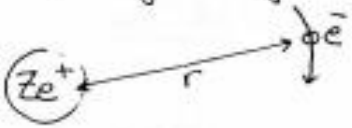
7. Electronic Spectroscopy

7.1. Atomic Spectroscopy

< Hydrogen-like atoms (H, He^+, Li^{++}, ⋯) neglecting any spin coupling effect >

$$\hat{H} = -\frac{\hbar^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}$$



$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\,Y_{lm}(\theta,\phi)$$

$$R_{nl}(r) = \left\{\left(\frac{2Z}{na_0}\right)^{3/2}\frac{(n-l-1)!}{2n[(n+l)!]^3}\right\}^{1/2} e^{-\frac{Zr}{na_0}}\underbrace{\left(\frac{2Zr}{na_0}\right)^{l} L^{2l+1}\left(\frac{2Zr}{na_0}\right)}_{L^{2l+1}_{n-l-1}\left(\frac{2Zr}{na_0}\right)}$$

L^{2l+1} : Laguerre Function

$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{1/2} e^{-Zr/a_0}$$

$$R_{20} = 2\left(\frac{Z}{a_0}\right)^{3/2}\left(1-\frac{Zr}{2a_0}\right) e^{-Zr/2a_0}$$

$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}}\, e^{im\phi}\, \underbrace{P_l^m(\cos\theta)}_{\text{associated Legendre Polynomial}}$$

$Y_{00} = \frac{1}{\sqrt{4\pi}} \longrightarrow$ s orbital

$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\, e^{\pm i\phi} \sin\theta \longrightarrow P_x,\ P_y$

$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \longrightarrow P_z$

$Y_{2\pm2} = \sqrt{\frac{15}{32\pi}}\, e^{\pm 2i\phi} \sin^2\theta \longrightarrow d_{z^2-y^2},\ d_{xy}$

$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}\, e^{\pm i\phi} \sin\theta\cos\theta \rightsquigarrow d_{yz},\ d_{zx}$

$Y_{2,0} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \rightsquigarrow d_{z^2}$

$l=0$;	S (Sharp)
$l=1$;	P (principal)
$l=2$;	D (Diffused)
$l=3$;	F (Fundamental
⋮	
$l=4$	G
$l=5$	H
⋮	

에너지.

$$E_n = -\frac{1}{2n^2}\frac{\mu Z^2 e^4}{(4\pi\varepsilon_0)^2\hbar^2} = -\frac{1}{2}\mu c^2\left(\frac{Z\alpha}{n}\right)^2$$

where $\alpha = \frac{e^2}{(4\pi\varepsilon_0)\hbar c} = \frac{1}{137}$; Fine Structure Constant

$a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{m_e e^2}$; Bohr radius 52.9 pm

$$E_n = -\frac{hc\,R_H}{n^2}$$

where $R_H = \left[\frac{\mu Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\right]/hc$ ($= \underset{\text{for } Z=1}{109678\ \text{cm}^{-1}}$); Rydberg Constant

$R_\infty = R_H\left(1+\frac{m_e}{m_p}\right) = \left[\frac{m_e Z^2 e^4}{2(4\pi\varepsilon_0)^2\hbar^2}\right]/hc$

($= \underset{\text{for } Z=1}{109737.3\ \text{cm}^{-1}}$) ; Practical Rydberg Constant

For transition between $n_2 \to n_1$

$$\Delta E = hc\,R_H\left\{\frac{1}{n_1^2}-\frac{1}{n_2^2}\right\} \quad \therefore\ \tilde{\nu} = R_H\left\{\frac{1}{n_1^2}-\frac{1}{n_2^2}\right\}$$

$n_1 = 1,\ n_2 = 2, 3, 4, \ldots$; Lyman Series (u.v)

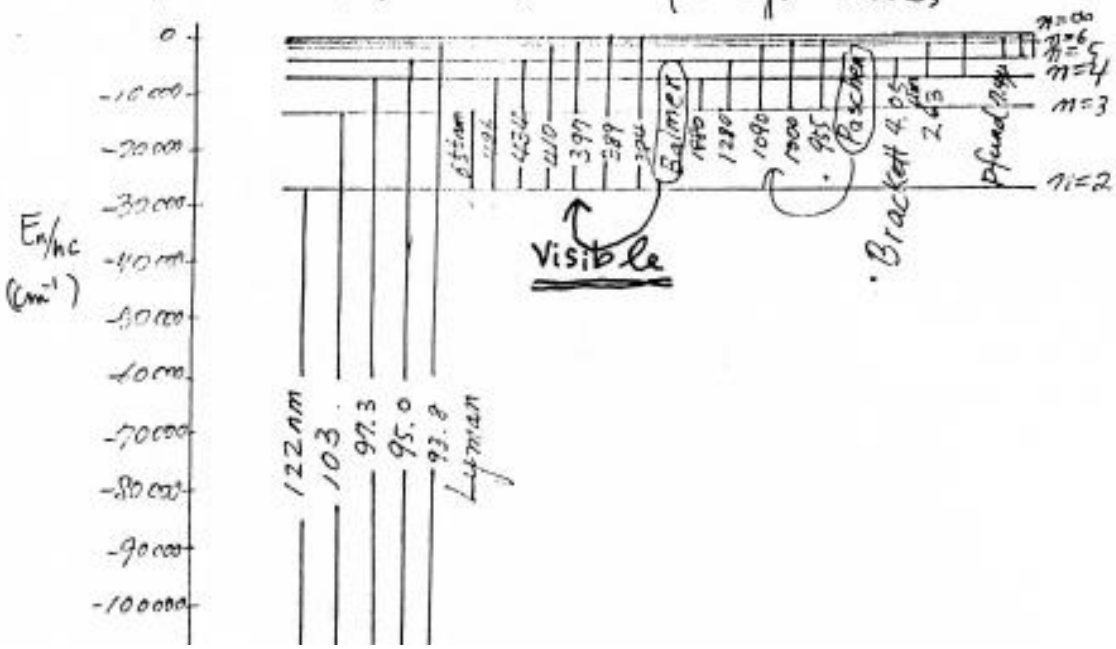
$n_1 = 2,\ n_2 = 3, 4, 5, \ldots$; Balmer Series (visible)

$n_1 = 3,\ n_2 = 4, 5, 6, \ldots$; Paschen Series (near IR)

$n_1 = 4,\ n_2 = 5, 6, 7, \ldots$; Brackett Series (mid IR)

$n_1 = 5,\ n_2 = 6, 7, 8, \ldots$; Pfund Series (Far IR)

$n_1 = 6,\ n_2 = 7, 8, 9, \ldots$; Humphreys Series



Series limit ; $\tilde{\nu}_{limit} = \frac{R_H}{n_1^2}$

Ionization energy $= (\tilde{\nu}_{limit})_{n_1=1} hc = R_H(hc)$

degeneracy n ; 자연수, $1 \le n < \infty$

l ; $0, 1, 2, \cdots, (n-1)$, $(n-1)$개

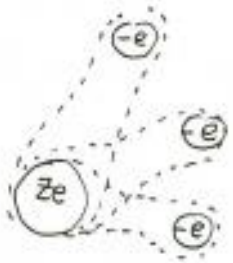
m_l ; $-l, -(l-1), \cdots, 0, \cdots, l-1, l$, $(2l+1)$개

m_s ; $\frac{1}{2}, -\frac{1}{2}$

< polyelectronic Atoms neglecting spin coupling effects >

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

$$\simeq -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 - \sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \sum_i V(r_i)$$



Self-consistent field (SCF) Method.

$$\psi(n_1 l_1 m_1 m_{s_1}; n_2 l_2 m_2 m_{s_2}; \cdots) = \| \psi_{n_1 l_1 m_1 m_{s_1}}(1)\, \psi_{n_2 l_2 m_2 m_3}(2)\, \psi_{n_3 l_3 m_3 m_{s_3}}(3) \cdots \|$$

$$= \frac{1}{\sqrt{N!}} \begin{bmatrix} \psi_{n_1 l_1 m_1 m_{s_1}}(1) & \psi_{n_1 l_1 m_1 m_{s_1}}(2) & \psi_{n_1 l_1 m_1 m_{s_1}}(3) & \cdots & \psi_{n_N l_N m_N m_{s_N}}(N) \\ \psi_{n_2 l_2 m_2 m_{s_2}}(1) & \psi_{n_2 l_2 m_2 m_{s_2}}(2) & \psi_{n_1 l_1 m_1 m_{s_1}}(3) & \cdots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{n_N l_N m_N m_{s_N}}(1) & \cdots & \cdots & \cdots & \psi_{n_N l_N m_N m_{s_N}}(N) \end{bmatrix}$$

(slater determinant)

각각의 $\psi_{n l m m_s}$ (one electron wavefunction)을 orbital이라 한다

* Effect of electron-electron repulsion term $\sum_i V(r_i)$ (Slater's Method)

1) Shielding effect σ

$$Z^* = Z - \sigma$$

σ is dependent on n and l in the following way, $\sigma = \sum_j \sigma_j$

① For an electron in a group outside the one of interest, $\sigma_j = 0$

② From each other electron in the group of interest, $\sigma_j = 0.35$
But if the electron is 1s, $\sigma_j = 0.30$

③ From each other electron inside the one of interest, $\sigma_j = 1.00$

$\sigma_j = 1.00$ if d or f

$\sigma_j = 0.85$ from electron in the next inner group if the electron of interest is s or p

$\sigma_j = 1.00$ for all deeper electrons.

2) Reduced $n \rightarrow n^*$

n	1	2	3	4	5	6	...
n^*	1	2	3	3.7	4.0	4.2	..

3) Slater's atomic orbital

$$\psi_{nlmm_s}(r,\theta,\phi) = N r^{n^*-1} e^{-\frac{Z^* r}{n^* a_0}} Y_{lm_l}(\theta,\phi)$$

Energy ;

$$E_{\{n_1 l_1 m_1 m_{s_1};\, n_2 l_2 m_2 m_{s_2};\, \cdots\}} =$$

$$\sum_i \Big\{ \underbrace{\underbrace{\langle n_i l_i m_i m_{s_i} | -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_i} | n_i l_i m_i m_{s_i} \rangle}_{\text{dependent on } n_i} + \underbrace{\langle n_i l_i m_i m_{s_i} | V(r_i) | n_i l_i m_i m_{s_i} \rangle}_{\text{dependent on } n_i, l_i \text{ (and } m_i, m_{s_i} \text{ when consider magnetic effect)}}}_{\text{orbital energy of } i\text{-th electron}} \Big\}$$

$\sum_i$ (orbital energy of i) becomes very large when quantum numbers of i and j electrons are all the same. $\Rightarrow$ Paul's exclusion Principle

Order of orbital energies

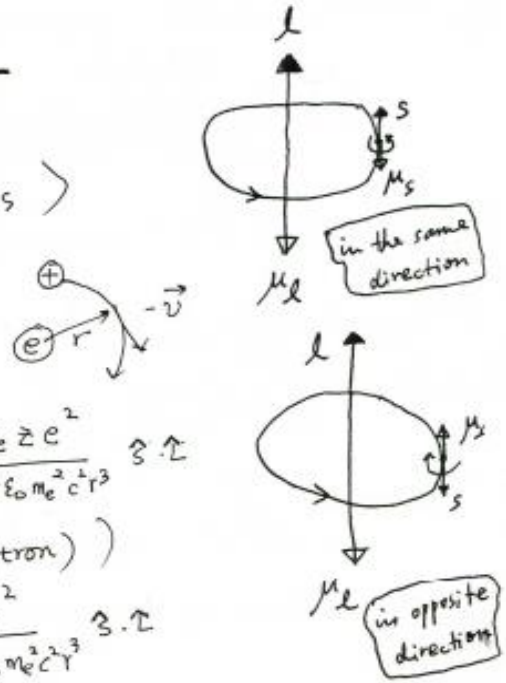
$1s < 2s < 2p < 3s < 3p < 4s < 3d < \cdots$

$\Rightarrow$ Periodic Table.

E_i

1s

〈 Fine structure of Hydrogen-like atoms 〉



① Spin-orbit Coupling Effect.

$$\hat{H}'_{s\text{-}o} = -\vec{\mu}_s \cdot \vec{B}$$

$$= -\left(\frac{g_e |e|}{2m_e c}\hat{s}\right)\cdot\left(-\frac{Ze^2}{4\pi\varepsilon_0 m_e c\, r^3}\hat{l}\right) = \frac{g_e Z e^2}{8\pi\varepsilon_0 m_e^2 c^2 r^3}\,\hat{s}\cdot\hat{l}$$

($g_e = 2.00232$ (g-factor of electron))

⇒ 1926 Thomas 보정 ; $\hat{H}'_{s\text{-}o} = \dfrac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2 r^3}\,\hat{s}\cdot\hat{l}$

$$= \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2 r^3}\left\{(\hat{s}+\hat{l})^2 - \hat{s}^2 - \hat{l}^2\right\} = \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2 r^3}\left\{\hat{J}^2 - \hat{s}^2 - \hat{l}^2\right\}$$

그러므로 $\hat{H}_{s\text{-}o}$에 의한 에너지 보정값을 $|n l m m_s\rangle$의 linear combination인 $|n l s j m_j\rangle$의 기대치로서 나타내는 것이 가능하다. (양자역학적 결과) 단, j는 $|l-s| \le j \le l+s$ 의 제한을 갖는다.

P.W. Atkins, 'Molecular Quantum Mechanics」 9장 3절 참조.

$$E'_{s\text{-}o} = \langle n\,l\,s\,j\,m_j | \hat{H}_{s\text{-}o} | n\,l\,s\,j\,m_j \rangle$$

$$= \frac{Ze^2}{8\pi\varepsilon_0 m_e^2 c^2} \left\{ j(j+1) - s(s+1) - l(l+1) \right\} \hbar^2 \underbrace{\langle n\,l\,s\,j\,m_j | \frac{1}{r^3} | n\,l\,s\,j\,m_j \rangle}_{= \left(\frac{Z^3}{(l+1)\,a_0^3 n^3 l (l+\frac{1}{2})} \right)}$$

$$= \frac{\hbar^2 Z^4 e^2}{8\pi\varepsilon_0 m_e^2 a_0^3 c^2} \frac{\left\{ j(j+1) - l(l+1) - s(s+1) \right\}}{n^3 l (l+1)(l+\frac{1}{2})}$$

$$\left(\begin{array}{ll} j = l + \frac{1}{2} \text{ 일 때} & j(j+1) - l(l+1) - s(s+1) = l \\ j = l - \frac{1}{2} \text{ 일 때} & j(j+1) - l(l+1) - s(s+1) = -l-1 \end{array} \right)$$

$$\therefore E'_{s\text{-}o} = \frac{\hbar^2 Z^4 e^2}{8\pi\varepsilon_0 m_e^2 c^2 a_0^3 n^3} \frac{\left\{ \begin{matrix} l \\ -l-1 \end{matrix} \right\}}{l(l+\frac{1}{2})(l+1)} \simeq \frac{1}{4} m_e c^2 (Z\alpha)^4 \frac{\left\{ \begin{matrix} l \\ -l-1 \end{matrix} \right\}}{n^3 l (l+\frac{1}{2})(l+1)}$$

② 특수상대론적 보정 (relativistic effect, electrodynamic effect)

$$E = (m_e^2c^4 + P_e^2c^2)^{1/2} \simeq m_ec^2\left(1+\frac{P^2}{m_e^2c^2}\right)^{1/2} \simeq m_ec^2 + \frac{P^2}{2m_e} - \frac{P^4}{8m_e^3c^2}$$

$$\hat{H} = \frac{P^2}{2m_e} - \frac{Ze^2}{4\pi\varepsilon_0 r} - \underbrace{\frac{P^4}{8m_e^3c^2}}_{\hat{H}'_{rel}}$$

$$\hat{H}_{rel} = -\frac{P^4}{8m_e^3c^2} = -\frac{1}{2m_ec^2}\left(\frac{P^2}{2m_e}\right)^2 = -\frac{1}{2m_ec^2}\left(\hat{H}^0 + \frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2$$

$$E'_{rel} = \langle n\ell m|\hat{H}'_{rel}|n\ell m\rangle = -\frac{1}{2m_ec^2}\langle n\ell m|E_n^{(0)2} + 2E_n^{(0)}\frac{Ze^2}{4\pi\varepsilon_0 r} + \left(\frac{Ze^2}{4\pi\varepsilon_0 r}\right)^2|n\ell m_\ell\rangle$$

$$= -\frac{1}{2m_ec^2}\left(E_n^{(0)2} + \frac{Ze^2}{2\pi\varepsilon_0}E_n^{(0)}\underbrace{\langle n\ell m|\tfrac{1}{r}|n\ell m\rangle}_{\left(\frac{4\pi\varepsilon_0 Z}{n^2a_0}\right)} + \frac{Z^2e^4}{16\pi^2\varepsilon_0^2}\underbrace{\langle n\ell m|\tfrac{1}{r^2}|n\ell m\rangle}_{\left(\frac{16\pi^2\varepsilon_0^2Z^2}{a_0^2n^3(\ell+\frac{1}{2})}\right)}\right)$$

$$= -\frac{1}{2m_ec^2}\left[E_n^{(0)2} - 4E_n^{(0)2} + \frac{Z^2e^4}{a_0^2n^3(\ell+\frac{1}{2})}\right]$$

$$= -\frac{1}{2m_ec^2}\left[-3E_n^{(0)2} + \frac{n}{(\ell+\frac{1}{2})}(-2E_n^{(0)})^2\right] = -\frac{1}{2}m_ec^2\frac{(Z\alpha)^4}{n^3}\left\{\frac{1}{\ell+\frac{1}{2}} - \frac{3}{4n}\right\}$$

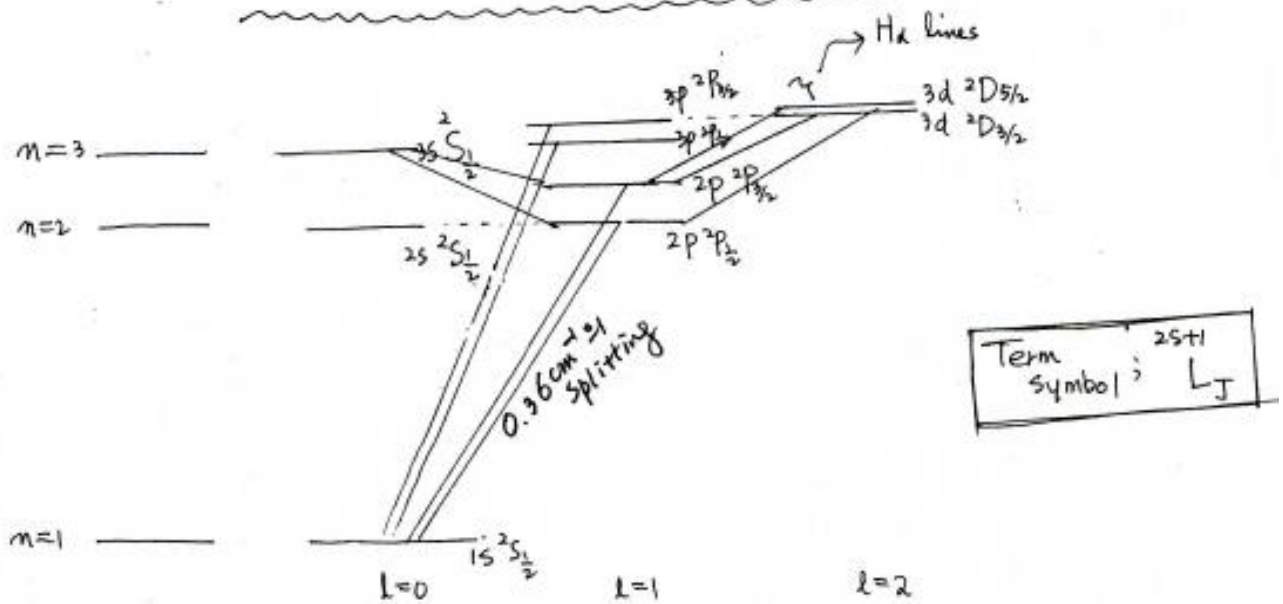
E'_{rel} 과 E'_{s-o} 는 order of magnitude 가 같다.

$$E'_{rel} + E'_{s-o} = -\frac{1}{2} m_e c^2 \frac{(Z\alpha)^4}{n^3}\left[\frac{1}{l+\frac{1}{2}} - \frac{3}{4n} - \frac{\left\{\begin{matrix} l \\ -l-1 \end{matrix}\right\}}{2l\left(l+\frac{1}{2}\right)(l+1)}\right]$$

$$= -\frac{1}{2} m_e c^2 \frac{(Z\alpha)^4}{n^3}\left[-\frac{3}{4n} + \frac{1}{\left\{\begin{matrix} l+1 \\ l \end{matrix}\right\}}\right]$$

$$\frac{O(E'_{rel}+E'_{s-o})}{O(E_n^{(0)})} \sim (Z\alpha)^2$$

$$E_n = -\frac{1}{2} m_e c^2 \frac{(Z\alpha)^4}{n^2} - \frac{1}{2} m_e c^2 \frac{(Z\alpha)^4}{n^3}\left[\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right] + \cdots$$

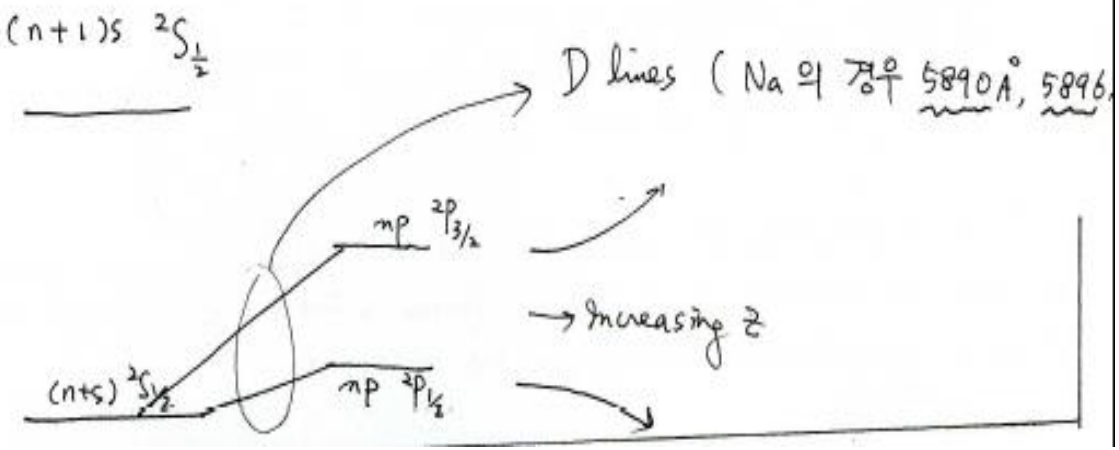


정표 The spectra of alkali Metal Atoms

① Shielding Effect → Z 대신 Z^* $1 \le Z \le Z^*$

Z^* 는 l 값에 따라 다르다, l이 클수록 Z^*가 증가

② Z^4에 비례해서 E'_{s-o}가 커진다.



<Coupling of Angular Momenta>

Each type of angular momentum, electron spin, electron orbital motion or nuclear spin, produce a magnetic moment. The magnetic moments interach with another through the magnetic field associated with the motions (spin or orbital) of electron (or nucleus). This is called coupling.

The perturbed Hamiltonian for polyelectronic atom is thus:

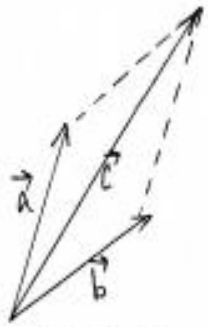
$$\hat{H}' = \sum_{i<j} A_{ij}\, \hat{l}_i \hat{l}_j + \sum_{i<j} B_{ij}\, \hat{s}_i \hat{s}_j + \sum_{i<j} C_{ij}\, \hat{s}_i \hat{l}_j$$ (neglecting nuclear spin effe

The expectation value is then:

$$E = \langle l_1\, m_1\, m_{s_1}\, ;\, l_2\, m_2\, m_{s_2}\, ;\, \cdots \left| \sum_{ij} A_{ij}\, \hat{l}_i \hat{l}_j + \sum_{i<j} B_{ij}\, \hat{s}_i \hat{s}_j + \sum_{i<j} C_{ij}\, l_i s_j \right| l_1\, m_1\, m_{s_1}\, ;\, l_2\, m_2\, m_{s_2}\, ;\, \cdots \rangle$$

However, there are too many quantum numbers to describe the state!! $\Rightarrow$ We need an approximation to which reduced quantum numbers can describe the state.

< physical meaning of the coupling >



$\vec{c} = \vec{a} + \vec{b}$

If strong coupling occurs between $\vec{a}$ and $\vec{b}$, $\vec{c}$ is fixed in space while $\vec{a}$ moves and $\vec{b}$ follows $\vec{c} - \vec{a}$ and vice versa. This results in the precession of both $\vec{a}$ and $\vec{b}$ around $\vec{c}$.

The rate of precession increases with the strength of coupling.

$\vec{c}$ is in practice precessing about an arbitrary direction in space. But when an electric or magnetic field is introduced in this direction, the space quantization effect can be observed.

Term energy를 결정하는 Hund의 thumb Rule.

(Rule 1) The term with the maximum multiplicity lies lowest in energy

(Rule 2) For a given multiplicity, the term with the largest value of L lies lowest in energy

(Rule 3) For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.

예) np^2 의 경우, $l_1 = l_2 = 1 \quad \therefore L = 2, 1, 0$ D.A. McQuarrie & J.D. Simon pp 296 – 300

$s_1 = s_2 = \frac{1}{2} \quad \therefore S = 1, 0$

However, $L=1$ (antisymmetric w.r.t. interchange of two electrons) couples with $S=1$ (symmetric spin)

$^{2S+1}L_J$

$L=2, S=0 \Rightarrow J=2 \quad \boxed{^1D_2}$

$L=1, S=1 \Rightarrow J=2,1,0, \quad \boxed{^3P_2 \mid {}^3P_1 \mid {}^3P_0}$

$L=0, S=0 \Rightarrow J=0 \quad \boxed{^1S_0}$

The order of lowest energy is $^3P_0, {}^3P_1, {}^3P_2, {}^1D_2, {}^1S_0$

j-j-coupling

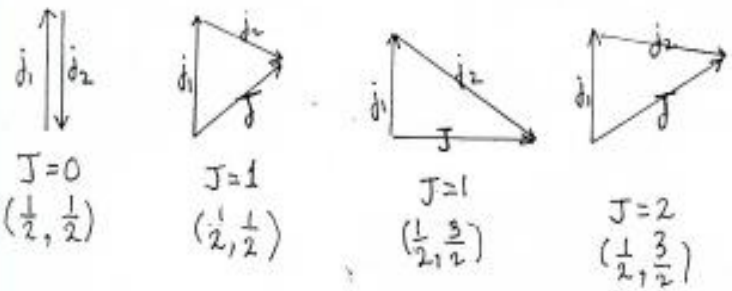
When $C_{ij} \gg A_{ij}, B_{ij}$, it is appropriate to describe the system with $|j_1, j_2, \cdots J\, m_J\rangle$ instead of $|l_1, m_1\, m_{s_1}; l_2\, m_2\, m_{s_2}; \cdots\rangle$.

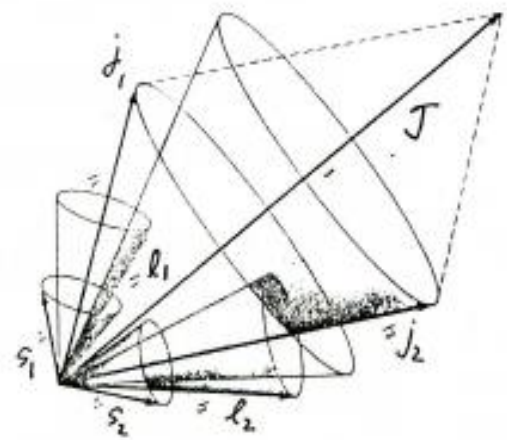
$j_1 = l_1 + s_1, \ldots |l_1 - s_1|$

$j_2 = l_2 + s_2, \cdots |l_2 - s_2|$

$\vdots$

$J = j_1 + j_2 \cdots, |j_1 - j_2|$





This implies that $|a, b, c, m_c\rangle$ can describe the system instead of $|a, m_a, b, m_b\rangle$. In other words $|a, b, c, m_c\rangle$ is a linear combination of $|a, m_a, b, m_b\rangle$ with different m_a and m_b. For both $|a, b, c, m_c\rangle$ and $|a, m_a, b, m_b\rangle$ to describe identical system, quantum mechanics shows that only c's satisfying

$$c = a+b, \cdots, |a-b|$$

are possible.

1) Russel-Sanders Coupling limit

When $A_{ij}, B_{ij} \gg C_{ij}$, it is appropriate to describe the system with $|LSJm_J\rangle$ instead of $|l_1 m_1 m_{s_1}; l_2 m_2 m_{s_2}; \cdots\rangle$.

$$L = l_1 + l_2, l_1 + l_2 - 1, \cdots, |l_1 - l_2| \quad \text{(for 2-electron)}$$

$$S = s_1 + s_2, s_1 + s_2 - 1, \cdots, |s_1 - s_2| \quad \text{(for 2-electron)}$$

$$J = L+S, L+S-1, \cdots, |L-S|$$

The expectation value is then,

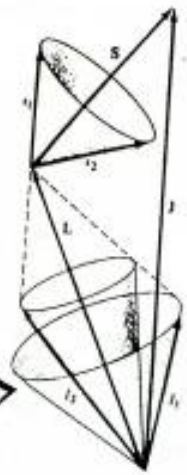
$$E = \langle LSJm_J | A_{L l_1 l_2 \ldots} \hat{L}^2 + B_{S s_1 s_2 \ldots} \hat{S}^2 + C_{JLS} \hat{L}\cdot\hat{S} | LSJm_J \rangle$$

$$= L(L+1)\hbar^2 \langle LSJm_J | A_{L l_1 l_2 \ldots} | LSJm_J \rangle$$

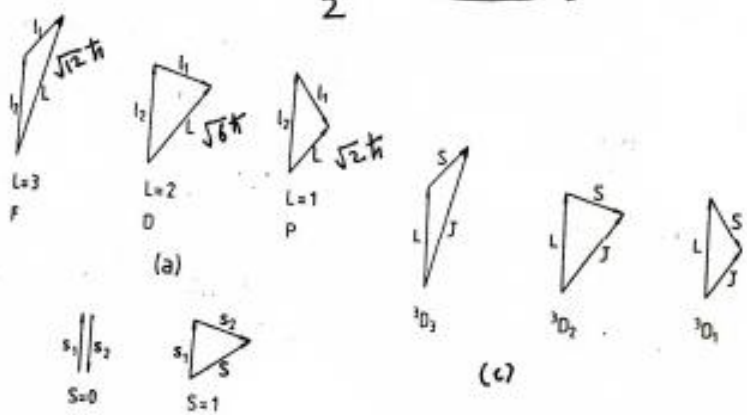
$$+ S(S+1)\hbar^2 \langle LSJm_J | B_{S s_1 s_2 \ldots} | LSJm_J \rangle$$

He in the highly excited configuration $2p^1 3d^1$

$$+ \left\{ \frac{J(J+1) - L(L+1) - S(S+1)}{2} \right\} \hbar^2 \langle LSJm_J | C_{JLS} | LSJm_J \rangle$$



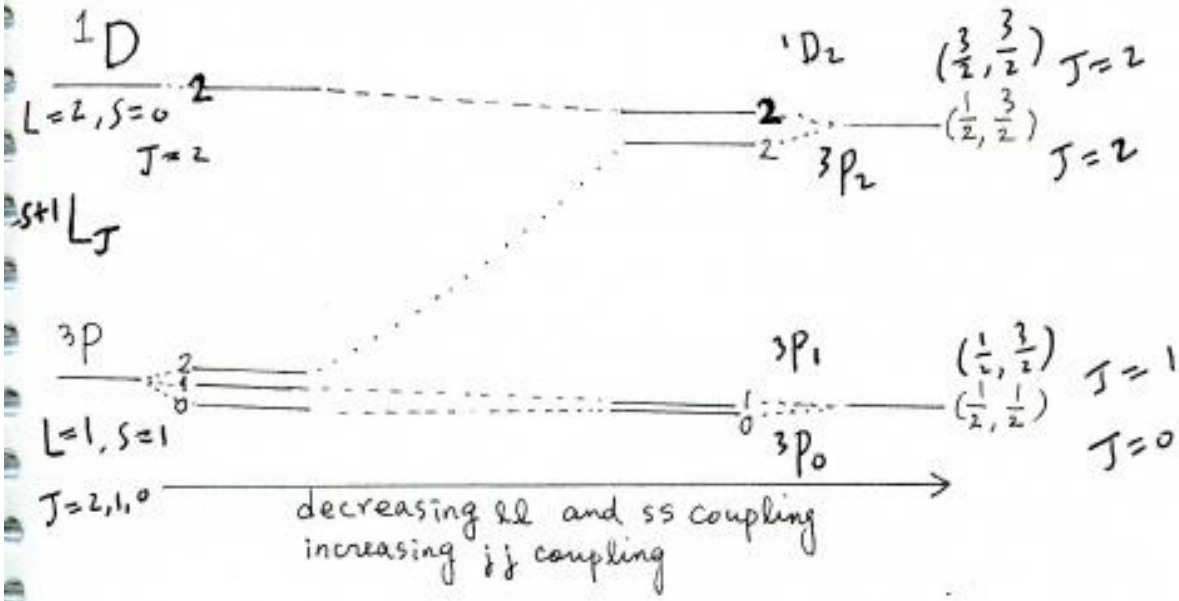
$l_1 = 1$
$l_2 = 2$
의 경우
⇒



Term Symbol

$^{2S+1}L_J$

Correlation with Russel-Saunders Coupling and j-j coupling



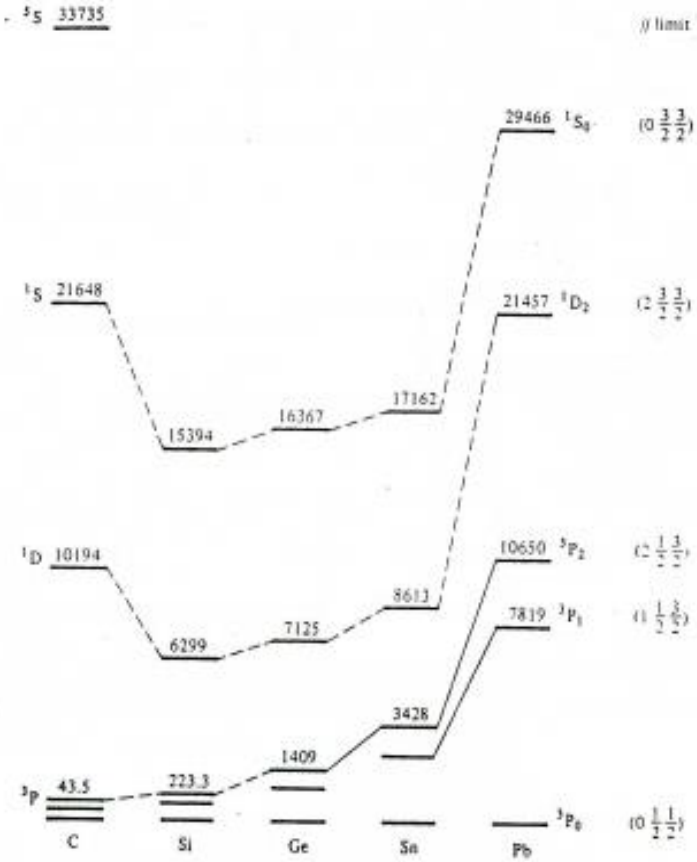


Figure 2.6
Energy levels for neutral atoms of the fourth column of the periodic table. All states arise from the p^2 configuration except for the ^5S, which arises from sp^3. Energies and splittings in this figure and in figures 2.7 and 2.8 are all in cm^{-1}. The right-hand (high Z) terms are labeled with the jj limit quantum numbers.

7.1.3. Spectra of Alkali Metal Atoms

1) Term value

$\begin{cases} \text{Nucleus} + (Z-1) \text{ core electrons} \Rightarrow \text{net charge of } +e \\ 1 \text{ valence electron} \end{cases}$

Therefore alkali Metal Atom's term value is dependent on the state of one valence electron.

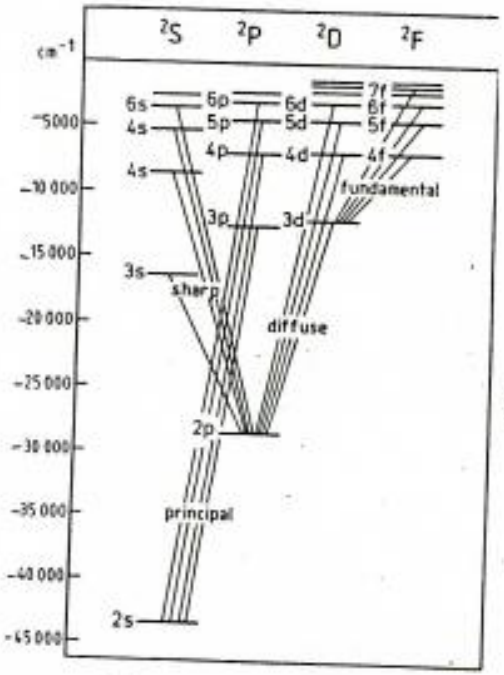
예) Li의 경우

Configuration	States
$1s^2 2s^1$	$^2S_{1/2}$
$1s^2 ns^1$ $(n=3, 4, \cdots)$	$^2S_{1/2}$
$1s^2 np^1$ $(n=2, 3, \cdots)$	$^2P_{1/2}$, $^2P_{3/2}$
$1s^2 nd^1$ $(n=3, 4, \cdots)$	$^2D_{3/2}$, $^2D_{5/2}$
$1s^2 nf^1$ $(n=3, 4, \cdots)$	$^2F_{5/2}$, $^2F_{7/2}$

2) Selection Rule

(a) Δn is unrestricted

(b) $\Delta l = \pm 1$



Grotrian diagram for lithium

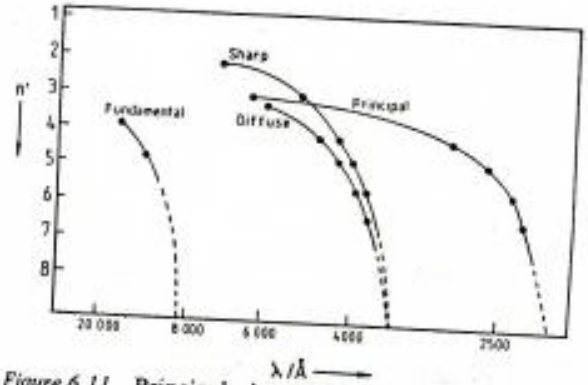
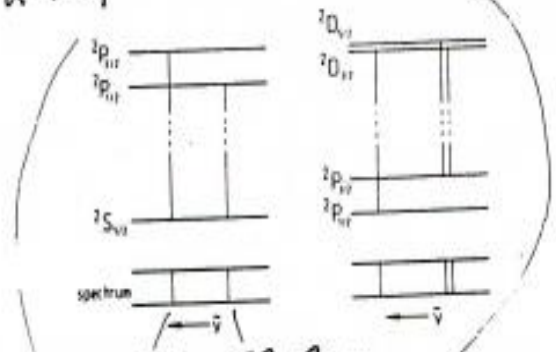


Figure 6.11 Principal, sharp, diffuse and fundamental series in the emission spectrum of the lithium atom

(C) $\Delta J = 0, \pm 1$ except $J = 0 \not\leftrightarrow J = 0$

a simple doublet a compound doublet



588.995 589.592 nm

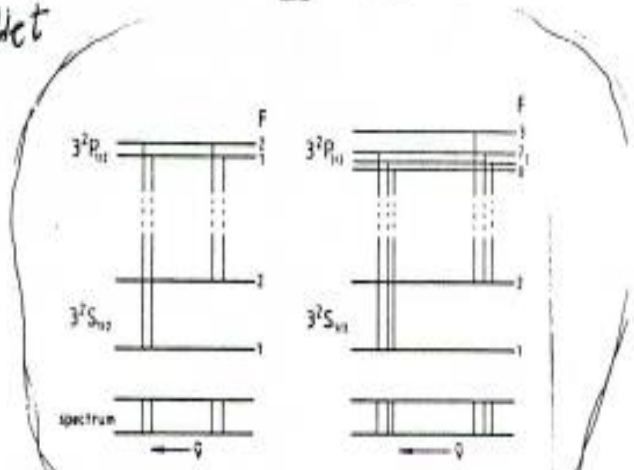
Fine Structure

Sodium D lines

principal series

Sodium atom

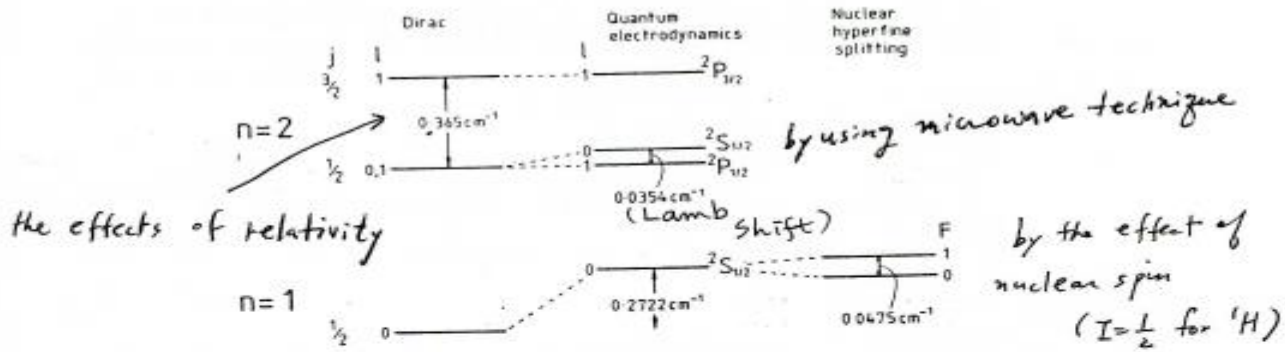
diffuse series



Nuclear Hyperfine Structure

by the effect of nuclear spin

7.1.4. Spectrum of the Hydrogen Atom



by using microwave technique

the effects of relativity

by the effect of nuclear spin ($I=\frac{1}{2}$ for ^1H)

The $n=1$ and $n=2$ levels of the hydrogen atom

7.1.5. Spectra of Helium and the Alkaline Earth Metal Atoms (Two electron system)

$$\psi_e = \psi_e^{o}\,\psi_e^{s}$$

ψ_e^{s} → electron spin wave function

ψ_e^{o} → electron orbital wave function.

ψ_e ↑ Total electronic wave function

$$\psi_e^{s} = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right] \text{ ; antisymmetric}$$

$$\left.\begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right] \end{array}\right\} \text{symmetric.}$$

$$\psi_e^0 = \frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) + \chi_a(2)\chi_b(1)\right]$$

$$\frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)\right]$$

for example $1s^1 2p^1$ config. of He

Total wavefunction should be antisymmetric w.r.t the exchange of fermion.

$$\therefore \psi_e = \underbrace{\frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) + \chi_a(2)\chi_b(1)\right]\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]}_{\text{singlet}}$$

$$= \frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)\right]\alpha(1)\alpha(2)$$

$$\frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)\right]\beta(1)\beta(2)$$

$$\frac{1}{\sqrt{2}}\left[\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)\right]\left[\alpha(1)\beta(2) + \beta(1)\alpha(2)\right]$$

same energy states before the fine structure is considered $\rightarrow$ triplet.

예) He의 경우

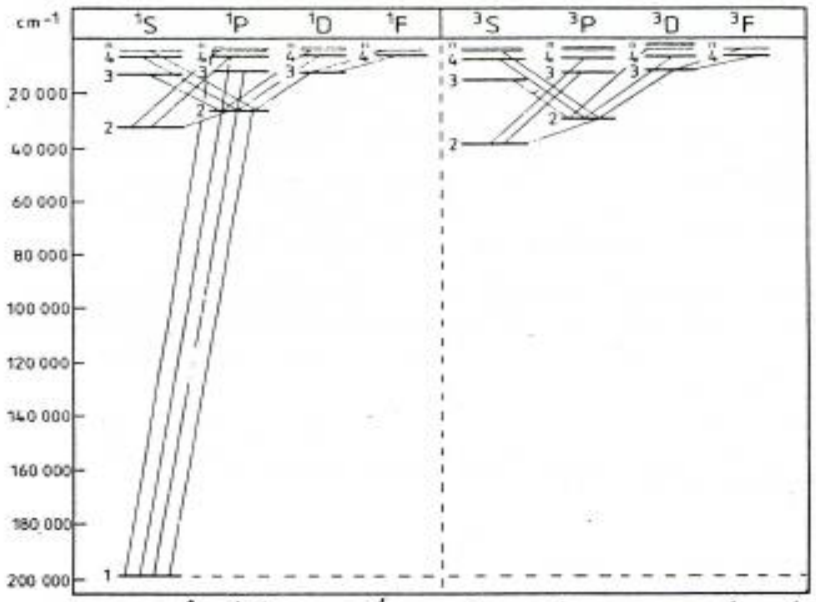
ground state ($1s^2$)에서는 $\psi_e^0 = \chi_a(1)\chi_b(2)$

즉 symmetric orbital ~~ea~~ wave function을 갖으므로 singlet term 이다. 그렇지만 excited state에서는 ($1s^1 \chi^1$) triplet 상태가 에너지가 더 낮다.

Selection Rules are $\Delta l = \pm 1$, for the promoted electron

$\Delta S = 0$

$\Delta J = 0, \pm 1$, except $J=0 \not\leftrightarrow J=0$



Grotrian diagram for helium. The scale is too small to show splittings due to spin-orbit coupling

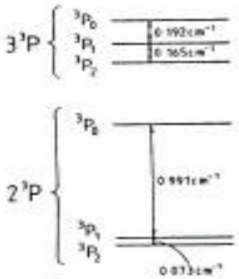


Figure 6.18 The unusual 2^3P and 3^3P multiplet splittings in the helium atom

a simple triplet

a compound triplet

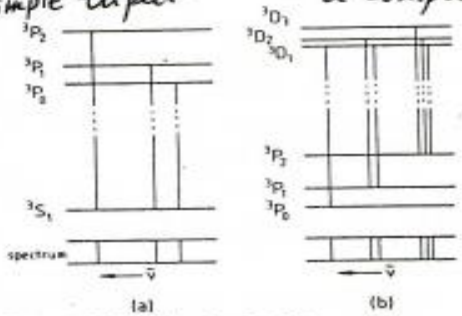


Figure 6.19 (a) A simple triplet, and (b) a compound triplet in the spectrum of, for example, an alkaline earth metal atom

7.1.6. Spectra of Other Polyelectronic Atoms

Selection Rules ① $\Delta L = 0, \pm 1$, except $L=0 \not\leftrightarrow L=0$

② $\Delta J = 0, \pm 1$, except $J=0 \not\leftrightarrow J=0$

③ $\Delta S = 0$

④ Laporte Selection Rule

$\text{even}\left(\sum_i l_i\right) \longleftrightarrow \text{odd}\left(\sum_i l_i\right)$ [even $\not\leftrightarrow$ even, odd $\not\leftrightarrow$ odd]

∴ Transition is forbidden between states arising from the same configuration.

$C: 1s^2 2s^2 2p^2 \longrightarrow {}^1S, {}^3P, {}^1D$ 174

Ex) $C: 1s^2 2s^2 2p^1 3d^1$ gives ${}^{1,3}P$, ${}^{1,3}D$, ${}^{1,3}F$.

exited state

But ${}^1P \not\leftrightarrow {}^1D$, ${}^3D \not\leftrightarrow {}^3F$ etc.

consider only the ΔS and ΔL selection rules ${}^1P \longleftrightarrow {}^1D$

($1s^2 2s^2 2p^1 3d^1 \left(\sum_i l_i = 3\right) \not\longleftrightarrow 1s^2 2s^2 3d^1 4f^1 \left(\sum_i l_i = 5\right)$

but the Laporte rule forbids it. ${}^1P \not\leftrightarrow {}^1D$

7.2. Electronic Spectroscopy of Diatomic Molecules

7.2.1 Molecular Orbitals

Linear Combination of Atomic Orbitals (LCAO)

$$\underbrace{\psi}_{\text{Molecular orbital}} = \sum_i c_i \underbrace{\chi_i}_{\text{atomic orbital}}$$

For effective linear combination.

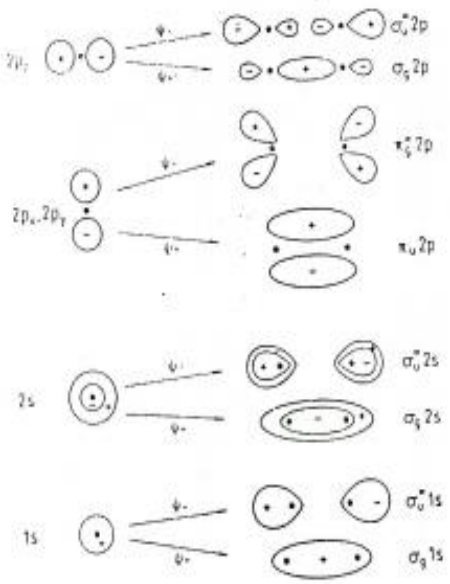
1. The energies of the AO must be comparable.
2. The AO should overlap as much as possible
3. The AOs must have the same symmetry property w.r.t certain symmetry elements of the molecule.

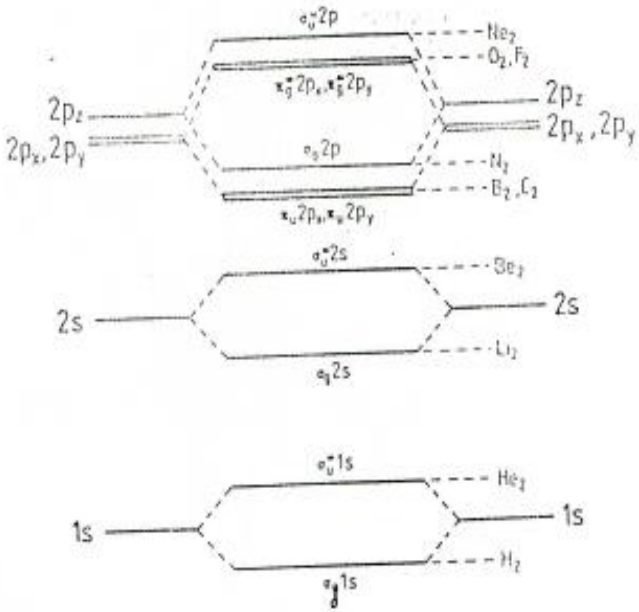
<Homonuclear diatomic molecule>

$\psi = c_1\chi_1 + c_2\chi_2$ 를 trial function 으로 사용하면

결과 $\Rightarrow$ $$E_\pm = \frac{H_{11} \pm H_{12}}{1 \pm S_{12}}$$ where $H_{ij} = \langle \chi_i | H | \chi_j \rangle$, $S_{ij} = \langle \chi_i | \chi_j \rangle$

$$\psi_\pm = \frac{1}{\sqrt{2}}(\chi_1 \pm \chi_2)$$


2p_z
σ_u*2p
σ_g2p
π_g*2p
2p_x,2p_y
π_u2p
2s
σ_u*2s
σ_g2s
1s
σ_u*1s
σ_g1s


σ_u*2p
Ne_2
O_2,F_2
π_g*2p_x,π_g*2p_y
2p_z
2p_x,2p_y
σ_g2p
N_2
B_2,C_2
π_u2p_x,π_u2p_y
σ_u*2s
Be_2
2s
Li_2
σ_g2s
σ_u*1s
He_2
1s
H_2
σ_g1s

$D_{\infty h}$

Molecule	Ground Electronic State		Excited Electronic State	
	Configuration	Symmetry	Configuration	Symmetry
H_2	$(\sigma_g 1s)^2$, B.O=1	Σ_g^+	$(\sigma_g 1s)^1(\sigma_u 1s)^1$ B.O=0	$\sigma_g^+ \times \sigma_u^- = \Sigma_u^-$
He_2	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2$, B.O=0	Σ_g^+	$(\sigma_g 1s)^2(\sigma_u^* 1s)^1(\sigma_g 2s)^1$, B.O=1	$\sigma_u^- \times \sigma_g^+ = \Sigma_u^-$
Be_2	$[He_2](\sigma_g 2s)^2(\sigma_u^* 2s)^2$, B.O=0	Σ_g^+	$[He_2](\sigma_g 2s)^2(\sigma_u^* 2s)^1(\pi_u 2p)^1$ B.O=1	$\sigma_u^- \times \pi_u = \pi_g$
B_2	$[Be_2](\pi_u 2p_x)^1(\pi_u 2p_y)^1$, B.O=1	$\pi_u \times \pi_u = {}^3\Sigma_g^- + {}^1\Sigma_g^+ + {}^1\Delta_g$	$[Be_2](\pi_u 2p)^1(\sigma_g 2p)^1$, B.O=1	$\pi_u \times \sigma_g^+ = \pi_u$
C_2	$[Be_2](\pi_u 2p_x)^2(\pi_u 2p_y)^2$, B.O=2	Σ_g^+	$[Be_2](\pi_u 2p)^3(\sigma_g 2p)^1$, B.O=2	$\pi_u \times \sigma_g^+ = \pi_u$
N_2	$[Be_2](\pi_u 2p_x)^2(\pi_u 2p_y)^2(\sigma_g 2p)^2$ B.O=3	Σ_g^+	$[Be_2](\pi_u 2p_x)^2(\pi_u 2p_y)^2(\sigma_g 2p)^1(\pi_g 2p)^1$, B.O=3	$\sigma_g^+ \times \pi_g = \pi_g$
O_2	$[Be_2](\sigma_g 2p)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p_x)^1(\pi_g^* 2p_y)^1$, B.O=2	$\pi_g \times \pi_g = {}^3\Sigma_g^- + {}^1\Sigma_g^+ + {}^1\Delta_g$	$[Be_2](\sigma_g 2p)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p)^1(\sigma_u^* 2p)^1$ B.O=2	$\pi_g \times \Sigma_u^- = \pi_u$
			혼은	
			$[Be_2](\sigma_g 2p)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p)^2$ B.O=2	$\pi_u \times \pi_g = {}^3\Sigma_u^- + {}^1\Sigma_u^+ + {}^1\Delta_u$
F_2	$[Be_2](\sigma_g 2p)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p_x)^2(\pi_g^* 2p_y)^2$, B.O=1	Σ_g^+	$[Be_2](\sigma_g 2p)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g 2p)^3(\sigma_g^* 2p)^1$	$\pi_g \times \sigma_g^- = \pi_g$

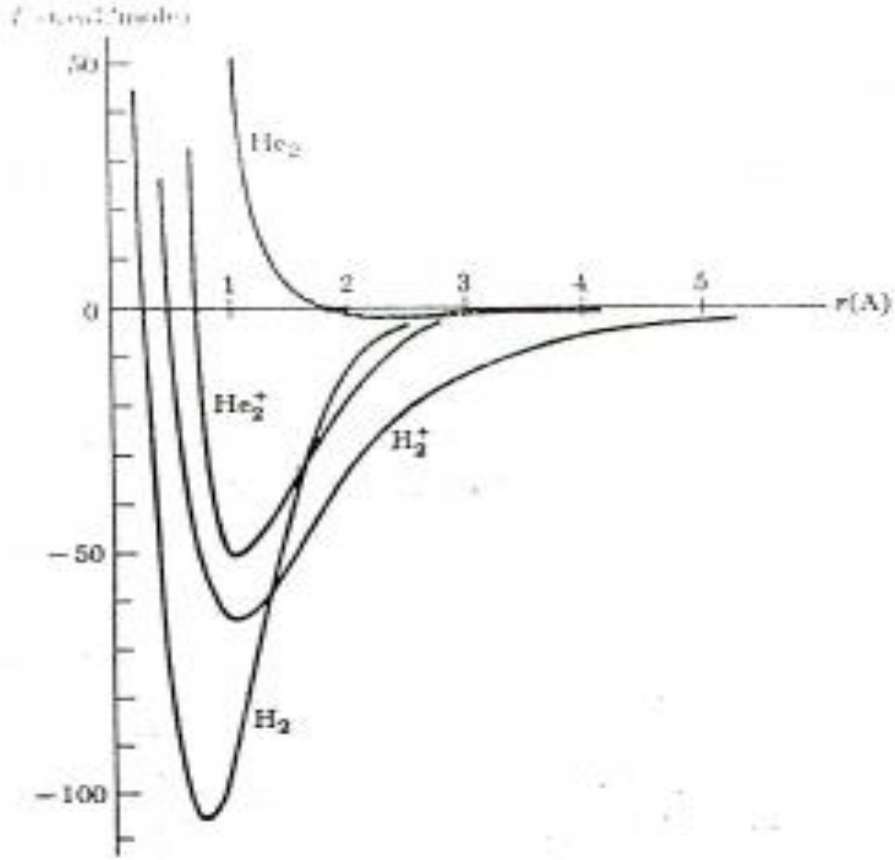
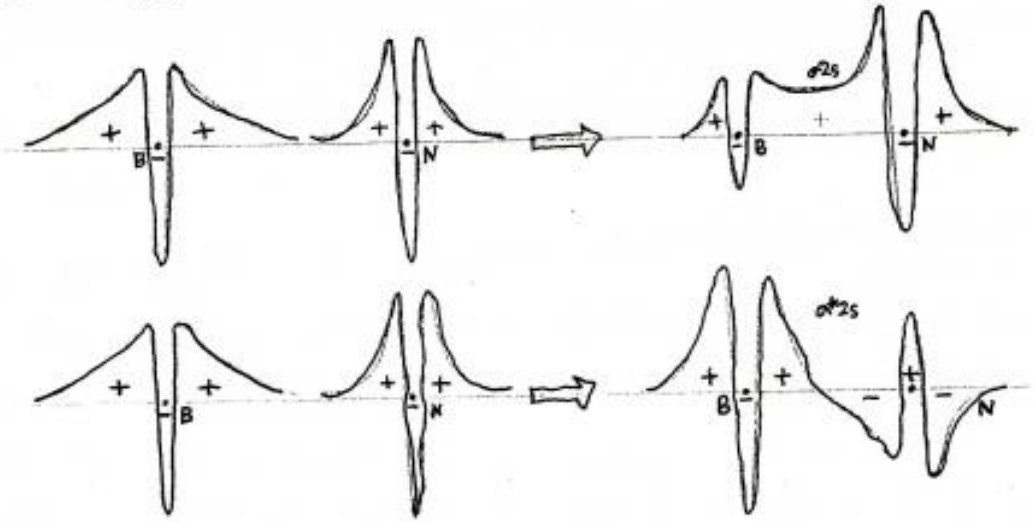
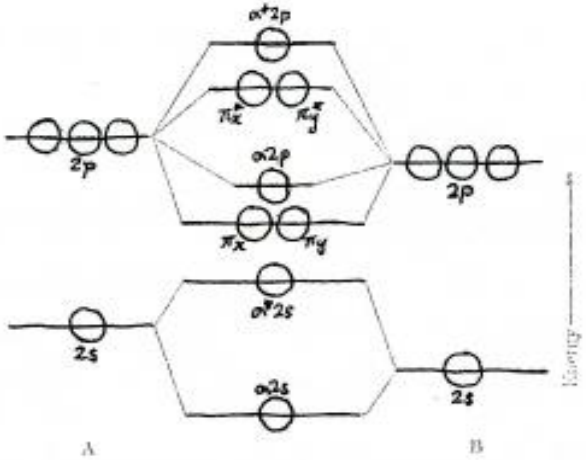

50
0
−50
−100
1
2
3
4
5
r(A)
He2
He2+
H2+
H2

Table 6.6 Electronic states arising from ground configurations in which there is more than one electron or vacancy in a degenerate orbital

Point group	*Configuration*	*States*
C_3	$(e)^2$	$^3A + {}^1A + {}^1E$
C_4	$(e)^2$	$^3A + {}^1A + {}^1B + {}^1B$
C_5	$(e_1)^2$	$^3A + {}^1A + {}^1E_2$
	$(e_2)^2$	$^3A + {}^1A + {}^1E_1$
C_6	$(e_1)^2$ and $(e_2)^2$	$^3A + {}^1A + {}^1E_2$
C_7	$(e_1)^2$	$^3A + {}^1A + {}^1E_2$
	$(e_2)^2$	$^3A + {}^1A + {}^1E_3$
	$(e_3)^2$	$^3A + {}^1A + {}^1E_1$
C_8	$(e_1)^2$ and $(e_3)^2$	$^3A + {}^1A + {}^1E_2$
	$(e_2)^2$	$^3A + {}^1A + {}^1B + {}^1B$
C_{3v}	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1E$
C_{4v}	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$
C_{5v}	$(e_1)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
	$(e_2)^2$	$^3A_2 + {}^1A_1 + {}^1E_1$
C_{6v}	$(e_1)^2$ and $(e_2)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
$C_{\infty v}$	$(\pi)^2$	$^1\Sigma^+ + {}^3\Sigma^- + {}^1\Delta$
	$(\delta)^2$	$^1\Sigma^+ + {}^3\Sigma^- + {}^1\Gamma$
D_3	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1E$
D_4	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$
D_5	$(e_1)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
	$(e_2)^2$	$^3A_2 + {}^1A_1 + {}^1E_1$
D_6	$(e_1)^2$ and $(e_2)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
C_{3h}	$(e'')^2$ and $(e^*)^2$	$^3A'' + {}^1A'' + {}^1E''$
C_{4h}	$(e_g)^2$ and $(e_u)^2$	$^3A_g + {}^1A_g + {}^1B_g + {}^1B_g$
C_{5h}	$(e_1'')^2$ and $(e_1^*)^2$	$^3A'' + {}^1A'' + {}^1E_2''$
	$(e_2'')^2$ and $(e_2^*)^2$	$^3A'' + {}^1A'' + {}^1E_1''$
C_{6h}	$(e_{1g})^2$, $(e_{1u})^2$, $(e_{2g})^2$ and $(e_{2u})^2$	$^3A_g + {}^1A_g + {}^1E_{2g}$
D_{2d}	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$
D_{3d}	$(e_g)^2$ and $(e_u)^2$	$^3A_{2g} + {}^1A_{1g} + {}^1E_g$
D_{4d}	$(e_1)^2$ and $(e_3)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
	$(e_2)^2$	$^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$
D_{5d}	$(e_{1g})^2$ and $(e_{1u})^2$	$^3A_{2g} + {}^1A_{1g} + {}^1E_{2g}$
	$(e_{2g})^2$ and $(e_{2u})^2$	$^3A_{2g} + {}^1A_{1g} + {}^1E_{1g}$
D_{6d}	$(e_1)^2$ and $(e_5)^2$	$^3A_2 + {}^1A_1 + {}^1E_2$
	$(e_2)^2$ and $(e_4)^2$	$^3A_2 + {}^1A_1 + {}^1E_4$
	$(e_3)^2$	$^3A_2 + {}^1A_1 + {}^1B_1 + {}^1B_2$
D_{3h}	$(e')^2$ and $(e'')^2$	$^3A_2' + {}^1A_1' + {}^1E''$
D_{4h}	$(e_g)^2$ and $(e_u)^2$	$^3A_{2g} + {}^1A_{1g} + {}^1B_{1g} + {}^1B_{2g}$
D_{5h}	$(e_1')^2$ and $(e_1'')^2$	$^3A_2' + {}^1A_1' + {}^1E_2''$
	$(e_2')^2$ and $(e_2'')^2$	$^3A_2' + {}^1A_1' + {}^1E_1''$
D_{6h}	$(e_{1g})^2$, $(e_{1u})^2$, $(e_{2g})^2$ and $(e_{2u})^2$	$^3A_{2g} + {}^1A_{1g} + {}^1E_{2g}$
$D_{\infty h}$	$(\pi_g)^2$ and $(\pi_u)^2$	$^3\Sigma_g^- + {}^1\Sigma_g^+ + {}^1\Delta_g$
	$(\delta_g)^2$ and $(\delta_u)^2$	$^3\Sigma_g^- + {}^1\Sigma_g^+ + {}^1\Gamma_g$
S_4	$(e)^2$	$^3A + {}^1A + {}^1B + {}^1B$
S_6	$(e_g)^2$ and $(e_u)^2$	$^3A_g + {}^1A_g + {}^1E_g$
S_8	$(e_1)^2$ and $(e_3)^2$	$^3A + {}^1A + {}^1E_2$
	$(e_2)^2$	$^3A + {}^1A + {}^1B + {}^1B$
T_d	$(t_1)^2$, $(t_1)^4$, $(t_2)^2$ and $(t_2)^4$	$^3T_1 + {}^1A_1 + {}^1E + {}^1T_2$
	$(t_1)^3$	$^4A_1 + {}^2E + {}^2T_1 + {}^2T_2$
	$(t_2)^3$	$^4A_2 + {}^2E + {}^2T_1 + {}^2T_2$
	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1E$
T	$(t)^2$ and $(t)^4$	$^3T + {}^1A + {}^1E + {}^1T$
	$(t)^3$	$^4A + {}^2E + {}^2T + {}^2T$
	$(e)^2$	$^3A + {}^1A + {}^1E$
O_h	$(t_{1g})^2$, $(t_{1u})^2$, $(t_{1g})^4$, $(t_{1u})^4$, $(t_{2g})^2$, $(t_{2u})^2$, $(t_{2g})^4$, $(t_{2u})^4$	$^3T_{1g} + {}^1A_{1g} + {}^1E_g + {}^1T_{2g}$
	$(t_{1g})^3$	$^4A_{1g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$
	$(t_{1u})^3$	$^4A_{1u} + {}^2E_u + {}^2T_{1u} + {}^2T_{2u}$
	$(t_{2g})^3$	$^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$
	$(t_{2u})^3$	$^4A_{2u} + {}^2E_u + {}^2T_{1u} + {}^2T_{2u}$
	$(e_g)^2$ and $(e_u)^2$	$^3A_{2g} + {}^1A_{1g} + {}^1E_g$
O	$(t_1)^2$, $(t_1)^4$, $(t_2)^2$ and $(t_2)^4$	$^3T_1 + {}^1A_1 + {}^1E + {}^1T_2$
	$(t_1)^3$	$^4A_1 + {}^2E + {}^2T_1 + {}^2T_2$
	$(t_2)^3$	$^4A_2 + {}^2E + {}^2T_1 + {}^2T_2$
	$(e)^2$	$^3A_2 + {}^1A_1 + {}^1E$

Heteronuclear Diatomic molecule





Molecule	Ground Electronic State		Excited Electronic State	
	Configuration	Symmetry	Configuration	Symmetry
BN	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^3$, B.O $= \frac{3}{2}$	Π	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^2(\sigma_{2p})^1$, B.O $= \frac{3}{2}$ . . . . . . 또는 $(\sigma_{2s})^2(\sigma^*_{2s})^1(\pi_{2p})^4$, B.O $= \frac{3}{2}$	$\pi \times \pi \times \sigma^+ = \Sigma^+ + {}^3\Sigma^- + \Delta$ . . . . . . Σ^-
CO	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$, B.O $= 3$	Σ^+	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^1(\pi^*_{2p})^1$ B.O $= 2$	$\sigma^+ \times \pi = \Pi$
NO	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^1$	$^2\Pi$	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\sigma^*_{2p})$ . . . . 또는 . . . . $(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^3(\pi^*_{2p})^2$	$^2\Sigma^-$ . . . $\Pi \times \Pi^2 = \Pi \times (\Sigma^+ + \Sigma^- + \Delta) = \Pi$ (?)

7.2.2. Classification of Electronic States of Diatomic Molecules

$$\vec{L} = \sum_i \vec{l_i}$$ → angular momentum of each electron

Total angular momentum of elections of diatomic molecule

component of Total angular momentum

$$M_L = \sum_i m_{li}$$ → Component of angular momentum of ith electron.

$M_L = -L, -L+1, \cdots, L-1, L$

Likewise,

$$\vec{S} = \sum_i \vec{S_i} \qquad M_S = \sum_i m_{si}, \qquad M_S = -S, -S+1, \cdots, S-1, S$$

< 유의해야 할점 >

① $\vec{L}$ and $\vec{S}$ are not coupled to each other

② $\vec{L}$ is coupled very strongly to electrostatic field produced by the two nuclei. Thus, $\vec{L}$ precesses about the internuclear axis so rapidly ⇒ $\vec{L}$ is not a good quantum number.

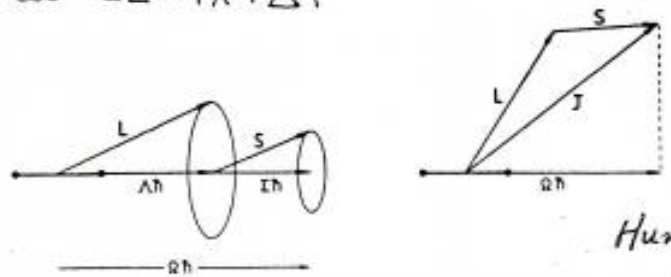
Lambda Λ But Λ $(= |M_L|)$ is defined. $\Lambda = 0, 1, 2, 3, \cdots$ $(\Sigma, \Pi, \Delta, \Phi, \cdots)$

③ $\vec{S}$ is coupled to magnetic field produced along the internuclear axis. ⇒ $\vec{S}$ is still a good quantum number.

Its component, Σ, can take $(2S+1)$ values.

$$\Sigma (= M_S) = -S, -S+1, \cdots, S-1, S$$

④ Spin-Orbit interaction $(\Delta E = A\Lambda\Sigma)$ now distinguishes $(2S+1)$ spin states. The quantum number Ω is defined $\Omega = |\Lambda + \Sigma|$



Hund's case (a)

Hund's case (c) when there is at least one highly charged nucleus in the molecule

(5) Term Symbol : $^{2S+1}\Lambda_{\Omega}$

(6) Hund's Rules applies to diatomic case as well as to atomic case

(7) Λ ($= \Sigma, \Pi, \Delta, \Phi,$) symbols also indicate symmetry of the electronic wavefunction of the point group.

예) H_2 의 경우 $(\sigma_g 1s)^2$, $m_{l_1}=0$, $m_{l_2}=0$, $\therefore M_L=0$

$m_{s_1}=\frac{1}{2}$, $m_{s_2}=-\frac{1}{2}$ $\therefore M_S=0$ $S=0$ $\therefore$ $^1\Sigma$

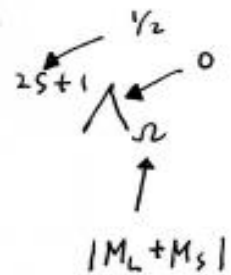
He_2^+ 의 경우 $(\sigma_g 1s)^2(\sigma_u^* 1s)^1$ $m_{l_1}=m_{l_2}=m_{l_3}=0$ $\therefore M_L=0$

$m_{s_1}=\frac{1}{2}$, $m_{s_2}=-\frac{1}{2}$, $m_{s_3}=\pm\frac{1}{2}$ $\therefore M_S=\pm\frac{1}{2}$ $S=1/2$

$\therefore {}^2\Sigma_{1/2}$

B_2 의 경우 $(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p_x)^1(\pi_u 2p_y)^1$

$m_l=\pm 1$, $m_s=\pm\frac{1}{2}$



	m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	M_L	M_S
①	+1	$\frac{1}{2}$	+1	$-\frac{1}{2}$	2	0
②	+1	$\frac{1}{2}$	−1	$\frac{1}{2}$	0	1
③	+1	$\frac{1}{2}$	−1	$-\frac{1}{2}$	0	0
④	+1	$-\frac{1}{2}$	−1	$\frac{1}{2}$	0	0
⑤	+1	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	0	−1
⑥	−1	$\frac{1}{2}$	−1	$-\frac{1}{2}$	2	0

①, ⑥ → $|M_L|=2$, $S=0$ ⇒ $^1\Delta$

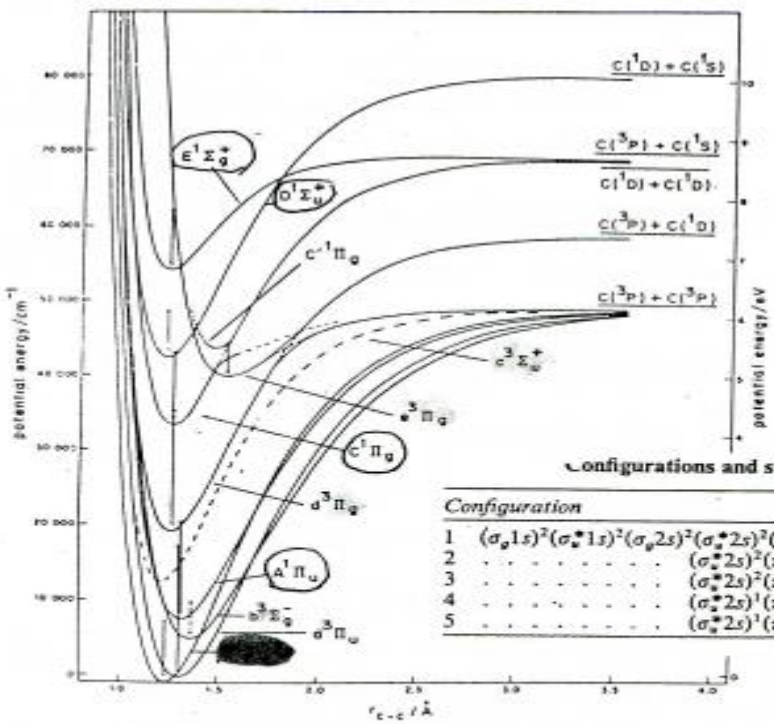
②, ③, ⑤ ⇒ $|M_L|=0$, $S=1$ ⇒ $^3\Sigma$ → lowest energy

④ → $|M_L|=0$, $S=0$ ⇒ $^1\Sigma$

7.2.3: Electronic Selection Rules

1. $\Delta\Lambda = 0, \pm 1$
2. $\Delta S = 0$
3. $\Delta\Sigma = 0$; $\Delta\Omega = 0, \pm 1$
4. $+ \not\leftrightarrow -$; $+ \leftrightarrow +$; $- \leftrightarrow -$
5. $g \leftrightarrow u$; $g \not\leftrightarrow g$; $u \not\leftrightarrow u$

7.2.5. Vibrational Coarse Structure



Configurations and states of the C_2 molecule

	Configuration	*States*
1	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4$	$X^1\Sigma_g^+$
2	. . . . . $(\sigma_u^* 2s)^2(\pi_u 2p)^3(\sigma_g 2p)^1$	$a^3\Pi_u$, $A^1\Pi_u$
3	. . . . . $(\sigma_u^* 2s)^2(\pi_u 2p)^2(\sigma_g 2p)^2$	$b^3\Sigma_g^-$, $E^1\Sigma_g^+$, $^1\Delta_g$
4	. . . . . $(\sigma_u^* 2s)^1(\pi_u 2p)^4(\sigma_g 2p)^1$	$c^3\Sigma_u^+$, $D^1\Sigma_u^+$
5	. . . . . $(\sigma_u^* 2s)^1(\pi_u 2p)^3(\sigma_g 2p)^2$	$d^3\Pi_g$, $C^1\Pi_g$

Figure 7.17 Potential energy curves for the ground and several excited states of C_2. (Reproduced, with permission, from Ballik, E. A., and Ramsay, D. A., *Astrophys. J.*, 137, 84, 1963 published by the University of Chicago Press; Copyright (1963) The American Astronomical Society.)

* Labelling Convention; ① The ground state is labelled X

② Higher states of the same multiplicity (as the ground state) are labelled A, B, C, ... in order of increasing energy

③ States with different multiplicity (from the ground state) are labelled a, b, c, ... in order of increasing energy.

Table 7.6 Electronic transitions observed in C_2.

Transition	Names associated	Spectral region/nm	Source of spectrum
$b^3\Sigma_g^- \rightarrow a^3\Pi_u$	Ballik–Ramsay	2700–1100	King furnace
$A^1\Pi_g \leftrightharpoons X^1\Sigma_g^+$	Phillips	1549– 672	Discharges
$d^3\Pi_g \leftrightharpoons a^3\Pi_u$	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
$D^1\Sigma_u^+ \leftrightharpoons X^1\Sigma_g^+$	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	

$$S = T + G(v) + F(J)$$

$F(J)$ → rotational term values

$G(v)$ → vibrational term values

T → electronic term values

(Ro) Vibronic Spectra : electronic transition + (ro) vibrational transiti

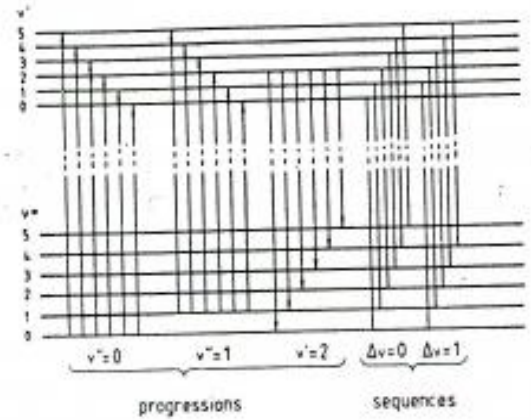
① $\Delta v = v' - v''$; unrestricted

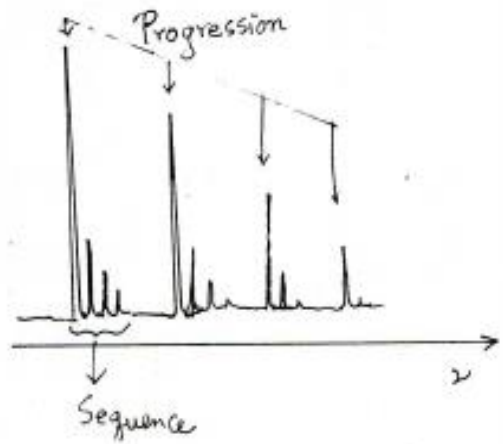
② Its intensity is governed by

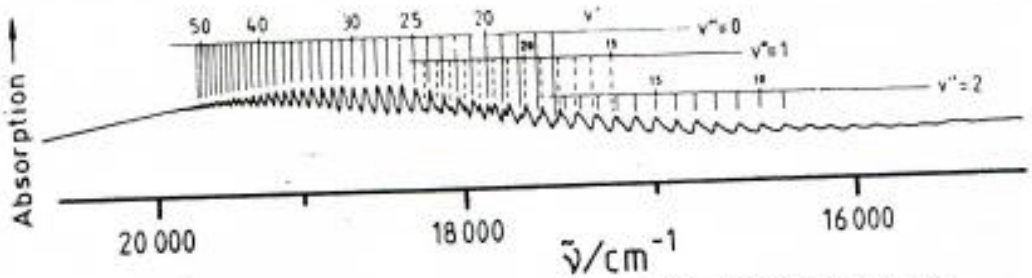
a) Boltzman factor : $\exp[-\{G(v'') - G(0)\} hc/kT]$

b) Franck Condon Factor

7.2.5.2. Progressions and sequences

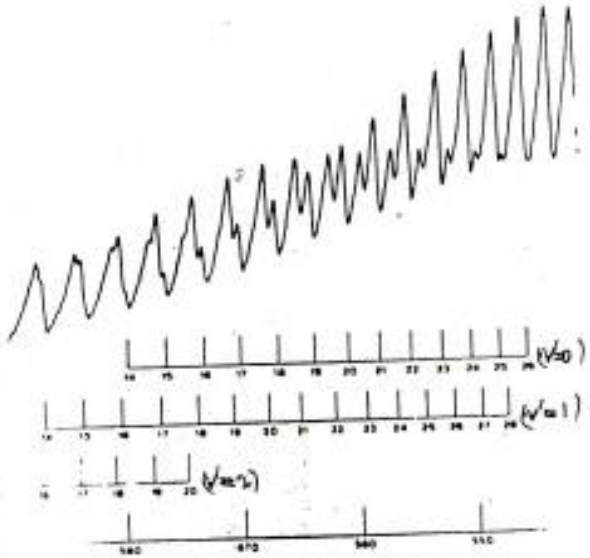






Progressions with $v'' = 0$, 1 and 2 in the $B^3\Pi_{0^+u} - X^1\Sigma_g^+$ system of the I_2 molecule

$\tilde{\nu}_e'' = 214.50\ cm^{-1}$



Overlapping of (v', 0), (v', 1) and (v', 2) bands in iodine

7.2.5.3. Franck Condon Principle.

$$\mu_{if} = \int \psi_e'^{*} \psi_v'^{*} \mu \psi_e'' \psi_v'' \, d\tau_{ev}$$

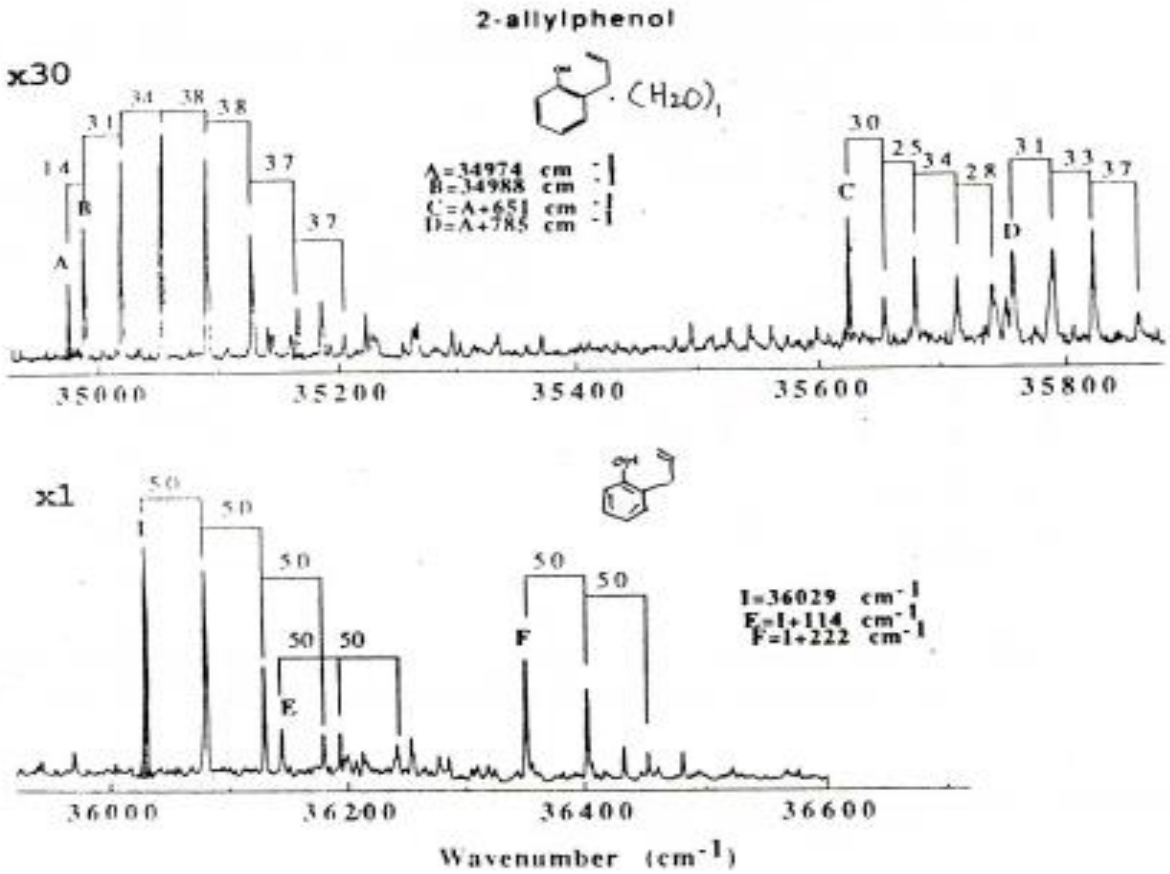
ψ_v'' → vibrational wave function in the ground electronic state

ψ_e'' → ground electronic wave function

$\psi_v'^{*}$ → vibrational wave function in the excited electronic state

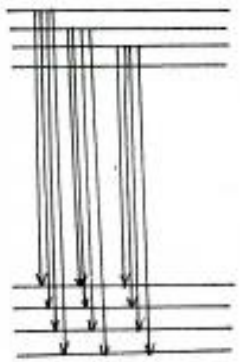
$\psi_e'^{*}$ → excited electronic wave function.

$$= \underbrace{\int \psi_e'^{*} \mu \psi_e'' \, d\tau_e}_{\text{electronic transition dipole moment.}} \cdot \underbrace{\int \psi_v'^{*} \psi_v'' \, d\tau_v}_{\text{Franck Condon Factor}}$$

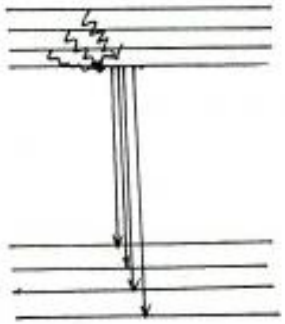

2-allylphenol
x30
(H2O)1
A=34974 cm-1
B=34988 cm-1
C=A+651 cm-1
D=A+785 cm-1
14
31
34
38
38
37
37
A
B
30
25
34
28
31
33
37
C
D
35000
35200
35400
35600
35800
x1
50
50
50
50
50
50
50
I
E
F
I=36029 cm-1
E=I+114 cm-1
F=I+222 cm-1
36000
36200
36400
36600
Wavenumber (cm-1)

c) Emission Spectra

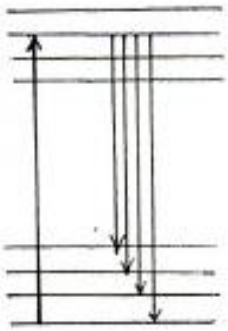
a) Random Preparation of Excited state (e.g. low pressure discharge)



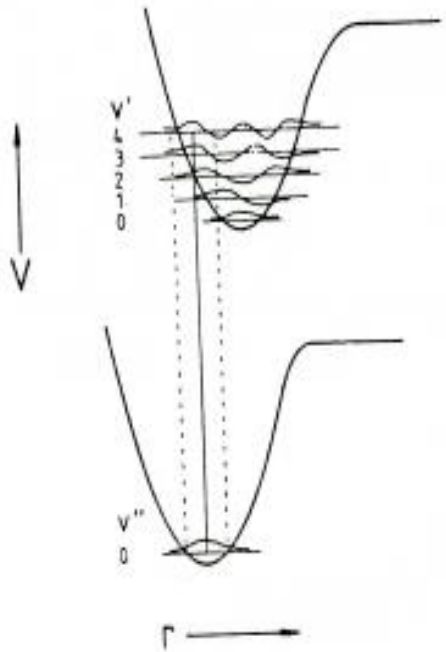
b) Random Preparation of Excited State followed by fast deactivation (e.g. high pressure discharge)



c) Laser Excitation at low pressure



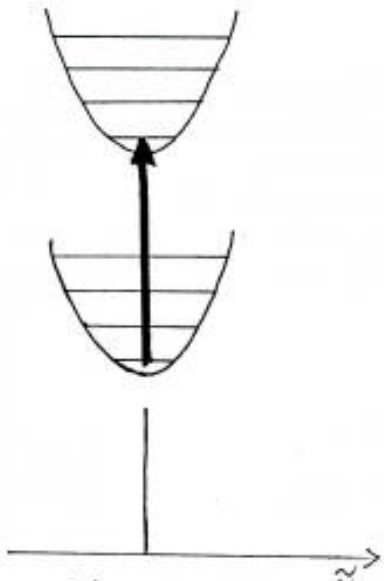
d) Laser Excitation at high pressure.



Franck Condon Factor of <u>the vertical transition</u> is maximum.

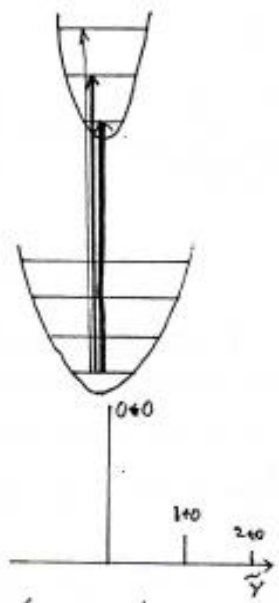
A) Excitation Spectra of Cold Molecule ($T \ll \frac{h\nu}{k}$)

a) $\tilde{\nu}_e' = \tilde{\nu}_e''$, $R_e' = R_e''$ 일 때



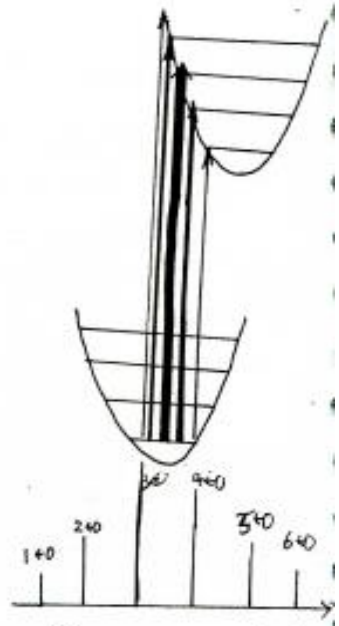
Only 0←0 transition is observed

b) $\tilde{\nu}_e' \neq \tilde{\nu}_e''$, $R_e' = R_e''$ 일 때
(Most Cases)



Some vibrational peaks are observed weakly

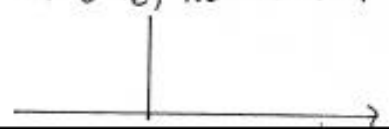
c) $R_e' \neq R_e''$ 일 때



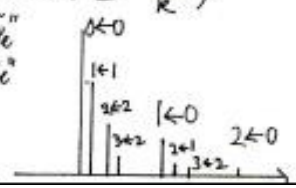
Strong Vibrational progression

B) Excitation Spectra of Hot Molecule ($T \gtrsim \frac{h\nu}{k}$)

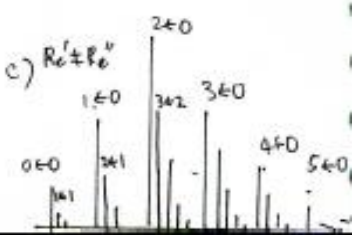
a) $\tilde{\nu}_e' = \nu_e''$, $R_e = R_e''$ 일 때



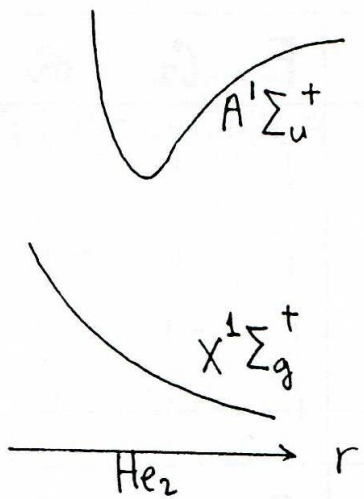
b) $\tilde{\nu}_e' \neq \tilde{\nu}_e''$
$R_e' = R_e''$

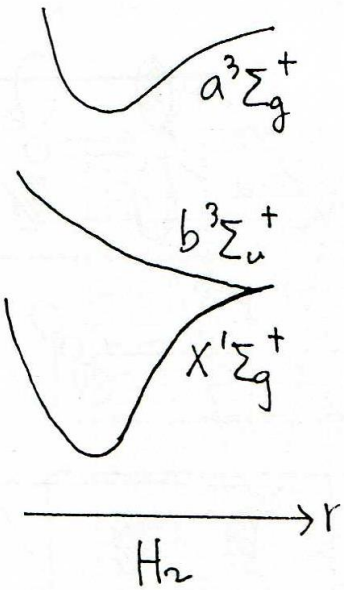


c) $R_e' \neq R_e''$



7.2.5.6. Repulsive States and Continuous Spectra.





7.3. Electronic Spectroscopy of Polyatomic Molecules

7.3.1.1. AH_2 molecules.

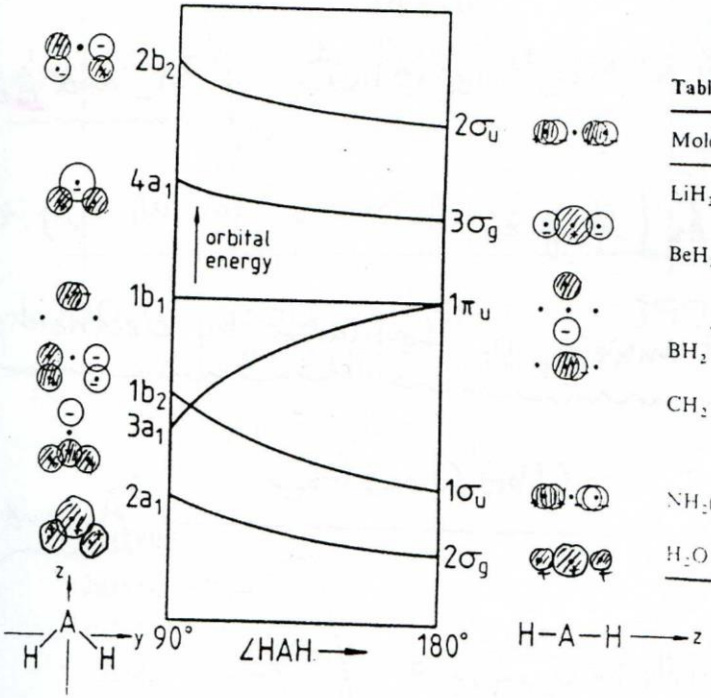


Figure 7.31 Walsh MO diagram for AH_2 molecules.

Table 7.8 Ground and excited configurations of some AH_2 molecules.

Molecule	Configuration	State	∠HAH
LiH_2	$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^1$	$\tilde{X}^2\Sigma_u^+$	180°(?)
	$(1a_1)^2(2a_1)^2(3a_1)^1$	$\tilde{A}^2A_1$	<180°(?)
BeH_2	$(1\sigma_g)^2(2\sigma_g)^2(1\sigma_u)^2$	$\tilde{X}^1\Sigma_g^+$	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°
	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^1$	$\tilde{X}^3B_1$	136
		$\tilde{b}^1B_1$	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°)
	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$	$\tilde{A}^2A_1$	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

1s − Pz − 1s

−1s + 2s − 1s

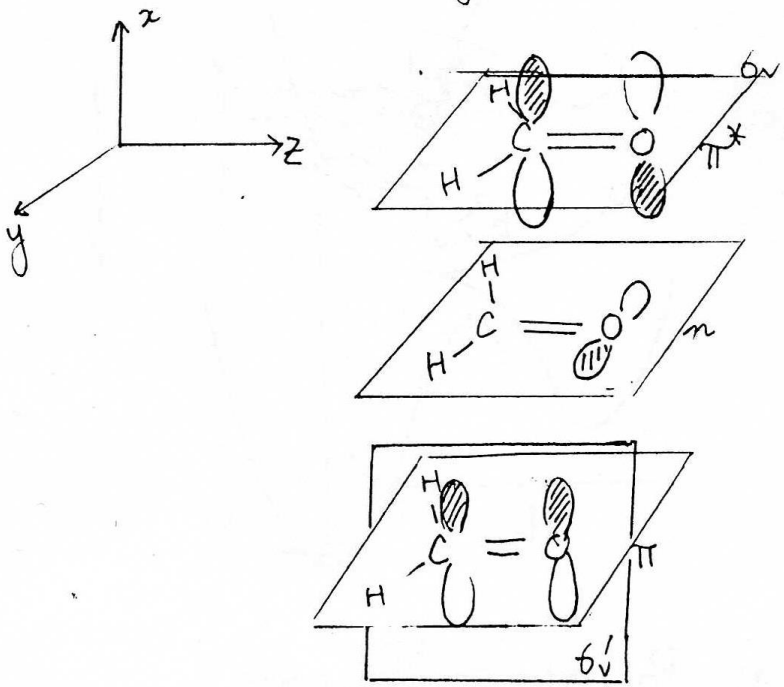
1s + Py + 1s

1s + Px + 1s

1s + Pz − 1s

1s + 2s + 1s

7.3.1.2. Formaldehyde (H_2CO)



C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z
A_2	1	1	−1	−1	
B_1	1	−1	1	−1	x
B_2	1	−1	−1	1	y
π	2	−2	−2	2	$\rightarrow 1b_2$
π^*	2	−2	−2	2	$\rightarrow 2b_2$
n	1	−1	1	−1	$\rightarrow 2b_1$

Ground state Configuration ; $\cdots (1b_2)^2 (2b_1)^2$ (π, n)

π^*
n
π

$X\,^1A_1$

Excited state Configuration ; $B_1 \times B_2$

a) $n\pi^*$ state $\begin{pmatrix} \uparrow \pi^* \\ \uparrow n \\ \downarrow\uparrow \pi \end{pmatrix}$; $\cdots (1b_2)^2 (2b_1)^1 (2b_2)^1$ $\therefore$ $^3A_2$ and $^1A_2$

However, $\mu_{if} \propto \langle A_2 | (x, y, z) | A_1 \rangle = 0$ for all x, y, z

Therefore, $n\pi^*$ transition is forbidden by electric dipole

b) $\pi\pi^*$ state $\begin{pmatrix} \uparrow \pi^* \\ \downarrow\uparrow n \\ \uparrow \pi \end{pmatrix}$; $\cdots (1b_2)^1 (2b_1)^2 (2b_2)^1$ $\therefore$ $^3A_1$ and $^1A_1$

$\mu_{if} \propto \langle A_1 | (x, y, z) | A_1 \rangle \neq 0$ for z

Therefore, $\pi\pi^*$ transition is allowed by electric dipole and polarized along C=O bond.

Typically $\varepsilon_{\pi\pi^*} = 10{,}000 \sim 50{,}000\ cm^{-1} M^{-1}$

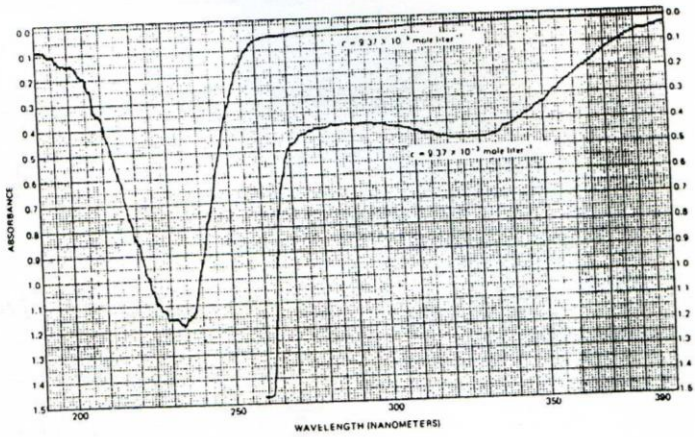
$\varepsilon_{n\pi^*} = 100 \sim 500\ cm^{-1} M^{-1}$

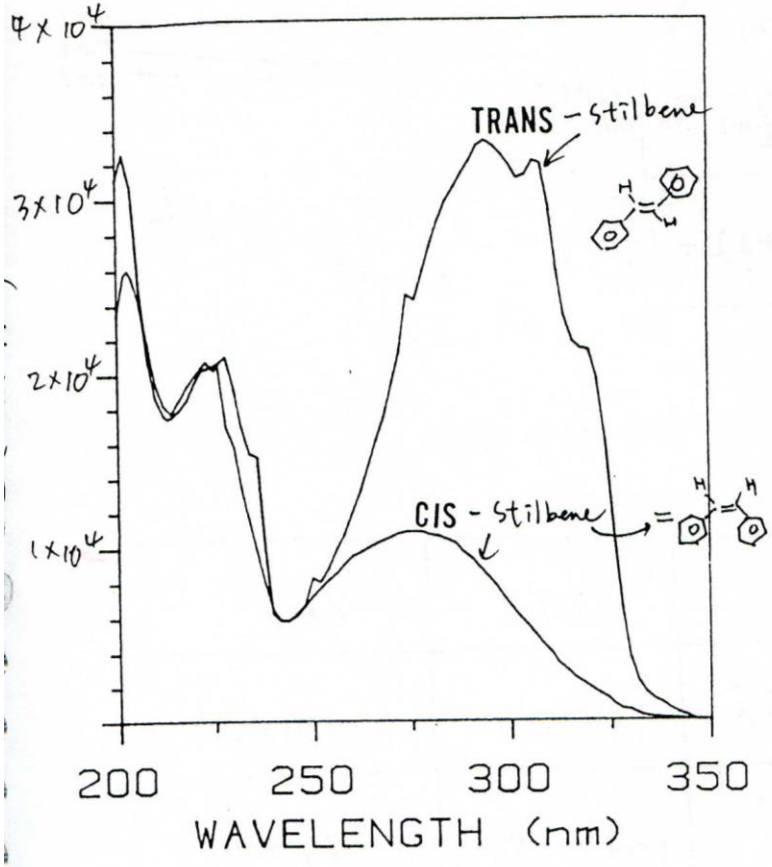
($n\pi^*$, $\pi\pi^*$ 의 예들)

$CH_3\overset{O}{\overset{\|}{C}}CH_3$ 의 경우 $\lambda_{\pi\pi^*} \sim 180nm$, $\lambda_{n\pi^*} \sim 280\ nm$.

$(CH_3)_2C=CH\overset{O}{\overset{\|}{C}}CH_3$ 의 경우 $\lambda_{\pi\pi^*} \sim 235nm$

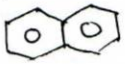
$\lambda_{n\pi^*} \sim 355nm$



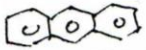


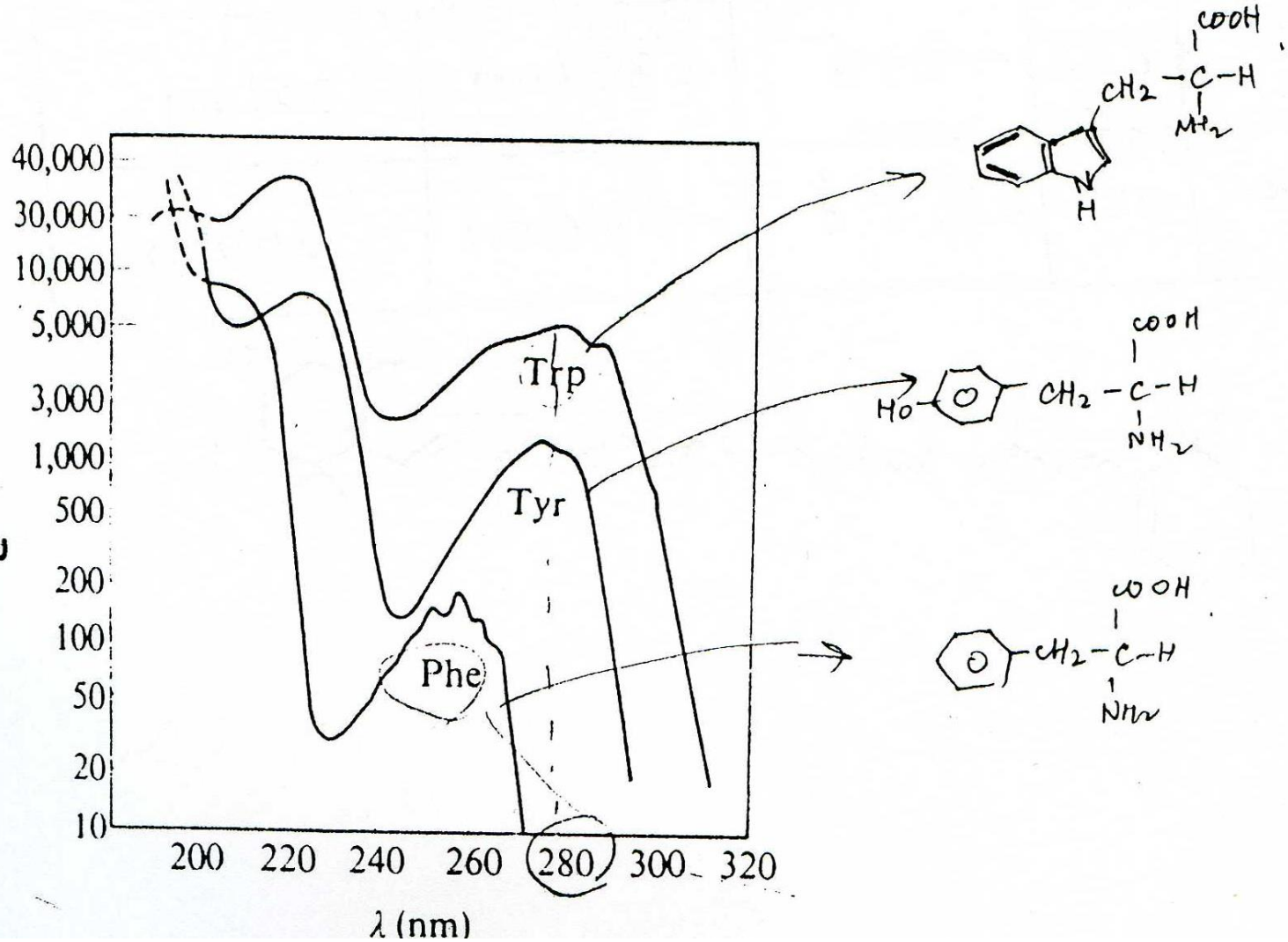
Benzene 의 경우 $\lambda_{\pi\pi^*} \sim 255nm$

Napthene 의 경우. $\lambda_{\pi\pi^*} \sim 310nm$



Anthracene 의 경우. $\lambda_{\pi\pi^*} \sim 375nm$



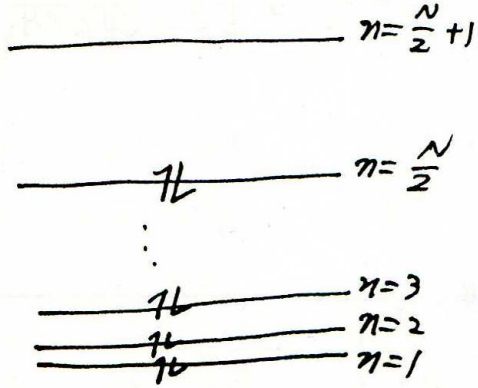

40,000
30,000
10,000
5,000
3,000
1,000
500
200
100
50
20
10
ε
Trp
Tyr
Phe
200
220
240
260
280
300
320
λ (nm)
COOH
CH2
C
H
NH2
H
HO
COOH
CH2
C
H
NH2
COOH
CH2
C
H
NH2

* particle in-a-box model for conjugated double bond

$R(CH{=}CH)_m R'$

1-dimensional particle in-a-box 에서

$$E_n = \frac{n^2 h^2}{8 m_e a^2} \quad (n = 1, 2, 3, \cdots)$$



분자가 N개의 π-전자를 가지고 있다면

$$\psi_{\frac{N}{2}} \rightarrow \text{HOMO}, \quad \psi_{\frac{N}{2}+1} \rightarrow \text{LUMO}$$

$$\Delta E = E_{\frac{N}{2}+1} - E_{\frac{N}{2}} = \frac{h^2}{8 m_e a^2}\left\{\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right\} = \frac{h^2(N+1)}{8 m_e a^2} = h\frac{c}{\lambda}$$

$$\therefore \lambda = \frac{8 m_e a^2 c}{h(N+1)}$$

Compound	N	a	λ_{calc}	λ_{exp}
Butadiene	4	~5.35 Å	~210 nm	217 nm
hexa-1,3,5-triene	6	~7.0 Å	~240 nm	244 nm
Octa-1,3,5,7-tetracene	8	~9.5 Å	~331 nm	303 nm
β-carotene	22	~17.5 Å	~440 nm	450 nm

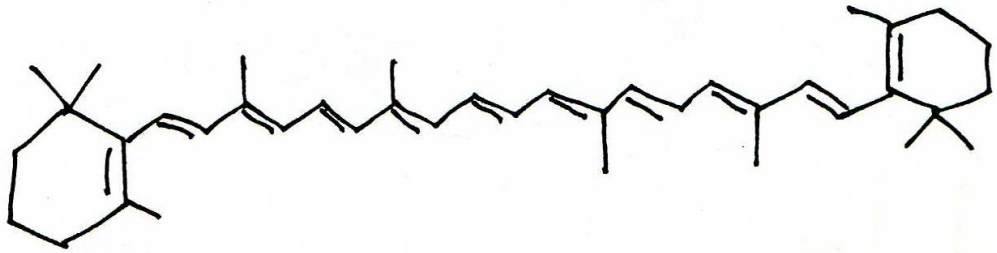
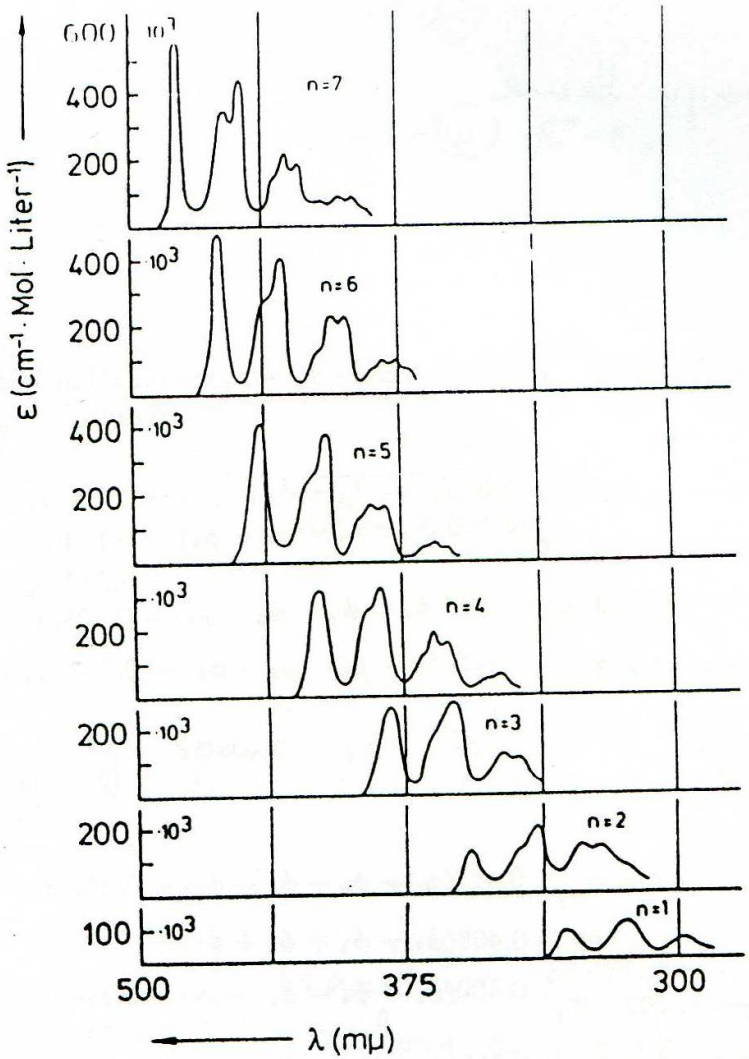


Fig. 14.22. Absorption spectra (long-wavelength part, lowest electronic transitions) of linear diphenyl polyenes, C_6H_5–(CH=CH)$_n$–C_6H_5 in solution at −196 °C, with n = 1 to 7. The absorption belongs to the polyene chain, –(CH=CH)$_n$, and can be understood to a good approximation on the basis of a model with an electron gas which is free to move along the chain. [After K.W. Hausser, R. Kuhn, and A. Smakula, Z. phys. Chem. B29, 371 (1935)]



C_6H_5–(CH=CH)$_n$–C_6H_5 at −196 °C

$n = 1$ to 7

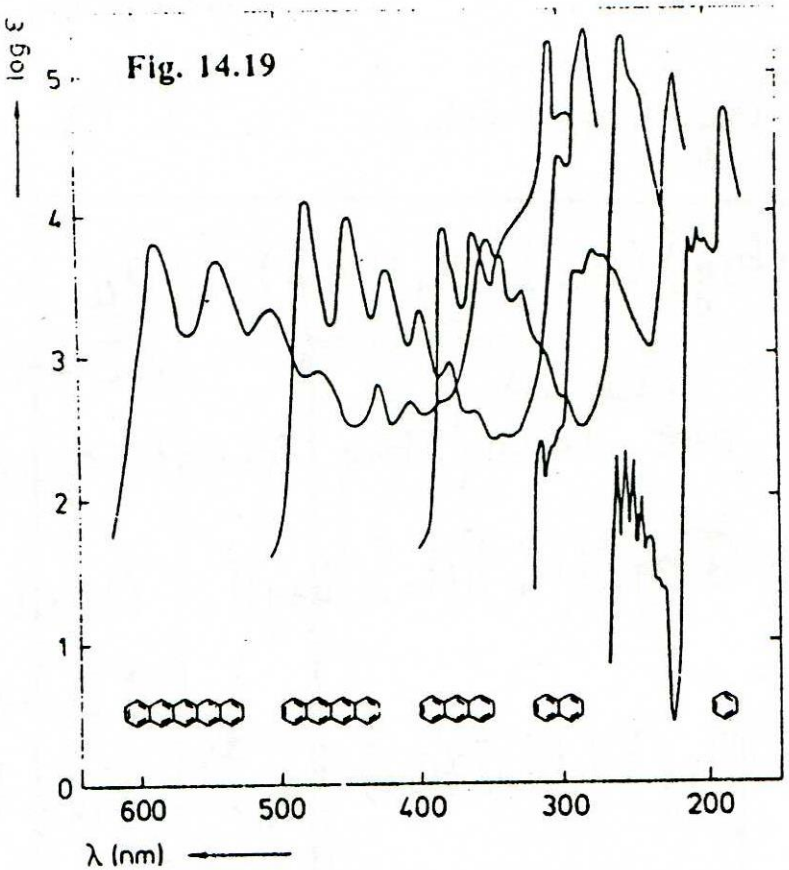


Fig. 14.19

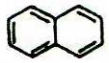
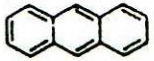
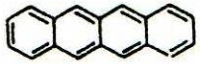
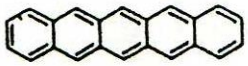
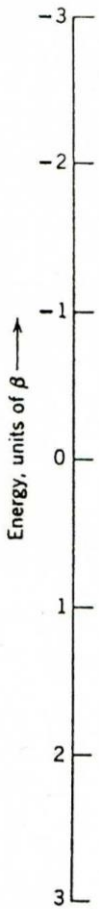
Molecule		Absorption
Benzene		2550 Å
Naphthaline		3150 Å
Anthracene		3800 Å
Tetracene		4800 Å
Pentacene		5800 Å

Fig. 14.20

* Napthalene의 경우

Hückel MO & Energy level (참고서적, Cotton, Chemical Applications of Group Theory)



$B_{3g}^{(3)}$ −2.303 $\psi_{10} = 0.301(\phi_1 - \phi_4 - \phi_5 + \phi_8) - 0.231(\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.461(\phi_9 - \phi_{10})$

$A_u^{(2)}$ −1.618 $\psi_9 = 0.263(\phi_1 - \phi_4 + \phi_5 - \phi_8) - 0.425(\phi_2 - \phi_3 + \phi_6 - \phi_7)$

$B_{1u}^{(3)}$ −1.303 $\psi_8 = 0.400(\phi_1 + \phi_4 + \phi_5 + \phi_8) - 0.174(\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.347(\phi_9 + \phi_{10})$

$B_{3g}^{(2)}$ −1.000 $\psi_7 = 0.408(\phi_2 - \phi_3 - \phi_6 + \phi_7) - 0.408(\phi_9 - \phi_{10})$

$B_{2g}^{(2)}$ −0.618 $\psi_6 = 0.425(\phi_1 + \phi_4 - \phi_5 - \phi_8) - 0.263(\phi_2 + \phi_3 - \phi_6 - \phi_7)$

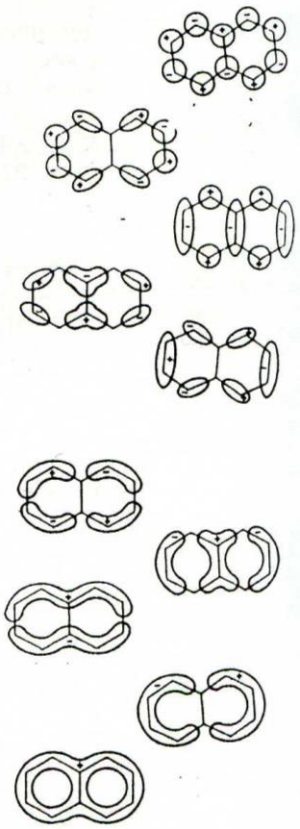
$A_u^{(1)}$ 0.618 $\psi_5 = 0.425(\phi_1 - \phi_4 + \phi_5 - \phi_8) + 0.263(\phi_2 - \phi_3 + \phi_6 - \phi_7)$

$B_{1u}^{(2)}$ 1.000 $\psi_4 = 0.408(\phi_2 + \phi_3 + \phi_6 + \phi_7) - 0.408(\phi_9 + \phi_{10})$

$B_{3g}^{(1)}$ 1.303 $\psi_3 = 0.400(\phi_1 - \phi_4 - \phi_5 + \phi_8) + 0.174(\phi_2 - \phi_3 - \phi_6 + \phi_7) + 0.347(\phi_9 - \phi_{10})$

$B_{2g}^{(1)}$ 1.618 $\psi_2 = 0.263(\phi_1 + \phi_4 - \phi_5 - \phi_8) + 0.425(\phi_2 + \phi_3 - \phi_6 - \phi_7)$

$B_{1u}^{(1)}$ 2.303 $\psi_1 = 0.301(\phi_1 + \phi_4 + \phi_5 + \phi_8) + 0.231(\phi_2 + \phi_3 + \phi_6 + \phi_7) + 0.461(\phi_9 + \phi_{10})$



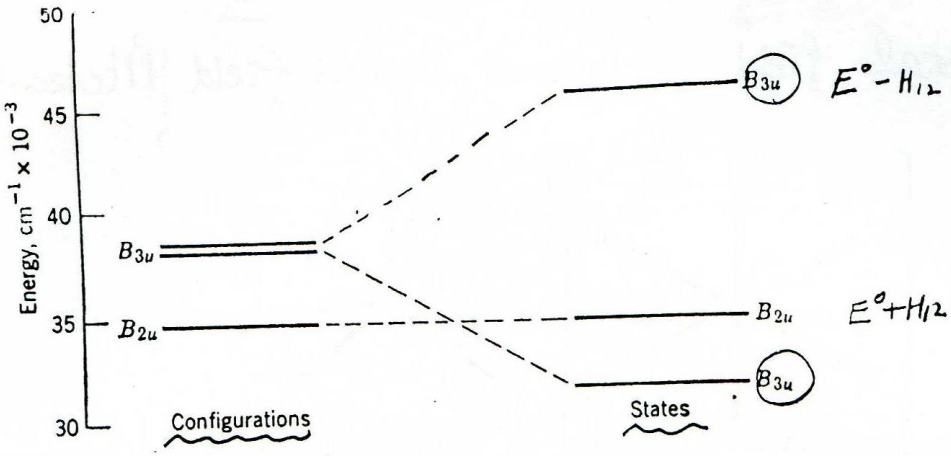
	Configuration	Symmetry
The ground state :	$\cdots(b_{1u})^2(b_{2g})^2(b_{3g})^2(b'_{1u})^2(a_u)^2$	$\tilde{X}\ ^1A_g$.
The first excited state.	$\cdots(b_{1u})^2(b_{2g})^2(b_{3g})^2(b'_{1u})^2(a_u)^1(b_{2g})^1$	$a_u \times b_{2g} = \underline{B_{2u}}$ $(\Delta E = -1.236\beta)$

(This is not really the lowest excited states)

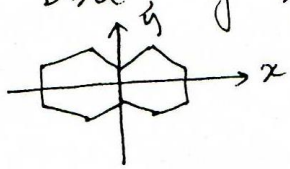
The higher excited state	$\cdots(b_{1u})^2(b_{2g})^2(b_{3g})^2(b'_{1u})^2(a_u)^1(b_{3g})^1$	$a_u \times b_{3g} = \underline{B_{3u}}$ $(\Delta E = -1.618\beta)$
	$\cdots(b_{1u})^2(b_{2g})^2(b_{3g})^2(b'_{1u})^1(a_u)^2(b_{2g})^1$	$b_{1u} \times b_{2g} = \underline{B_{3u}}$ $(\Delta E = -1.618\beta)$

* Configuration Interation.

$$\begin{vmatrix} E^0 - E & H_{12} \\ H_{21} & E^0 - E \end{vmatrix} = 0 \qquad H_{12} = \int \psi_{B_{3u}} \hat{\mathcal{H}} \cdot \psi'_{B_{3u}} \, d\tau$$



x spans as B_{3u}, y spans as B_{2u}, z spans as B_{1u}. in [



$\tilde{A}\,^1B_{3u} \leftarrow \tilde{X}\,^1A_{1g}$ is the lowest energy transition and is x-polarized.

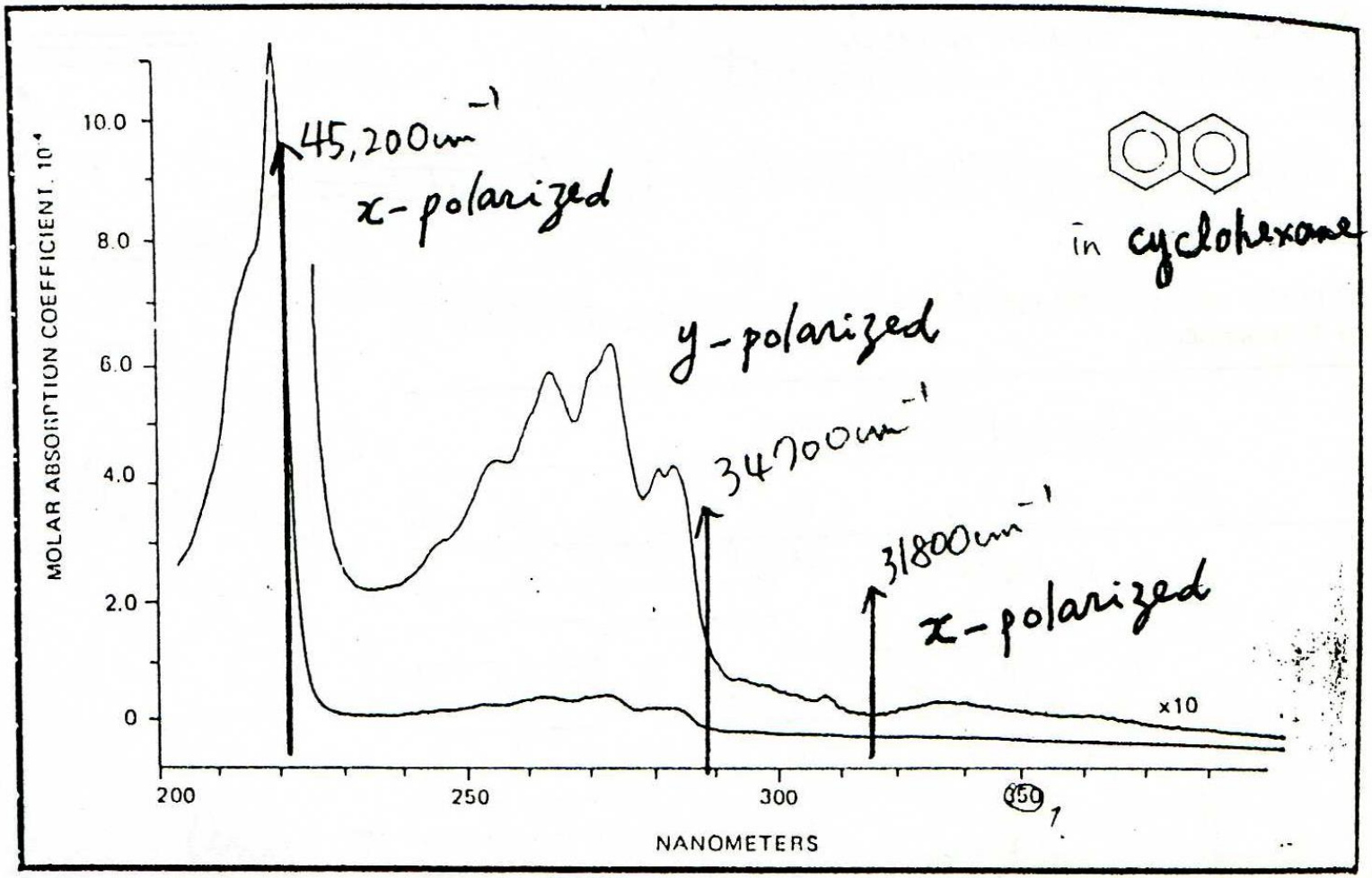
* long axis polarized 31,800 cm^{-1}

$\tilde{B}\,^1B_{2u} \leftarrow \tilde{X}\,^1A_{1g}$ is the 2nd lowest energy transition and is y-polarized

* short axis polarized 34,700 cm^{-1}

$\tilde{C}\,^1B_{3u} \leftarrow \tilde{X}\,^1A_{1g}$ is the 3rd lowest energy transition and is x polarized

* long axis polarized 45,200 cm^{-1}


MOLAR ABSORPTION COEFFICIENT, 10^4
10.0
8.0
6.0
4.0
2.0
0
200
250
300
350
NANOMETERS
45,200 cm^{-1}
x-polarized
y-polarized
34700 cm^{-1}
31800 cm^{-1}
x-polarized
x10
in cyclohexane

7.3.1.4 Crystal field and ligand field Molecular orbitals

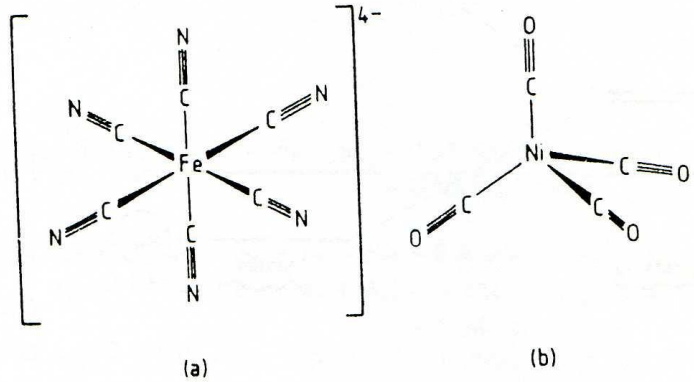


Figure 7.37 (a) Octahedral $[Fe(CN)_6]^{4-}$ and (b) tetrahedral $Ni(CO)_4$.

7.3.1.4 (a). Crystal field Theory

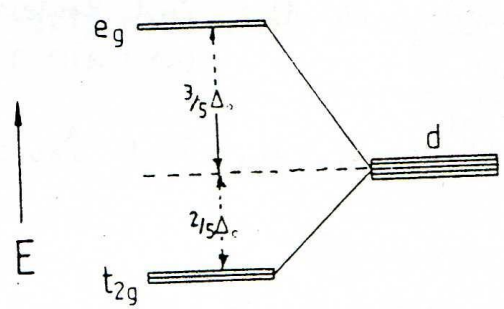
① Treat ligand as a negative point charge.

② Interaction between central d orbital with ligands is relatively weak

1) Octahedral Ligand Geometry

d_{z^2}, $d_{x^2-y^2}$ are destabilized.

d_{xy}, d_{yz}, d_{zx} are stabilized.



2). Tetragonal Ligand Geometry

d_{z^2}, $d_{x^2-y^2}$ are stabilized.

d_{xy}, d_{yz}, d_{zx} are destabilized

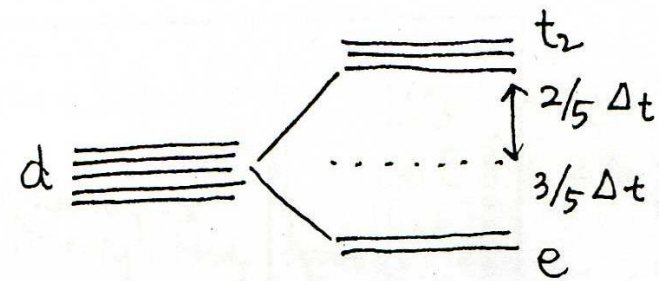


Table 7.9 Symmetry species of orbitals resulting from the splitting of *d* orbitals by various ligand arrangements.

Point group	*d* orbitals				
	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{yz}	d_{xz}
O_h	← e_g →		← t_{2g} →		
T_d	← e →		← t_2 →		
D_{3h}	a_1'	← e' →		← e'' →	
D_{4h}	a_{1g}	b_{1g}	b_{2g}	← e_g →	
$D_{\infty h}$	σ_g^+	← δ_g →		← π_g —	
C_{2v}	a_1	a_1	a_2	b_2	b_1
C_{3v}	a_1	a_1	a_2	← e →	
C_{4v}	a_1	b_1	b_2	← e →	
D_{2d}	a_1	b_1	b_2	← e →	
D_{4h}	a_1	← e_2 →		← e_3 →	

Sc Ti V Cr Mn Fe Co Ni Cu Zn

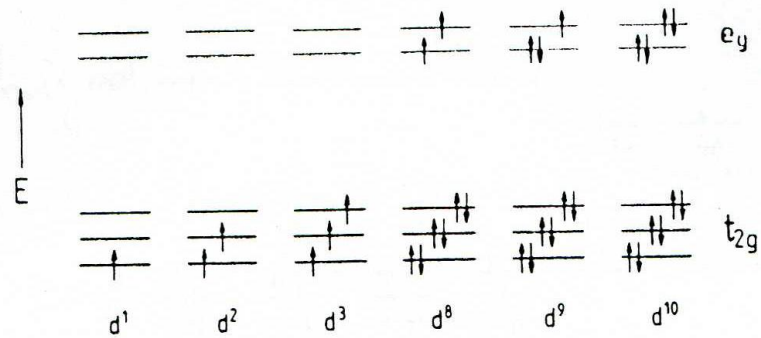


Figure 7.39 Electron configurations in d^1, d^2, d^3, d^8, d^9, and d^{10} octahedral complexes.

(electron fed up 의 단순한 경우들) $d^1 \sim d^3$, $d^8 \sim d^{10}$

① $[Ti(H_2O)_6^{3+}]$ 의 경우,

		configuration	Symmetry
	ground state.	$(t_{2g})^1$	$\tilde{X}\,^2T_{2g}$
	1st excited state	$(e_g)^1$	$\tilde{A}\,^2E_g$

However $\tilde{X}\,^2T_{2g} \leftarrow \tilde{A}\,^2E_g$ is forbidden since.

$T_{2g} \times E_g = T_{1g} + T_{2g}$ and (x, y, z) spans T_{1u} in O_h

However, $\tilde{A} \leftarrow \tilde{X}$ transition is observed weakly at about 500 nm due to vibronic interaction

② $[Cu(H_2O)_6]^{2+}$ 의 경우

	Configuration	Symmetry
Ground state	$(t_{2g})^6(e_g)^3$	$\tilde{X}\,^2E_g$
1st excited state	$(t_{2g})^5(e_g)^4$	$\tilde{A}\,^2T_{2g}$

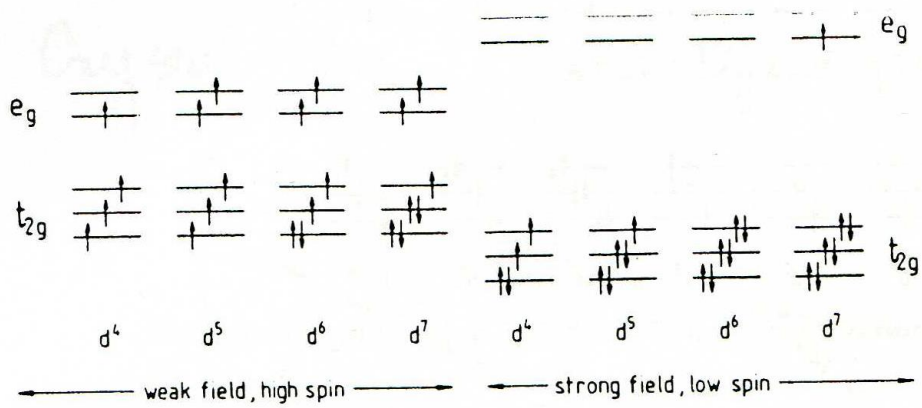
Again, $\tilde{A}\,^2T_{2g} \leftarrow \tilde{X}\,^2E_g$ is forbidden

However, $\tilde{A} \leftarrow \tilde{X}$ transition is observed weakly at 790nm and is responsible for the blue color of aqueous Cu^{2+} solution.

③ $[V(H_2O)_6]^{3+}$,

	Configuration	Symmetry
Ground state	$(t_{2g})^2$	$^3T_{1g} + {}^1A_{1g} + {}^1E_g + {}^1T_{2g}$
1st excited state	$(t_{2g})^1(e_g)^1$	$^{1,3}T_{1g} + {}^{1,3}T_{2g}$

Any Transitions are forbidden, but weak vibronic transitions are observed at 500nm ($\tilde{A}\,^3T_{2g} \leftarrow \tilde{X}\,^3T_{2g}$) and at 400 nm ($\tilde{B}\,^3T_{1g} \leftarrow \tilde{X}\,^3T_{2g}$)



(electron fed up 의 꽉 차 아픈 경우들) $d^4 \sim d^7$ electrons

④ $[Cr(H_2O)_6]^{2+}$ weak field, high spin

ground state 의 configuration ; $(t_{2g})^3(e_g)^1$

ground state 의 symmetry ; $(^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}) \times e_g$.

$$= {}^{3,5}E_g + {}^{1,3}A_{1g} + {}^{1,3}A_{2g} + {}^{1,3}E_g + {}^{1,3}T_{1g} + {}^{1,3}T_{2g} + {}^{1,3}T_{1g} + {}^{1,3}T_{2g}$$

$\tilde{X}\,{}^5E_g$ is the lowest ground state

1st excited state의 configuration $(t_{2g})^2(e_g)^2$

" symmetry ; many states are possible but $\tilde{A}\,^5T_{2g}$ is only quintet state.

$\tilde{A}\,^5T_{2g} \leftarrow \tilde{X}\,^5E_g$ is forbidden transition but weakly observed at about 700 nm.

⑤ $[Fe(CN)_6]^{4-}$ or $[Co(NH_3)_6]^{3+}$ strong field, low spin

	Configuration	Symmetry
Ground state	$(t_{2g})^6$	$\tilde{X}\,^1A_{1g}$
1st excited state	$(t_{2g})^5(e_g)^1$	$^{1,3}T_{1g} + {}^{1,3}T_{2g}$.

7.3.1.4 (b) Ligand Field Theory.

① Relatively strong interaction between ligands and central d orbital of metal.

② MOs of the ligand must be considered.

< σ MO의 경우 >.

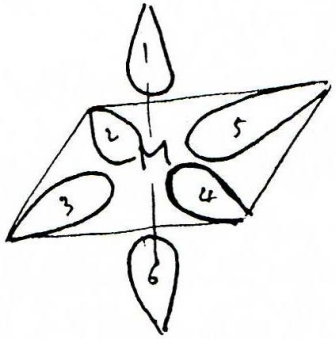
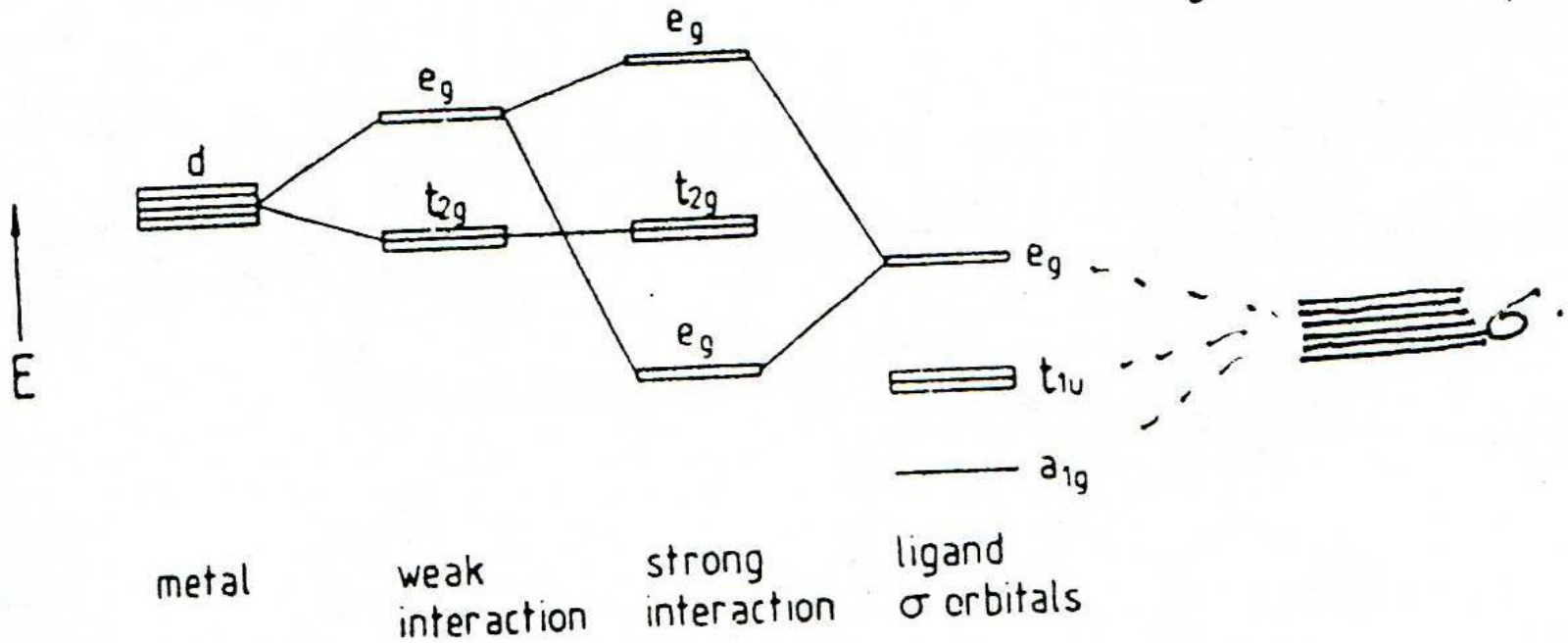


Table 7.10 Classification of σ ligand orbitals in various point groups.

Point group	σ orbital symmetry species
O_h	$a_{1g} + e_g + t_{1u}$ (in octahedral ML_6)
T_d	$a_1 + t_2$ (in tetrahedral ML_4)
D_{3h}	$2a_1' + a_2'' + e'$ (in trigonal bipyramidal ML_5)
D_{4h}	$a_{1g} + b_{1g} + e_u$ (in square planar ML_4)
	$2a_{1g} + a_{2u} + b_{1g} + e_u$ (in *trans*-octahedral ML_4L_2')
$D_{\infty h}$	$\sigma_g + \sigma_u$ (in linear ML_2)
C_{2v}	$a_1 + b_2$ (in non-linear ML_2)
	$2a_1 + b_1 + b_2$ (in tetrahedral ML_2L_2')
	$3a_1 + a_2 + b_1 + b_2$ (in *cis*-octahedral ML_4L_2')
C_{3v}	$2a_1 + e$ (in tetrahedral ML_3L')
	$2a_1 + 2e$ (in all-*cis*-octahedral ML_3L_3')
C_{4v}	$2a_1 + b_1 + e$ (in square pyramidal ML_4L')
	$3a_1 + b_1 + e$ (in octahedral ML_5L')
D_{2d}	$2a_1 + 2b_2 + 2e$ (in dodecahedral ML_8)
D_{4d}	$a_1 + b_2 + e_1 + e_2 + e_3$ (in square antiprism ML_8)

Octahedral Ligand Geometry OHK



7.3.2. Electronic and Vibronic Selection Rules.

① Spin Selection Rule.

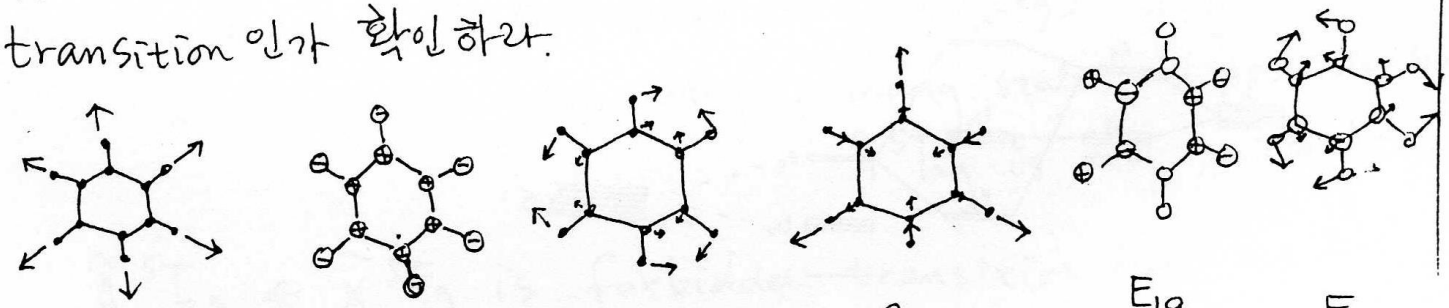
Conservation of spin selection ($\Delta S = 0$) are less important as heavier atoms are involved. For example, in benzene singlet $\leftrightarrow$ triplet transition is extremely weak but much more intense in iodobenzene.

② Transition dipolemoment in Vibronic Transitions.

$$\mu_{ev} = \int \psi_{ev}'^{*} \mu \psi_{ev} \, d\tau_{ev} = \int \psi_e'^{*} \psi_v'^{*} \mu \psi_e \psi_v \, d\tau_{ev}$$

The transition is allowed if $\Gamma(\psi_e' \psi_v') \times (x \text{ or } y \text{ or } z) \times \Gamma(\psi_e \psi_v)$ is totally symmetric.

예). Benzene 의 vibrational, electronic ground state 에서 1st excited electronic state 의 다음 vibration은 allowed transition 인가 확인하라.



A_{1g} A_{2u} B_{2u} B_{1u} E_{1g} E_{2g}

풀이). Benzene 의 vibrational electronic ground state 는 A_{1g} symmetry

" 1st excited electronic state 는 B_{2u}

$B_{2u} \times A_{1g} = B_{2u}$

$B_{2u} \times A_{2u} = B_{1g}$

$B_{2u} \times B_{2u} = A_{1g}$

$B_{2u} \times B_{1u} = A_{2g}$

$B_{2u} \times E_{1g} = E_{2u}$

$B_{2u} \times E_{2g} = E_{1u}$

(x, y) spans as E_{1u}, and z spans as A_{2u} in D_{6h}

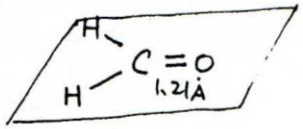
Therefore only E_{2g} vibration among the above 6 vibrations in the B_{2u} state is allowed from vibrational electronic ground state.

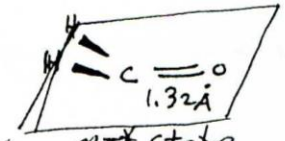
7.3.4. Vibrational coarse structure.

a). Progressions in totally symmetric vibrations

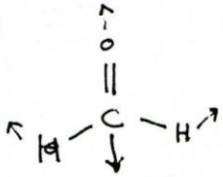
Vibrational progressions are strong when the vibrational coordinate involves big geometry change between ground electronic state and excited electronic state

예).

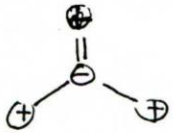




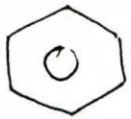
$n\pi^*$ state.



and



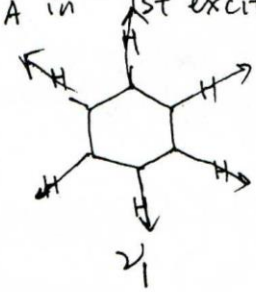
shows a strong vibrational progression



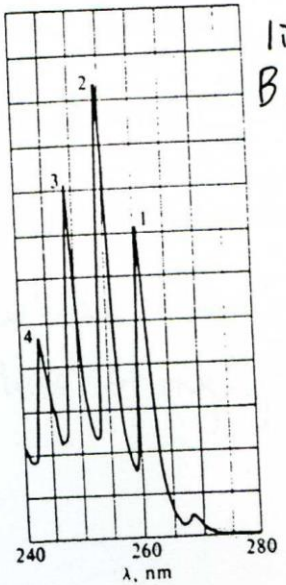
→ 1.397 Å in ground electronic state

1.434 Å in 1st excited electronic state.

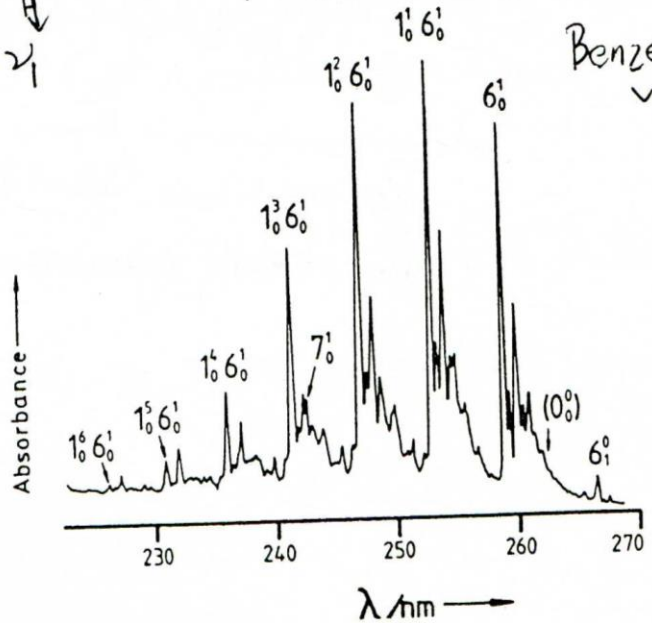
Benzene



shows a strong vibrational progression.



liquid Benzene



Benzene vapor.

Figure 7.42 Low resolution $\tilde{A}^1B_{2u} - \tilde{X}^1A_{1g}$ absorption spectrum of benzene.

7.3.4.2.(b). Non-totally symmetric vibrations.

Many vibronic transitions involving non-totally symmetric vibrations are allowed by symmetry, but only few has significant intensity. Why?

$\Rightarrow$ Herzberg-Teller distortion (Breakdown of Franck Condon Princip

$$\mu_{ev} = \iint \psi_e^{*\prime} \psi_v^{*\prime} \mu_e \psi_e \psi_v \, d\tau_e \, d\tau_v$$

$$\Rightarrow \left[\int \psi_e^{*\prime} \mu_e \psi_e \, d\tau_e \right] \left[\int \psi_v^{*\prime} \psi_v \, d\tau_v \right]$$

Franck-Condon approximation (Separation of variab was possible only whe electronic motion is m faster than nuclear motion)

$$\mu = \iint \psi_e'^{*} \psi_v'^{*} \left[(\mu_e)_{eq} + \sum_i \left(\frac{\partial \mu_e}{\partial Q_i} \right)_{eq} Q_i \right] \psi_e \psi_v \, d\tau_e \, d\tau_v .$$

$$= \left[\int \psi_e'^{*} \mu_e \psi_e \, d\tau_e \right] \left[\int \psi_v'^{*} \psi_v \, d\tau_v \right] \leftarrow \text{Franck Condon Factor}$$

$$+ \sum_i \frac{\partial}{\partial Q_i} \left[\int \psi_e'^{*} \mu_e \psi_e \, d\tau_e \right]_{eq} \left[\int \psi_v'^{*} Q_i \psi_v \, d\tau_v \right]$$

Responsible for transition intensity of non-totally symmetric vibrations.

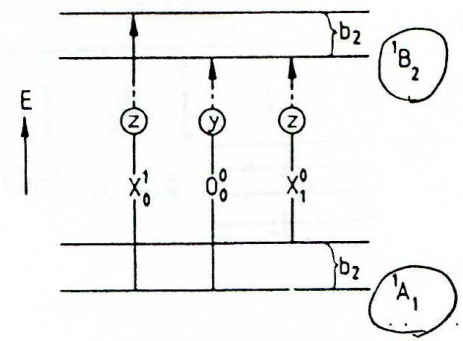
(examples)

① Chlorobenzene (C_{2v})

There are 10 b_2 vibrations. And transitions ground vibrational and electionic state to b_2 vibration in the 1st excited state is allowed by symmetry

$$B_2 \times B_2 \times A_1 \times A_1 = A_1 = \Gamma(z)$$

electronic ground state
vibrational ground state
electronic excited state
vibrational excited state.



But only ν_{29} vibration has significant intensity and the other 9 b_2 vibrations are not observed, because only $\frac{\partial}{\partial Q_i}\left[\int \psi_e^{*\prime} \mu_e \psi_e\right]_{eq}$ much greater than the corresponding terms for all the other b_2 vibrations

② Benzene of $\tilde{A}\,^1B_{2u} \leftarrow \tilde{X}\,^1A_{1g}$

0_0^0 band is symmetry forbidden, which means $\int \psi_e^{*\prime} \mu_e \psi_e \, d\tau_e = 0$

Therefore, $\mu_{ev} = \sum_i \frac{\partial}{\partial Q_i} \left[\int \psi_e^{*\prime} \mu_e \psi_e \, d\tau_e \right]_{eq} \left[\int \psi_v^* Q_i \psi_v \, d\tau_v \right]$ (i.e. Franck Condon term is neglected).

All transition intensity derives from non-Franck-Condon term and most of it through e_{2g} vibration ν_6. Since.

$B_{2u} \times e_{2g} = E_{1u} = \Gamma(x, y)$.

Only vibronic transitions involving ν_6 is strong since. $\frac{\partial}{\partial Q_6} \left[\psi_e^{*\prime} \mu_e \psi_e \, d\tau_e \right]$ is large, while other e_{2g} vibrations, ν_7, ν_8, ν_9 vibrations are much less strongly active.