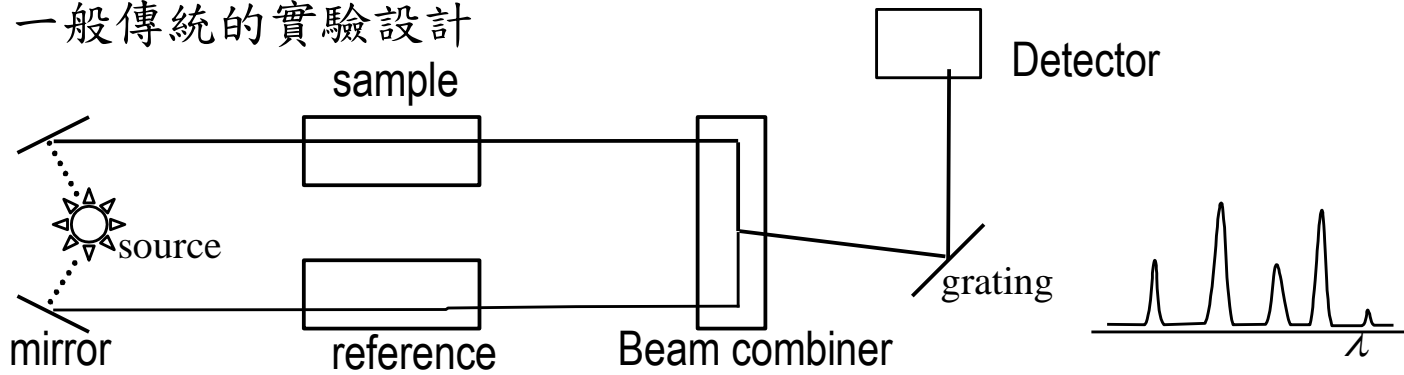# Chapter 12
Spectroscopy : Rotational and vibrational spectra

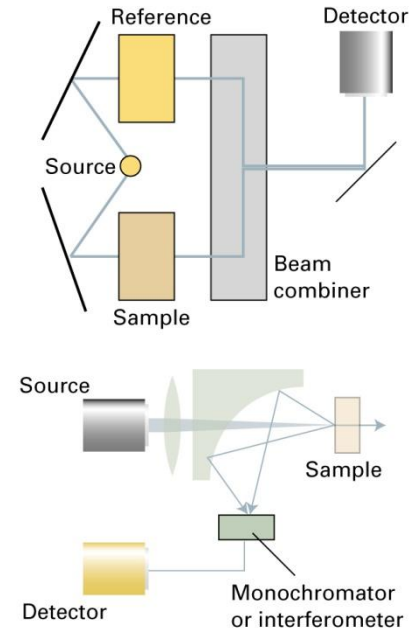量測光譜的實驗設計:

一般傳統的實驗設計
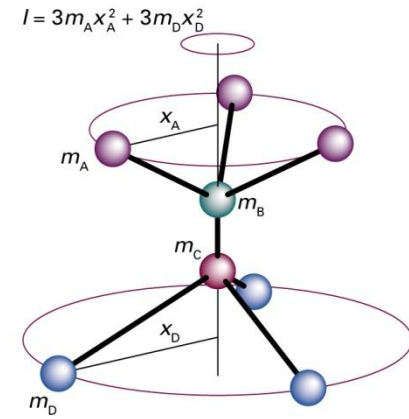
設備優點：設備簡單，裝置容易，數據直接，分析容易

缺點：對於比較弱的吸收訊號，不易觀察，resolution 不易提高
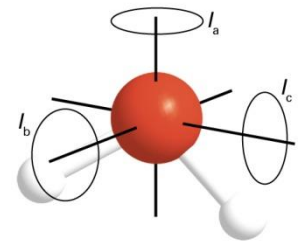
Pure rotation spectra

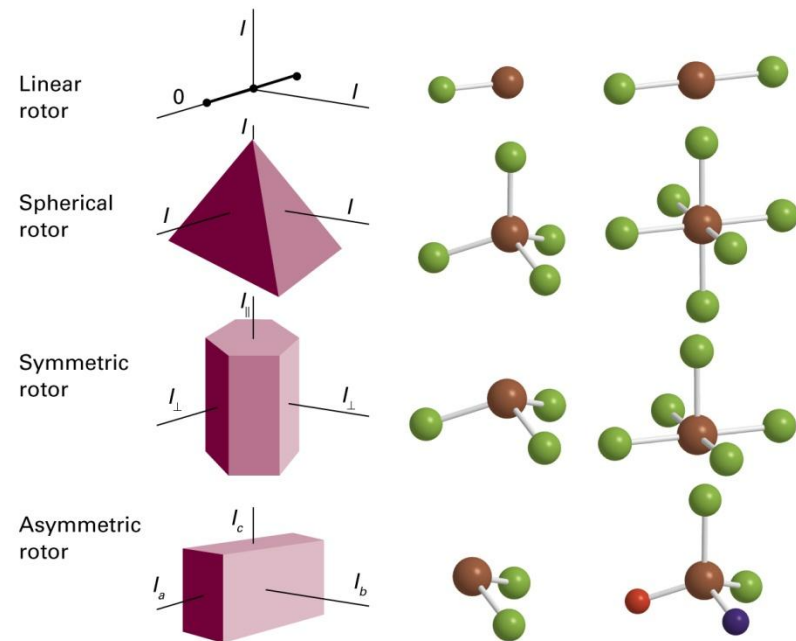因為轉動牽涉到轉動慣量，而分子轉動
慣量與鍵長鍵角有關，所以由轉動光譜
可以得知分子的鍵長鍵角等資訊

$$I = 3m_A x_A^2 + 3m_D x_D^2$$

轉動慣量，I，Moment of inertia …

$$I = \sum_i m_i \, r_i^2$$

r_i：i 粒子與轉軸的垂直距離

假設分子旋轉時，原子間的距離不拉長、不變形
=> 「*rigid rotor*」.

共可分成四種類型：
1. *Spherical rotor* （$I_a = I_b = I_c$）；CH_4, SF_6, SiH_4
2. *Symmetric rotor* （$I_a = I_b \neq I_c$）；NH_3, CH_3Cl, C_6H_6
　　又分為 *Oblate* （$I_a = I_b < I_c$）；C_6H_6, $CHCl_3$, NH_3
　　　　　　Prolate （$I_a = I_b > I_c$）；CH_3Cl
3. *Linear rotor* （$I_a = I_b , I_c = 0$）；CO_2, HCl
4. *Asymmetry rotor* （$I_a \neq I_b \neq I_c$）；H_2O, CH_3OH

1. *Diatomic molecules*
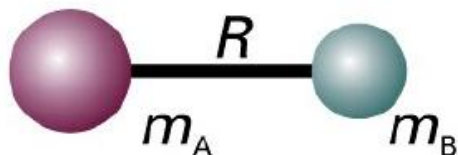
$$I = \mu R^2 \qquad \mu = \frac{m_A m_B}{m}$$

2. *Triatomic linear rotors*
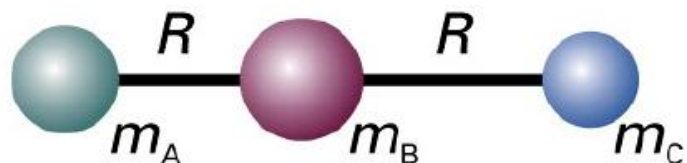
$$I = m_A R^2 + m_C R'^2 - \frac{(m_A R - m_C R')^2}{m}$$

$$I = 2 m_A R^2$$

Linear rotors have one moment of inertia

3. Symmetric rotors
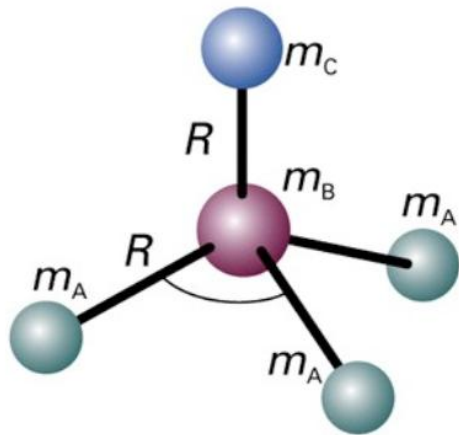
$$I_\| = 2m_A(1 - \cos\theta)R^2$$

$$I_\perp = m_A(1 - \cos\theta)R^2 + \frac{m_A}{m}(m_B + m_C)(1 + 2\cos\theta)R^2$$

$$+ \frac{m_C}{m}\{(3m_A + m_B)R' + 6m_A R[\tfrac{1}{3}(1 + 2\cos\theta)]^{1/2}\}R'$$
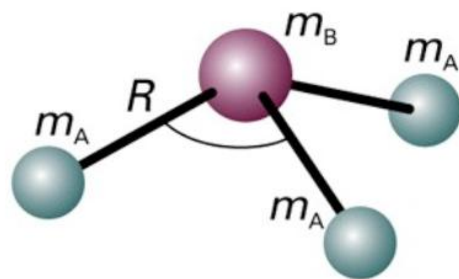
$$I_\| = 2m_A(1 - \cos\theta)R^2$$

$$I_\perp = m_A(1 - \cos\theta)R^2 + \frac{m_A m_B}{m}(1 + 2\cos\theta)R^2$$
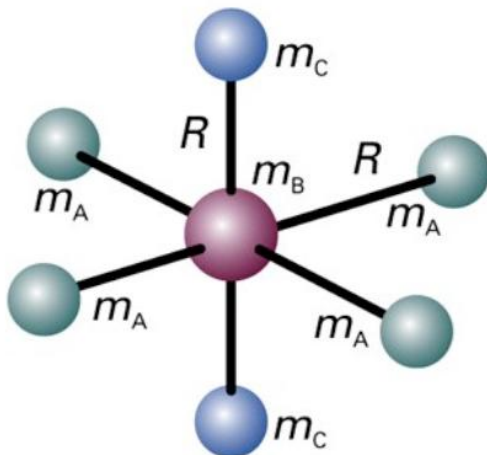
$$I_\| = 4m_A R^2$$

$$I_\perp = 2m_A R^2 + 2m_C R'^2$$

Symmetric rotors have two equal moments of inertia

4. Spherical rotors

$$I = \tfrac{8}{3} m_A R^2$$

$$I = 4 m_A R^2$$

Spherical rotors have three equal moments of inertia

Calculate the moment of inertia of an H_2O molecule around the axis defined by the bisector of the HOH angle (**1**). The HOH bond angle is 104.5° and the bond length is 95.7 pm.
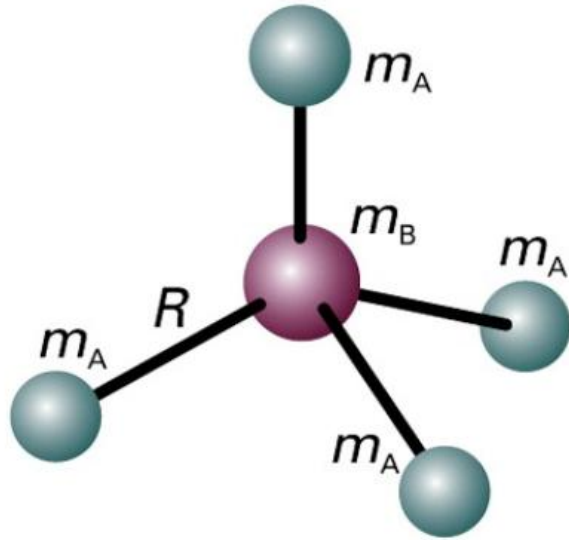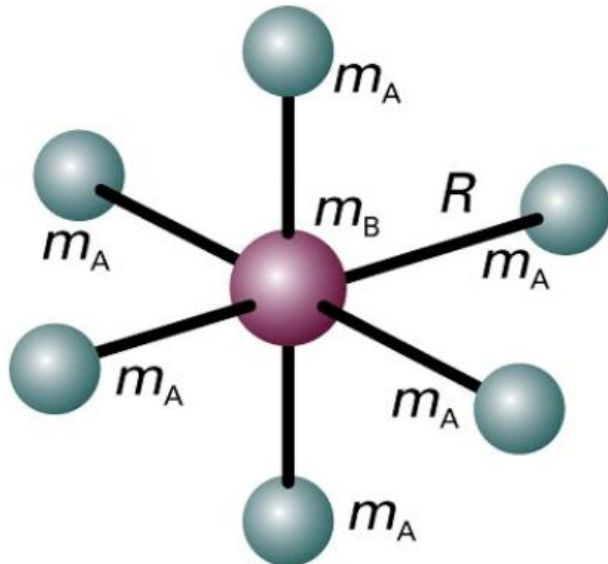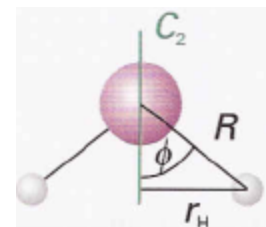

Method According to eqn 13.20, the moment of inertia is the sum of the masses multiplied by the squares of their distances from the axis of rotation. The latter can be expressed by using trigonometry and the bond angle and bond length.

Answer From eqn 13.20,

$$I = \sum_i m_i r_i^2 = m_H r_H^2 + 0 + m_H r_H^2 = 2m_H r_H^2$$

If the bond angle of the molecule is denoted 2ϕ and the bond length is R, trigonometry gives $r_H = R \sin \phi$. It follows that

$$I = 2m_H R^2 \sin^2 \phi$$

Substitution of the data gives

$$I = 2 \times (1.67 \times 10^{-27} \text{ kg}) \times (9.57 \times 10^{-11} \text{ m})^2 \times \sin^2 52.3° = 1.91 \times 10^{-47} \text{ kg m}^2$$

Note that the mass of the O atom makes no contribution to the moment of inertia for this mode of rotation as the atom is immobile while the H atoms circulate around it.

The rotational energy levels：

繞一轉軸a, 以ω_a的角速度轉動時，
其轉動能量:

$$E_a = \frac{1}{2} I_a w_a^2$$

a axis
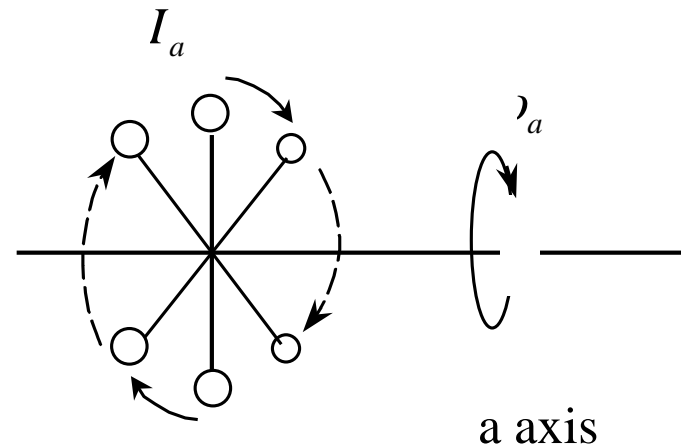
at three rotational axises,

$$E = E_a + E_b + E_c = \frac{1}{2} I_a w_a^2 + \frac{1}{2} I_b w_b^2 + \frac{1}{2} I_c w_c^2$$

當 $I_a = I_b = I_c = I$ (spherical)， $E = \dfrac{J_a^2 + J_b^2 + J_c^2}{2I} = \dfrac{\mathbf{J}^2}{2I}$,

其中$\mathbf{J}^2 = J_a^2 + J_b^2 + J_c^2$

$\mathbf{J}$：magnitude of the total angular momentum

由量子力學觀點,任何轉動體,其magnitude of the angular momentum

$\mathbf{J}^2 = J(J+1)\hbar^2$, or $\mathbf{J} = \sqrt{J(J+1)}\ \hbar$, 其中 J 為 $rotational\ guantum\ number$, $J = 0,1,2,\cdots$

∴ 對 spherical rotor, 其 $E_J = \dfrac{J(J+1)\hbar^2}{2I}$

令 $B = \dfrac{\hbar}{4\pi c I}$, 稱 B為 $rotational\ constant$. 則 $hcB = \dfrac{\hbar^2}{2I}$

則 $E_J = hcBJ(J+1)$, J =0, 1, 2,......

or $\dfrac{E_J}{hc} = BJ(J+1) \rightarrow$ 單位為 cm^{-1} (wave number) or $F(J) = BJ(J+1)$

$F(J) = BJ(J+1)$ 稱rotational quantum number為J的旋轉能量以cm^{-1}為單位。

則separation of adjacent levels is $F(J) - F(J-1) = 2BJ$

separation隨 J 值增加而增大，但光譜圖，
恰相當規則的等線間隔譜圖。(實際上，
分子譜線並非完全等間隔 並非完全rigid rotor)
因為B與I成反比，(由實驗譜線求出B以後，
可求得I，進而得知分子的鍵長及鍵角)。
所以對大的分子而言(I大, 則小B)，
其rotation energy spacing變小，
同時I越大(越轉不動)
其rotation energy相對變小。
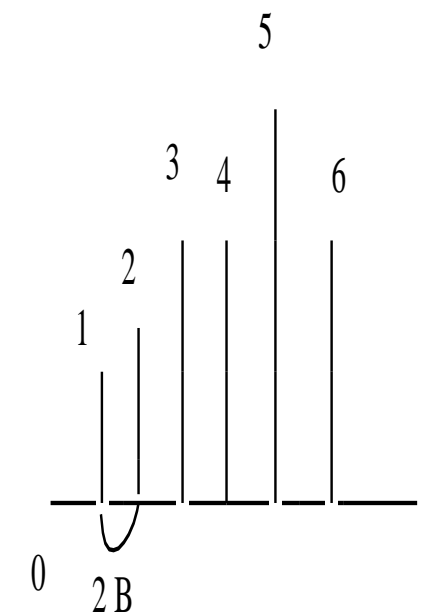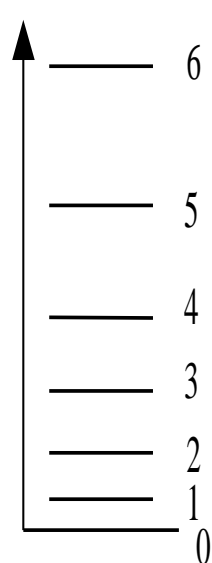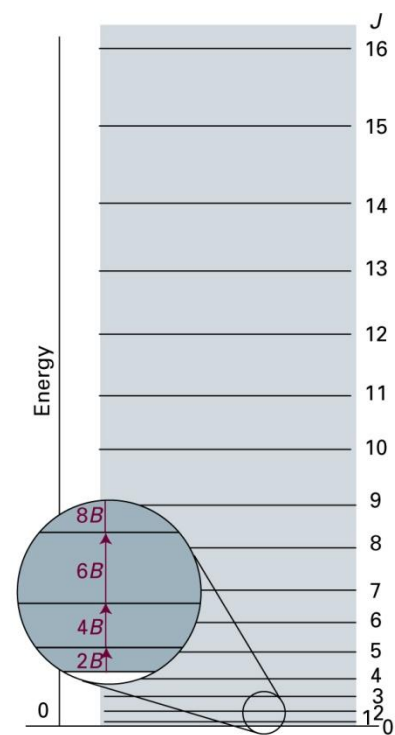
Symmetric rotors：

　　這樣的分子有一principal rotation axis or 稱figure axis。 該轉軸的轉動慣量，特別以 $I_{//}$ 表示.其他另外兩個轉軸相互對等，並垂直於該 figure axis，以 $I_{\perp}$ 表示.

　　oblate： $I_{//} > I_{\perp}$ （eg. C_6H_6 ）

　　　（重原子集中在垂直主軸 面上）

　　prolate： $I_{//} < I_{\perp}$ （eg. CH_3Cl）

　　　（重原子集中在主軸上）

　　該rotor的轉動能量：

$$E = \frac{J_a^2 + J_b^2}{2I_{\perp}} + \frac{J_c^2}{2I_{//}} = \frac{\mathbf{J}^2 - J_c^2}{2I_{\perp}} + \frac{J_c^2}{2I_{//}} = \frac{\mathbf{J}^2}{2I_{\perp}} + (\frac{1}{2I_{//}} - \frac{1}{2I_{\perp}})J_c^2 \ , \quad \mathbf{J}^2 = J_a^2 + J_b^2 + J_c^2$$

$$F(J,K) = BJ(J+1) + (A-B)K^2, \ J =, 0, 1, 2 \text{、、、}, \ K=0, \pm 1, \pm 2, \ldots\ldots, \pm J$$

令 $A = \dfrac{\hbar}{4\pi c I_{//}}$, $B = \dfrac{\hbar}{4\pi c I_{\perp}}$ K is the quantum number used to signify a

component on the principal axis, (而M_J is reserved for a component on an externally defined axis) ,K值可視為是分子旋轉時其angular momentum quantum number 在分子主軸上的分量。

(而K^2剛好為$J_c^{\ 2}$,   ∵ $J_c^{\ 2}$是定義為該分子的principal axis上的角動量平方。亦即為total angular momentum 平方,$\mathbf{J}^2$,在principal axis上的分量。

∴ $K^2\hbar^2$與$J_c^{\ 2}\hbar^2$是不謀而合,但M_J則是$\mathbf{J}$在外加的or任意指定的一個方向上的可能分量,其值亦為0, $\pm 1, \pm 2, \pm J$),J 為quantum number (符號表示正,反轉)。(而 total angular momentum 大小, $\mathbf{J} = \sqrt{J(J+1)}\ \hbar$)
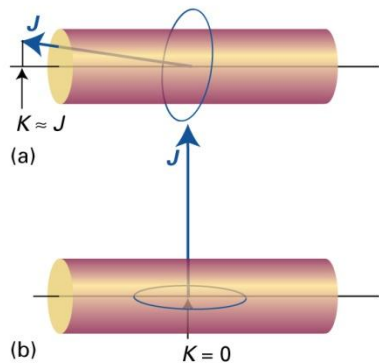
不管是oblate or prolate，其推導結果是一樣的式子，所不同的是A與B

的大小不一樣, 而定義 ： $A = \dfrac{\hbar}{4\pi c I_{//}}$, $B = \dfrac{\hbar}{4\pi c I_{\perp}}$

在oblate分子, $I_{//} > I_{\perp} \therefore$ A＜B.
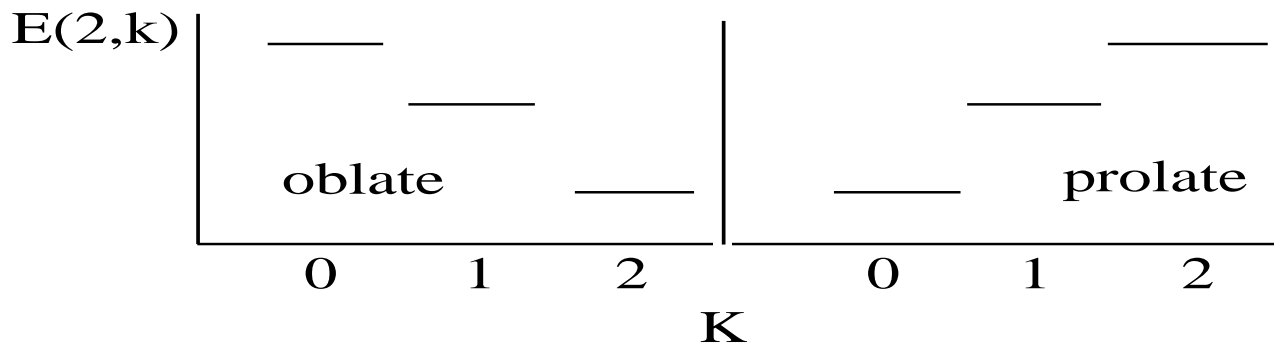
而prolate分子, $I_{//} < I_{\perp} \therefore$ A＞B.

如何由光譜分辨該分子是 oblate or prolate？
在光譜中, rotation energy, $F(J,K) = BJ(J+1) + (A-B)K^2$

For **oblate**, $\because$A＜B. $\therefore$當J相同而K不同時, eg. J =2, K可以等於0, 1, 2.
其能階, 隨K值增加而下降.
For **prolate**, $\because$A ＞ B. $\therefore$當J相同而K不同時, eg. J =2, K可以等於0, 1, 2.
其能階，隨K值增加而上升。

A $^{14}NH_3$ molecule is a symmetric rotor with bond length 101.2 pm and HNH bond angle 106.7°. Calculate its rotational terms.

Method Begin by calculating the rotational constants A and B by using the expressions for moments of inertia given in Table 13.1. Then use eqn 13.29 to find the rotational terms.

Answer Substitution of $m_A = 1.0078$ u, $m_B = 14.0031$ u, $R = 101.2$ pm, and $\theta = 106.7°$ into the second of the symmetric rotor expressions in Table 13.1 gives $I_\parallel = 4.4128 \times 10^{-47}$ kg m^2 and $I_\perp = 2.8059 \times 10^{-47}$ kg m^2. Hence, $A = 6.344$ cm^{-1} and $B = 9.977$ cm^{-1}. It follows from eqn 13.29 that

$$F(J,K)/cm^{-1} = 9.977J(J+1) - 3.633K^2$$

Upon multiplication by c, $F(J,K)$ acquires units of frequency:

$$F(J,K)/GHz = 299.1J(J+1) - 108.9K^2$$

For $J = 1$, the energy needed for the molecule to rotate mainly about its figure axis $(K = \pm J)$ is equivalent to 16.32 cm^{-1} (489.3 GHz), but end-over-end rotation $(K = 0)$ corresponds to 19.95 cm^{-1} (598.1 GHz).

For M$_J$ 的變化：
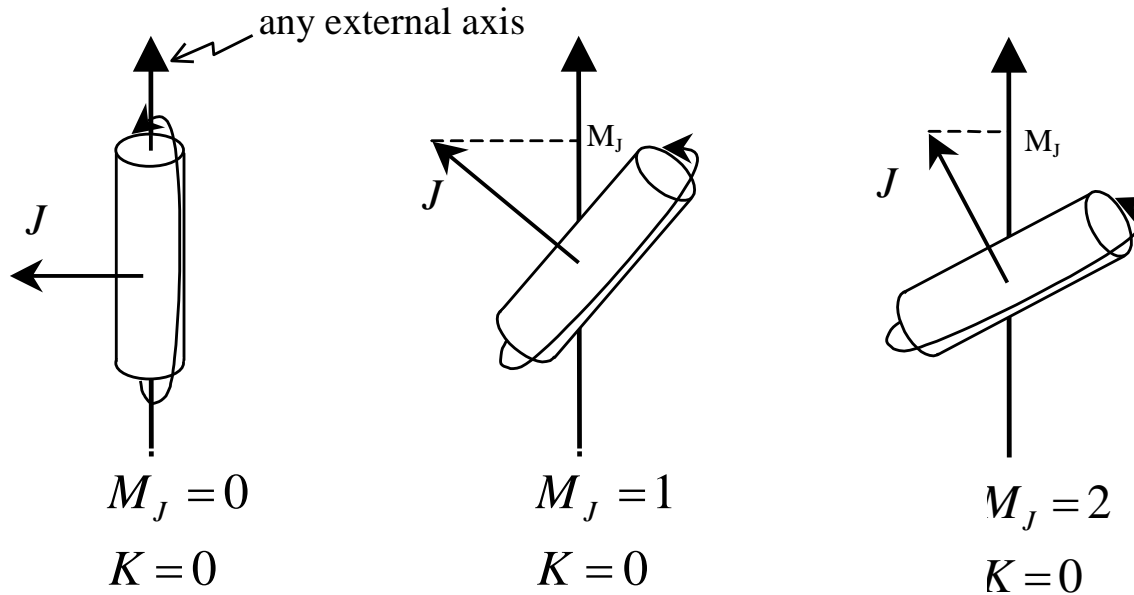
For linear rotor：
∵主軸的 $I_{//}$=0　∴在主軸上 E_{rot}=0，亦即K= 0
∴, $F(J,K) = BJ(J+1)$　J=0，1，2，、、、而每個值，有**2J+1**個
degeneracies.

Rotational transitions：

Typical values of B for small molecules介於**0.1-10㎝⁻¹**間。(eg. NF_3 為 0.356㎝⁻¹ , HCl 為10.59㎝⁻¹)，因此其躍遷譜線介於microwave region。

Selection rules：

必須具備有permanent dipole的分子，才會有吸收。(∵轉動時，dipole會 fluctuating，在電場作用下(攪動電場)產生resonance效應). ∴一般未具有 dipole的分子, N_2, O_2, H_2, CO_2及spherical molecule CH_4, 不能有rotational transition (除非旋轉時變形，而有dipole產生)。

Of the molecules N_2, CO_2, OCS, H_2O, $CH_2=CH_2$, C_6H_6, only OCS and H_2O are polar, so only these two molecules have microwave spectra.
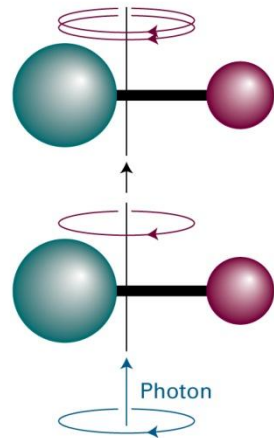
Selection rule為 (可以由angular momentum 守恆的定律來理解)。

$$\Delta J = \pm 1, \quad \Delta M_J = 0, \pm 1$$

transition moment 經推導得：

$$\left| \mu_{J+1, J} \right|^2 = \left(\frac{J+1}{2J+1} \right) \mu^2 \rightarrow \frac{1}{2} \mu^2 \ for \ J \ \rangle\rangle 1 \ (\mu \ 為 dipole \ moment)$$

∴permanent dipole 越強者, 其rotation transition越強。

一般rotation光譜，譜線接近等間隔，但intensity的分布稍須留意，並非ground state 的population最大。 其

$$N_J \propto N g_J e^{\frac{-E_J}{kT}}$$
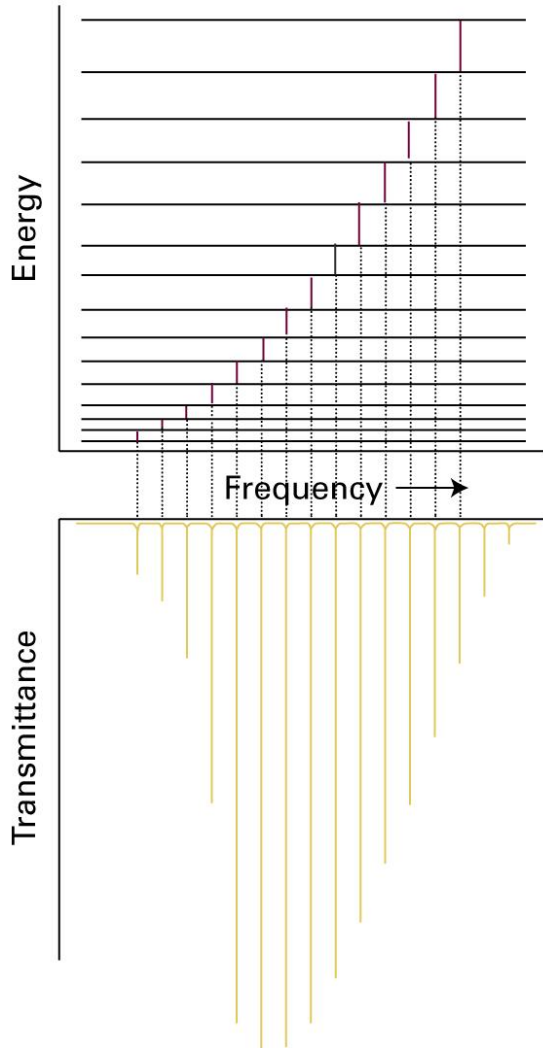
其中g_J為degeneracy of level J. (通常2J+1個)

N為total number of molecules.

經計算得知，the value of J for the most highly populated rotational energy level in a linear molecular is

$$J_{max} \approx \left(\frac{kT}{2hcB} \right)^{\frac{1}{2}} - \frac{1}{2},$$

eg. OCS, B=0.2cm⁻¹, kT＝1000hcB (at room T) ∴ $J_{max} \approx 22$

Nuclear statistics and rotational states

CO_2 為什麼只存在有even J的rotational states？
這是由Pauli principle所推導而出的(如同Pauli principle去除一些不存在的electronic states一樣)。
其所依的公式：

$$\frac{odd\ J\ 的\ intensity}{even\ J\ 的\ intensity} = \begin{cases} \dfrac{(I+1)}{I} & \rightarrow & for\ half-spin\ nuclei \\ \\ \dfrac{I}{(I+1)} & \rightarrow & for\ integer-spin\ nuclei \end{cases}$$
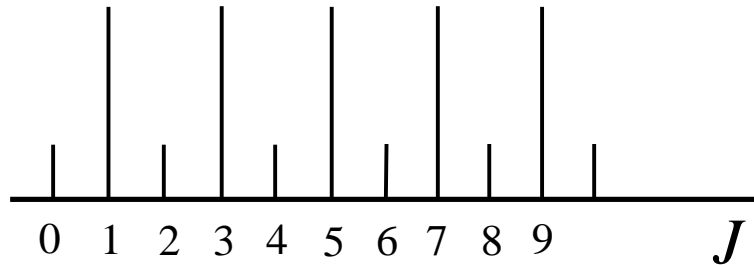
依上式，for O 原子核，$I = 0$
$\therefore$ 對O_2分子odd J rotational states 與 even J者的intensity比？

$$\frac{odd\ J}{even\ J} = \frac{0}{1} = 0. \quad \therefore\ 只存在有\ even\ J\ states.$$

對氫原子而言，Ｉ=1/2　∴對H_2分子odd J與even J又如何?

$\dfrac{odd\ J}{even\ J}=\dfrac{\frac{1}{2}+1}{\frac{1}{2}}=\dfrac{3}{1}$，即$H_2$ rotation spectrum其中odd J intensity為even J的3倍。

原理：H-H(equivalent nuclei)相互交換(∵轉動), overall wavefN一定要變號, (Pauli principle), 而overall wavefN中包含nuclear spin wavefN, vibration wavefN , rotation wavefN and electronic wavefN。其中vibration及electronic wavefN不會因交換原子核位置而發生任何改變, 因此overall wavefN 變號與否完全決定於nuclear spin wavefN 與rotation wavefN。

對H原子而言，nuclear spin Ⅰ=1/2, ∴存在有兩種nuclear spin 即α及β,因此對H-H分子而言,其可能存在的nuclear spin方式有4種，如右所示。

$H_{(1)}-H_{(2)}$

α α

β β

α β ⎫
　　⎬ ⟹   α(1)β(2)＋β(1)α(2)；
β α ⎭   α(1)β(2)－β(1)α(2)
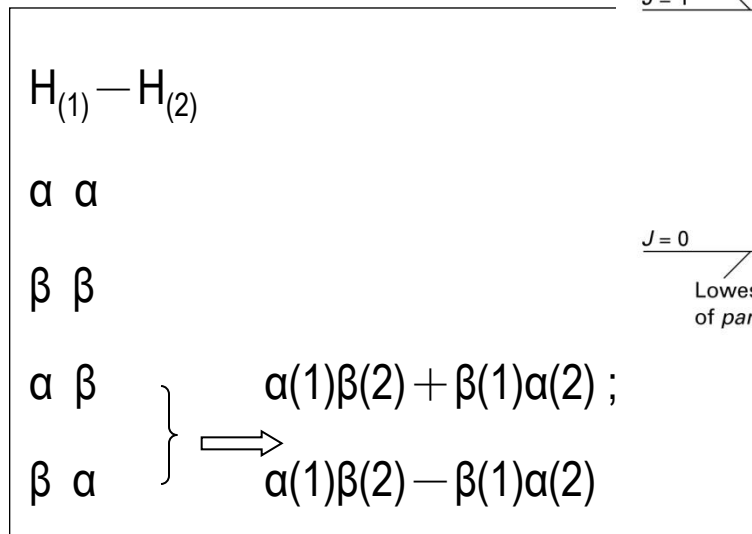
其中有3種在H(1)－H(2)　H(2)－H(1)是完全對稱，亦即『α(1)α(2)』；『β(1)β(2)』；『α(1)β(2)＋β(1)α(2)』。

只有一種是反對稱，即『α(1)β(2)－β(1)α(2)』。
若H－H nuclear spin的排法是前述3種者，稱ortho-hydrogen (ortho-H_2)，則其rotation時，nuclear spin wavefN不變號。
若H－H nuclear spin的排法是後述1種者，稱para-hydrogen (para-H_2)，則其rotation時，nuclear spin wavefN會變號。

然而rotation wavefN 的形式是$(-1)^J$, 亦即當J為偶數時旋轉不變號 (如AO中的s, d,…) ; 反之，當J為奇數時旋轉會變號(如AO中的p, f,…)。由Pauli principle可知H原子核為fermion (Ⅰ=1/2)，∴核交換後overall wavefunction必須變號。

∴ortho-H_2 必須配odd J rotation states，亦即ortho-H_2只能存在odd J rotation states, (偶數不存在) ; 同樣的，para-H_2只能存在even J rotation states。然而在整個所有可能組合中，ortho-H_2與para-H_2的量比為3：1，因此其所顯現出來的odd J與even J rotation states的比為3：1。如圖12.20 p461。

同理CO_2的case,

O – C – O

(1)   (2)

O – C – O

(2)   (1)
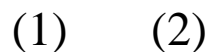
(應可了解為何只存在even J rotation states的原因了)
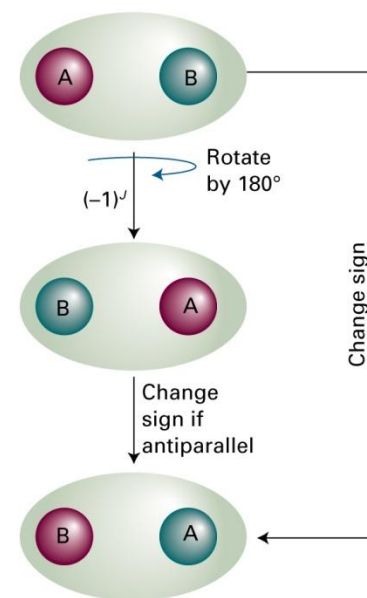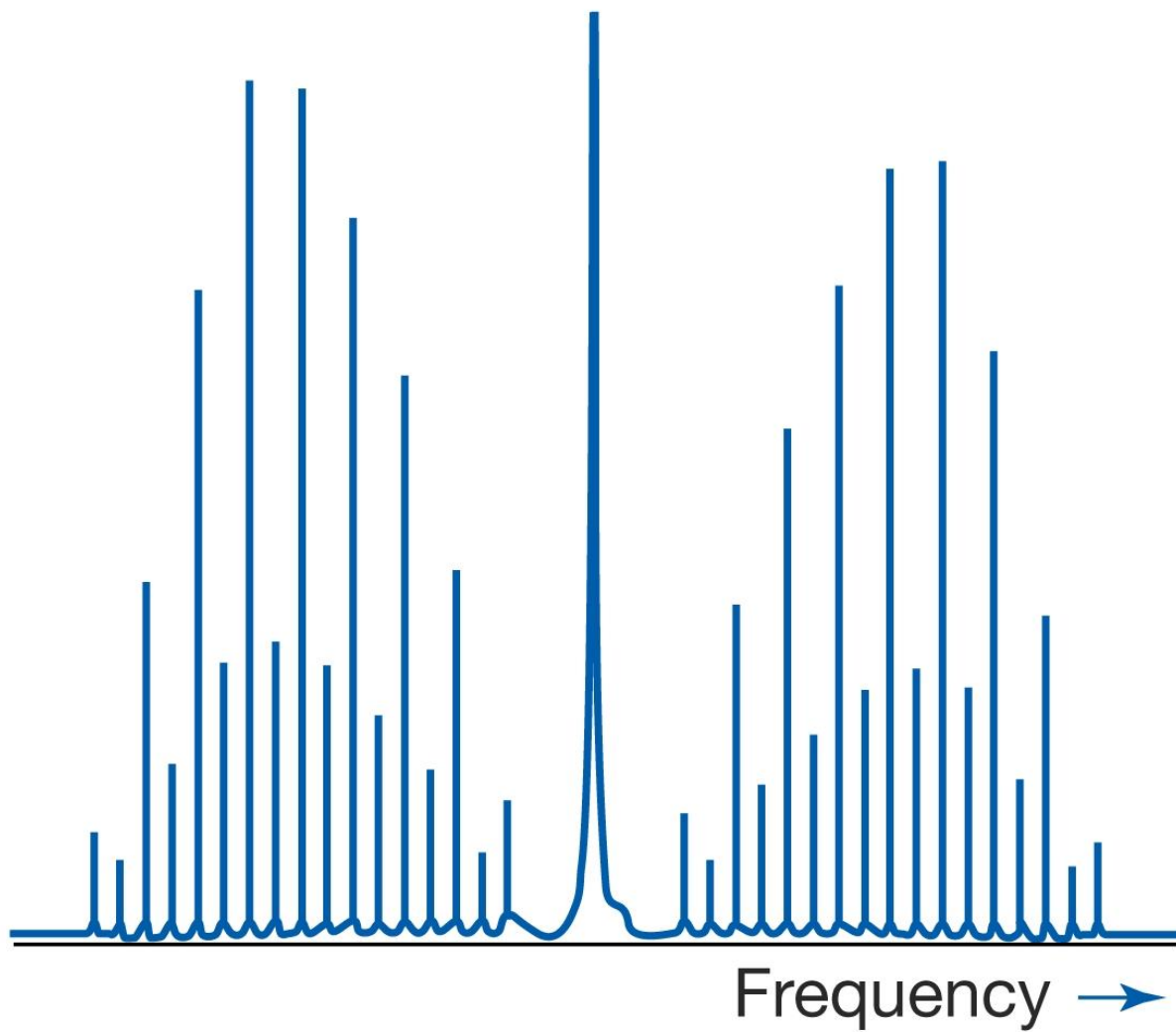
H_2 rotational Raman spectrum, the ratio of odd J and even J is 3:1

Molecular vibration：

m_1 m_2 reduce to u

$u = m_1 m_2 / (m_1 + m_2)$

$-x$ x $-x$ x
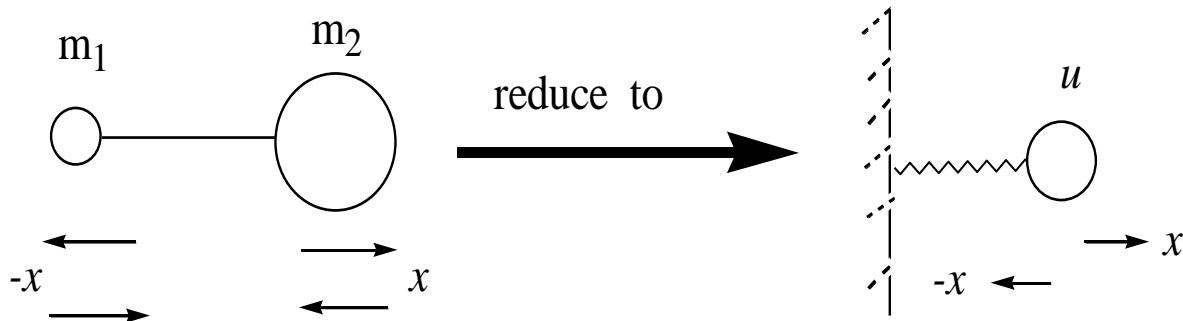
Ideal case：harmonic vibrational motion(諧和振動)

potential energy V(x)

ideal case

real case

$-x$ R_e $+x$ R
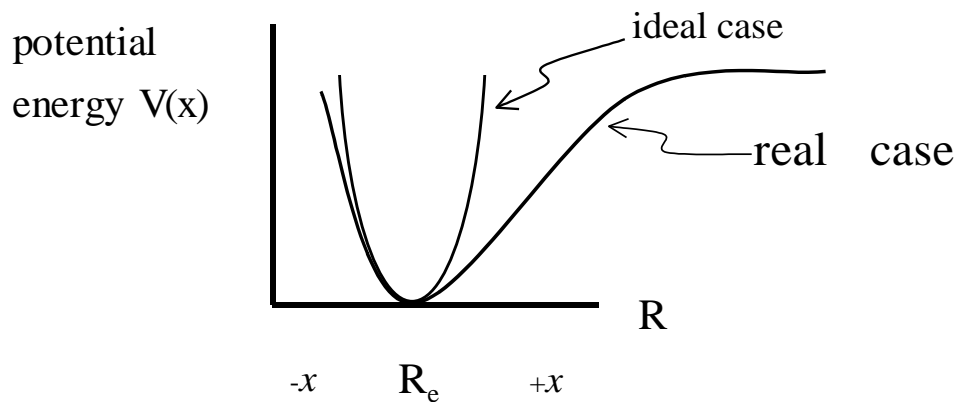
一般諧和振動的位能

$$V(x) = \frac{1}{2} k x^2$$

k：force const

x：(R － R_e)伸長量
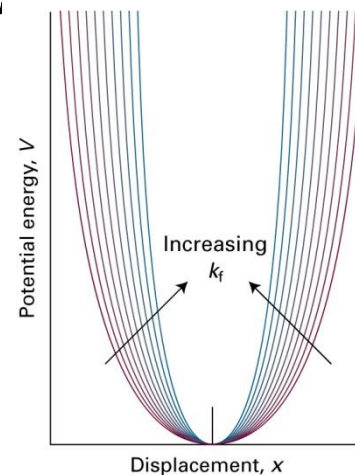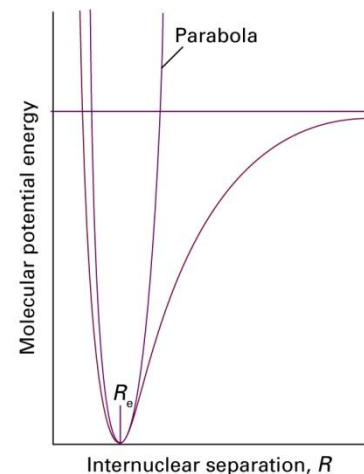
其解與前面所談的vibration motion的解完全一樣。

$$E_\upsilon = (\upsilon + \tfrac{1}{2})h\nu \quad \text{or} \quad E_\upsilon = (\upsilon + \tfrac{1}{2})\hbar\omega$$

$\psi(\nu)$ 即為Hermit polynomial gaussian fN的形式
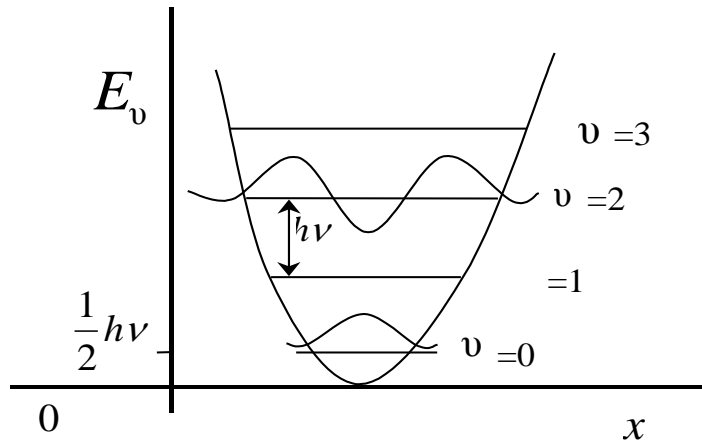
以wave number 表示能量 $\quad \dfrac{E_\upsilon}{hc} = G(\upsilon) = (\upsilon + \dfrac{1}{2})\tilde{v}$, $\qquad \tilde{v} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu}}$

分子的振動光譜涉及到能階間的躍遷。

大多數分子的振動頻率處於紅外線(Infrared Radiation)區間。因此若能符合該區間的頻率而產生能階躍遷者，稱 IR active。然而對於電磁波能產生吸收者，必須是在振動時能產生dipole moment 的變化，才能與電磁波的電場產生共振。分子本身不一定須具備permanent dipole，但至少須於振動時有dipole moment。例如：CO_2分子，不具有permanent dipole，但其一些振動模式會有dipole moment的變化：

$\delta -$ $\delta +$ $\delta -$

如   O--C--O   O--C--O   ；反之，   O--C--O   則無dipole moment的變化。

因此前兩種modes為IR active，後一種為IR inactive。同樣很多雙原子分子，如：H_2, O_2, N_2….是否為IR active，HCl又如何？

the electric dipole moment of the molecule must change when the atoms are displaced relative to one another

$$dipole\ moment\ \mu = R\delta q \qquad q:電荷量$$

$$而 R = R_e + \chi$$

$$\therefore \mu = R_e\delta q + \chi\delta q = \mu_0 + \chi\delta q$$

transition dipole moment：

$$\left\langle \upsilon_f |\mu|\upsilon_i \right\rangle = \mu_0\left\langle \upsilon_f |\upsilon_i \right\rangle + \delta q\left\langle \upsilon_f |\chi|\upsilon_i \right\rangle = 0 + \left\langle \upsilon_f |\chi|\upsilon_i \right\rangle\delta q, \quad \because \left\langle \upsilon_f \right| 與 \left| \upsilon_i \right\rangle 是 orthogonal$$

$$而\, \delta q = \frac{d\mu}{d\chi} \quad \therefore \left\langle \upsilon_f |\mu|\upsilon_i \right\rangle = \left\langle \upsilon_f |\chi|\upsilon_i \right\rangle\left(\frac{d\mu}{d\chi} \right)$$

因此只要 du/dx≠0，則transition dipole moment≠0，就會有躍遷。
証明了分子的振動若有dipole moment的變化，就IR active。

Vibration transition 的 selection rule，$\Delta \upsilon = \pm\, 1$

証明

$$\left\langle \upsilon_f \left| \chi \right| \upsilon_i \right\rangle = N_{\upsilon_f} N_{\upsilon_i} \int_{-\infty}^{\infty} H_{\upsilon_f} \chi\, H_{\upsilon_i} e^{-y^2} dx \qquad 而 \chi = \alpha\, y$$

$$= \alpha^2 N_{\upsilon_f} N_{\upsilon_i} \int_{-\infty}^{\infty} H_{\upsilon_f}\, y\, H_{\upsilon_i} e^{-y^2} dy$$

依據 recursion rule：$yH_\upsilon = \upsilon H_{\upsilon-1} + \dfrac{1}{2} H_{\upsilon+1}$，代入上式，

$$\left\langle \upsilon_f \left| \chi \right| \upsilon_i \right\rangle = \alpha^2 N_{\upsilon_f} N_{\upsilon_i} \left\{ \upsilon_i \int_{-\infty}^{\infty} H_{\upsilon_f} H_{\upsilon_i-1} e^{-y^2} dy + \int_{-\infty}^{\infty} H_{\upsilon_f} H_{\upsilon_i+1} e^{-y^2} dy \right\}$$

由以前所述Hermit polynomial f_N 知：

$$\int H_{\upsilon_f} H_{\upsilon_i-1} e^{-y^2} dy = 0, \quad 除非 \upsilon_f = \upsilon_i - 1$$

$$\int H_{\upsilon_f} H_{\upsilon_i+1} e^{-y^2} dy = 0, \quad 除非 \upsilon_f = \upsilon_i + 1$$

，由此証出 $\quad \Delta \upsilon = \pm 1$

vibration transition能量若以wave number方式表示：

$\Delta G_{\upsilon+1/2} = G(\upsilon+1) - G(\upsilon) = \tilde{\nu}$ ，表示 $\upsilon+1 \leftarrow \upsilon$，如前述落在紅外線區間，400~4000㎝$^{-1}$，在一般室溫下，$kT/hC \approx 200\ cm^{-1}$。由此可見大多數分子在室溫下皆處於ground vibrational state(υ=0)。所以vibration transition的發生皆為fundamental transition, (Δ υ=±1)。所以只有單一光譜(一條譜線)。
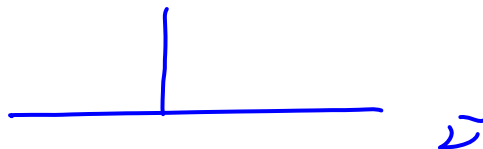
對於vibration放射光譜而言e.g. $H_2+F_2 \rightarrow 2\ HF^*$；$HF^*$ 可能處於高的vibration states.(如： υ=5, 4, 3,⋯), 但仍然出現接近單一光譜(5→4, 4→3,⋯) why?(這是理想諧和振動下等能階的現象)，實際分子就有機會產生多條很靠近的線譜，why?(不諧和?)
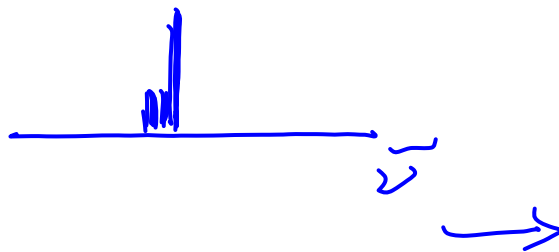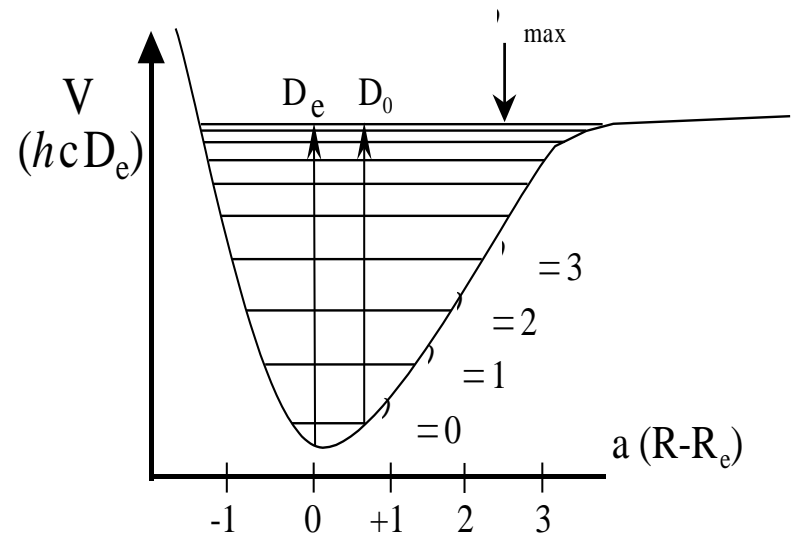
Anharmonicity
The motion becomes anharmonic.
亦即拉得太長後，restoring force
不和位移成正比(不遵守虎克定律)，
其能階間隔(在high v)會越來越小。
其位能曲線也不再是理想的拋物線
如左圖，Morse寫了一函數來近似
此位能曲線,稱為Morse potential。

$$V = hcD_e \{1 - e^{-a(R-R_e)}\}^2 \ , a = (\frac{\mu\omega^2}{2hcD_e})^{1/2}$$

D_e：The depth of the potential minimum.
D_0：Dissociation energy.
μ：reduced mass.

Morse potential:
$$V(r) = D_e \left(1 - e^{-a(r-r_e)}\right)^2 \qquad a = \sqrt{k_e/2D_e}$$

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial r^2} + V(r)\right)\Psi(v) = E(v)\Psi(v), \qquad x = ar; \; x_e = ar_e; \; \lambda = \frac{\sqrt{2mD_e}}{a\hbar}; \; \varepsilon_v = \frac{2m}{a^2\hbar^2}E(v).$$

$$\left(-\frac{\partial^2}{\partial x^2} + V(x)\right)\Psi_n(x) = \varepsilon_n \Psi_n(x), \qquad V(x) = \lambda^2 \left(e^{-2(x-x_e)} - 2e^{-(x-x_e)}\right).$$
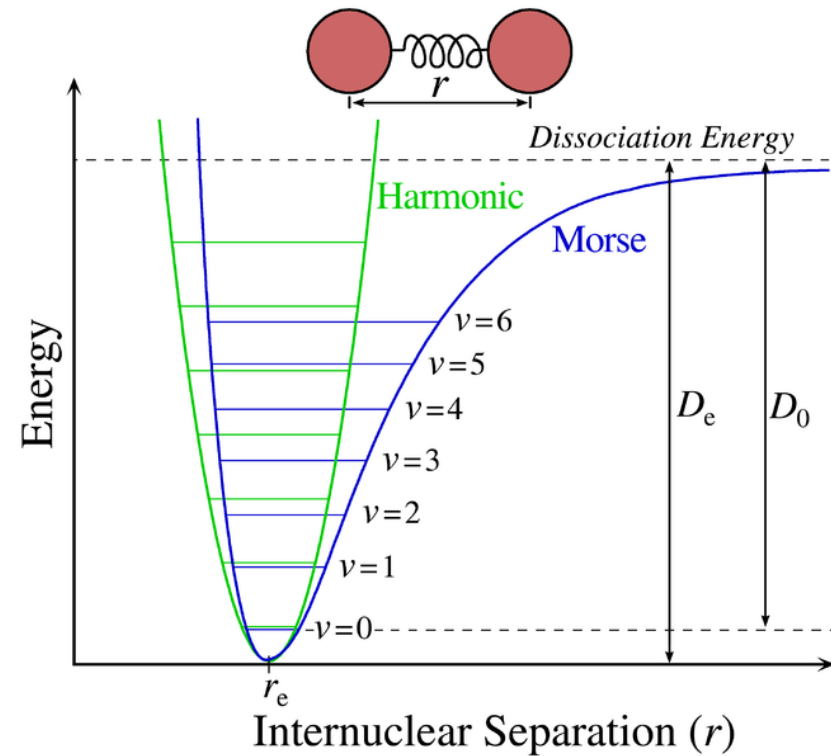
$$\varepsilon_n = -\left(\lambda - n - \frac{1}{2}\right)^2$$

$$\Psi_n(z) = N_n z^{\lambda - n - \frac{1}{2}} e^{-\frac{1}{2}z} L_n^{2\lambda - 2n - 1}(z),$$

$$z = 2\lambda e^{-(x-x_e)}$$

$$N_n = n! \left[\frac{a(2\lambda - 2n - 1)}{\Gamma(n+1)\Gamma(2\lambda - n)}\right]^{\frac{1}{2}}$$

$$L_n^\alpha(z) = \frac{z^{-\alpha}e^z}{n!}\frac{d^n}{dz^n}\left(z^{n+\alpha}e^{-z}\right) = \frac{\Gamma(\alpha+2)/\Gamma(\alpha-n+2)}{\Gamma(n+1)} \, {}_1F_1(-n, \alpha+1, z),$$

Energy vs Internuclear Separation (r) diagram showing Harmonic and Morse potentials, vibrational levels $v=0$ through $v=6$, Dissociation Energy, D_e, D_0, and r_e.

若將此 Morse potential V，代入 Schödinger equation 中的位能項(以前假設為純諧和振動時為 $\frac{1}{2}kx^2$)，再解一次可得能階為 $G(\upsilon) = (\upsilon + \frac{1}{2})\tilde{\nu} - (\upsilon + \frac{1}{2})^2 x_e \tilde{\nu}$　其中 $x_e = \frac{\tilde{\nu}}{4D_e}$ ，稱為 anharmonicity const. 而 υ 值從 0,1,2,3,.... υ_{max}（有限個），依上式的振動位能假設模式振動者，稱 Morse oscillator，很常被接受使用。

然而更具體完整的能階表示法如下：（∵不一定完全符合Morse potential）

$$G(\upsilon) = (\upsilon + \frac{1}{2})\tilde{\nu} - (\upsilon + \frac{1}{2})^2 x_e \tilde{\nu} + (\upsilon + \frac{1}{2})^3 y_e \tilde{\nu} + \cdots\cdots$$

其中 χ_e，稱first anhaomonicity const，y_e 稱2nd anhaomonicity const,......更高層次的 anharmonic的校正，這些皆是用來fit實驗的譜線data，以求得更精確的D₀。若依上式，則vibration transition energy for $\Delta\upsilon = $ +1，

$$G(\upsilon+1) - G(\upsilon) = \Delta G_{\upsilon+\frac{1}{2}} = \tilde{\nu} - 2(\upsilon+1)x_e\tilde{\nu} + ... \qquad (\upsilon = 0,1,2,3,....)$$

∴只要 $x_e \neq 0$，則1←0，2←1，3←2，的譜線就非單一，而且會有overtones，2←0，3←0，....稱1st，2nd....overtones，雖然違反selection rule($\Delta\upsilon = +1$)(為什麼能存在？)其能量，1st overtone：$G(\upsilon+2) - G(\upsilon) = 2\tilde{\nu} - 2(2\upsilon+3)x_e\tilde{\nu} + ...$

$\therefore$For an anharmonic oscillator，$\Delta \upsilon$ 為任何整數值，皆可能被允許，但當 $\Delta \upsilon = \pm 1$ 時，transition probability最大，信號最強，其他overtone的信號相對減弱，更高更弱。
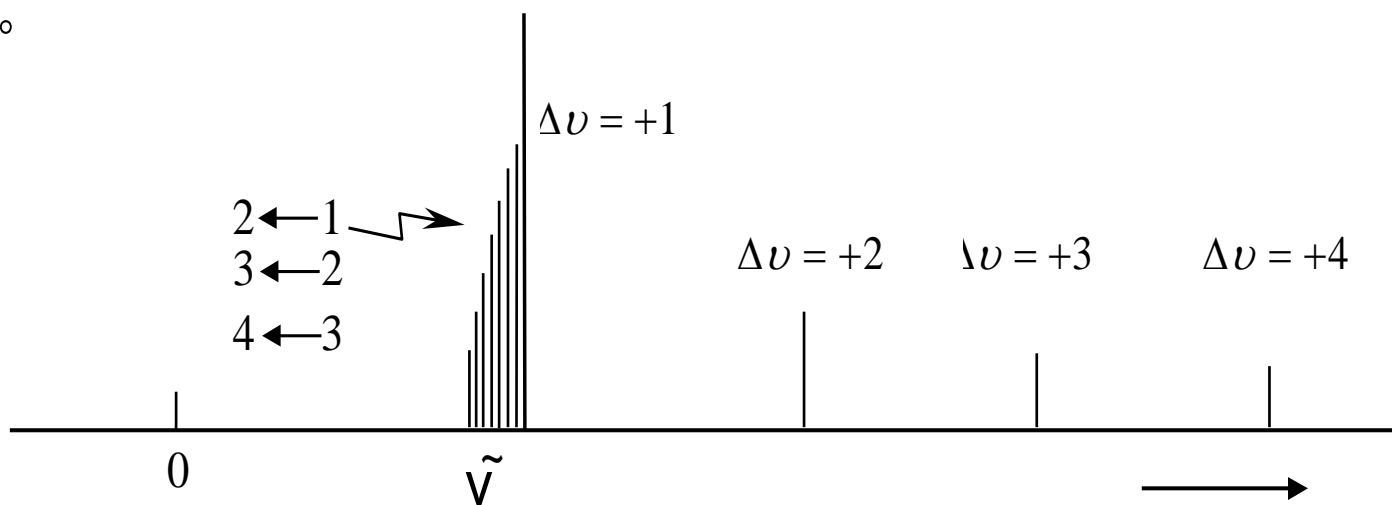
Vibration-rotation spectra

視為分子在rotate的過程中，突然受到vibration的干擾，而改變其rotate的速度（或狀態），猶如溜冰者，在這spin時，突然將其手臂縮起來（或張開）而影響到轉速，因此得到的spectra，稱vibration-rotation spectra，其selection rule為 $\Delta \upsilon = \pm 1, \Delta J = \pm 1$，對某些電子狀態在分子主軸上已帶有一個angular momentum的狀況下，如 $^2\Pi$ state，（NO分子），其vib-rot selection rule也存在於 $\Delta J = 0$，其transition能階：
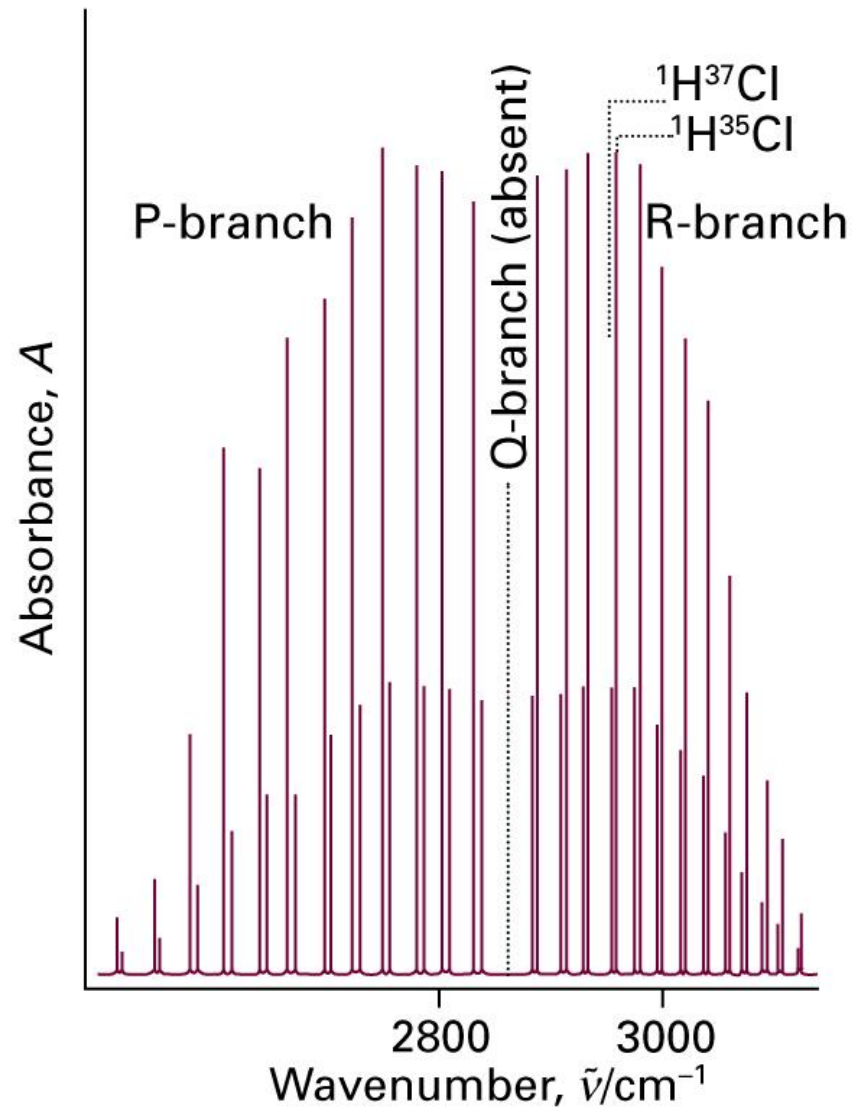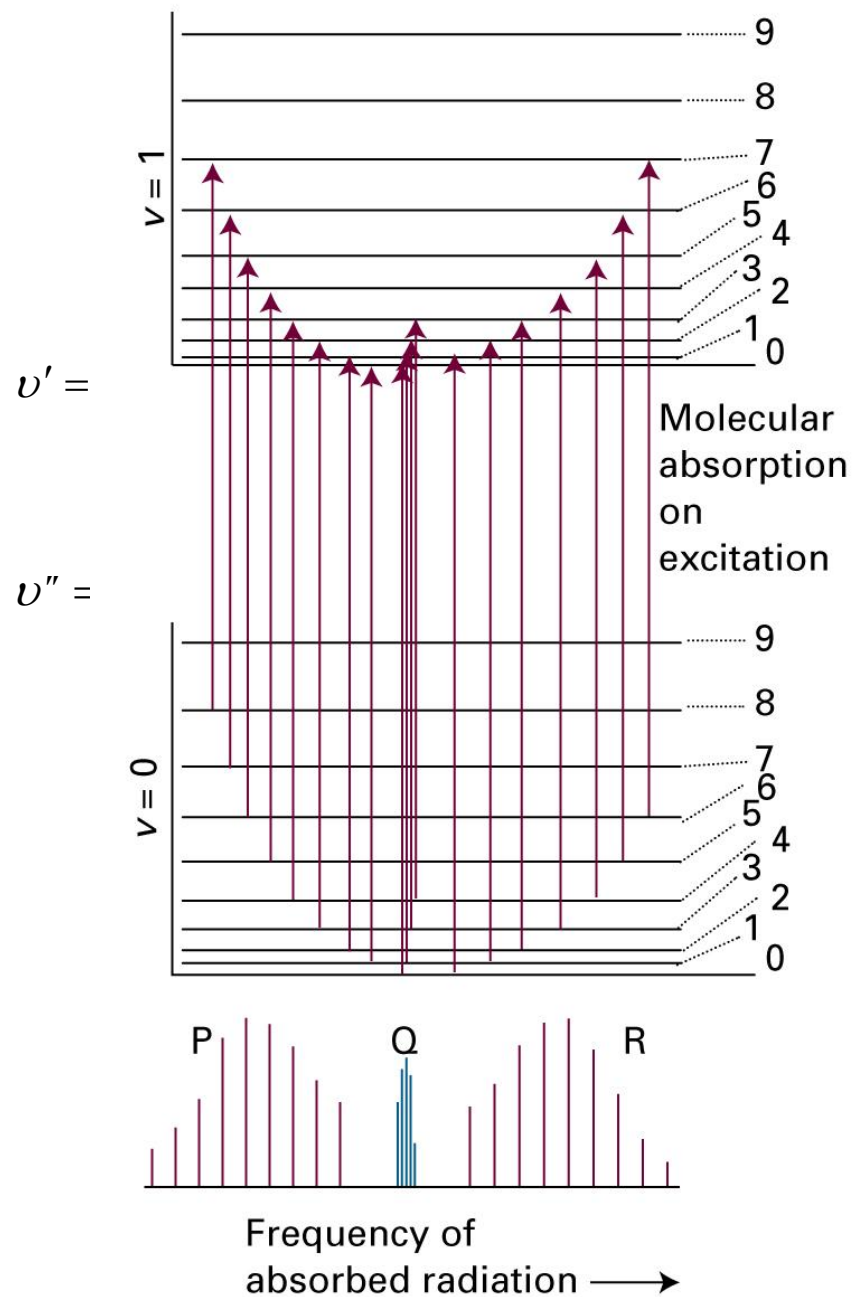
$$S(\upsilon, J) = G(\upsilon) + F(J)$$
$$= (\upsilon + \frac{1}{2})\widetilde{v} + BJ(J+1) \qquad （完全不考慮anharmonicity）$$

$\therefore \Delta \upsilon = +1, \quad \Delta J = -1 \qquad \widetilde{v}_p = S(\upsilon+1, J-1) - S(\upsilon, J) = \widetilde{v} - 2BJ \qquad J = 1, 2, 3$

$\Delta \upsilon = +1, \quad \Delta J = 0 \qquad \widetilde{v}_Q = S(\upsilon+1, J) - S(\upsilon, J) = \widetilde{v}$

$\Delta \upsilon = +1, \quad \Delta J = +1 \qquad \widetilde{v}_R = S(\upsilon+1, J+1) - S(\upsilon, J) = \widetilde{v} + 2B(J+1) \qquad J = 0, 1, 2, 3$

$v' =$

$v = 1$

9
8
7
6
5
4
3
2
1
0

Molecular
absorption
on
excitation

$v'' =$

$v = 0$

9
8
7
6
5
4
3
2
1
0

P   Q   R

Frequency of
absorbed radiation ⟶

Absorbance, A

P-branch   Q-branch (absent)   R-branch

$^1H^{37}Cl$
$^1H^{35}Cl$

2800   3000

Wavenumber, $\tilde{\nu}$/cm^{-1}
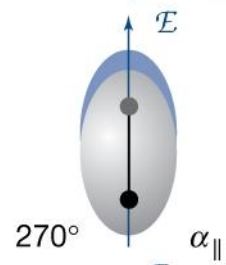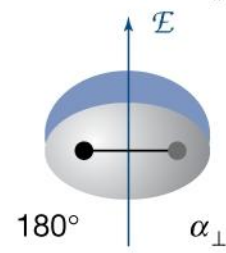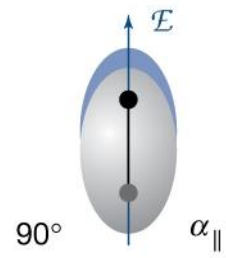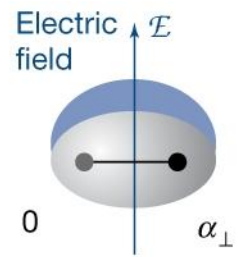
Rotational Raman Spectra

Selection rule：the molecule must be anisotropically polarizable.(不管該分子是否具有永久極性）

 ε (electric field)
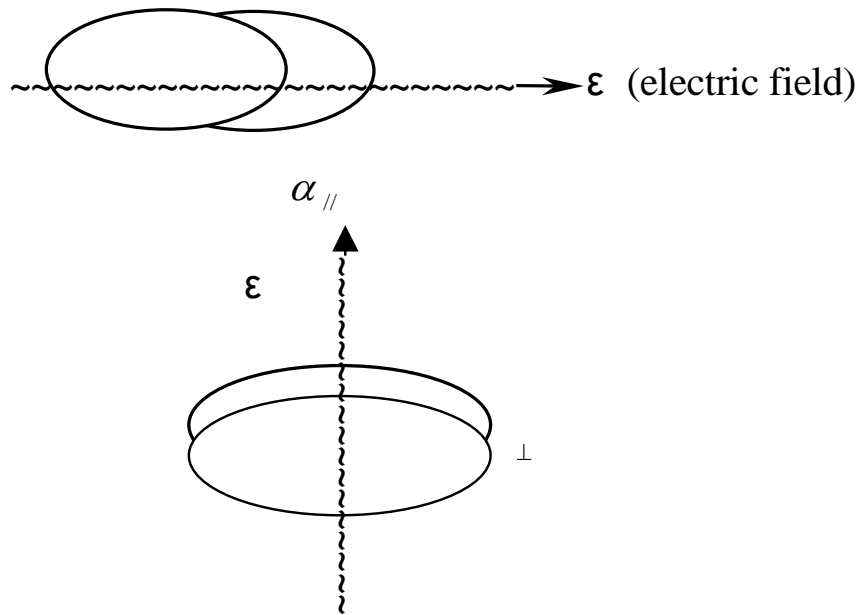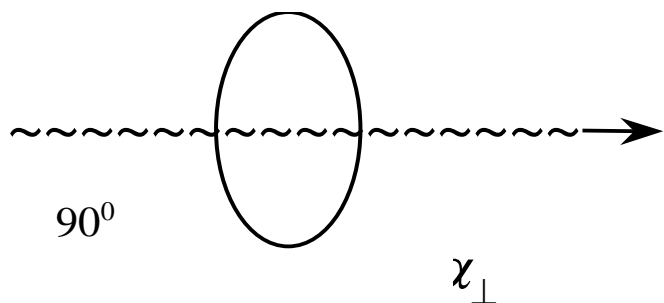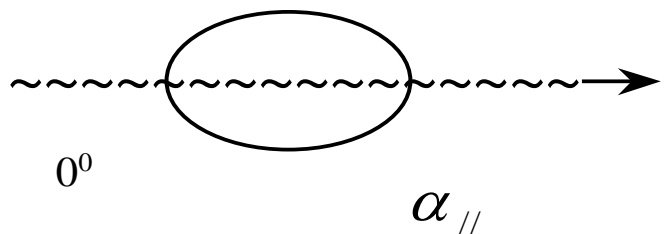
"平行"是表示與分子主軸平行的被極化方向。

$\alpha_{//}$

ε

⊥

若 $\alpha_{//} \neq \alpha_{\perp}$ 就稱為 anisotropically

polarizable.

直線分子皆具如此特性，唯 spherical molecule，如 CH_4、SF_6，其 $\alpha_{//} = \alpha_{\perp}$ 不但是 Raman inactive，也是 microwave inactive（純 rotation spectrum 而言）

Electric field $\mathcal{E}$

0      $\alpha_{\perp}$

$\mathcal{E}$

90° $\alpha_{\parallel}$

$\mathcal{E}$

180° $\alpha_{\perp}$

$\mathcal{E}$

270° $\alpha_{\parallel}$

$\mathcal{E}$

360° $\alpha_{\perp}$

Raman shift 的數學證明：

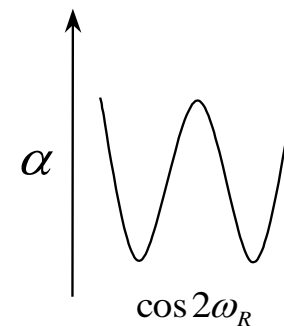

0^0

$\alpha_{//}$

90^0

$\chi_{\perp}$

180^0

$\alpha_{//}$
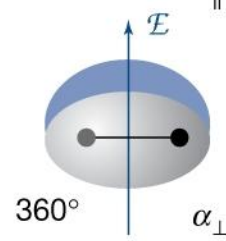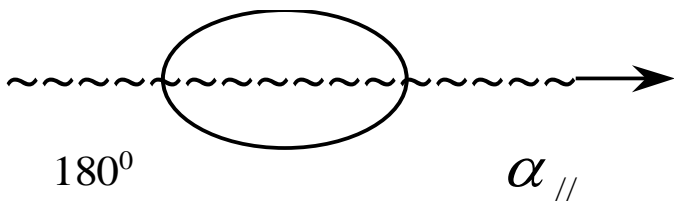
該 ε 產生的 induced dipole, μ.

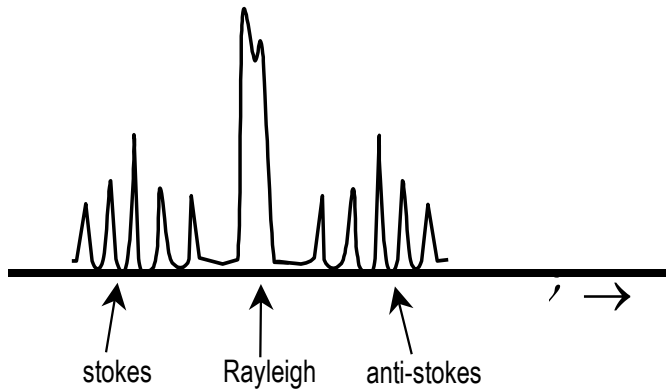$$\mu = \alpha\varepsilon(t) = \alpha\varepsilon_0 \cos \omega_i t$$

α :polarizability ω_i :入

射光的 frequency

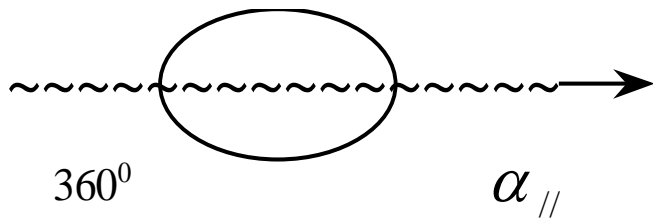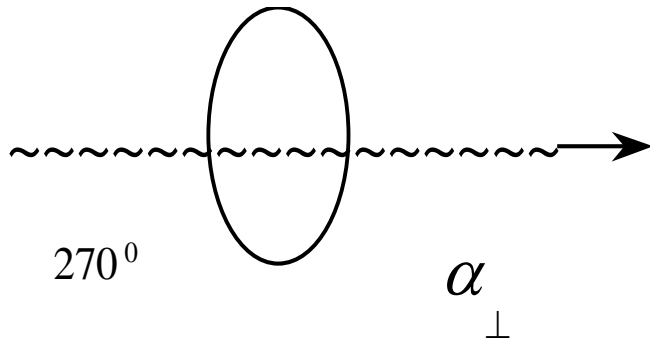α

$\cos 2\omega_R$

$$\alpha = \alpha_0 + \Delta\alpha \cos 2w_R t$$

$$\Delta\alpha = \alpha_{//} - \alpha_{\perp}$$

ω_R :分子的轉動頻率

$2\omega_R$ 是表示分子轉動一週，其 α 值有 2 次回到原點。

270^0 $\alpha_{\perp}$

360^0 $\alpha_{//}$

stokes   Rayleigh   anti-stokes

將 α 值代入上式

$$\therefore \; \mu = (\alpha_0 + \Delta\alpha \cos 2\omega_R t) \times (\varepsilon_0 \cos \omega_i t)$$

$$= \alpha_0 \varepsilon_0 \cos \omega_i t + \varepsilon_0 \Delta\alpha \cos 2\omega_R t \cos \omega_i t$$

$$= \alpha_0 \varepsilon_0 \cos \omega_i t$$

$$+ \frac{1}{2}\varepsilon_0 \Delta\alpha \left\{ \cos(\omega_i + 2\omega_R)t + \cos(\omega_i - 2\omega_R)t \right\}$$

說明 induced dipole has a component oscillating 於

3個 freq.

$$\omega_i \rightarrow \text{ Rayleigh}$$

$$\omega_i + 2\omega_R \rightarrow \text{ anti-stoke}$$

$$\omega_i - 2\omega_R \rightarrow \text{ stoke}$$

由上面式子，得知 $\Delta\alpha \neq 0$ 的前提下，才會有Raman scattering, $(\omega_i \pm 2\omega_R)$,否則只有Rayleigh scattering, ω_i。一般而言，一束光子射入一sample中能被分子scattered的概率是$1:10^5$，非常小。

$\therefore$Raman的強度很弱，一直到Laser發明後，才被發現我們可以依據上述原理，預測直線形分子的Raman轉動譜線。$\Delta J = \pm 2$，亦即分子被光子撞擊並彈開光子後，其轉動角動量增加或減少2個quantum number for $\Delta J = +2$. (stokes or anti-stokes?)

$$\tilde{v}(J+2 \leftarrow J) = \tilde{v}_i - \left\{F(J+2) - F(J)\right\} = v_i - 2B(2J+3)$$

譜線在小於入射光的低頻區，間距from $\tilde{v}_i$ 從6B,10B,14B,...對應於J＝0,1,2,....。stokes lines間的間距為4B。

for $\Delta J = -2$（分子角動量少掉2個quantum number，丟給了光子）

$$\tilde{v}(J-2,J) = \tilde{v}_i + \{F(J) - F(J-2)\} = v_i + 2B(2J-1)$$

譜線在大於入射光的高頻區。間距from $\tilde{v}_i$ 從6B,10B,14B,....

對應於J＝2,3,4,....。 anti-stokes lines間的間距為4B。

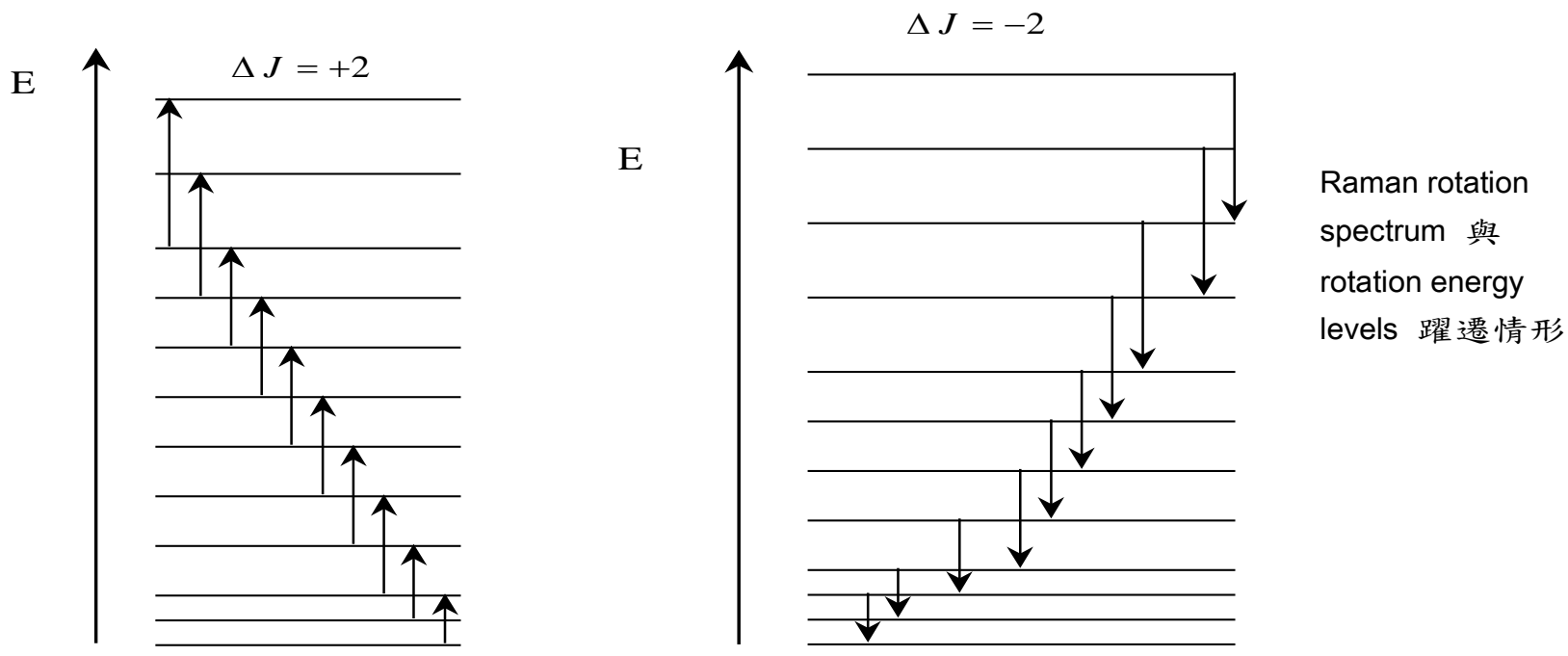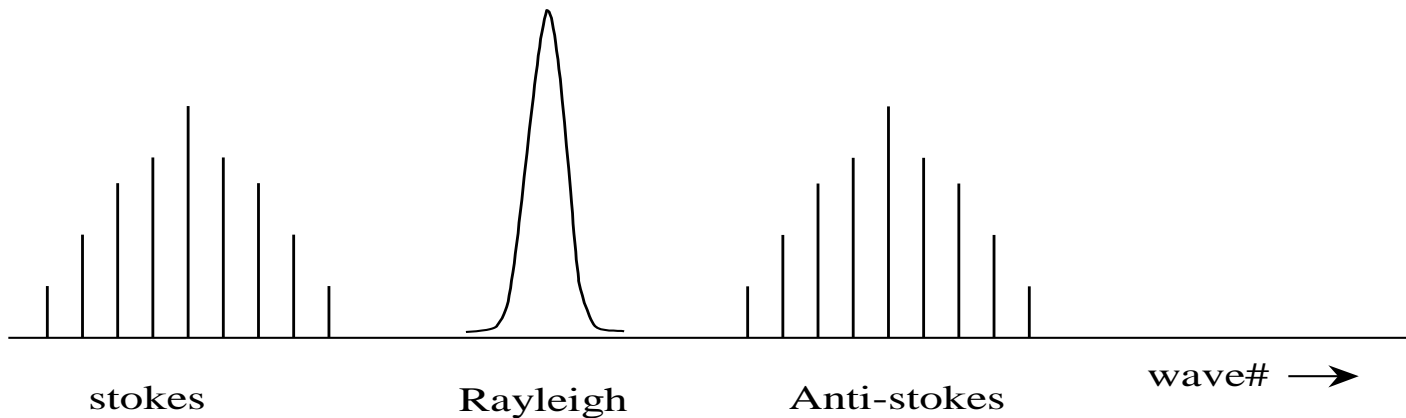由B值可以求出 $I_\perp, (B = \dfrac{\hbar}{4\pi CI}), \quad I = \mu R^2.$

可求出分子的鍵長等information。

Rotation Raman spectrum
Stokes lines, $\Delta J = +2$,
Anti-Stokes lines, $\Delta J = -2$
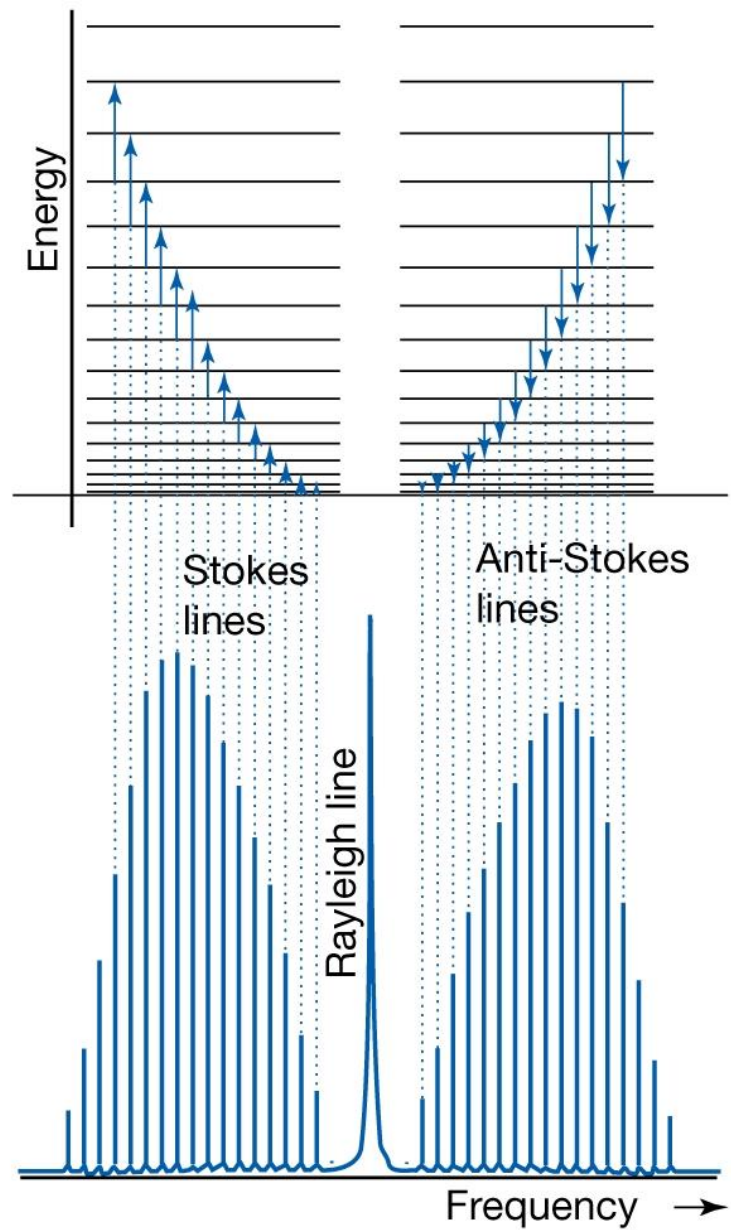
Raman rotation spectrum & rotation energy levels 越遷情形如下圖所示：

$\Delta J = +2$

E

$\Delta J = -2$

E

Raman rotation spectrum 與 rotation energy levels 躍遷情形

stokes   Rayleigh   Anti-stokes   wave# →

Vibration Raman spectra of diatomic molecules

要注意的一點是，只有stokes lines可以觀察到（why?），在Harmonic approx.下，specific selection rule for Raman transition is $\Delta v = \pm 1$。然而只存在$\Delta v = +1$可觀察到。$\Delta v = -1$(very very weak, unless at high temp.)在$\Delta v = +1$的spectrum中，in gas phase, these lines have branch structure arising from simultaneous rotational trasitions that accompany the vibrational excitation.

$\therefore \Delta J = 0, \pm 2$ 有三個branches：

$$O \Rightarrow (\Delta J = -2); \quad Q \Rightarrow (\Delta J = 0); \quad S \Rightarrow (\Delta J = +2)$$

$$\tilde{v}_O(J) = \tilde{v}_i - \tilde{v} - 2B + 4BJ$$

$$\tilde{v}_Q(J) = \tilde{v}_i - \tilde{v}$$

$$\tilde{v}_S(J) = \tilde{v}_i - \tilde{v} - 6B - 4BJ$$

($\tilde{v}$ 為vibration fundamental wave number)

$\Delta J = -2$ $\Delta J = 0$ $\Delta J = +2$

$\upsilon\,'=1,\,J'=0$

$\upsilon\,''=0,\,J''=0$

O   Q   S

?   ?

wave#   Stokes lines
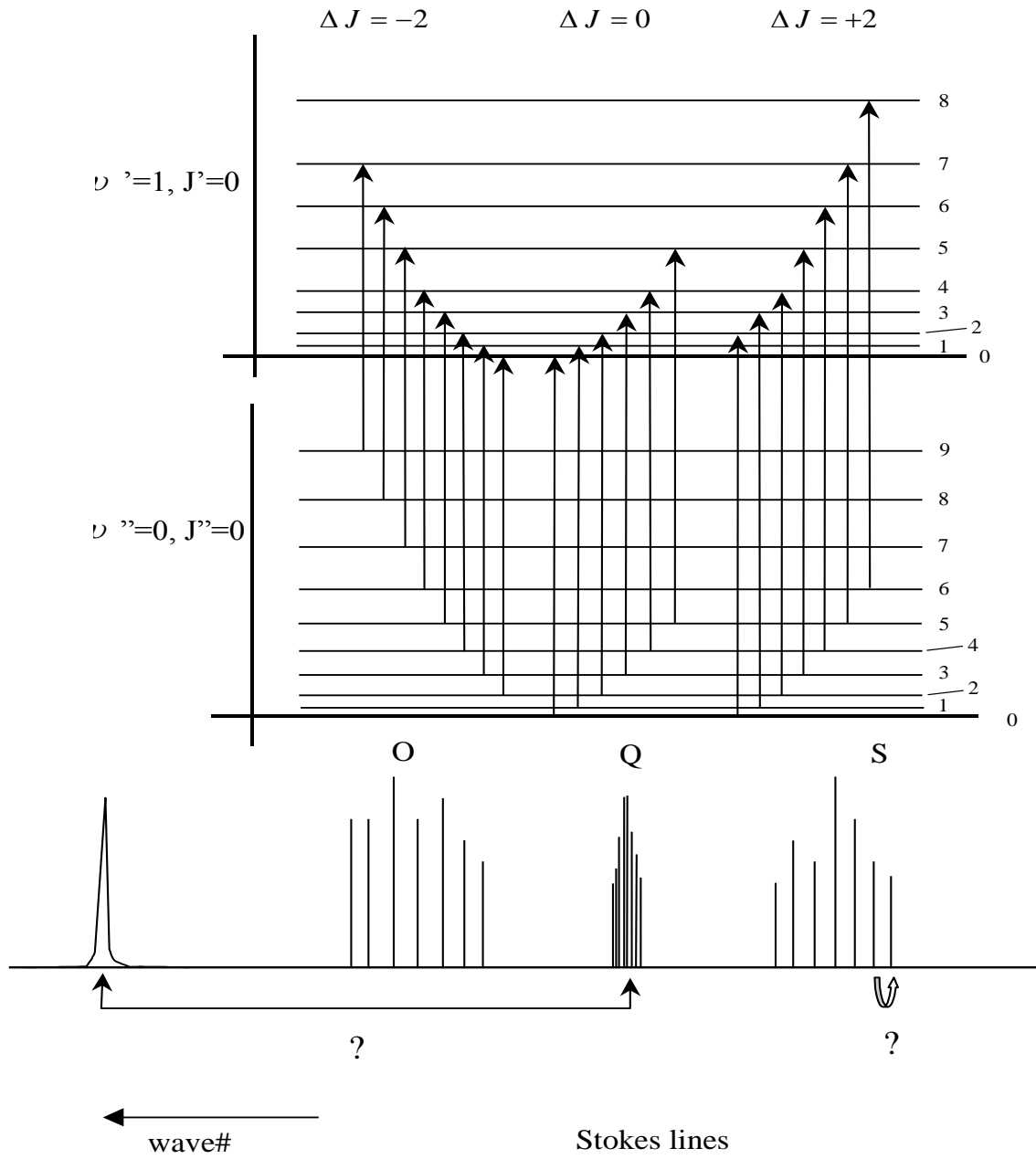
Vibrational Raman spectra of polyatomic molecules

polyatomic molecule 通常有3N-5 (linear) or 3N-6 (nonlinear)個vibration modes，這些 modes中，若在轉動或振動過程中，polarizability有改變者，即為Raman active。

(但在Infrared振動光譜，則是看該振動mode有否改變dipole moment,亦即$\frac{d\mu}{dx}$是 否不等於零，不等於零才會infrared active)。

欲判斷這些mode的光譜特性，通常可以從該分子所屬的character table 來 看，在table的最右欄內，有列一些所屬symmetry species代表性的functions.

Raman active：以具有與 x^2, xy, xz,...等quadratic form 相同對稱性的normal modes 屬之。

Infrared active：以具有與 x, y, z 相同對稱性的normal modes 屬之。

通常，all totally symmetric vibrations (不管屬於何種point group) are Raman active。

Exclusion rule：

如果分子具有對稱中心 , i, then no modes can be both infrared and Raman active，

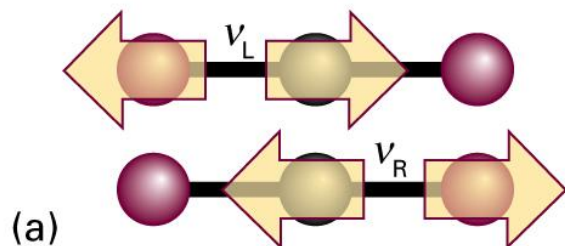check CO_2, H_2O, CH_4.

Resonance Raman spectra

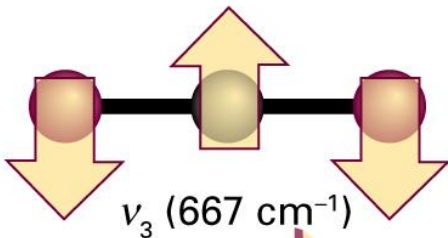挑選特別的入射光能量，使其剛好為電子躍升(electronic transition)的能階差，這樣可以產生相當強的 scattered radiation。
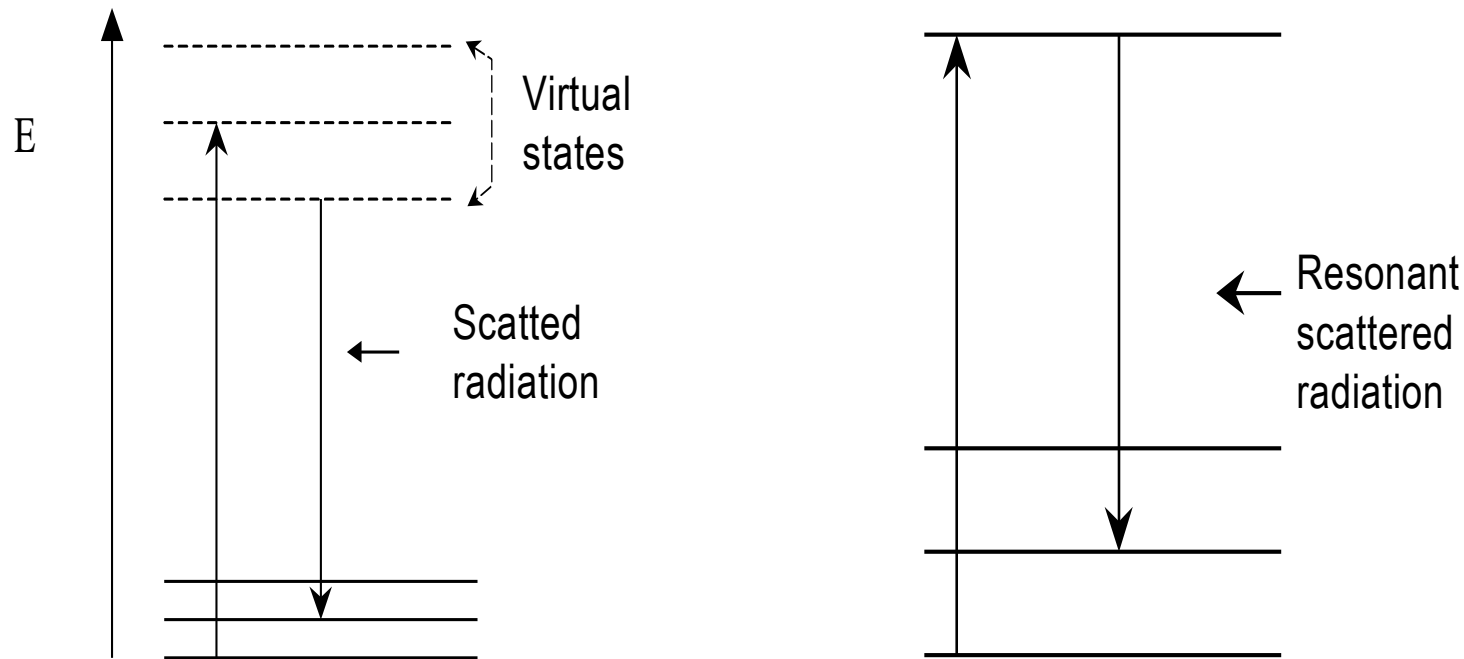
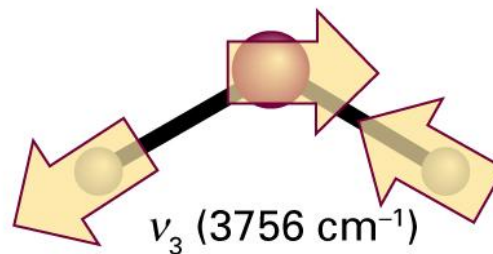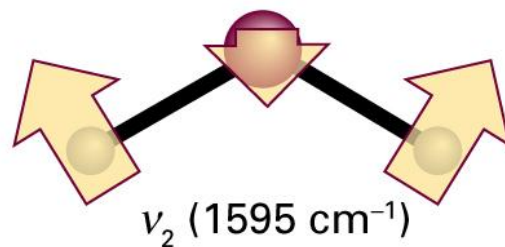由這些較強的 scattered radiation 中，可以從 stokes lines 中分析到不同 quanta 的 vibration transitions。

3N – 5 (linear molecule), or, 3N – 6 (non-linear molecule)
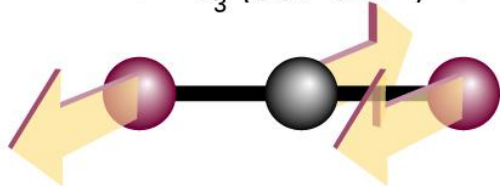

(a)
v_L
v_R

v_1 (1388 cm^{-1})

v_2 (2349 cm^{-1})

(b)

v_3 (667 cm^{-1})

(c)

v_1 (3652 cm^{-1})

v_2 (1595 cm^{-1})

v_3 (3756 cm^{-1})

motion corresponding to a normal mode should be accompanied by a change of dipole moment

parallel and perpendicular bands: dipole moment change is parallel and perpendicular, respectively, to the principal axis

a Q branch is observed in perpendicular band; a parallel band does not have a Q branch.

The vibrational spectra of different groups in a molecule give rise to absorptions at characteristic frequencies because a normal mode of even a very large molecule is often dominated by the motion of a small group of atoms.
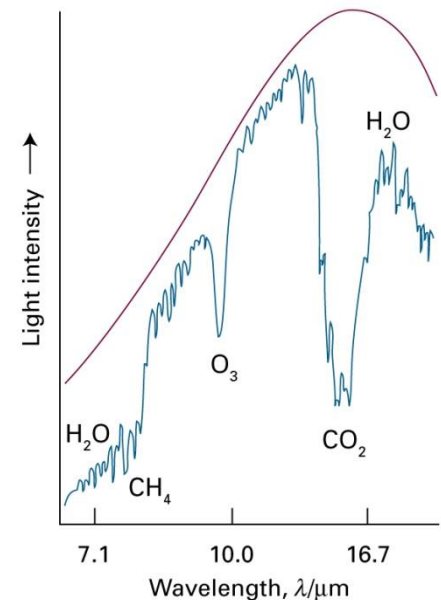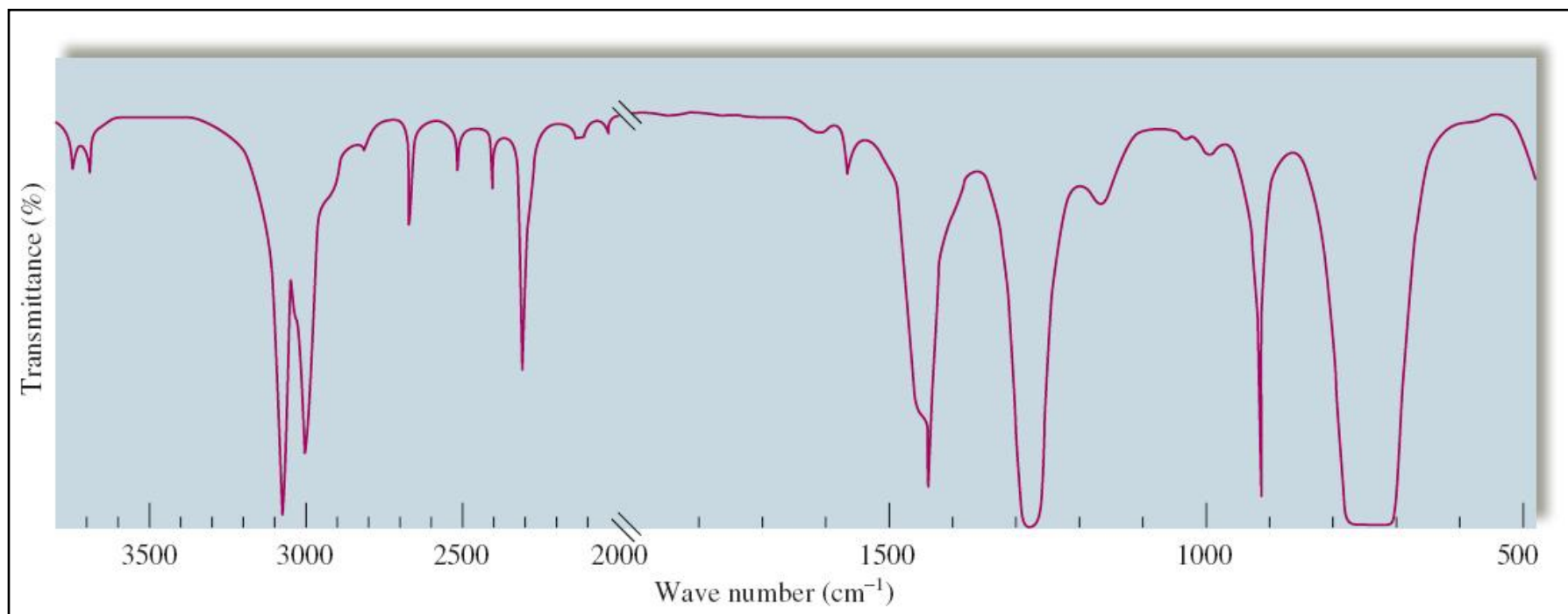
FIGURE 14.61

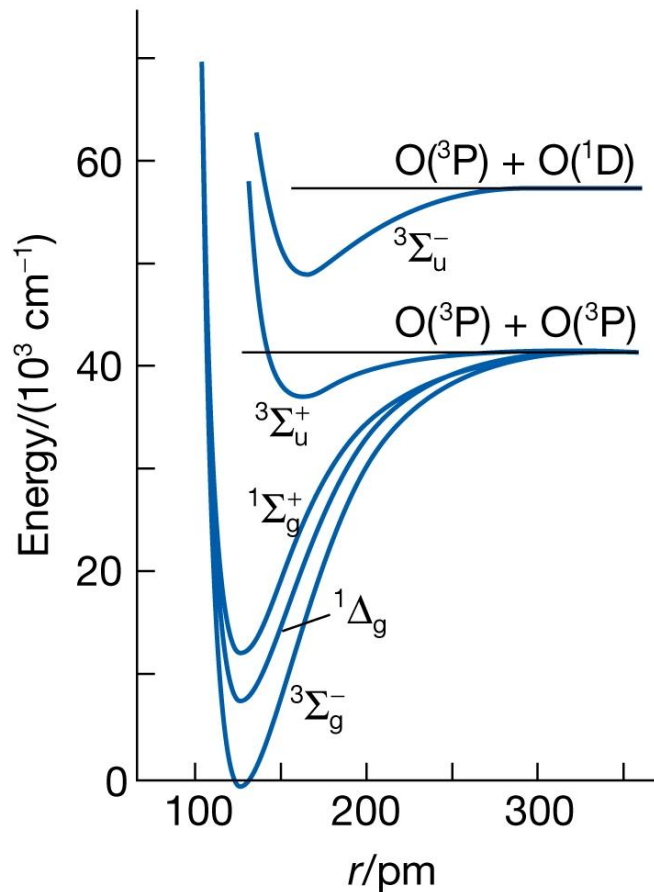The infrared spectrum of CH_2Cl_2. (The wave number scale changes on this spectrum at 2000 cm^{-1}.)

TABLE 14.1

Characteristic Stretching Frequency Ranges for Several Common Types of Bonds

Bond	Frequency Range (cm^{-1})
C—H	2850–3300
C=C	1640–1680
C≡C	2100–2260
C—O	1080–1300
C=O	1690–1760
O—H	3610–3640

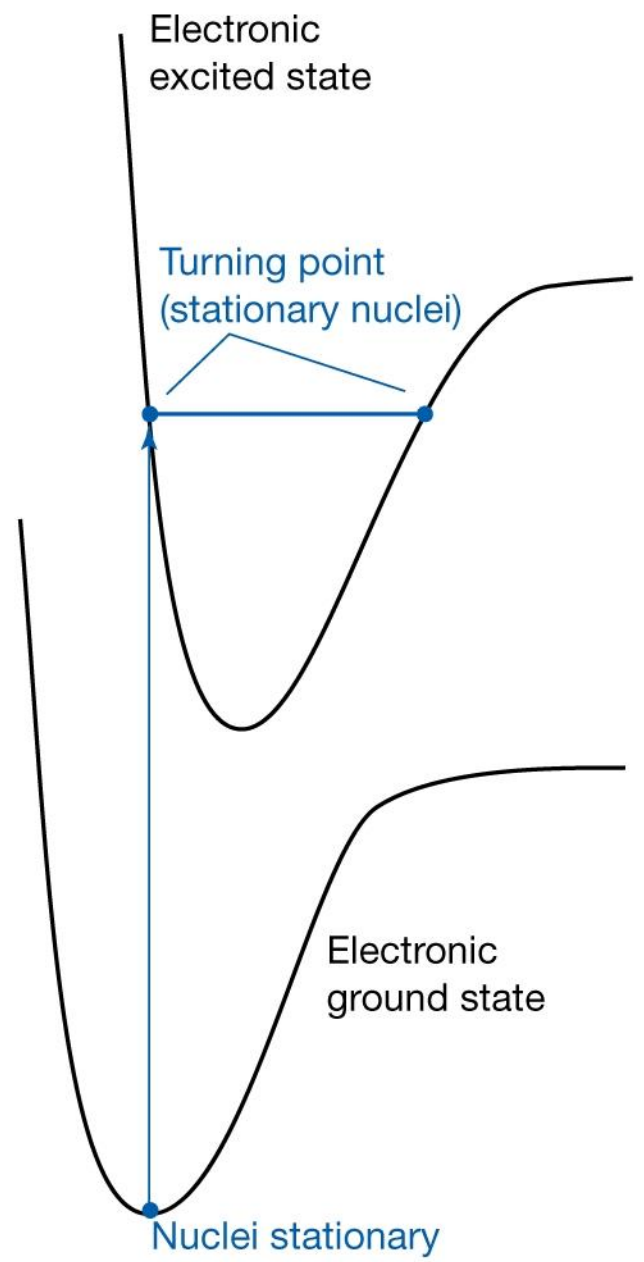## Electronic Transitions

Selection rules:
see p 494,

$$\Delta \Lambda = 0, \Delta S = 0,$$

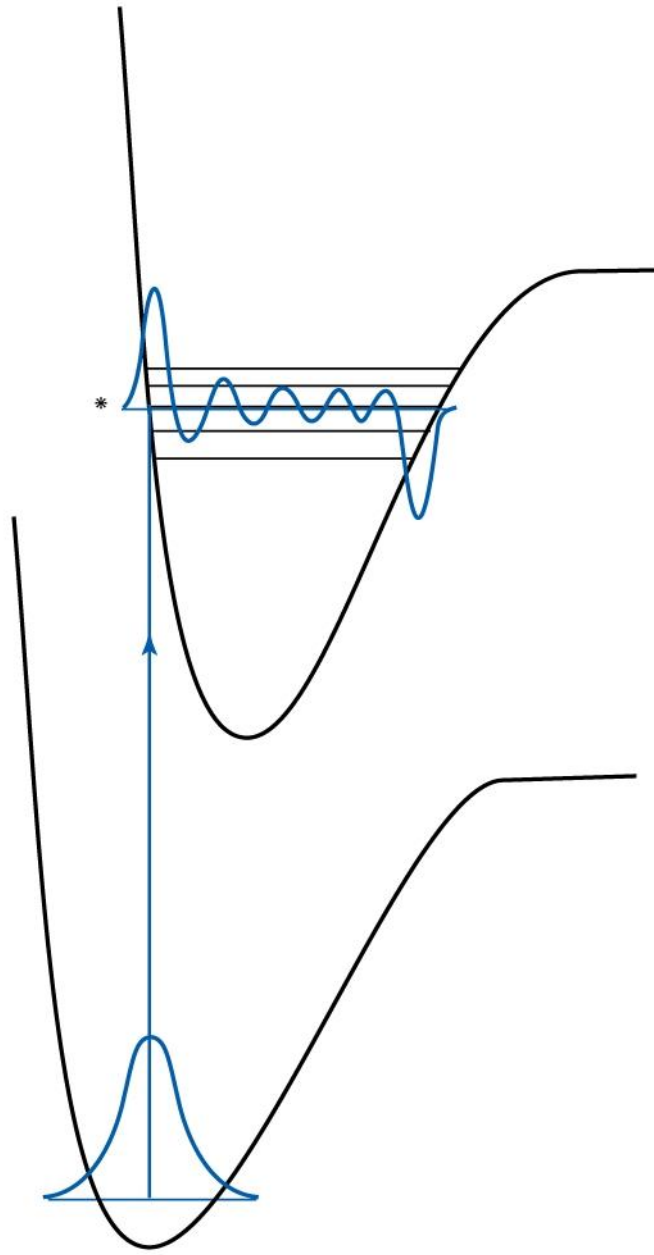$$\Delta \Sigma = 0, \Delta \Omega = 0, \pm 1$$

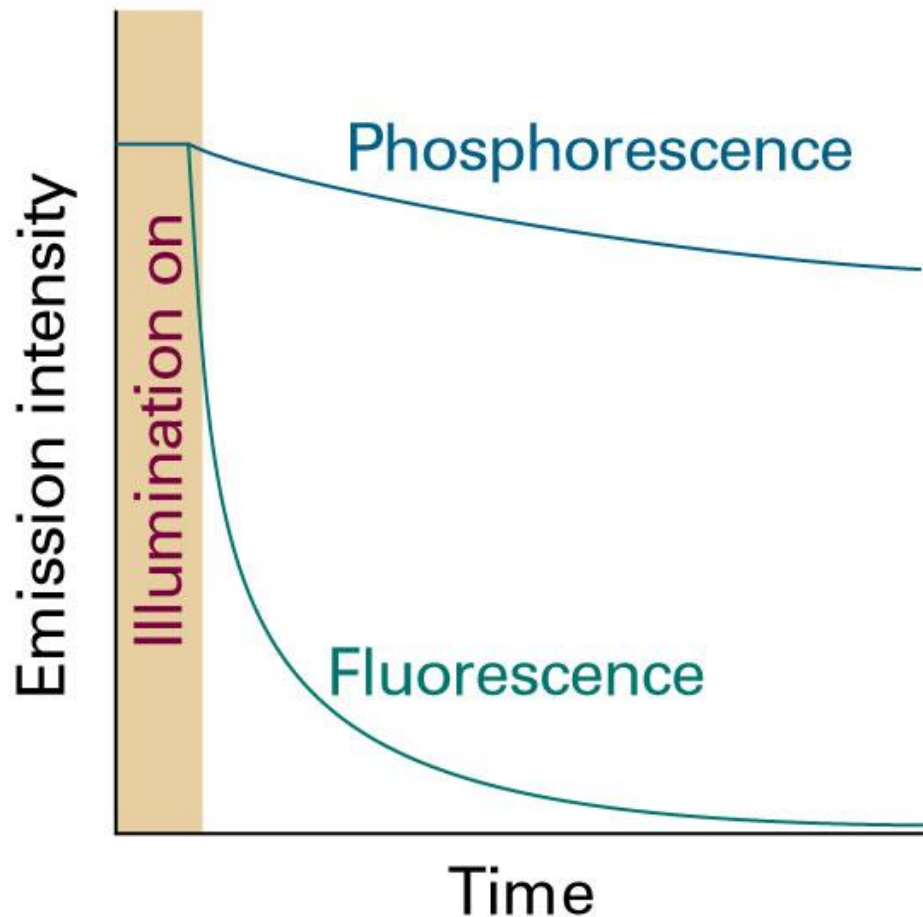$$\Sigma^+ \rightarrow \Sigma^+, \Sigma^- \rightarrow \Sigma^-$$

$$u \rightarrow g, g \rightarrow u$$
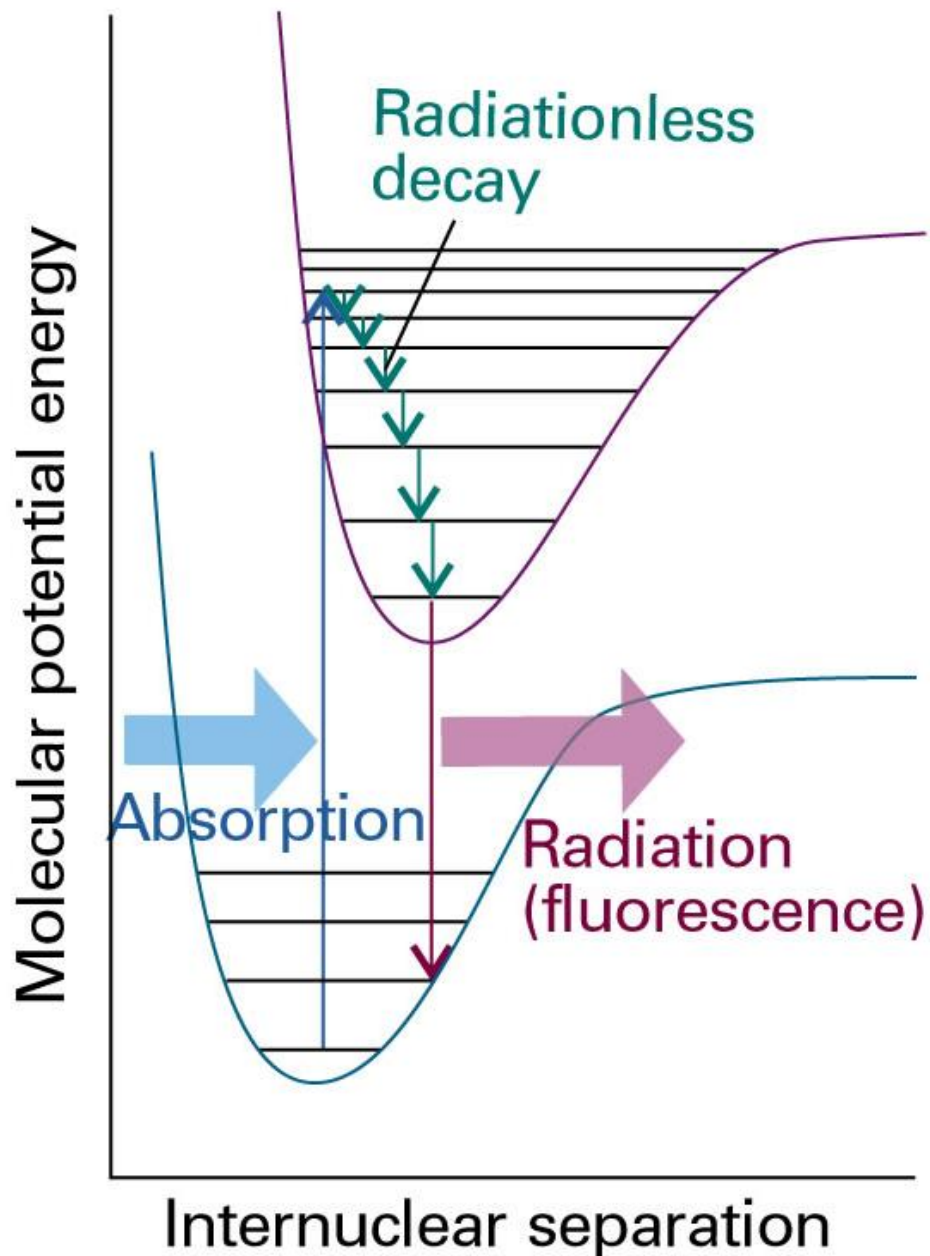
Franck-Condon principle
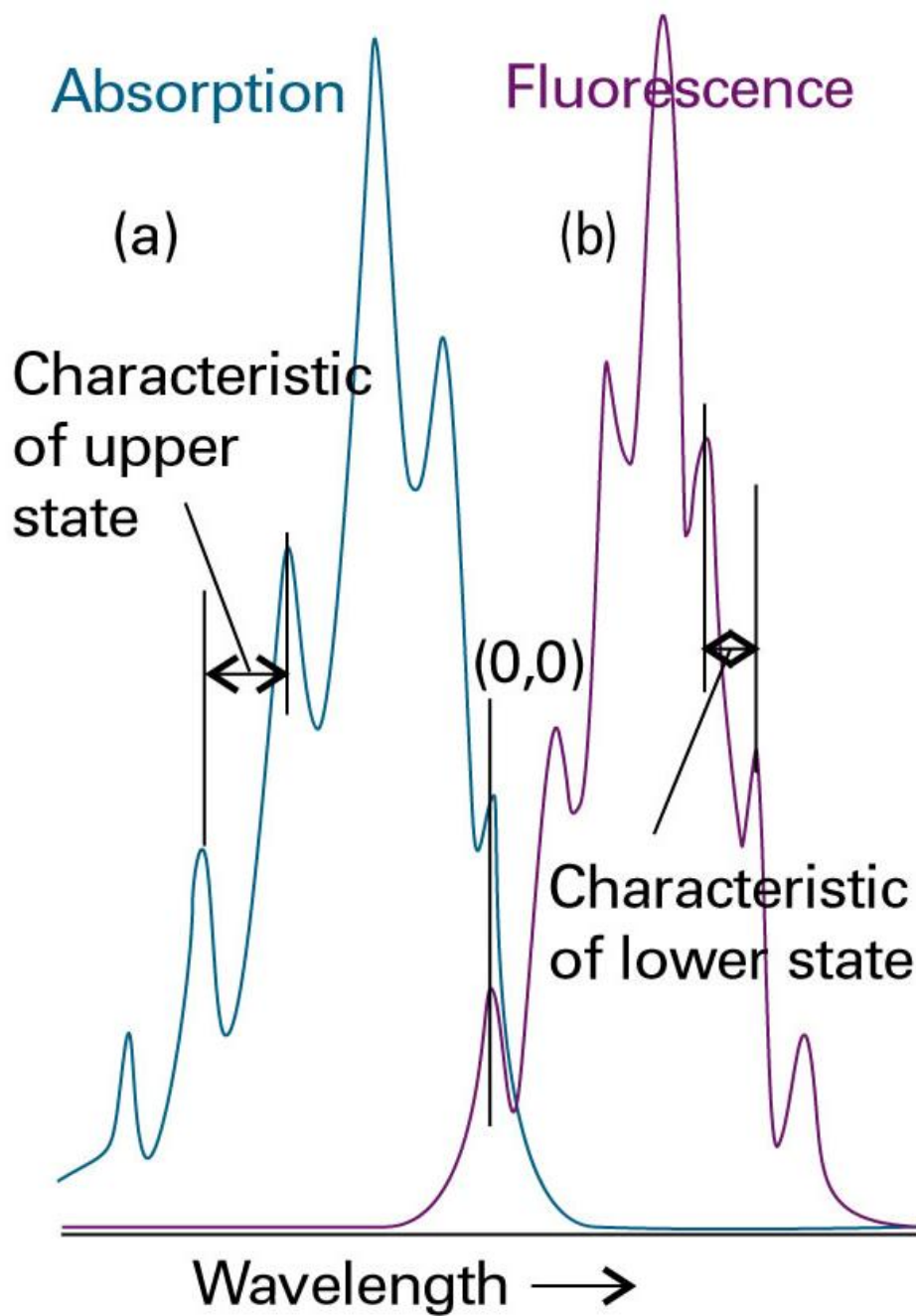
Franck Condon
factor calculation

Fig. 14.20 The empirical (observation-based) distinction between fluorescence and phosphorescence is that the former is extinguished very quickly after the exciting source is removed, whereas the latter continues with relatively slowly diminishing intensity.
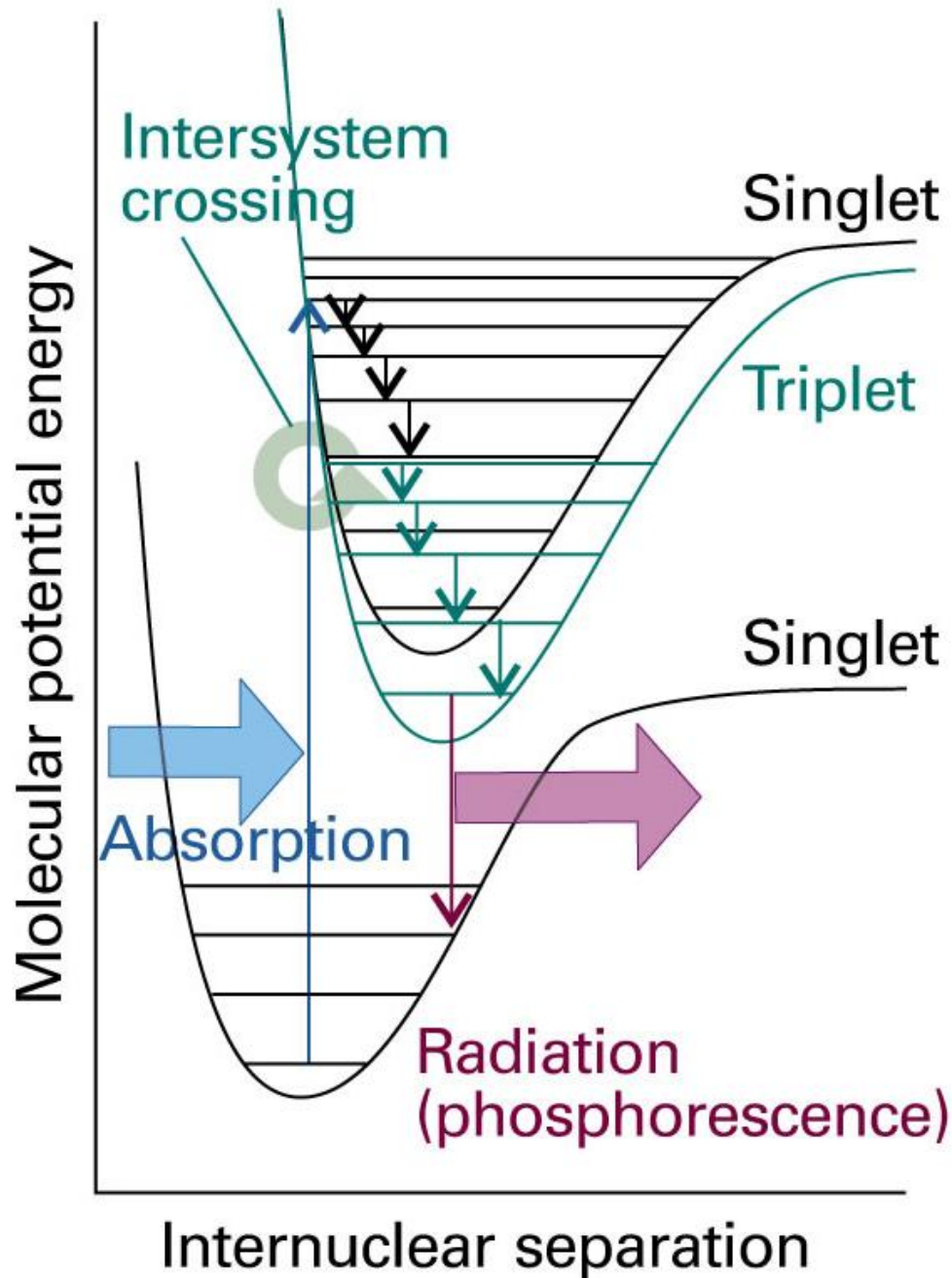
Fig. 14.21 The sequence of steps leading to fluorescence. After the initial absorption, the upper vibrational states undergo radiationless decay by giving up energy to the surroundings. A radiative transition then occurs from the vibrational ground state of the upper electronic state.

Chapter 13. Molecular spectroscopy 2: electronic transitions

Absorption

Fluorescence

(a)

(b)

Characteristic of upper state

(0,0)

Characteristic of lower state

Wavelength →

Fig. 14.22 An absorption spectrum (a) shows a vibrational structure characteristic of the upper state. A fluorescence spectrum (b) shows a structure characteristic of the lower state; it is also displaced to lower frequencies (but the 0−0 transitions are coincident) and resembles a mirror image of the absorption.

Chapter 13. Molecular spectroscopy 2: electronic transitions

P.505

Fig. 14.24 The sequence of steps leading to phosphorescence. The important step is the intersystem crossing, the switch from a singlet state to a triplet state brought about by spin–orbit coupling. The triplet state acts as a slowly radiating reservoir because the return to the ground state is spin-forbidden.
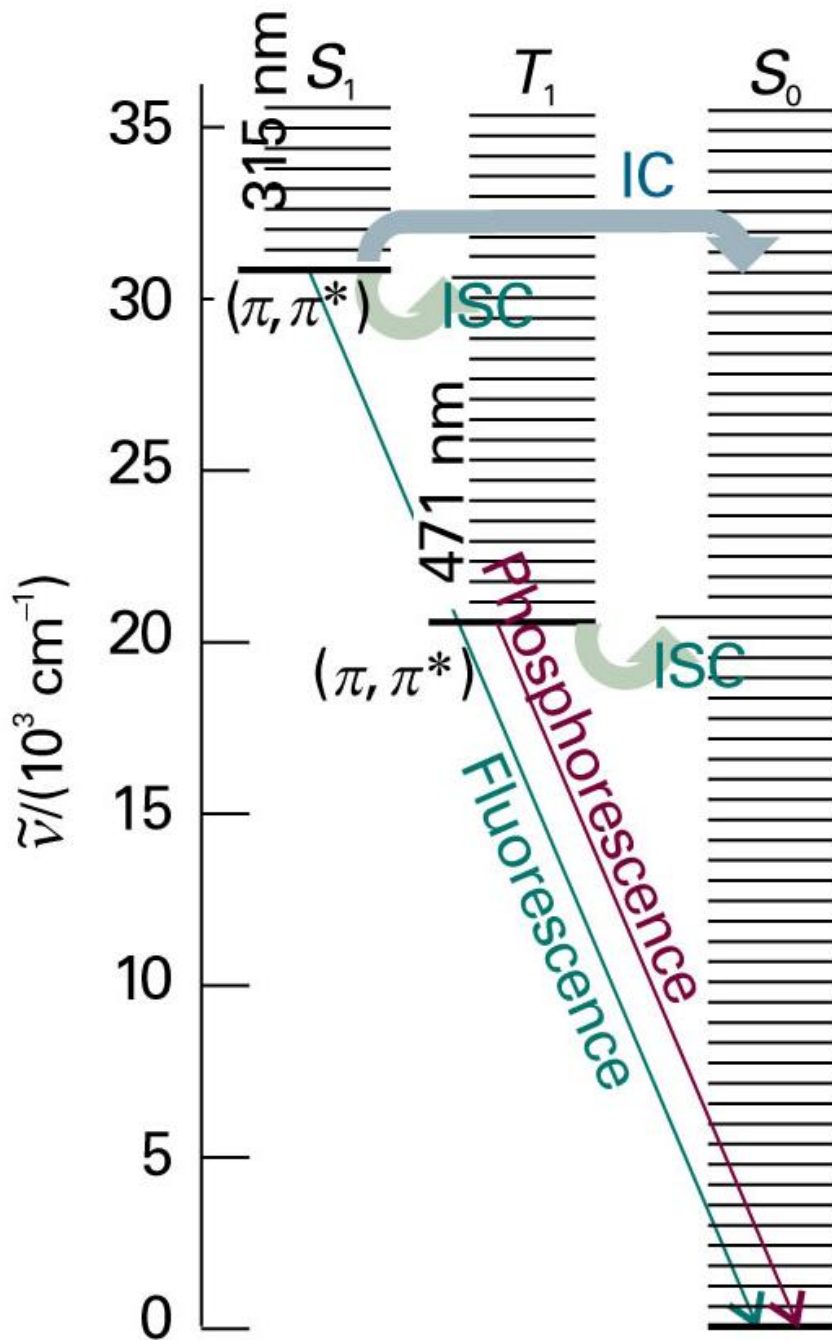
Fig. 14.25 A Jablonski diagram (here, for naphthalene) is a simplified portrayal of the relative positions of the electronic energy levels of a molecule. Vibrational levels of states of a given electronic state lie above each other, but the relative horizontal locations of the columns bear no relation to the nuclear separations in the states. The ground vibrational states of each electronic state are correctly located vertically but the other vibrational states are shown only schematically. (IC: internal conversion; ISC: intersystem crossing.)

Chapter 13. Molecular spectroscopy 2: electronic transitions
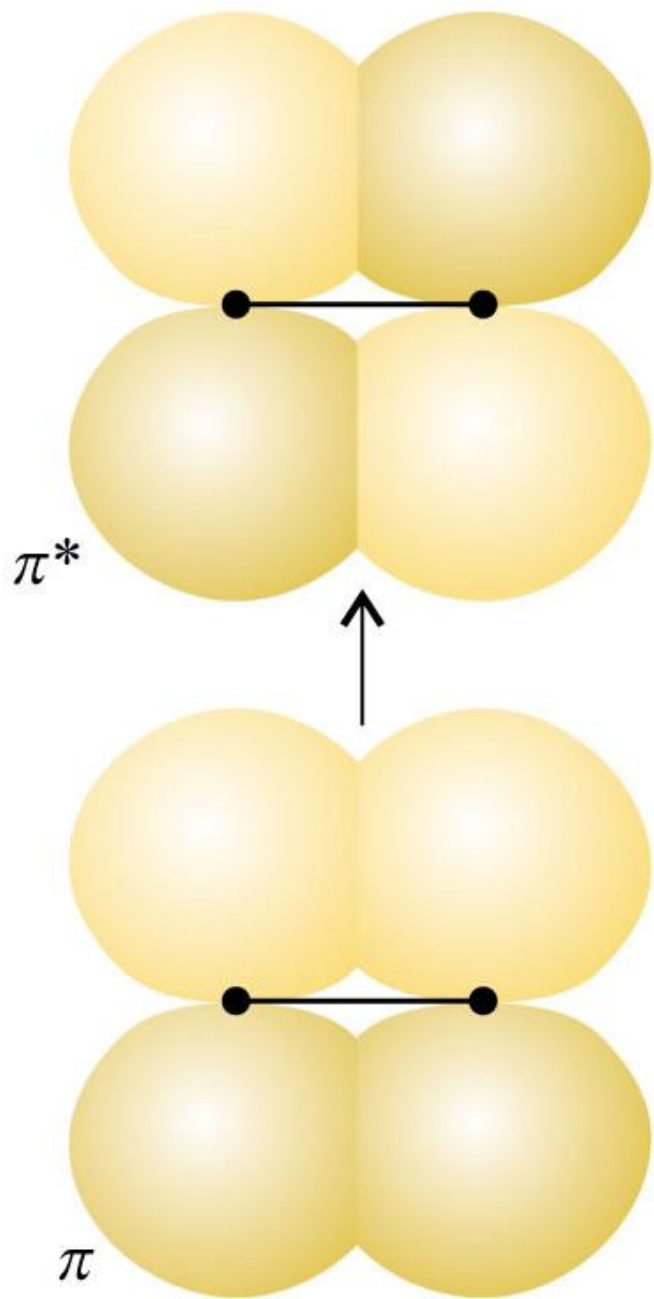
Photo-dissociation scheme and its spectrum
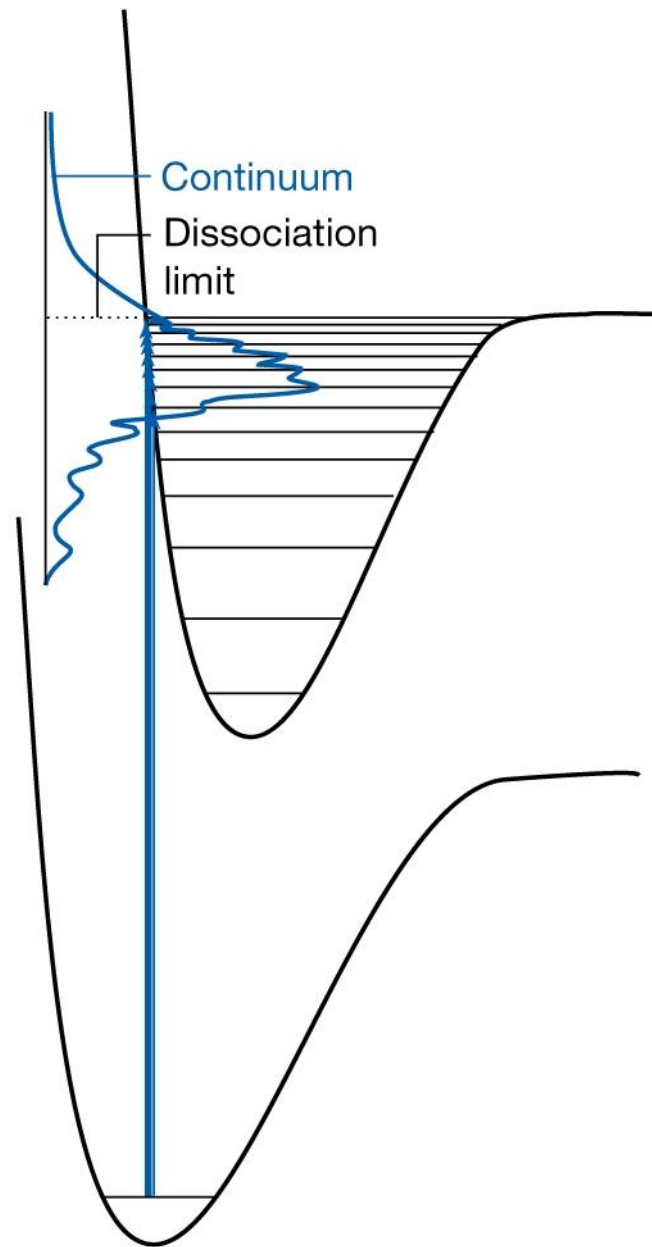
Pre-dissociation scheme and its spectrum
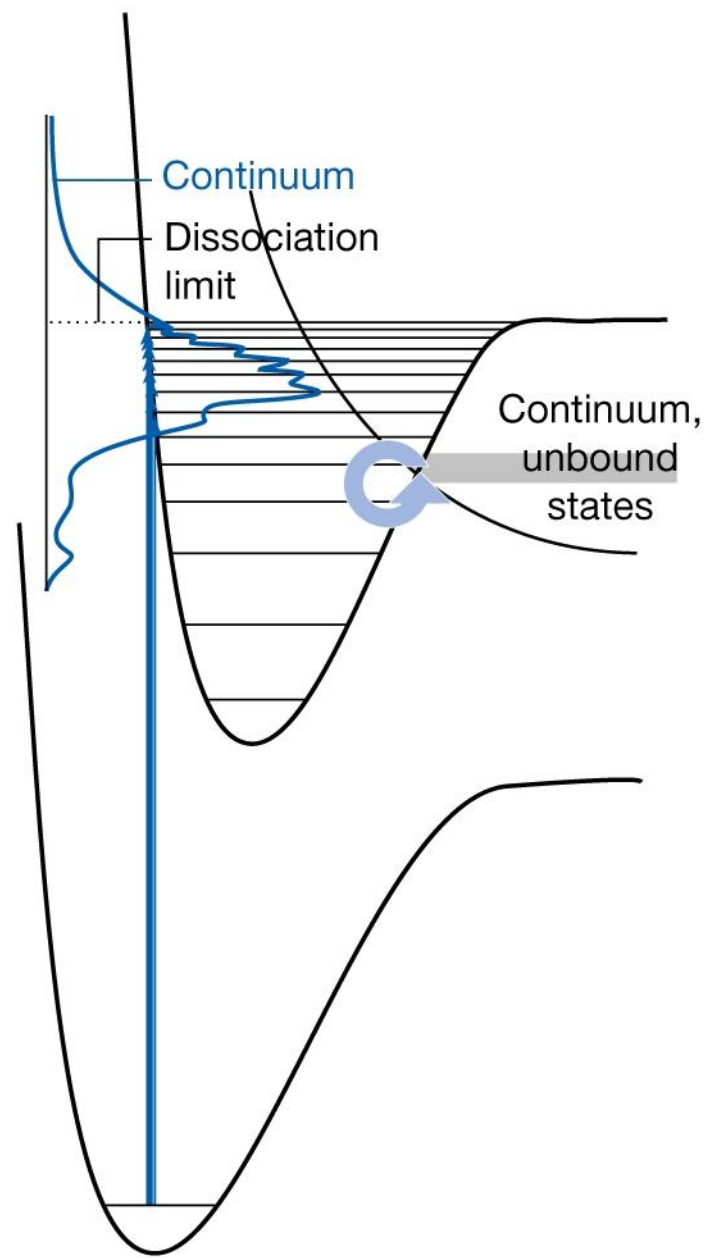
(d) $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ transition

對C=C bond的電子，$\pi^* \leftarrow \pi$ 有發生的機率，其波長範圍在 180nm(7 e.v.)左右，但若其conjugate system夠長的話，波長可以遷移到可見光的範圍。

在人體眼球中有一"visual purple" 其為一含11-cis-retinal的蛋白質，含有很長的conjugte double bond 其中第11個C的 $\pi \rightarrow \pi^*$在500nm的位置吸收，然後發生isomerization形成11-trans-retinal ，此一轉變產生一nerve impulse而傳至大腦瞭解見到光。

π^*

π

Fig. 14.14 A C=C double bond acts as a chromophore. One of its important transitions is the $\pi^* \leftarrow \pi$ transition illustrated here, in which an electron is promoted from a π orbital to the corresponding antibonding orbital.

Chapter 14. Molecular spectroscopy 2: electronic transitions
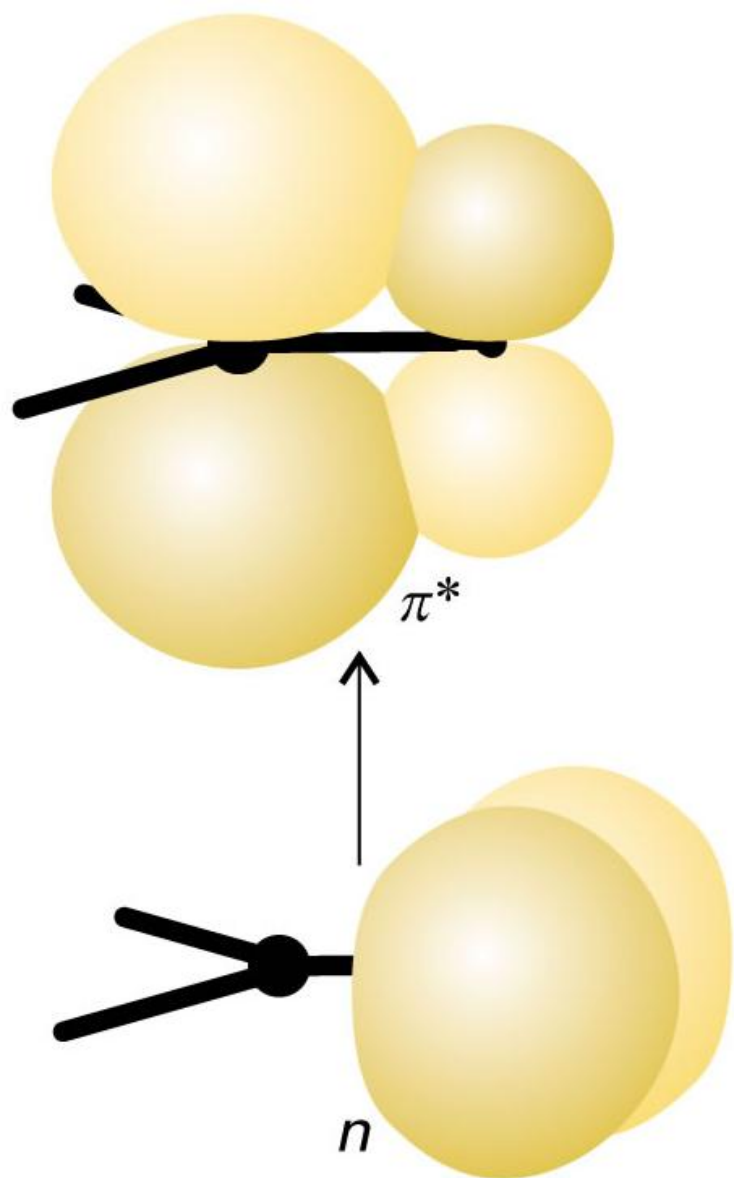
Fig. 14.15 A carbonyl group (C=O) acts as a chromophore primarily on account of the excitation of a nonbonding O lone-pair electron to an antibonding CO π orbital.

Synoptic table 14.3* Absorption characteristics of some groups and molecules

Group	$\tilde{v}/\text{cm}^{-1}$	λ_{max}/nm	$\varepsilon/(\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1})$
$C{=}C\ (\pi^\star \leftarrow \pi)$	61 000	163	5 000
	57 300	174	15 500
$C{=}O\ (\pi^\star \leftarrow n)$	35 000–37 000	270–290	10–20
$H_2O\ (\pi^\star \leftarrow n)$	60 000	167	7 000

* More values are given in the *Data section.*

Table 14.3 Absorption characteristics of some groups and molecules

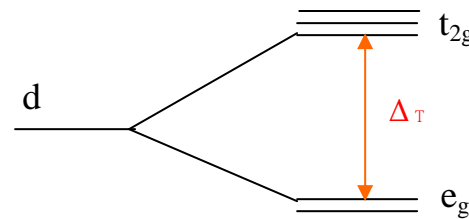| Group	$\tilde{v}_{max}/(10^4 \text{ cm}^{-1})$	λ_{max}/nm	$\varepsilon_{max}/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$
C=C ($\pi^\star \leftarrow \pi$)	6.10	163	1.5×10^4
	5.73	174	5.5×10^3
C=O ($\pi^\star \leftarrow n$)	3.7–3.5	270–290	10–20
—N=N—	2.9	350	15
	>3.9	<260	Strong
—NO$_2$	3.6	280	10
	4.8	210	1.0×10^4
C$_6$H$_5$—	3.9	255	200
	5.0	200	6.3×10^3
	5.5	180	1.0×10^5
$[\text{Cu(OH}_2)_6]^{2+}$(aq)	1.2	810	10
$[\text{Cu(NH}_3)_4]^{2+}$(aq)	1.7	600	50
H$_2$O ($\pi^\star \leftarrow n$)	6.0	167	7.0×10^3

.(1) d-d transitions
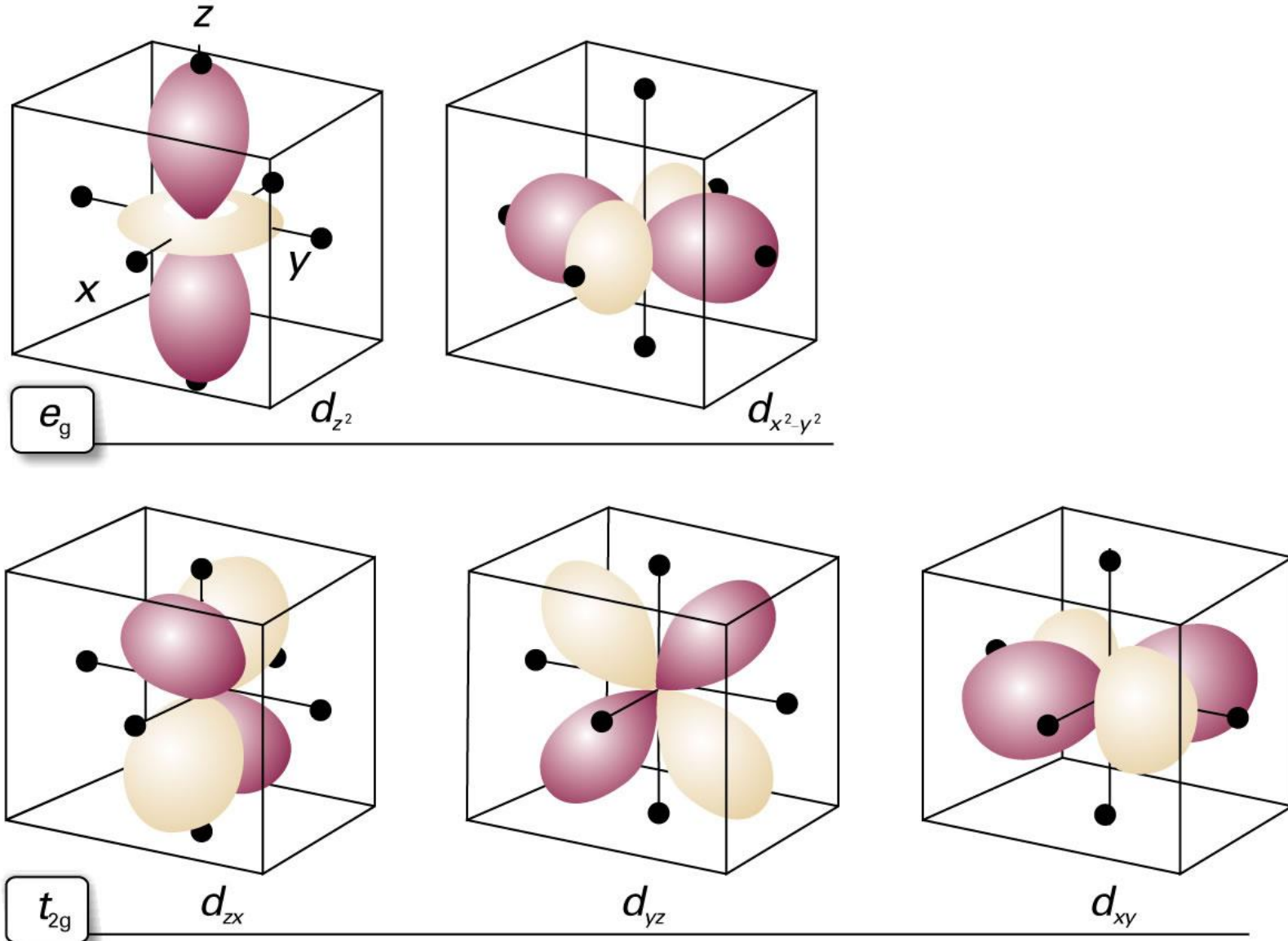
此為大部分過渡金屬具有色彩的原因，其transition λ 發生在可見光範圍

e.g.   for $Ti(OH_2)_6^{3+}$
$$\Delta_o \approx 20000 \text{ cm}^{-1}$$
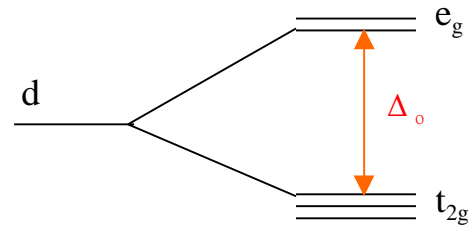
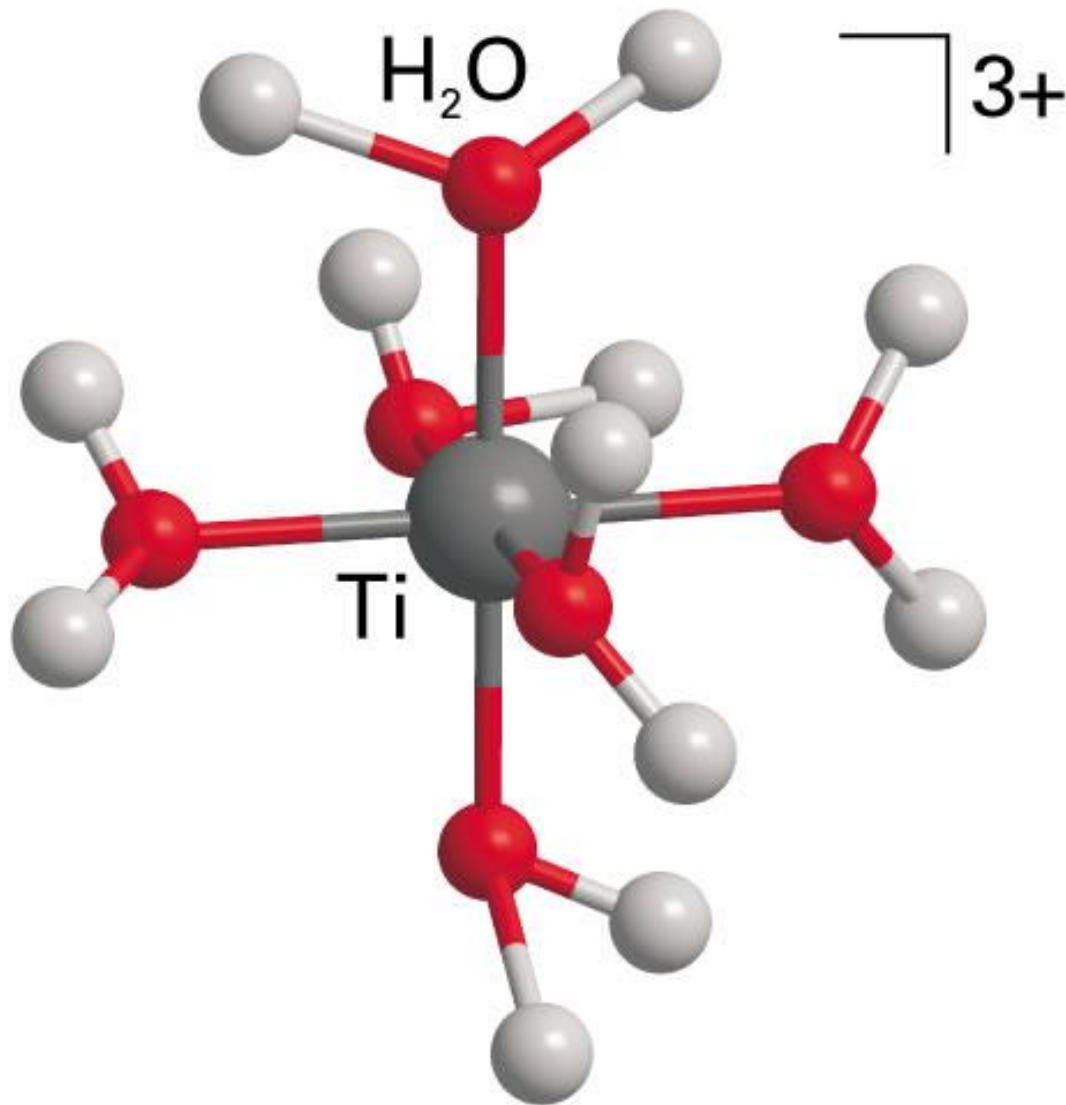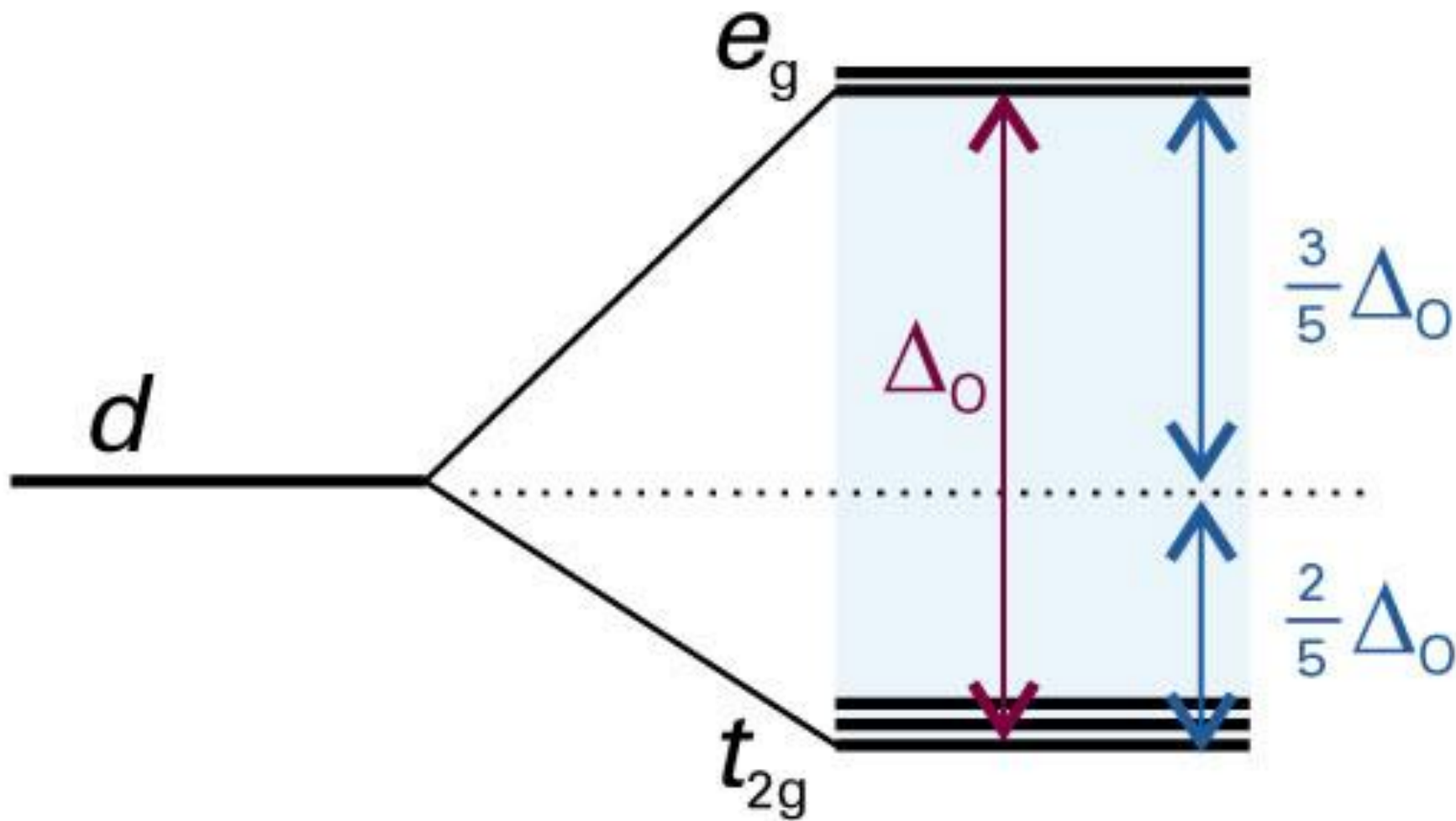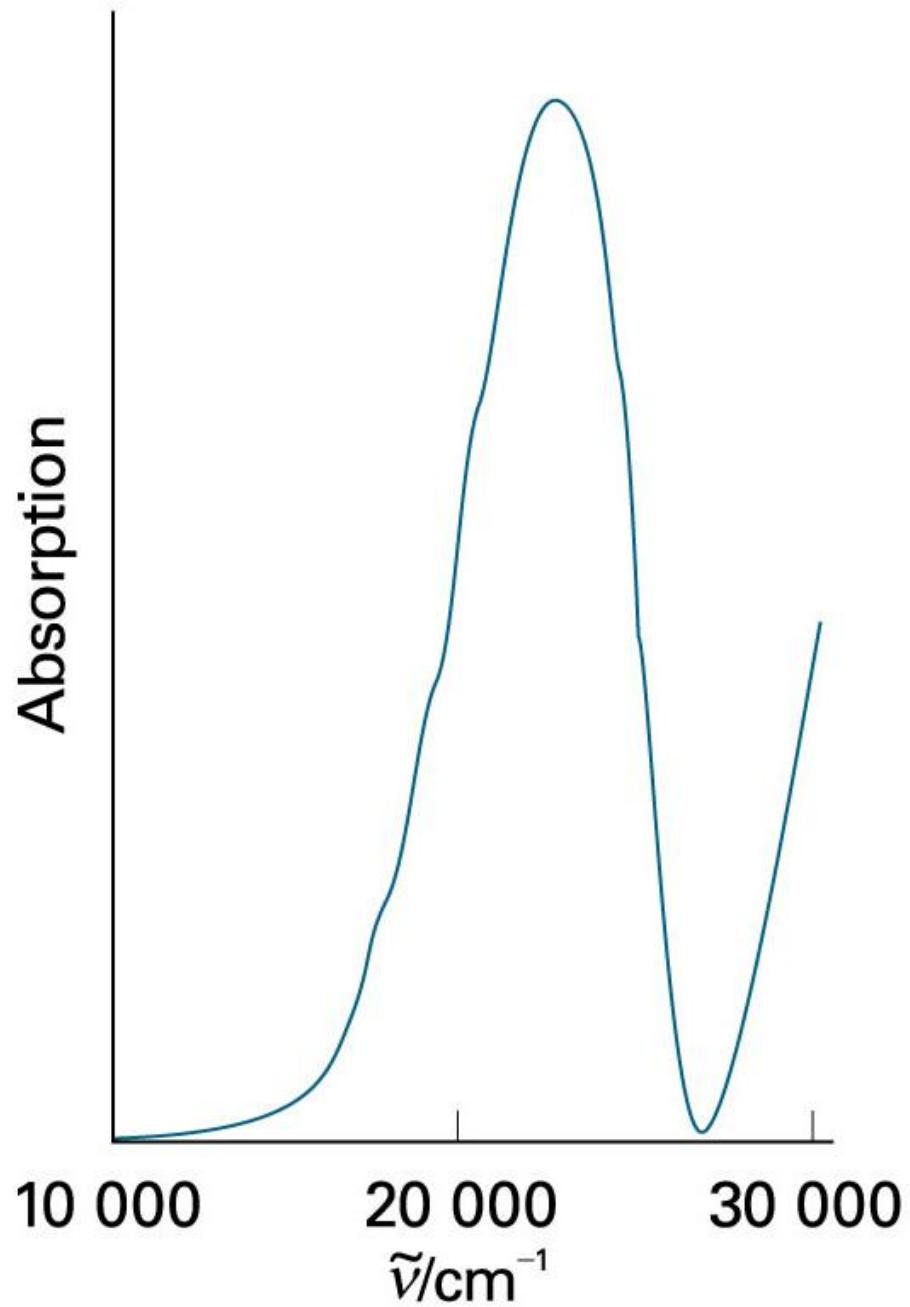for $Ni(OH_2)_4^{2+}$
$\Delta_T \approx$ 亦在可見光的範圍

Fig. 14.12 The classification of *d*-orbitals in an octahedral environment.

H_2O

$3+$

Ti

1 $[Ti(OH_2)_6]^{3+}$

2

Fig. 14.13 The electronic absorption spectrum of $[Ti(OH_2)_6]^{3+}$ in aqueous solution.

(2) <u>Vibronic Transitions:</u> A transition that derives its intensity from an asymmetrical vibration of a molecule is called a vibronic transition.

依據Laporte selection rule ，g↮g，μ ↮μ

然而因此種comlex分子發生振動時，就將此對稱中心破壞掉，

∴μ 和g就不存在了，因此在d-d transition中g↔g仍可以發生

e.g.參圖p494 Fig 13.5

vibronic (vibration & electronic) transition

因為 vibration而引發的 electronic transition 皆稱為vibronic

transition

L　A　S　E　R　_

  Light

  Amplification　 by

  Stimulated

  Emission　 of

  Radiation

雷射是一種光的放大，經由刺激(誘導)幅射所導至。

它和鐳扯不上關係，無放射性。

Emission (輻射)的種類:

.(1)Spontaneous Emission

自發輻射

.(2)Stimulated Emssion

刺激(誘導)輻射

產生雷射光的原理:

必要條件:

.(1)媒體 (midium)

可以是原子、分子、離子、氣體、液體或固體。
構成所謂固態、液態氣態,原子、分子及離子雷
射的名稱。

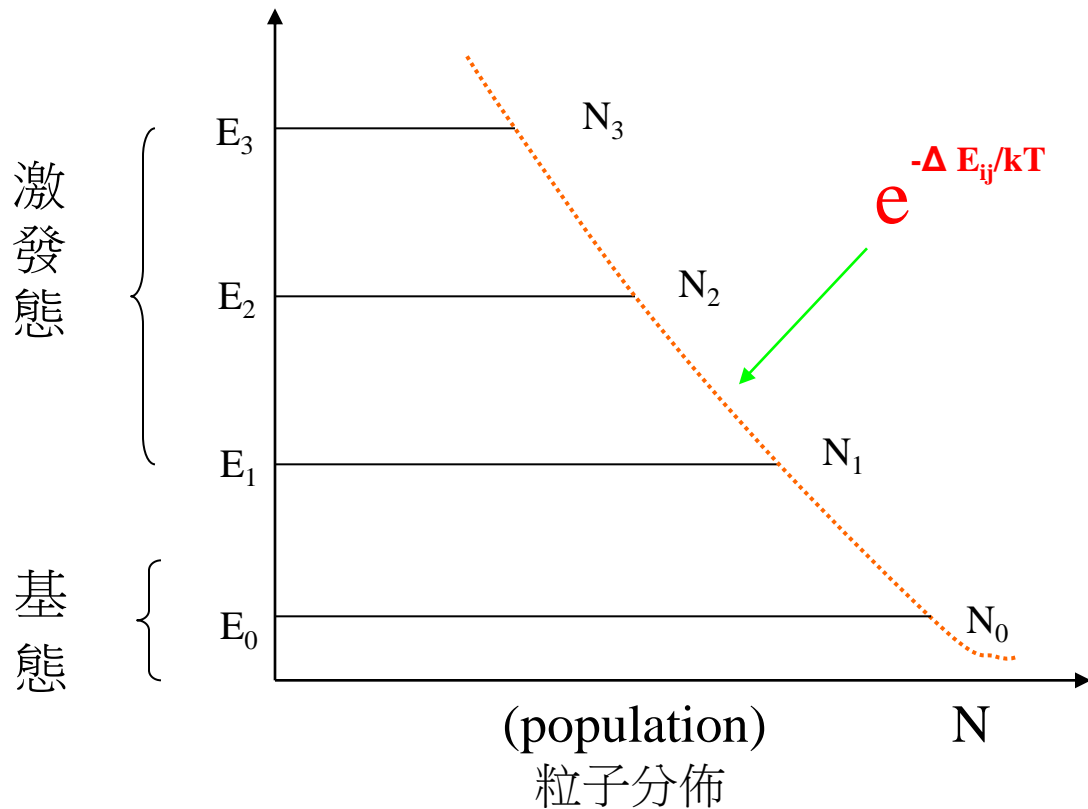.(2)能階粒子分佈反轉 (population inversion)

.(3)震盪裝置 (oscillation)
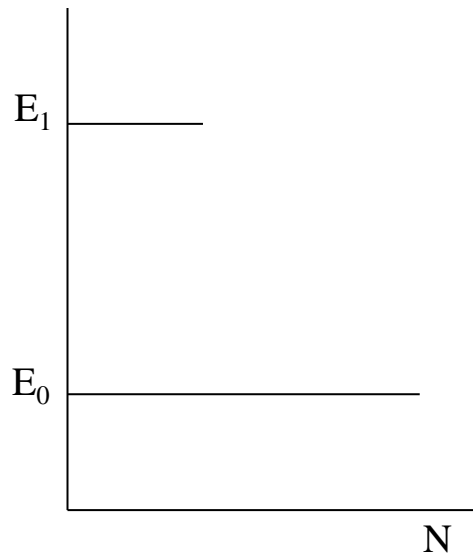
(laser cavity)

(feed-back)

Boltaman Distribution
(波耳茲曼能階粒子分佈律)

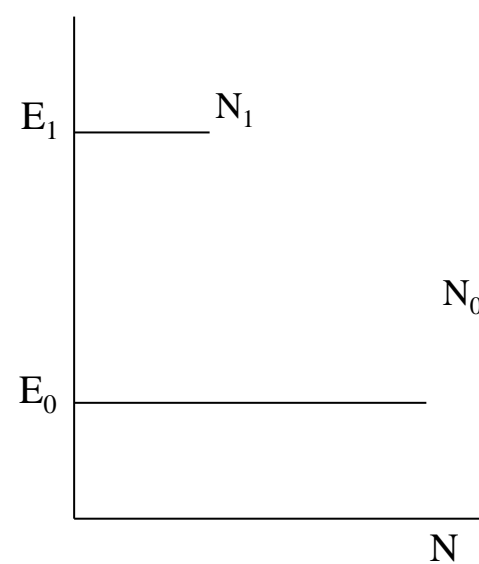$$\frac{N_j}{N_i} = e^{-\Delta E_{ij}/kT}$$

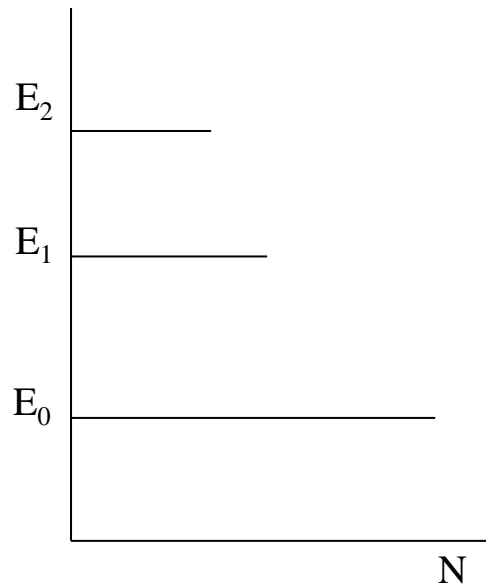# 何謂能階粒子分佈反轉 (population inversion)

Two-energy-level system

E_1

E_0

N

No pumping

E_1 N_1

E_0 N_0

N

Pumping (maximum)

No population inversion

$N_1 = N_0$

沒有雷射光

Three-energy-level system

E_2

E_1

E_0

N

No pumping

E_2 N_2

Fast decay N_1

E_1

∗ Laser
transition

E_0 N_0

N
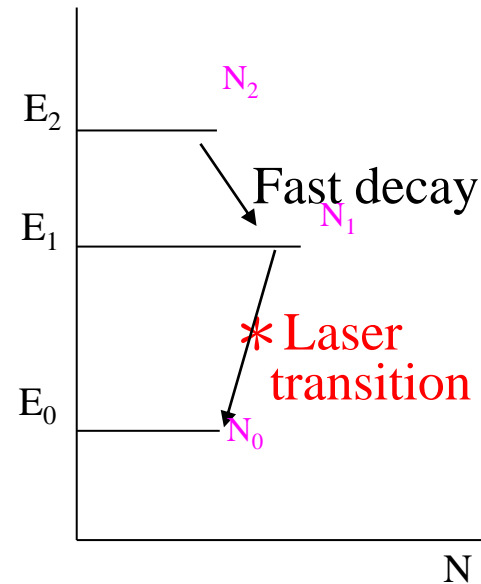
pumping

population
inversion

$N_1 > N_0$

雷射光($h\upsilon_{10}$)

Four-energy-level system

pump

population
inversion

$N_2 > N_1$

Feedback

聲 波 放 大

AMP

reflected light w..es

光 放 大

inverted laser medium

laser output beam

特定波長才能被放大
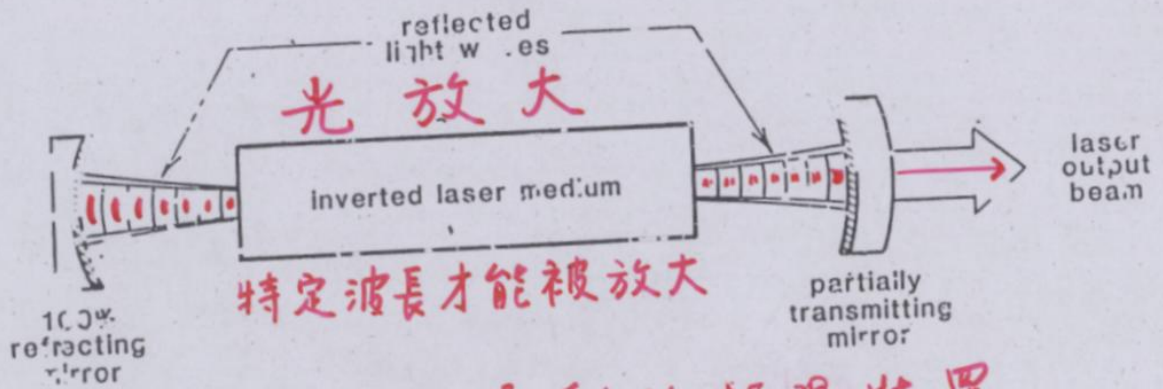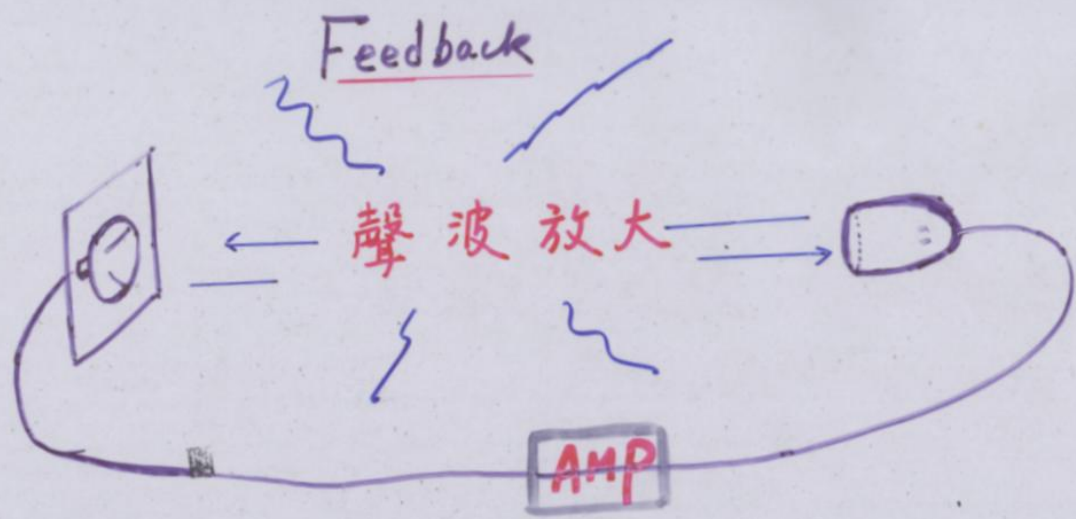
100% refracting mirror

partially transmitting mirror
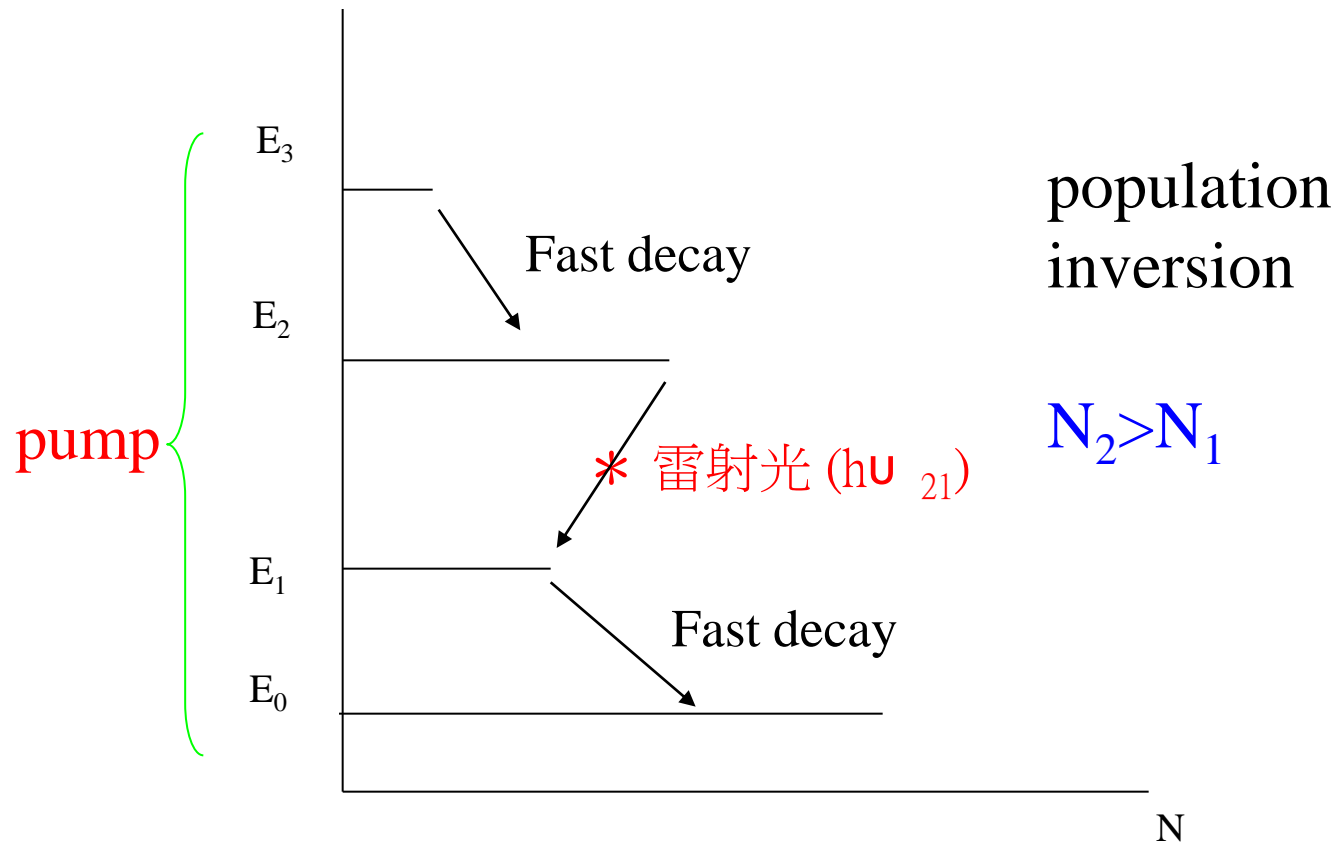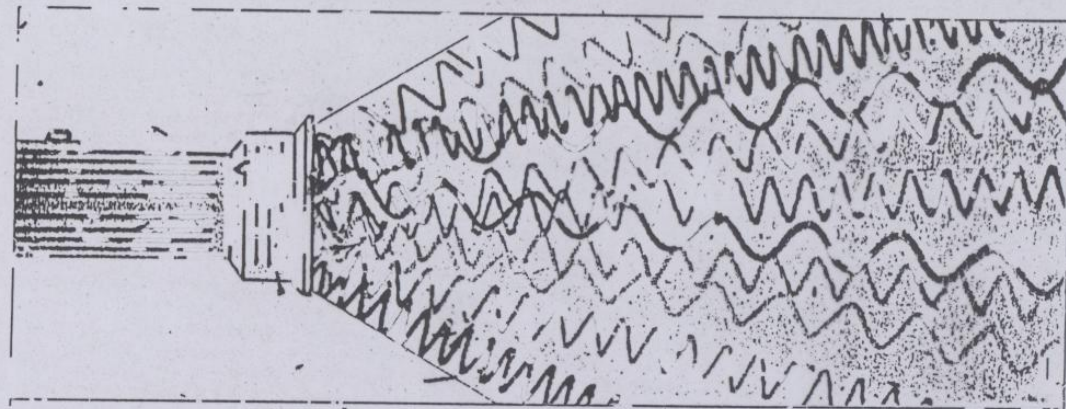
FIGURE 1.4
Laser oscillation.

產生雷射的振盪裝置

Laser 振當裝置

雷射光的特性:

(1) 高強度性 (intense)

(2) 高單光性 (monochromatic)

(3) 高同調性 (coherent)

(4) 高平行(方向)性 (directional)

(5) 高偏極光性 (polarized)

非一般光所能及

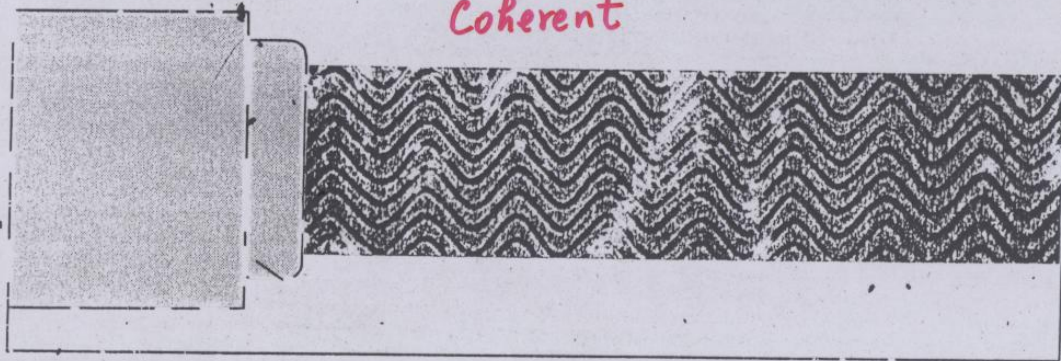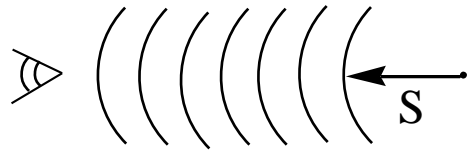Incoherent

普
通
光

Coherent

雷
射
光

FIGURE 1.42

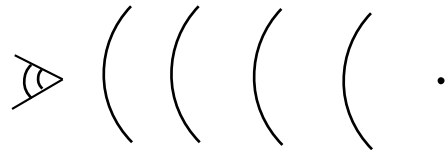Incoherent light from a flashlight (top) and coherent light from a laser (bottom).

Linewidth

有很多效應會影響到譜線的width (頻寬)

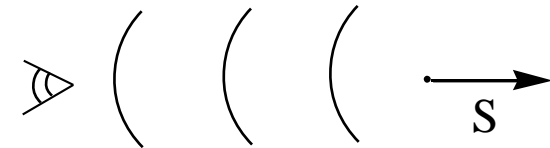（a）Doppler broadening (都卜勒效應產生的加寬)

$$v_{approaching} = \frac{v}{1 - s/c}$$

$$v = v$$

$$v_{receding} = \frac{v}{1 + s/c}$$

C：光速

v：光頻

S：發光體的移動速率

粒子處於各種不同方向及速度的分佈情形，其分佈曲線就似Gaussian function($\propto e^{-ax^2}$)

$\therefore$得到的Doppler shift profile.

就似Gaussian function　(bell-shape）

在同狀況下，質量越輕的氣體，其 Doppler broadening 的寬度越大。for N_2 分子在 300K時，其

$$\delta v \big/ v = 2.3 \times 10^{-6}$$
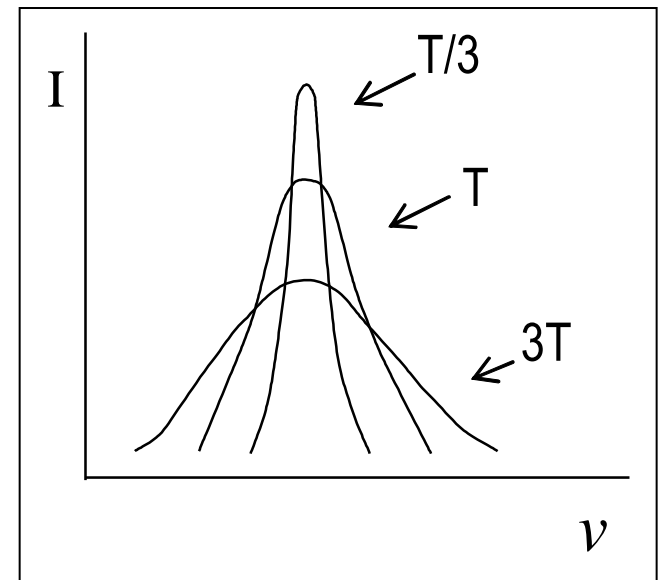
若是針對 rotation transition wave number ~ 1cm^{-1} (30 GHz)
則其 $\delta v = 3.0 \times 10^{10} \times 2.3 \times 10^{-6} = 70 kHz$ …其 δv 隨溫度升高
而變大 $\therefore$若要得到清晰尖銳光譜，通常皆在低溫下進行。

（b）lifetime broadening (or natural lifetime broadeing)

是完全依照 Heisenberg uncertainty principle，依據 state lifetime 的長短，對該 state 所處能階明確度的判別 ： $\Delta E \cdot \Delta t \geq \hbar$

$\because \Delta E = h c \Delta v \quad \geq \dfrac{\hbar}{\Delta t}$

$\therefore \Delta v = \dfrac{\dfrac{1}{2\pi c}}{\tau} \quad \approx \quad 5.3 \times 10^{-12} \quad \dfrac{cm^{-1}}{\tau_{\sec}} = \quad 5.3 \quad \dfrac{cm^{-1}}{\tau_{picosecond}}$

$(\quad \tau = \Delta t \quad)$

所以lifetime越短的state，其 $\Delta \tilde{v}$ 越大，越 broad(與溫度無關)然而其受控於nature (∵其 會spontaneous emission)，亦即electronic transition linewidth比vibrational or rotational transition linewidth來得大的多（why?）一般 electronic transition lifetime約10^{-8} sec

$$\Rightarrow \ \Delta \tilde{v} \approx 5 \times 10^{-4} cm^{-1} = 15 MH_Z \quad \text{而 rotational state natural}$$

lifetime 約10^3 sec $\Rightarrow \Delta \tilde{v} = 5 \times 10^{-15} cm^{-1} = 10^{-4} Hz$

除此之外，尚有collision deactivation , 引出所謂 collision lifetime(亦即相隔多久會被撞) , τ_{col} ，而 所謂collision linewidth $\Delta E_{col} \approx \dfrac{\hbar}{\tau_{col}}$ 。
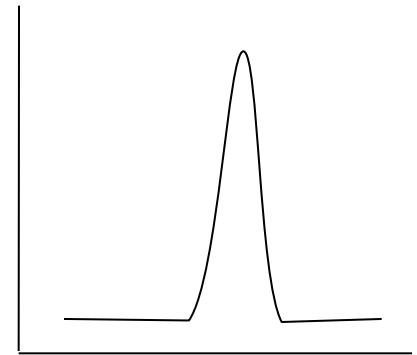
依據熱力學計算粒子碰撞頻率 z

$\therefore$碰撞間隔時間 $\propto \dfrac{1}{z}$, $\therefore \tau_{col} = \dfrac{1}{z}$ ，與粒子存在的 pressure 有關 ；

$\therefore \Delta E_{col}$ 與 pressure 有關

如何減低linewidth ？

lifetime broadening line shape 為 Lorentzian line shape

Absorption intensities

- 1. Stimulated absorption:
- transition from lower state to higher state.
- The transition rate:

$w = B\rho$, where B is called Einstein coefficient

of stimulated absorption, and

$\rho \mathrm{d}\upsilon$ is the energy density of radiation in the

frequency range υ to $\upsilon + \mathrm{d}\upsilon$, υ is the frequency of transition.

When the molecule is exposed to a black-body radiation

from a source of temperature T, ρ is given by the

Planck distribution : $\rho = \dfrac{8\pi h\upsilon^3 / c^3}{e^{h\upsilon / kT} - 1}$

- The total rate of absorption W, is proportional to the number of molecules being excited, W=Nw.
- Einstein considered that the radiation was also albe to induce the molecule in the upper state to the lower state: $w' = B' \rho$
- B' is called Einstein coefficient of stimulated emission.