, \ldots$

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

$excited \;\; states \;\; w/ \;\; different \;\; spins \;\; as \;\; GS: a, b, c, \ldots$

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

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

# * Vibrational structures in electronic spectra

## - Potential energy curves: $C_2$ case

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

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

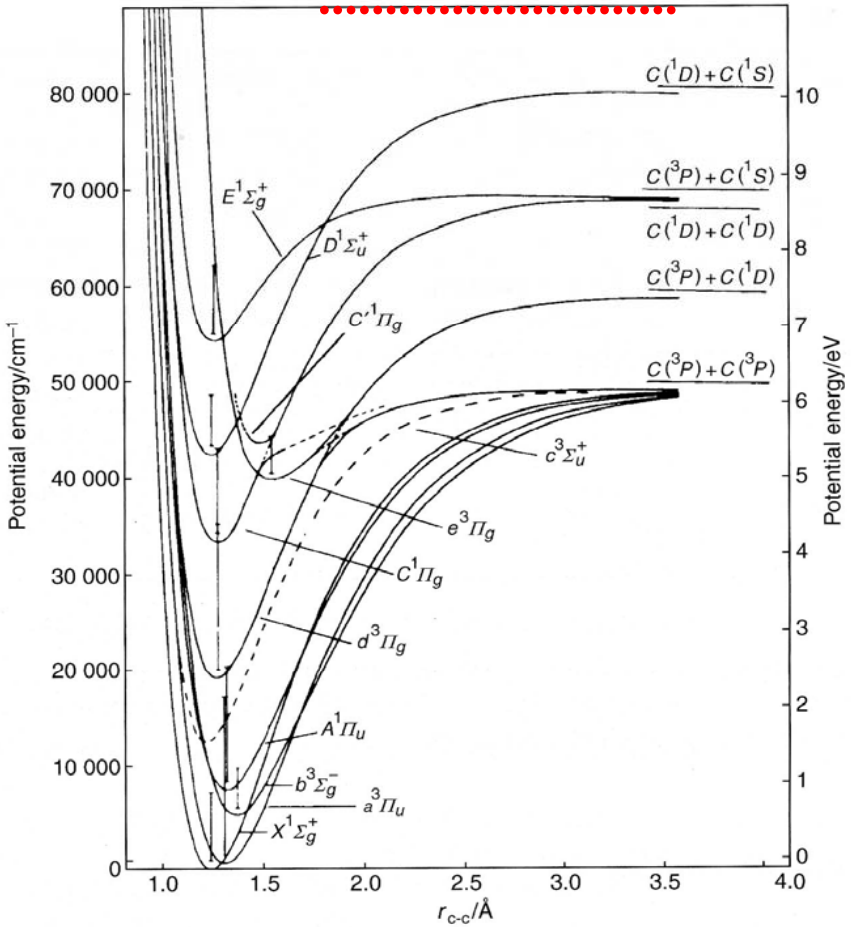
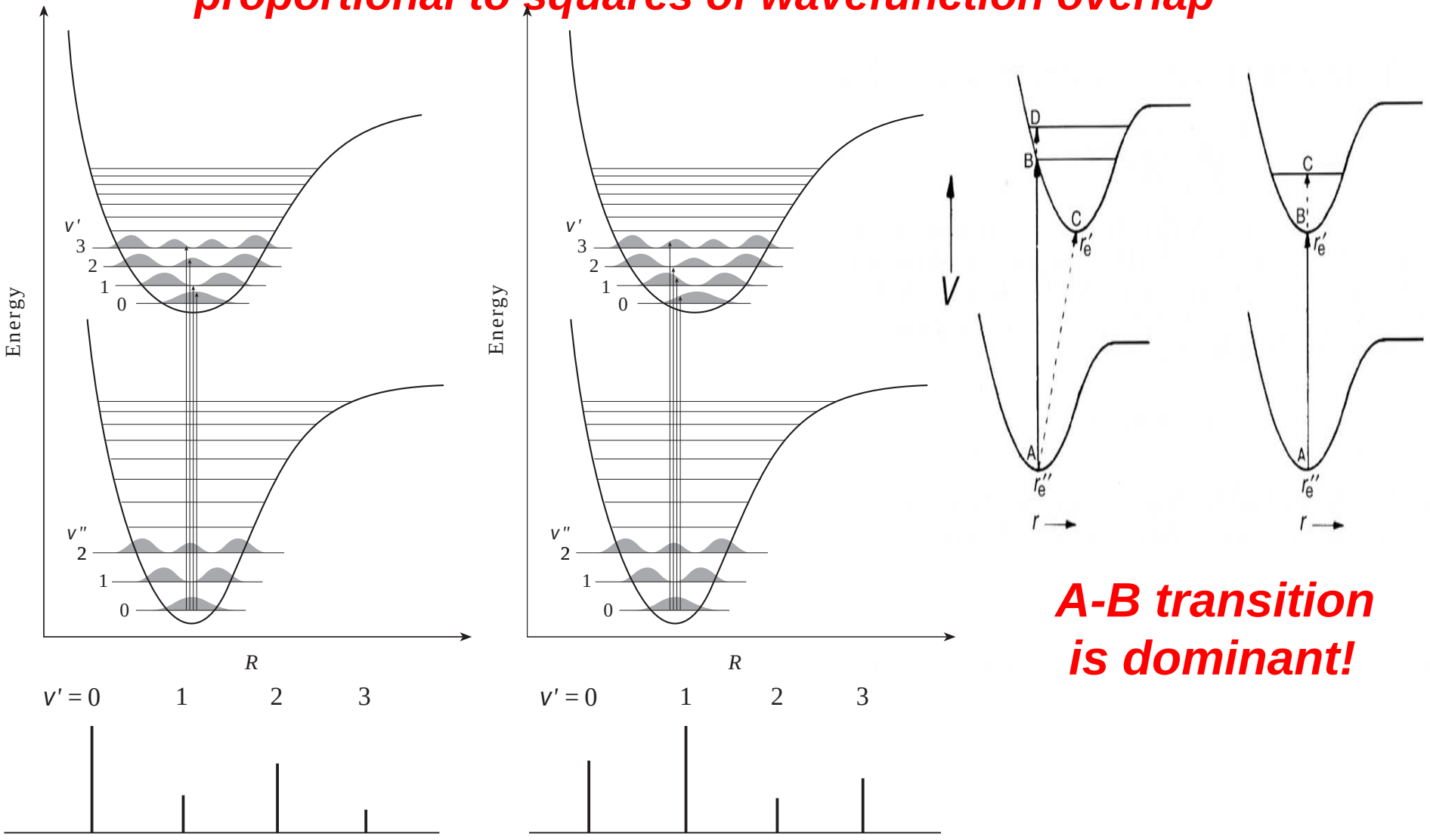



**Table 7.6** Electronic transitions observed in $C_2$

| Transition | Names associated | Special region/nm | Source of spectrum |
|---|---|---|---|
| $b^3\Sigma_g^- \rightarrow a^3\Pi_u$ | Ballik–Ramsay | 2700–1100 | King furnace |
| $A^1\Pi_g \rightleftarrows X^1\Sigma_g^+$ | Phillips | 1549–672 | Discharges |
| $d^3\Pi_g \rightleftarrows a^3\Pi_u$ | 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 |
| $D^1\Sigma_u^+ \rightleftarrows X^1\Sigma_g^+$ | 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 ↔ vertical transition in PES picture… Transition intensity is proportional to squares of wavefunction overlap"***




***A-B transition is dominant!***

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

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

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

$$= \int_r \int_R \psi^*_{\varepsilon'}(r;R)\psi^*_{v'}(R)\{\mu_e + \mu_N\}\psi_{\varepsilon''}(r;R)\psi_{v''}(R)\, dr\, dR$$

$$= \int_R \psi^*_{v'}(R)\underbrace{\left\{\int_r \psi^*_{\varepsilon'}(r;R)\ \mu_e\ \psi_{\varepsilon''}(r;R)dr\right\}}_{M_{\varepsilon'\varepsilon''}(R)}\psi_{v''}(R)\, dR$$

$$+ \int_R \psi^*_{v'}(R)\,\mu_N \underbrace{\left\{\int_r \psi^*_{\varepsilon'}(r;R)\ \psi_{\varepsilon''}(r;R)dr\right\}}_{\delta_{\varepsilon'\varepsilon''}}\psi_{v''}(R)\, dR$$

$$= \langle v' | M_{\varepsilon'\varepsilon''}(R) | v'' \rangle + \langle v' | \mu_N | v'' \rangle \delta_{\varepsilon'\varepsilon''}$$

**Pure vibrational transitions**

***if*** $M_{\varepsilon'\varepsilon''}(R) \approx M_{\varepsilon'\varepsilon''}(R_{eq})$,

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

$$= M_{\varepsilon'\varepsilon''}(R_{eq})\, S(v',v'') \leftarrow S : \textit{overlap integral}$$

***Intensity*** $I_{\varepsilon' v',\varepsilon'' v''} \propto |M_{\varepsilon' v',\varepsilon'' v''}|^2 = |M_{\varepsilon'\varepsilon''}(R_{eq})|^2 \underbrace{|S(v',v'')|^2}$

**Franck-Condon factor**

# *Vibronic spectral pattern informs shape of potential energy curve*

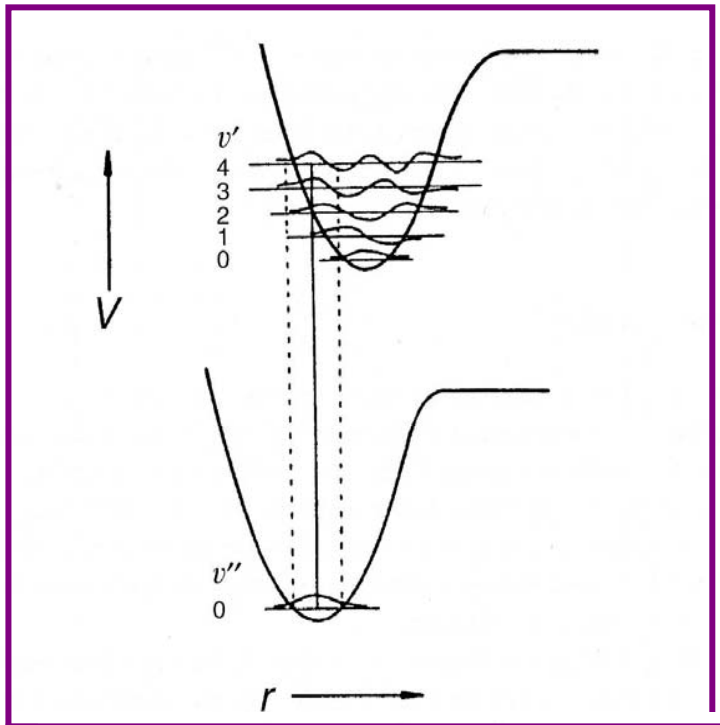
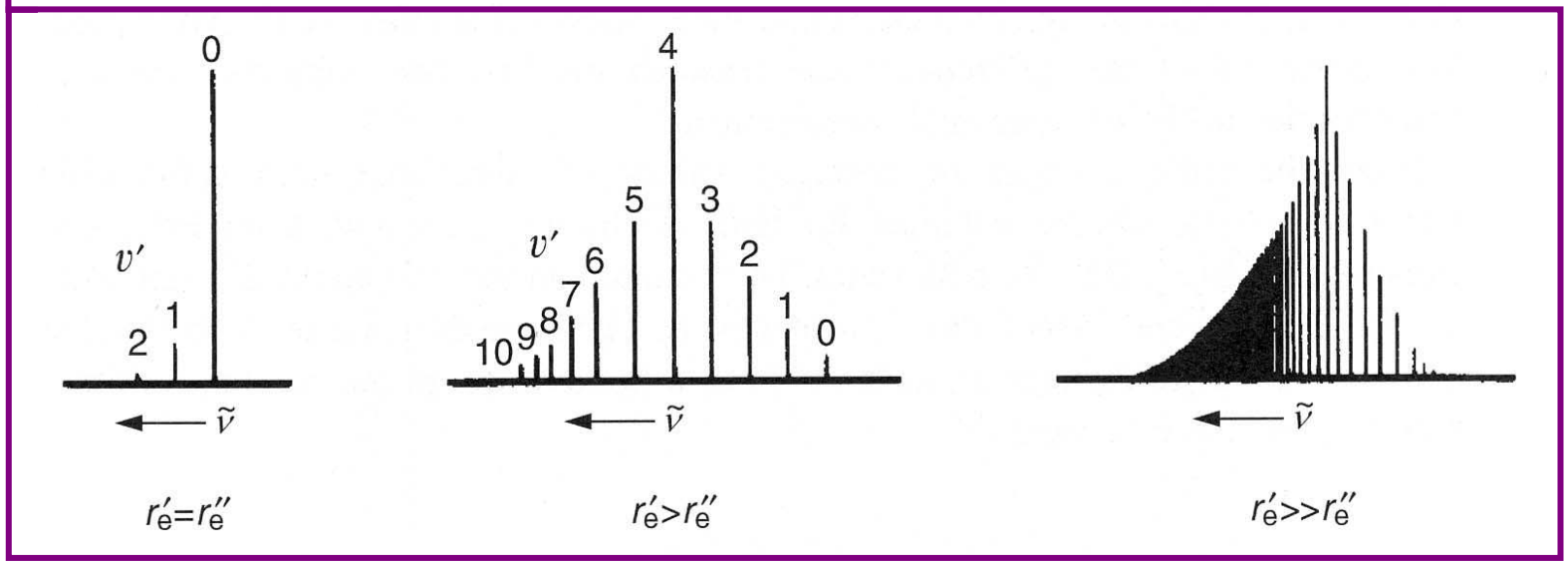


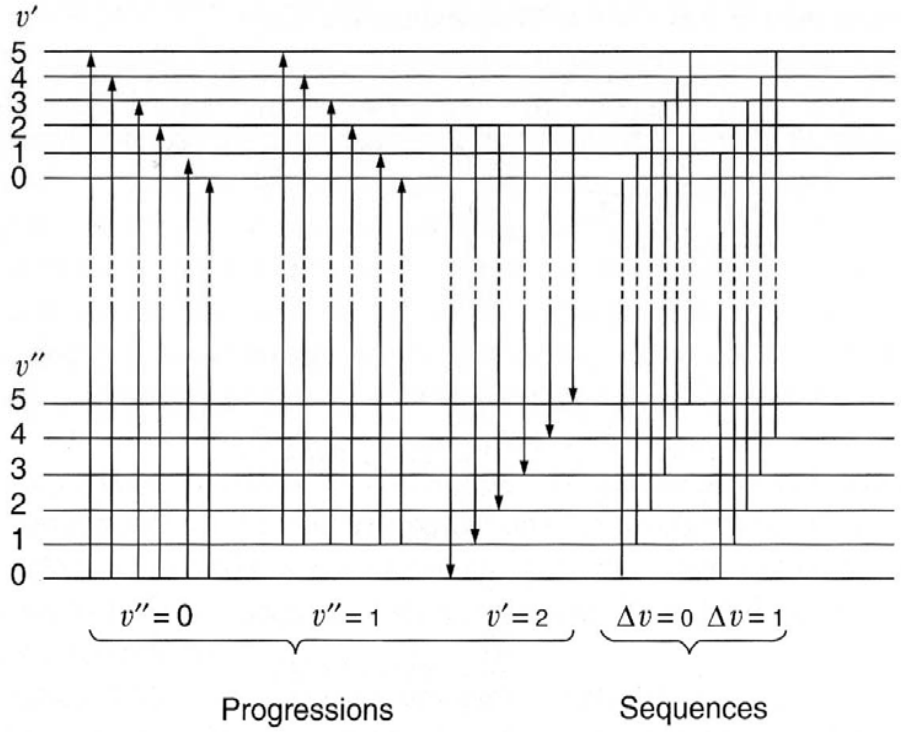

**TABLE 13.5**

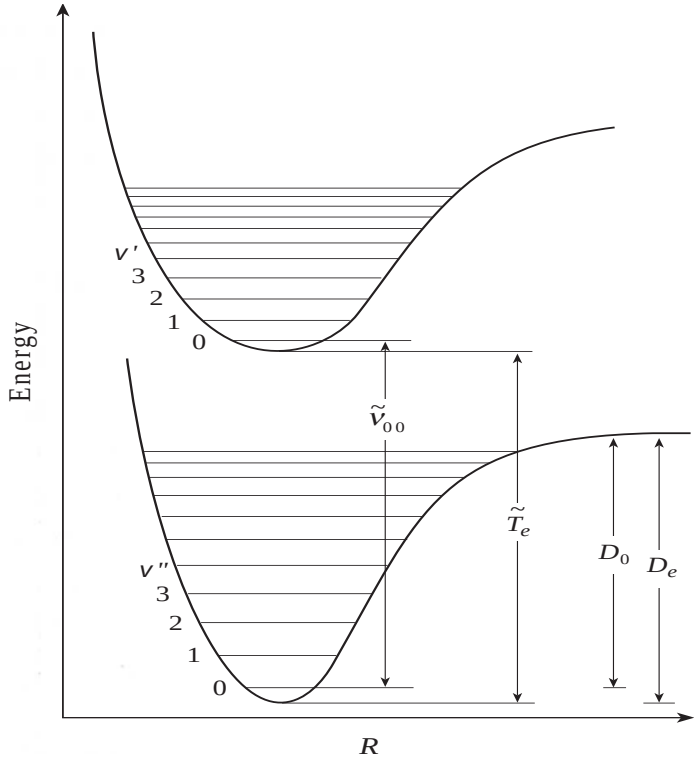
The equilibrium bond lengths for various electronic states of $O_2$.

| Electronic state | $\tilde{T}_e$/cm$^{-1}$ | $R_e$/pm |
|---|---|---|
| $^3\Sigma_g^-$ | 0 | 120.74 |
| $^1\Delta_g$ | 7 918.1 | 121.55 |
| $^1\Sigma_g^+$ | 13 195.2 | 122.67 |
| $^3\Sigma_u^+$ | 36 096 | 142 |
| $^3\Sigma_u^-$ | 49 802 | 160 |



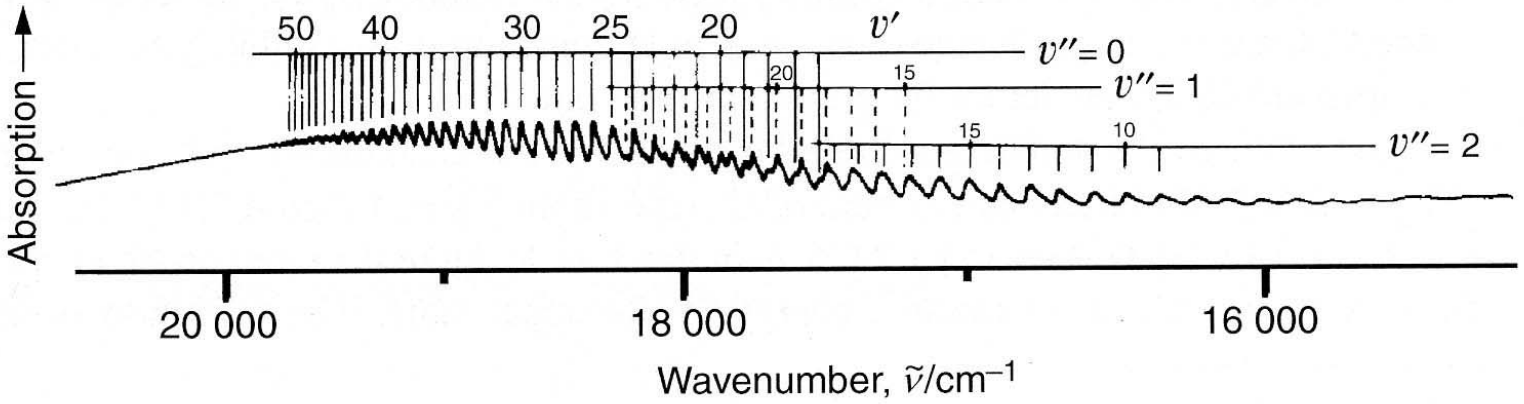
## * Vibrational progressions: $\Delta v = \pm$ *(any integers)*




*"progressions of vibrational bands"*

$$\tilde{\nu}_{obs}(v'' = 0) = T_e + G(v') - G(v'' = 0)$$



# - Deslandres table:

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

| $v'$ | $v''$ | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | | 1 | | 2 | | 3 | | 4 | | 5 | | 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 | | — |

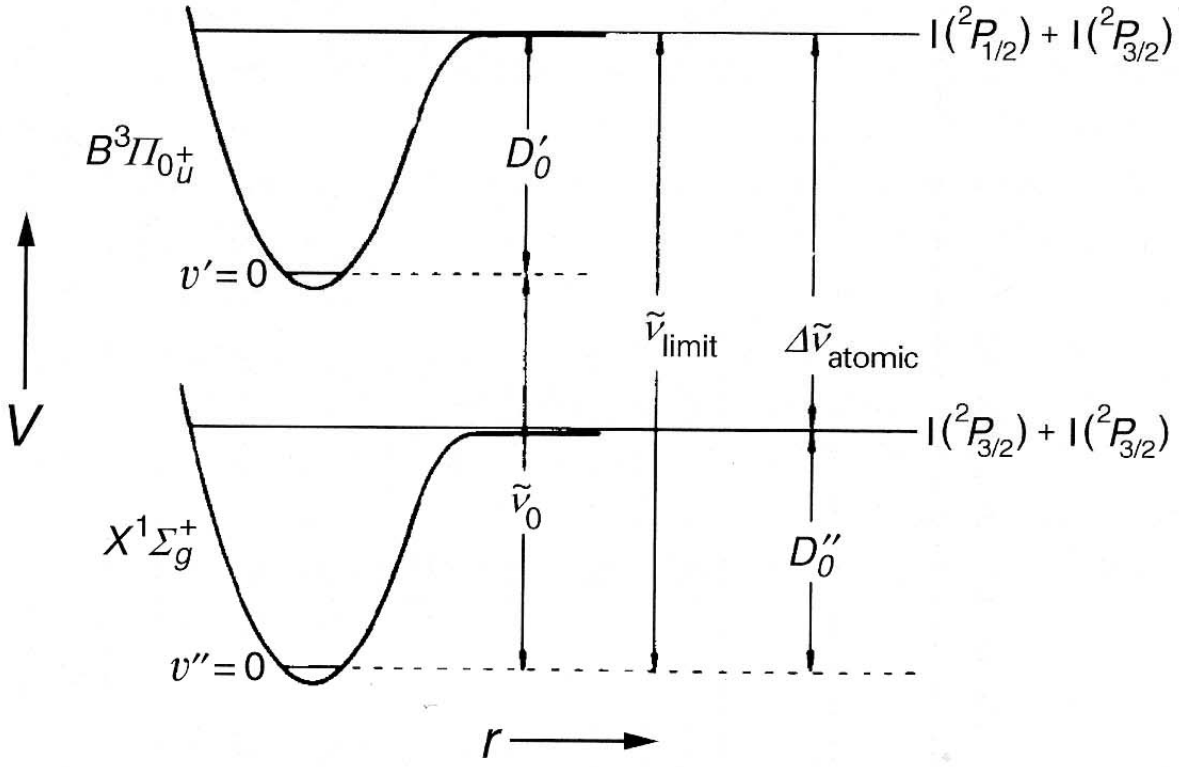
[a] Units are $cm^{-1}$ throughout. Measurements are of band heads, formed by the rotational structure, not band origins. Figures in parentheses are differences; variations in differences (e.g. between the first two columns) are a result of uncertainties in experimental measurements.

***Vibrational spacing in excited electronic state***

***Vibrational spacing in ground electronic state***

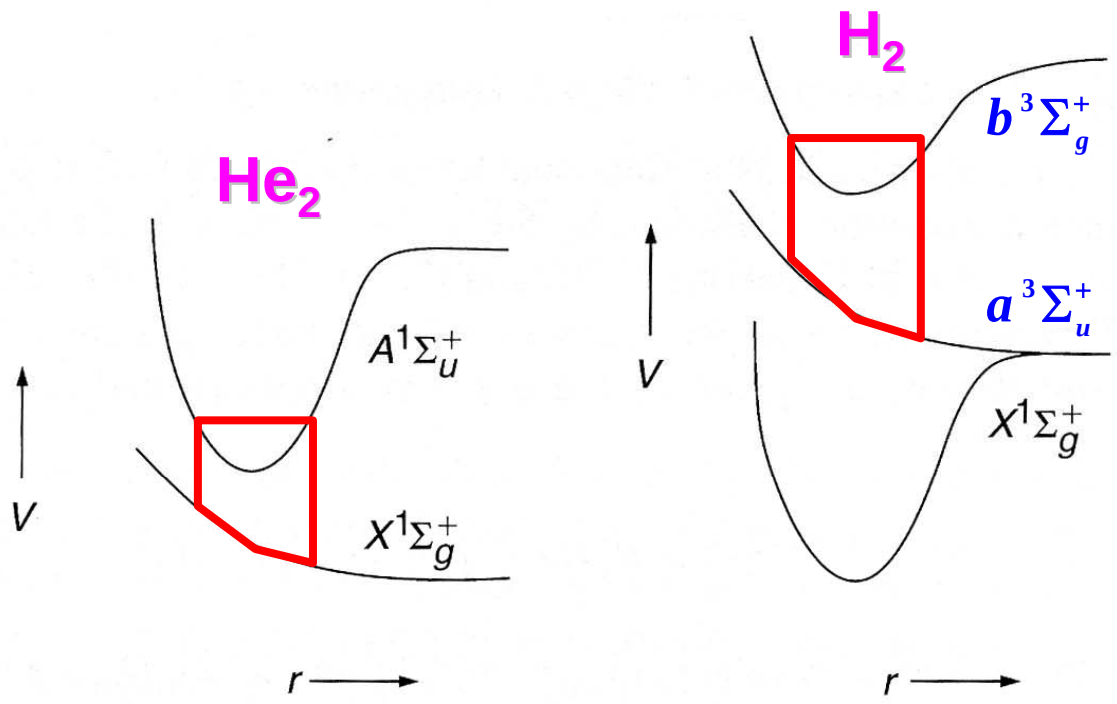
## - Determination of dissociation energies:

### use of Birge-Sponer extrapolation




$$\tilde{\nu}_{limit} = D_0' + \tilde{\nu}_0 = D_0'' + \Delta\tilde{\nu}_{atomic}$$

## - Repulsive states and continuous spectra:




***Continuous spectra***

$He_2 : (\sigma_g 1s)^2 (\sigma_u^* 1s)^2 \ \therefore X\,^1\Sigma_g^+$

$(\sigma_g 1s)^2 (\sigma_u^* 1s)^1 (\sigma_g 2s)^1 \ \therefore \sigma_u \otimes \sigma_g = A\,^1\Sigma_u^+,\ a\,^3\Sigma_u^+$

$H_2 : (\sigma_g 1s)^2 \ \therefore X\,^1\Sigma_g^+$

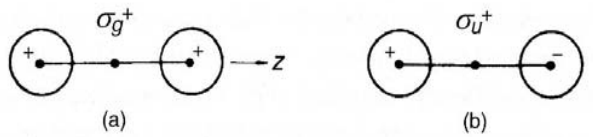
$(\sigma_g 1s)^1 (\sigma_u^* 1s)^1 \ \therefore \ \sigma_g \otimes \sigma_u = A\,^1\Sigma_u^+,\ a\,^3\Sigma_u^+$

$(\sigma_g 1s)^1 (\sigma_g 2s)^1 \ \therefore \ \sigma_g \otimes \sigma_g = B\,^1\Sigma_g^+,\ b\,^3\Sigma_g^+$

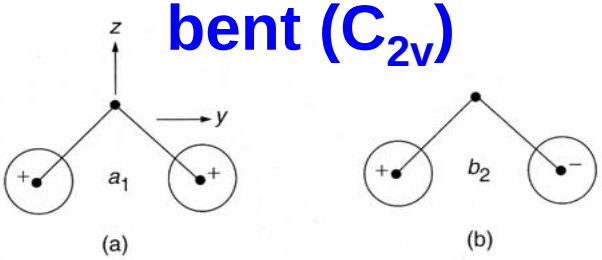
# Spectra of Polyatomic Molecules

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

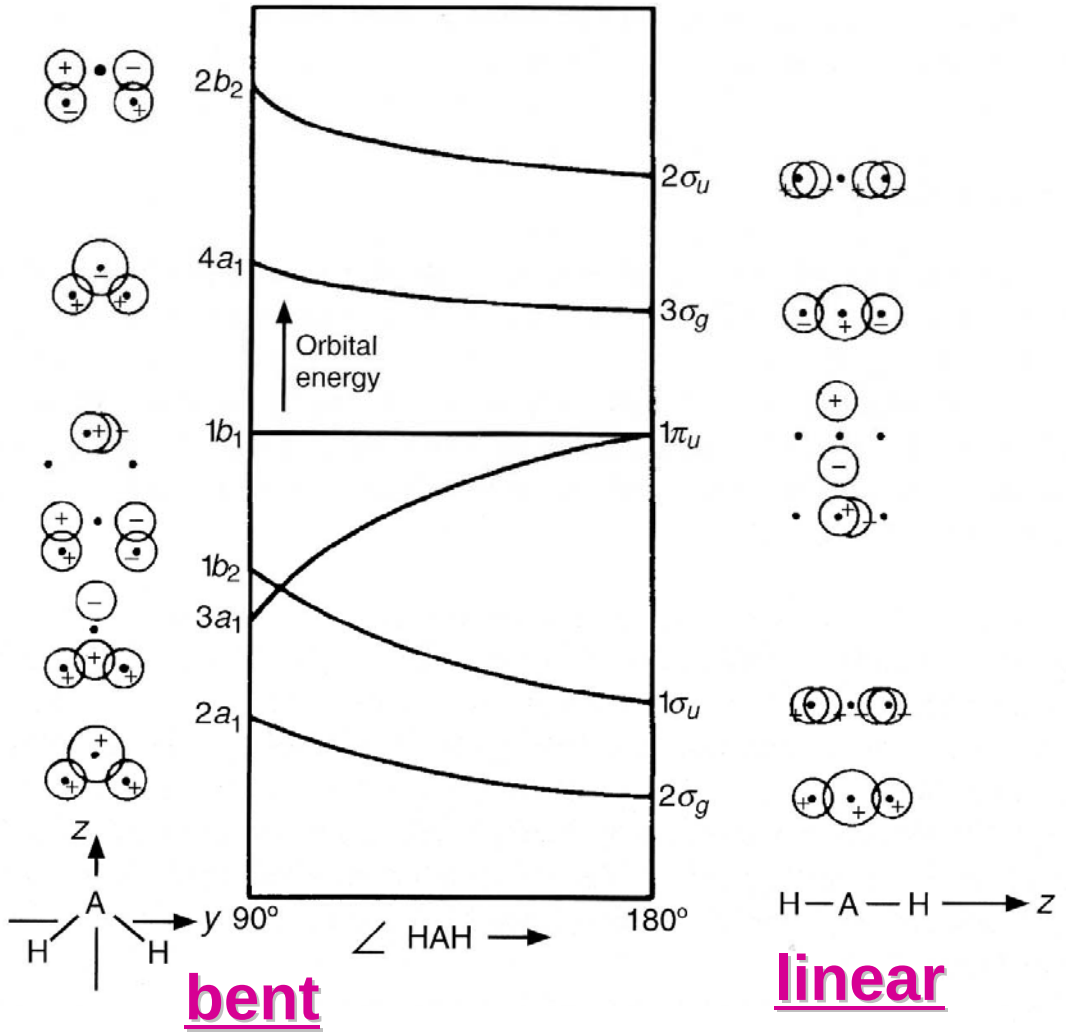
## linear ($D_{\infty h}$)




## bent ($C_{2v}$)




## Walsh diagram



## *Labelling of Polyatomics: $\tilde{X}$, $\tilde{A}$, $\tilde{B}$,..., $\tilde{a}$,$\tilde{b}$,...*

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

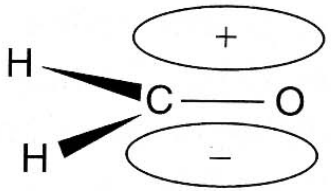
**Table 7.8** Ground and excited configurations of some $AH_2$ molecules

| Molecule | Configuration | State | ∠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° |
| $NH_2$ ($H_2O^+$) | $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$ | $\tilde{X}^2B_1$ | 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°) |
| $H_2O$ | $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ | $\tilde{X}^1A_1$ | 104.5° |

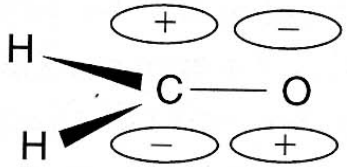
[a] The question marks indicate uncertainty, as the molecule is an unknown species.

## * $H_2CO$ case:

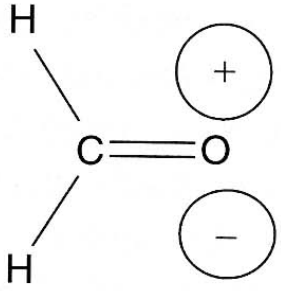
**"12 valence electrons, three σ-bonds, 1π-bond"**




**$1b_1(\pi)$**




**$2b_1(\pi^*)$**




**$2b_2(n)$**

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

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

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

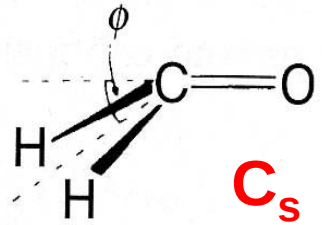
*(weak transition ∵ forbidden by symmetry)*

*; blue – shifted by hydrogen bonding*

**$(2b_1)^1$ $\pi^*$ electron favor bent geometry :**

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

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




**$C_s$**

## * Conjugated molecules:

### - Hückel MO theory:

$$\hat{H}_{el} = \hat{H}_{\sigma} + \hat{H}_{\pi}, \quad \psi_{el} = \psi_{\sigma}\psi_{\pi} \leftarrow \textit{assume } \sigma - \pi \textit{ separability}$$

*for* $\pi$ *– electrons only*

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

$$\hat{H}^{eff}\phi = E\phi, \quad \phi_i = \sum_{j=1}^{n} C_{ij}\chi_j \leftarrow \chi_j : p_z - \textit{orbital on atom } j$$

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

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

$$(\textit{matrix form}) \quad (\underset{\approx}{\hat{H}}^{eff} - E\underset{\approx}{S})\underset{\approx}{C} = 0 \rightarrow \textit{secular determinant: } |\underset{\approx}{\hat{H}}^{eff} - E\underset{\approx}{S}| = 0$$

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

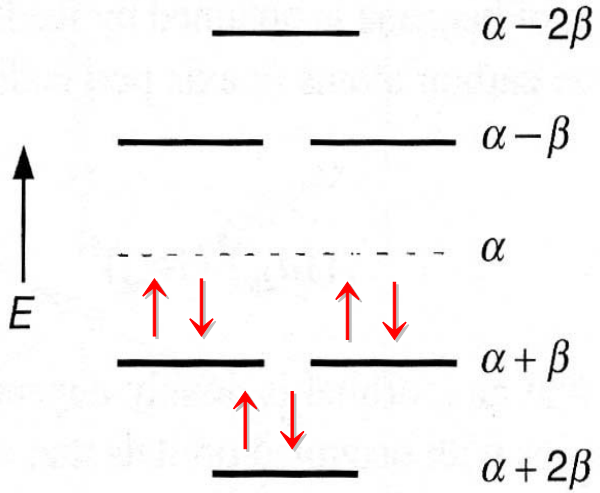
$$\hat{H}_{ij}^{eff} = \beta(\textit{adjacent}) \textit{ or } 0(\textit{others}) \,(\textit{resonance integral})$$

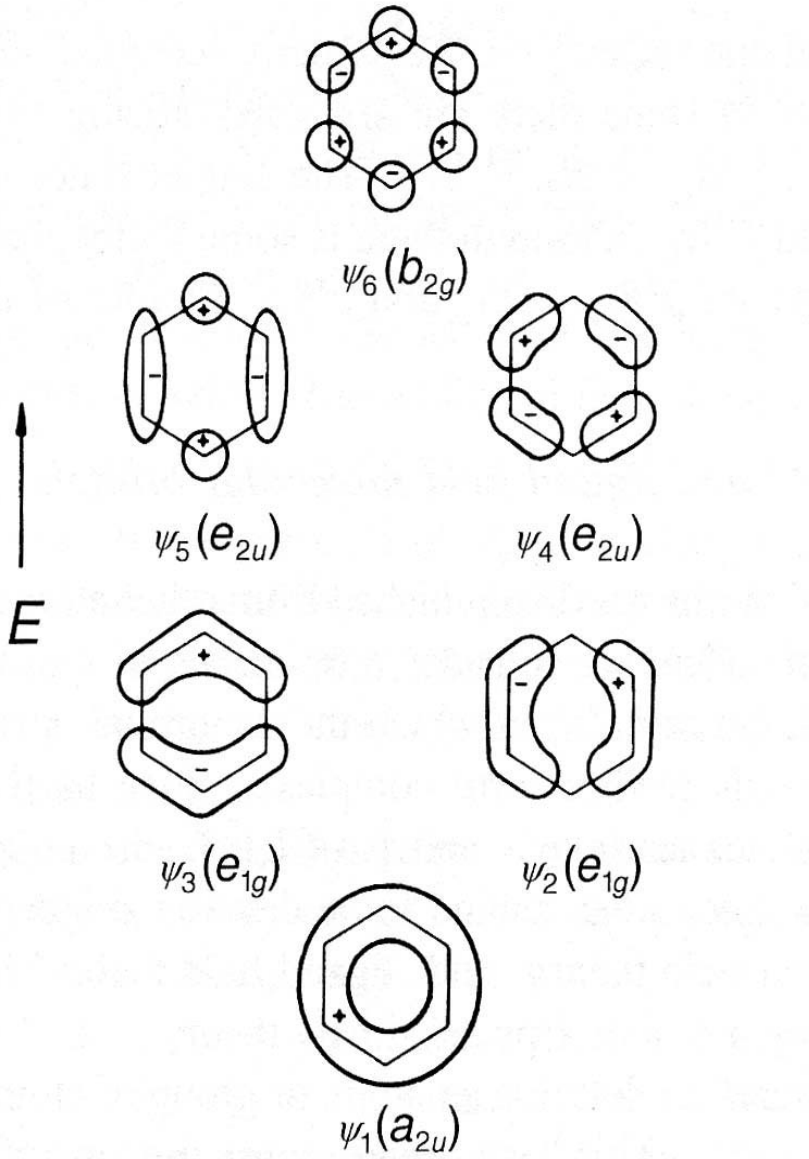
## Benzene Case:

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

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

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




Hückel molecular orbitals in benzene

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

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

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

***Electronic selection rule :***

$$\Delta S = 0,$$

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

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

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

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

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

## *Vibronic coupling :*

$\because$ *breakdown of Born – Oppenheimer approxim.*

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

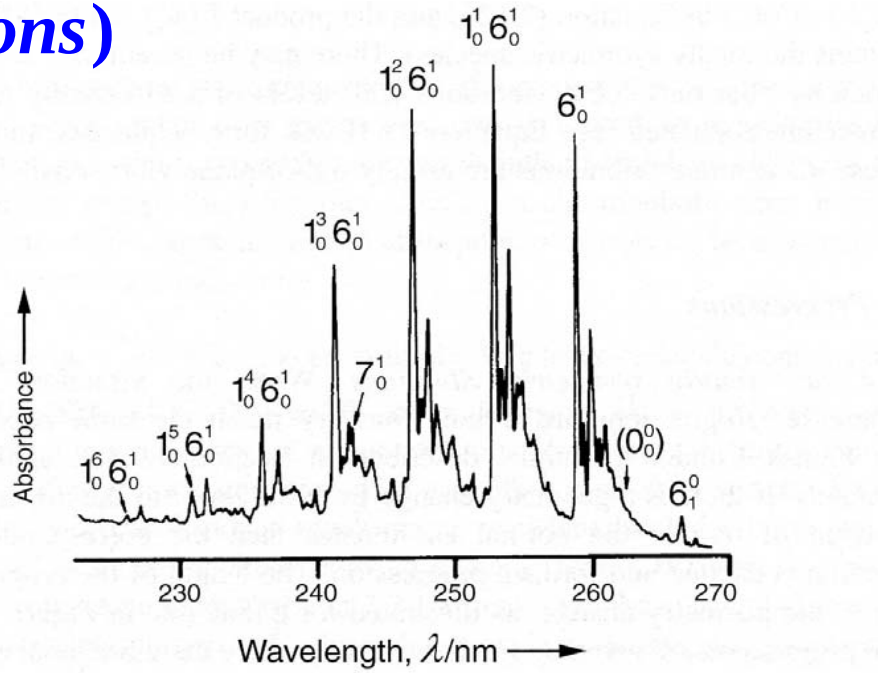
$$e.g.\ \tilde{X}\,{}^1A_{1g} \rightarrow \tilde{A}\,{}^1B_{2u},\ \ if\ \Gamma(\psi_v) = e_{2g}(v_6 = 1)$$

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

$$\therefore\ relaxed\ (1_0^n 6_0^1\ progressions)$$

*Benzene*

$\tilde{X}\,{}^1A_{1g} \rightarrow \tilde{A}\,{}^1B_{2u}$




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

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

$\pi^* \leftarrow \pi$ *transition*

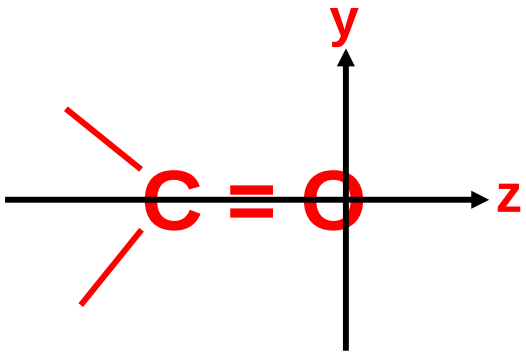
*e.g. Carbonyl* $\pi^* \leftarrow n$ *transition :*

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

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

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

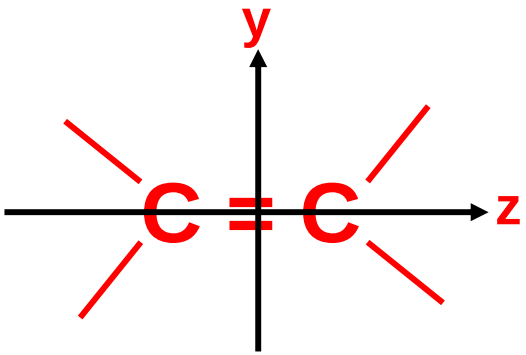
$\rightarrow$ *forbidden but relaxed by VB*



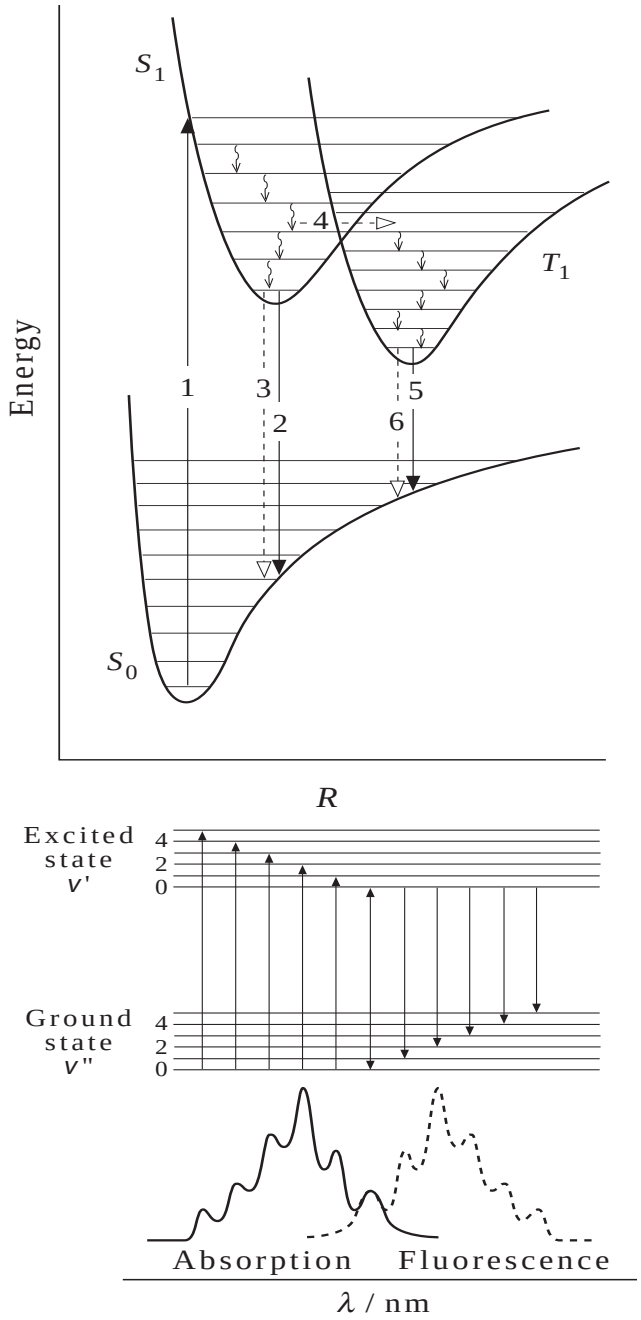

*Ethylene* $\pi^* \leftarrow \pi$ *transition :*

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

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



# Relaxation Processes of Electronically Excited Molecules



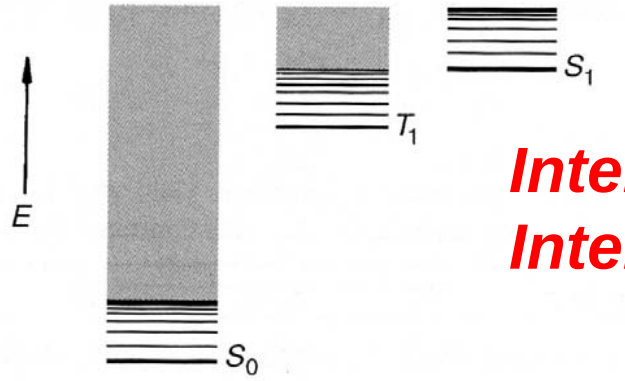




1. ***Absorption of $S_0$ to $S_1$ (Franck-Condon (FC); <$10^{-16}$ sec)***
   ***→ Rapid vibrational relaxation in $S_1$ (<ps)***
2. ***Fluorescence (FC) from $S_{1,v=0}$ to $S_{0,v'}$ ; mirror image of absorption spectra***
3. ***Nonradiative Internal Conversion from $S_{1,v=0}$ to highly excited vibrational states of $S_0$***
4. ***Intersystem Crossing ($S_1 \rightarrow T_1$); spin-orbit coupling → vibrational relaxation to $T_{1,v=0}$***
5. ***Phosphorescence ($T_1 \rightarrow S_0$; FC)***
6. ***Nonradiative Intersystem Crossing ($T_1 \rightarrow S_0$)***

| Process | Transition | Change in spin multiplicity | Time scale |
|---|---|---|---|
| Fluorescence | Radiative $S_1 \rightarrow S_0$ | 0 | $10^{-9}$ s |
| Internal conversion | Collisional $S_1 \rightarrow S_0$ | 0 | $10^{-7}$–$10^{-12}$ s |
| Vibrational relaxation | Collisional | | $10^{-14}$ s |
| Intersystem crossing | $S_1 \rightarrow T_1$ | 1 | $10^{-12}$–$10^{-6}$ s |
| Phosphoresence | $T_1 \rightarrow S_0$ | 1 | $10^{-7}$–$10^{-5}$ s |
| Intersystem crossing | $T_1 \rightarrow S_0$ | 1 | $10^{-8}$–$10^{-3}$ s |

## 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:

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

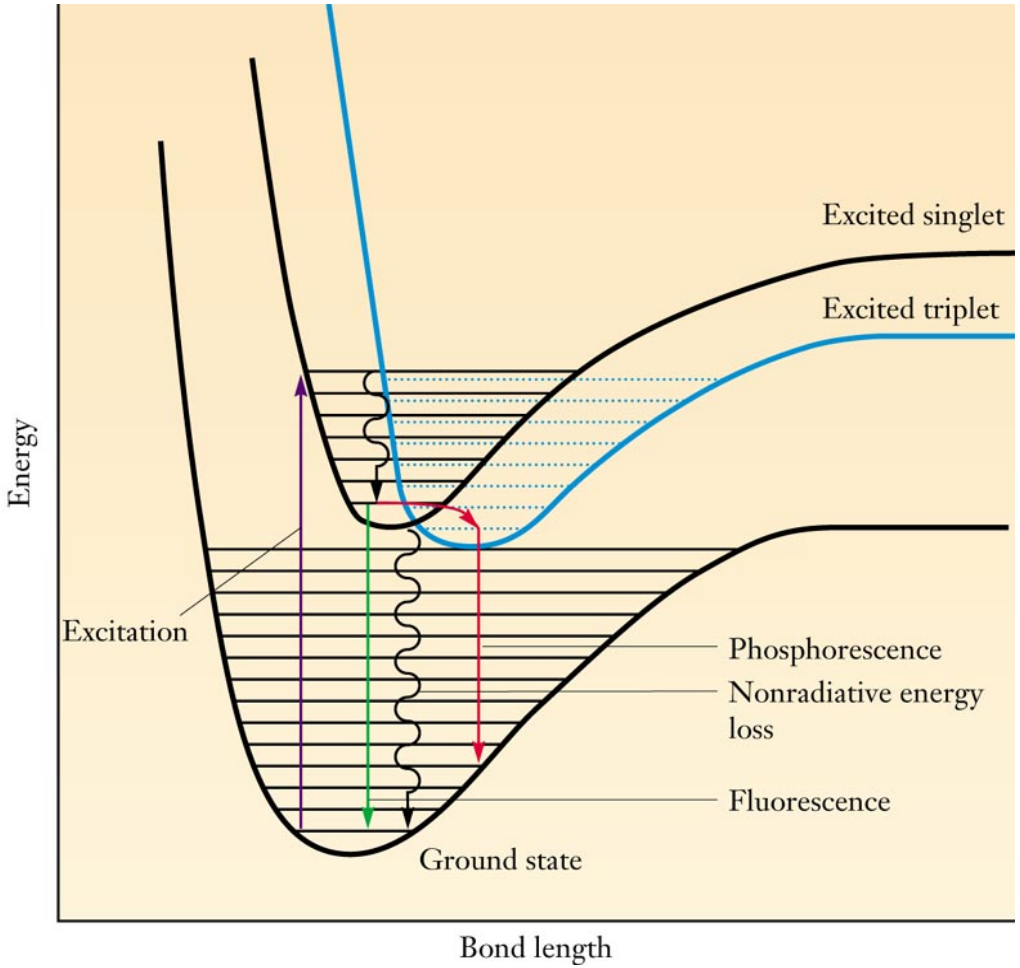
$$Fluorescence\ lifetime\ \tau_F = \frac{1}{k_r + k_{nr}}$$

**Table 7.11** Fluorescence quantum yield $\Phi_F$, fluorescence lifetime $\tau_F$, radiative, $k_r$, and non-radiative, $k_{nr}$, rate constants for the $S_1$ state of benzene

| Vibronic level | $\Phi_F$ | $\tau_F$/ns | $k_r/s^{-1}$ | $k_{nr}/s^{-1}$ |
|---|---|---|---|---|
| $0^0$ | 0.22 | 90 | $2.4 \times 10^{-6}$ | $8.7 \times 10^{-6}$ |
| $6^1$ | 0.27 | 80 | $3.4 \times 10^{-6}$ | $9.1 \times 10^{-6}$ |
| $1^1 6^1$ | 0.25 | 68 | $3.7 \times 10^{-6}$ | $11.0 \times 10^{-6}$ |

## * Spectral Broadening due to lifetimes of excited states:

$$\Delta E \bullet \tau \geq \hbar \rightarrow \Delta \nu \geq \frac{1}{2\pi\tau};\ k = \frac{1}{\tau}$$




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

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

$\leftarrow \tau_r, \tau_{nr}$ : *lifetimes*

$k_r, k_{nr}$ : *rate constants*

*(radiative, nonradiative)*

# Fermi Golden Rule

***"… a general formula to predict accurately the rate of transition from one quantum state to other quantum states in weak perturbation conditions by conserving the energies…"***

$$Time-dependent\ S-eqn:\ H\Psi(r,t)=i\hbar\frac{\partial\Psi}{\partial t}$$

$H_0\psi_m(r)=E_m\psi_m(r)$; *unperturbed hamiltonian*

$H=H_o+V(t)\ \leftarrow\ V(t)$: *time-dependent perturbation*

$$\Psi(r,t)=\sum_m C_m(t)\psi_m(r)$$

$|C_m(t)|^2=$ *probability of being in state* $\psi_m$ *at time* $t$

*Transition rate* $w_{m\to n}$ :

"*transition probability per unit time for a molecule to transfer from* $\psi_m$ *to* $\psi_n$"

$$w_{m\to n}=\frac{2\pi}{\hbar}|<\psi_m|V|\psi_n>|^2\ \delta(E_m-E_n)\ \text{"Fermi Golden Rule"}$$

$\leftarrow$ *delta function* $\delta(E_m-E_n)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}e^{i(E_m-E_n)t/\hbar}\,dt;\ \delta(\omega_m-\omega_n)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i(\omega_m-\omega_n)t}\,dt$

$\int_{-\infty}^{\infty}\delta(x)dx=1$ (*if* $x=0,\ \delta\to\infty$; *if* $x\neq 0,\ \delta\to 0$)

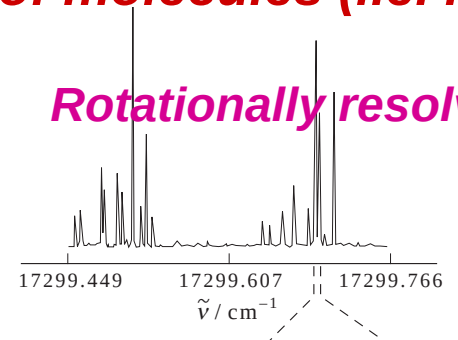
# Examples of Electronic Spectroscopy

## High Resolution Spectroscopy:

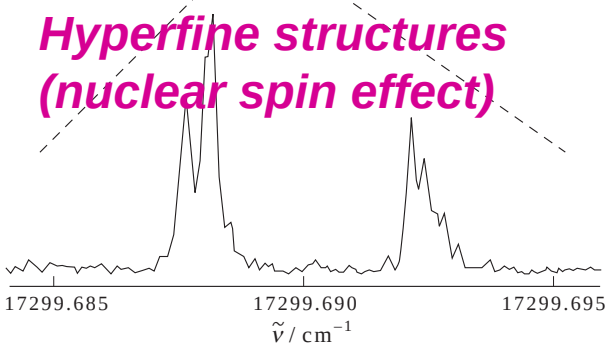
"frequency (or energy) domain"

***W/ CW lasers, high resolution spectra reveal full quantum states of molecules (i.e. rot, vib, ele, spin).***

***Rotationally resolved***




***Hyperfine structures (nuclear spin effect)***

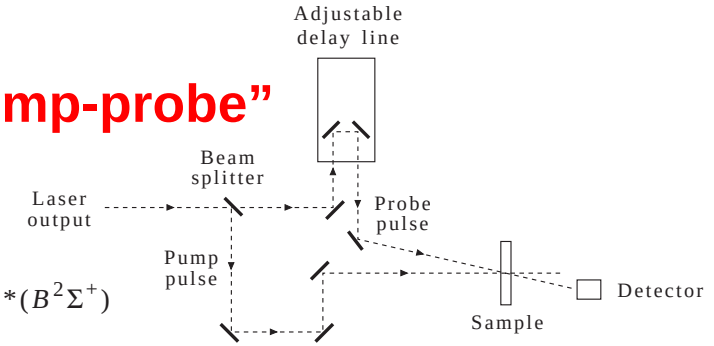



## Time-Resolved Spectroscopy:

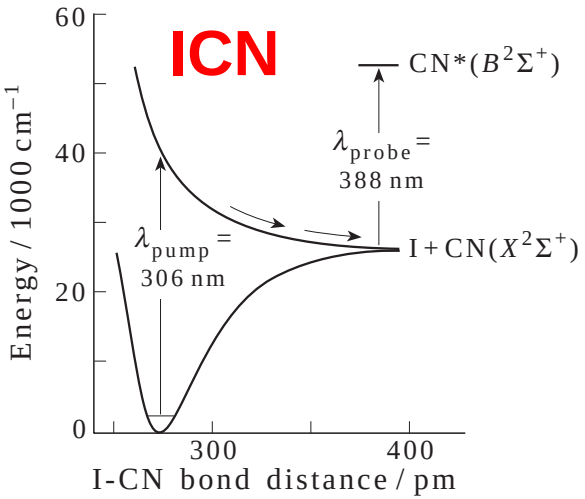
"time domain"

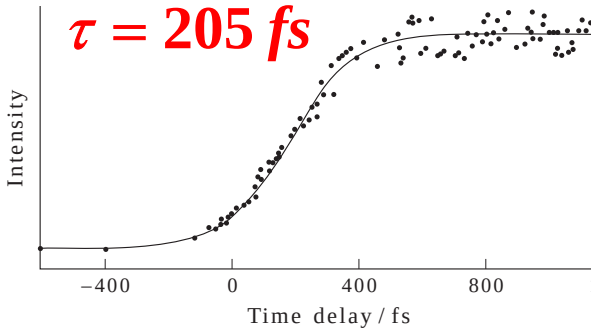
***W/ pulse lasers, reveal time-evolution of quantum states or reactions***

**"pump-probe"**




**ICN**




## Photochemical Reactions:

***Photodissociation, photoisomerization, Photodimerization,etc.***

$$*\text{quantum yield } \Phi = \frac{\#\text{ of molecules that undergo reaction}}{\#\text{ of photons absorbed}} \qquad \Phi_{fluores} = \frac{\#\text{ of fluorescence photons}}{\#\text{ of absorbed photons}}$$