6. Vibrationl Spectroscopy　（振動光譜）

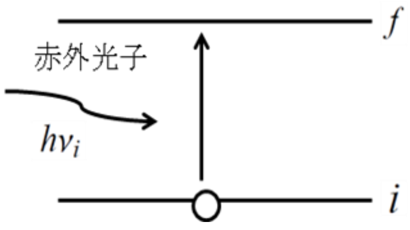
6.1 Infrared absorption and Raman scattering

Infrared absorption

Raman scattering

1) **Infrared absorption** 赤外吸収

Infrared photon



Final state with Energy E_f

Iinal state with Energy E_i

Energy conservation

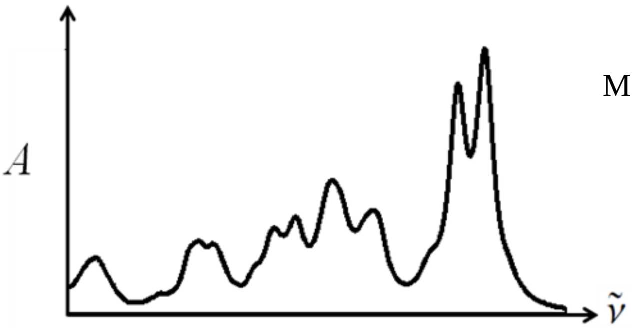
$$h\nu_i = E_f - E_i$$

Absorption intensity I

$$I \propto \left| \int \psi_f^* \mu \psi_i d\tau \right|$$

Einstein B coefficient

Absorbance



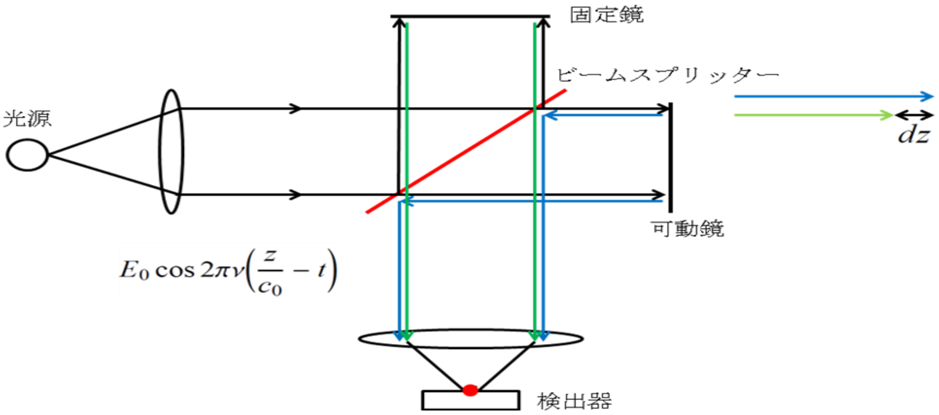
Wavenumber

Molecular fingerprint　(分子的指紋)

Infrared spectrometer

Dispersive spectrometer, prism or grating
FTIR

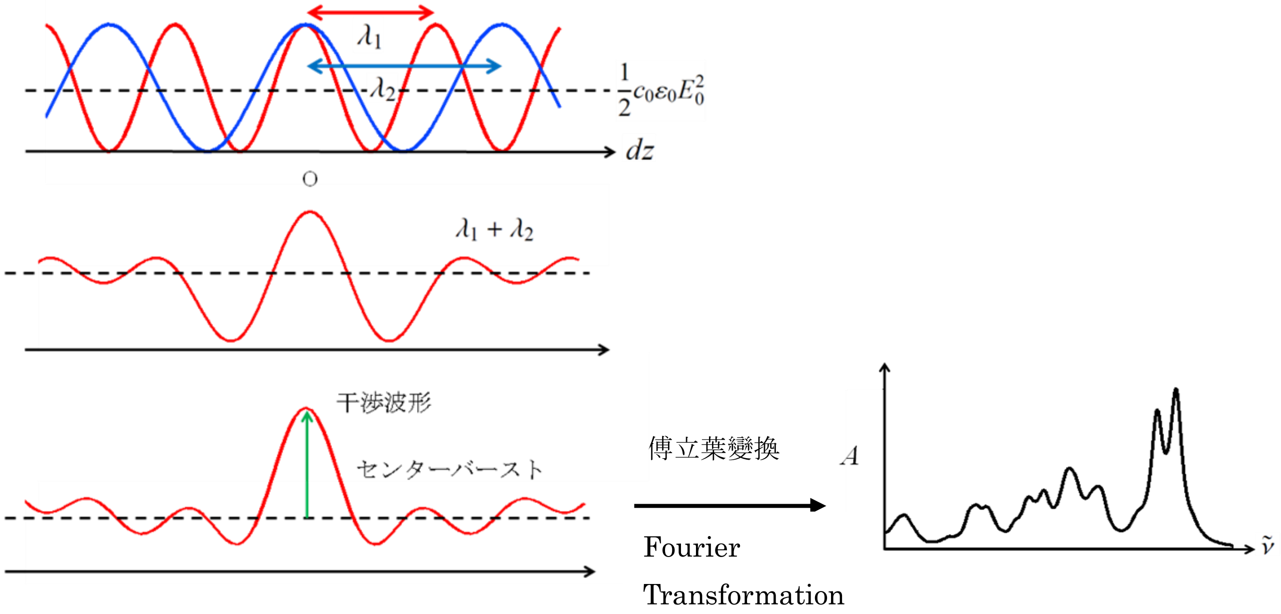
Michelson interferometer



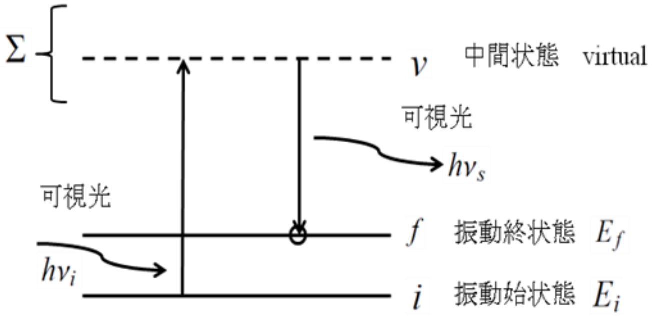
Light electric field on the detector

$$
\begin{aligned}
E &= E_A + E_B \\
&= \frac{1}{\sqrt{2}} E_0 \cos 2\pi\nu\left(\frac{z}{c_0} - t\right) + \frac{1}{\sqrt{2}} E_0 \cos 2\pi\nu\left(\frac{z+dz}{c_0} - t\right) \\
&= \sqrt{2} \cos \ \pi\nu\left(\frac{z}{c_0} - t + \frac{z+dz}{c_0} - t\right) \cos 2\pi\nu\left(\frac{-dz}{2c_0}\right) \\
&= \sqrt{2} \cos 2\pi\nu\left(\frac{z}{c_0} - t + \frac{dz}{2c_0}\right) \cos 2\pi\nu\left(\frac{dz}{2c_0}\right)
\end{aligned}
$$

$$
\begin{aligned}
I &= \overline{S}_z = c_0\varepsilon_0 \overline{E^2} \\
&= \frac{1}{2} c_0\varepsilon_0\left(\sqrt{2} E_0 \cos 2\pi\nu\left(\frac{dz}{2c_0}\right)\right)^2 = \frac{1}{2} c_0\varepsilon_0 E_0^2\left(1 + \cos 2\pi\nu\frac{dz}{c_0}\right) \\
&\qquad = \frac{1}{2} c_0\varepsilon_0 E_0^2\left(1 + \cos 2\pi\frac{dz}{\lambda}\right)
\end{aligned}
$$



2) Raman scattering 拉曼散射



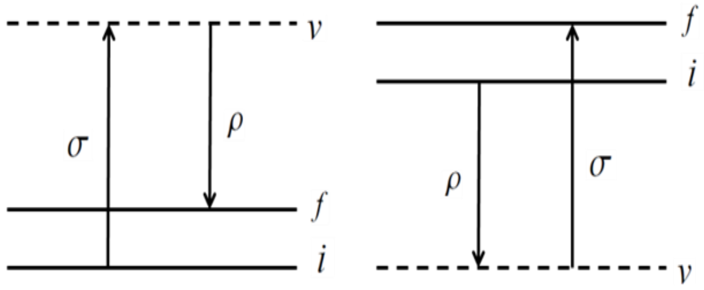
Energy conservation

$$\begin{cases} h\nu_i + E_i = h\nu_s + E_f \\ h\nu_i - h\nu_s = E_f - E_i \end{cases}$$

Intensity I

$$I \propto \left| \underbrace{\int \psi_f^* \mu \psi_v d\tau}_{v \to f} \underbrace{\int \psi_v^* \mu \psi_i d\tau}_{i \to v} \right|^2$$

$I \propto |a_{\rho\sigma}|^2$ $\quad a_{\rho\sigma}$: Raman scattering tensor



$$\rho = x, y, z$$
$$\sigma = x, y, z$$

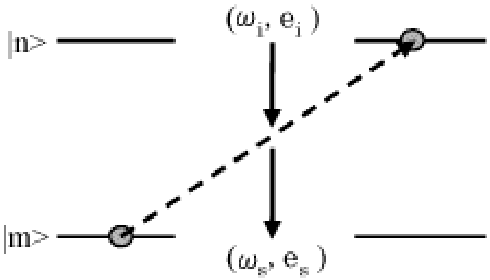
Kramers-Heisenberg-Dirac (KHD) formula

$$a_{\rho\sigma} = \sum_{v \neq i, f} \left\{ \frac{\int \psi_f^* \mu_\rho \psi_v d\tau \int \psi_v^* \mu_\sigma \psi_i d\tau}{E_v - E_i - h\nu_i} + \frac{\int \psi_f^* \mu_\sigma \psi_v d\tau \int \psi_v^* \mu_\rho \psi_i d\tau}{E_v - E_f + h\nu_i} \right\}$$

Quantum theory of Raman scattering

The initial and final states of Raman scattering 拉曼散射的始狀態和終狀態

In the quantum theory of Raman scattering, we calculate the probability for an optical process in which an incident photon with angular frequency ω_i and polarization vector e_i is annihilated and a new scattered photon with ω_s and e_s is created with a concomitant molecular transition from the initial state |m> to the final state |n>.



The photn number state is expressed as $|n_i,n_s>$, where n_i stands for the number of phtons with ω_i and e_i, n_s that for ω_s and e_s. The initial state |i> and the final state |f> of Raman scattering are expressed as the products of the photon and the molecular states as;

$|i>=|n_i,n_s>|m>$ (1)

$|f>=|n_i-1,n_s+1>|n>$. (2)

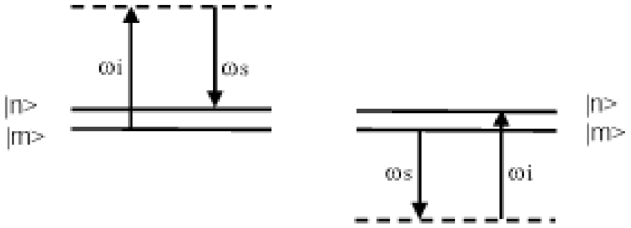
The intermediate states of Raman scattering 拉曼散射的中間狀態

The Raman scattering process is obtained as a second order perturbation of the light-matter interaction. There are two kinds of intermediate states that can combine the initial and final states by a one-photon transition.

$|v_1>=|n_i-1,n_s>|e>$ (3)

$|v_2>=|n_i,n_s+1>|e>$ (4)

$|v_1>$ corresponds to the state in which an incident photon is annihilated with a molecular transition from |m> to |e> (figure-a) and $|v_2>$ to that in which one scattered photon is created with |m> to |e> (figure-b).



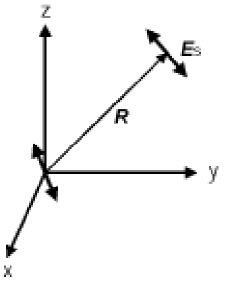
(a) (b)

The contribution of the second intermediate state is characteristic of Raman scattering that distinguishes Raman scattering from fluorescence.

In the quantum theory of Raman scattering, it is convenient to use photon flux F instead of intensity I, $I = h\omega C/2\pi$,where $h\omega/2\pi$ is the photon energy. F indicates the number of photons transmitted per unit time through unit area. The second order perturbation theory gives the following formula that connects the scattered photon number per unit time $F_s R^2$ and the incident photon flux F_i.

$$F_s R^2 = \frac{\omega_s^{3} \omega_i}{c^4} | e_s \alpha e_i |^2 \ F_i$$

$$\alpha_{\rho\sigma} = \sum_{e \neq m,n} \{ \frac{< m | D_\sigma | e >< e | D_\rho | n >}{E_e - E_m - E_i - i\Gamma_e} + \frac{< m | D_\rho | e >< e | D_\sigma | n >}{E_e - E_n + E_i + i\Gamma_e} \}$$



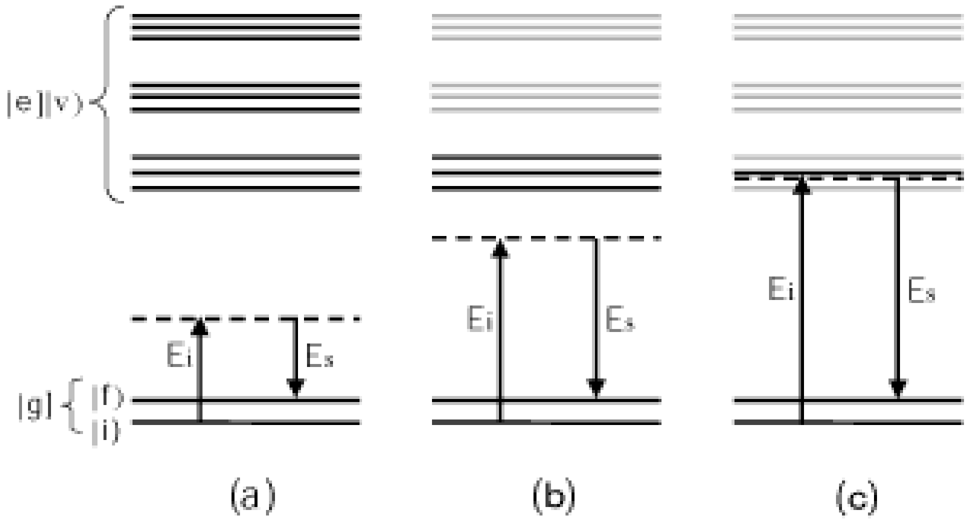
Here, $\boldsymbol{e}_i$ and $\boldsymbol{e}_s$ are the unit polarization vectors of the incident and scattered photons, a_{rs} is the Raman scattering tensor with s and r being (x,y,z), and D_s and D_r are the r and s components of the electric dipole moment.

Vibrational Raman scattering and electronic resonance

In vibrational Raman scattering in the ground electronic state, the initial, final and intermediate states are expressed as the products of the electronic and vibrational parts as,

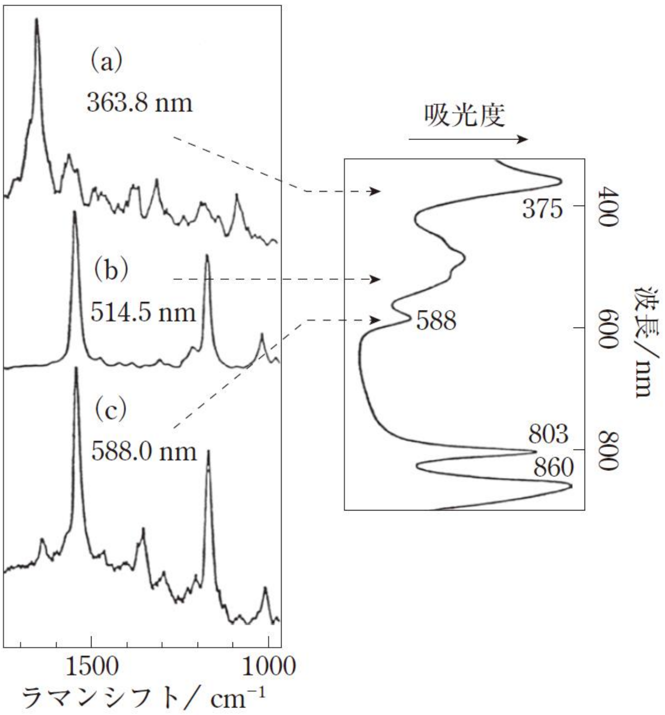
|m >=|g]|i) (7), |n>=|g]|f) (8), and |e>=|e]|v) (9)

where |] stands for electronic state and |) for vibrational state; |g] is the ground electronic state and |e] the excited electronic state(s), and |i), |f),|v) are the initial, final and intermediate vibrational states, respectively.



Off-resonance 非共振 Pre-resonance 前期共振 Rigorous resonance 真正共振

Resonance Raman scattering　共振拉曼散射



光合成細菌膜標準品的共振拉曼光譜（左）與電子吸收光譜（右）(a) 363.8nm，(b) 514.5nm，(c) 588.0nm 激發，（a）選擇性觀測細菌葉綠素，（b）選擇性觀測類胡蔔素，（c）觀測兩者

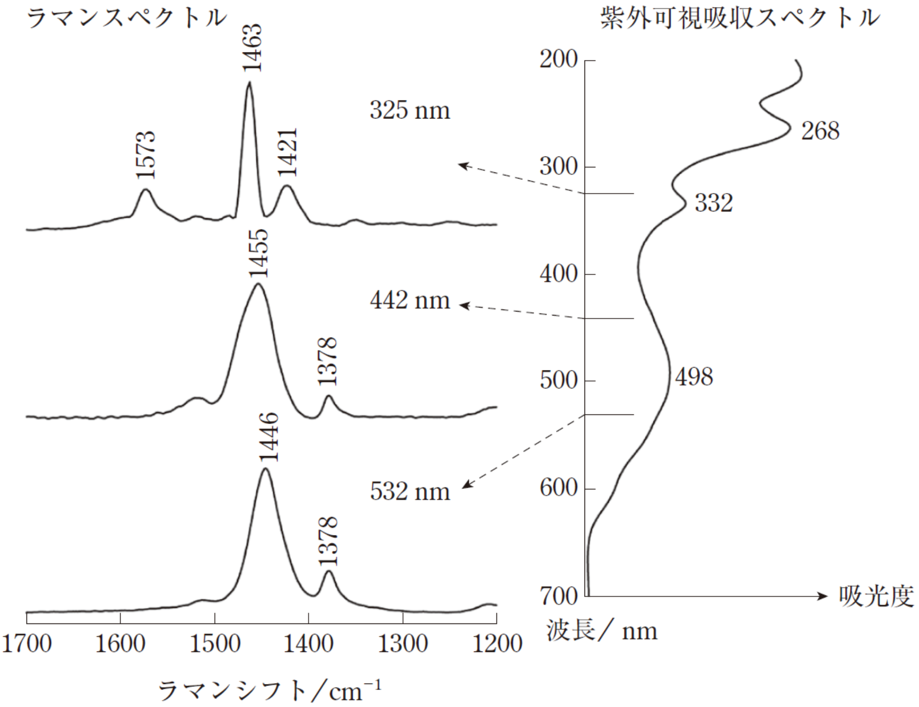


図 4.1.12　P3HT : PCBM 混合物（重量比 1 : 1）の紫外可視吸収スペクトルと共鳴ラマンスペクトル

In off-resonance Raman scattering (a), E_{ev}-E_{gi}» Ei and therefore many excited electronic states Σ |e] |v) contribute (virtual intermediate states). In pre-resonance Raman scattering, *E*i become close to E_{ev}-E_{gi} and the vibrational states of the lowest excited electronic state |e]Σ|v) play the role of interemediate states. In rigorous resonance Raman scattering, E_{ev}-E_{gi}~ *E*i and one particular vibronic state |e]|v) dominates the scattering process.

Placzek's polarizability theory of off-resonance Raman scattering

By introducing (7), (8), (9) into (6), we obtain the formula for vibrational Raman scattering.

$$\alpha_{\rho\sigma} = (i|[g|\sum_{e\neq g}\sum_{v}\{\frac{[g|D_\sigma|e]|v)(v|[e|D_\rho|g]}{E_{ev}-E_{gi}-E_i-i\Gamma_e} + \frac{[g|D_\rho|e]|v)(v|[e|D_\sigma|g]}{E_{ev}-E_{gf}+E_i+i\Gamma_e}\}|g]|f) \tag{10}$$

In off-resonance Raman scattering, E_{ev}-E_{gi}» E_i and therefore E_{ev}-E_{gi}-E_i is much larger than the vibrational energies. Then E_{ev}-E_{gi}-E_i+iΓ~ E_e-E_g-E_i holds with a good approximation. Then the closure property Σ|v><v|=1 simplifies (10) to the following form.

$$a_{\rho\sigma} \cong (i|\alpha_{\rho\sigma}|f)$$

$$\alpha_{\rho\sigma} = \sum_{e\neq g}\{\frac{[g|D_\sigma|e][e|D_\rho|g]}{E_e-E_g-E_i} + \frac{[g|D_\rho|e][e|D_\sigma|g]}{E_e-E_g+E_i}\} \tag{11}$$

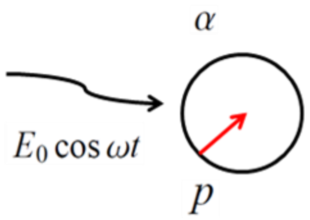
The Raman scattering tensor component a_{rs} is approximately given by the vibrational matrix element of the polarizability tensor component α_{rs} (Placzek polarizability theory).

Placzek polarizability theory

$$\begin{cases} h\nu_i << E_v - E_i & \text{Non-resonance condition} \\ i \text{ Is non-degenerate} & \text{Non-degenerate condition} \end{cases}$$

$$a_{\rho\sigma} \longrightarrow \int \psi_f^*(\mathbf{R})\alpha_{\rho\sigma}\psi_i(\mathbf{R})d\mathbf{R}$$

Classical model of the polarizability theory 極化率理論的古典力学



Dipole moment induced on the molecule

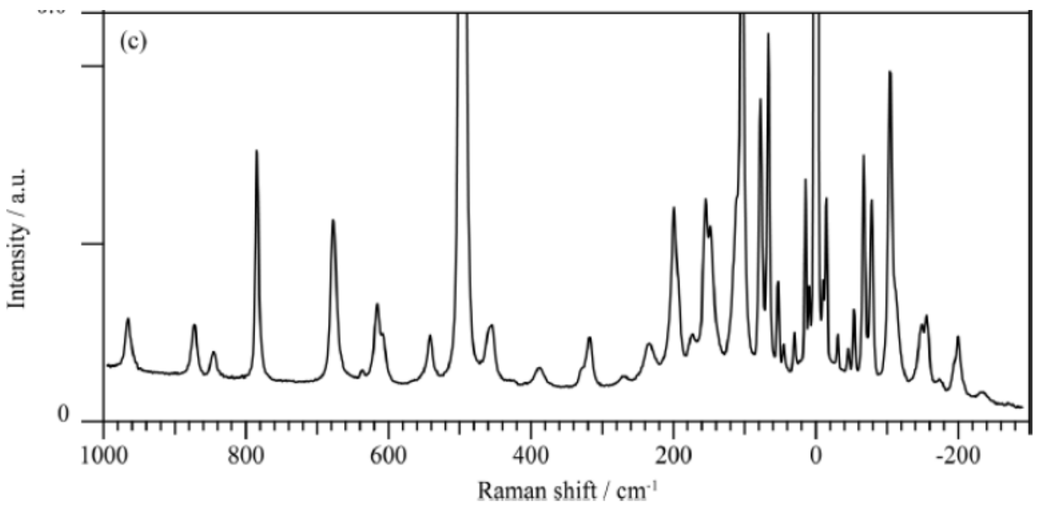
$$p = \varepsilon_0 \alpha E$$

α : polarizability

$$\alpha = \alpha_0 + \alpha_1 \cos 2\pi\nu t$$

ν : molecular vibrational frequency

$$\begin{aligned} p &= \varepsilon_0(\alpha_0 + \alpha_1 \cos 2\pi\nu t)E_0 \cos 2\pi\nu_i t \\ &= \varepsilon_0\alpha_0 E_0 \cos 2\pi\nu_i t && \longrightarrow \nu_s = \nu_i \\ &+ \frac{1}{2}\varepsilon_0\alpha_1 E_0 \cos 2\pi(\nu_i - \nu)t && \longrightarrow \nu_s = \nu_i - \nu \\ &+ \frac{1}{2}\varepsilon_0\alpha_1 E_0 \cos 2\pi(\nu_i + \nu)t && \longrightarrow \nu_s = \nu_i + \nu \end{aligned}$$



Stokes Raman scattering ←→ Anti-Stokes Raman scattering

H. Okajima, H. Hamaguchi, *Appl. Spectrosc.* **63**, 960 (2009).

Raman Shift $\equiv \nu_i - \nu_s$

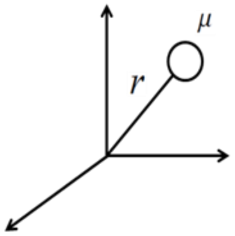
$$\frac{I_{AS}}{I_S} \propto e^{-\frac{h\nu}{kT}}$$

I_S : Stokes
I_{AS} : Anti-Stokes

6.2 Vibrational spectra of diatomic molecules

1) Harmonic approximation 諧振子近似

Born-Oppenheimer approximation



$$\text{Separation of} \begin{cases} \text{Electronic motion} \\ \text{Nuclear motion} \end{cases}$$

↓

$$\begin{cases} \text{vibration} \\ \text{rotation} \end{cases}$$

$$\left\{-\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)+E_e(r)\right\}\phi_v(r)=E_v\phi_v(r)$$

$$\phi_v(r)=\frac{\psi_v(r)}{r}$$

$$\frac{d}{dr}\phi_v(r)=-\frac{1}{r^2}\psi_v(r)+\frac{1}{r}\frac{d\psi_v(r)}{dr}$$

$$r^2\left(\frac{d}{dr}\phi_v(r)\right)=-\psi_v(r)+r\frac{d\psi_v(r)}{dr}$$

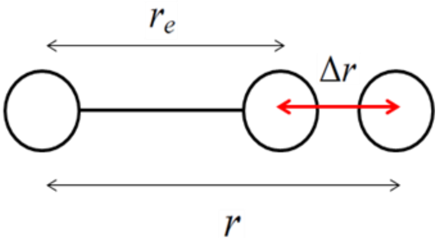
$$\frac{d}{dr}\left\{r^2\left(\frac{d}{dr}\phi_v(r)\right)\right\}=\cancel{-\frac{d\psi_v(r)}{dr}}+\cancel{\frac{d\psi_v(r)}{dr}}+r\frac{d^2\psi_v(r)}{dr^2}$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{r}\frac{d^2\psi_v(r)}{dr^2}+E_e(r)\frac{\psi_v(r)}{r}=E_v\frac{\psi_v(r)}{r}$$

$$\underbrace{-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(r)}{dr^2}}_{\text{Kinetic energy}}+\underbrace{E_e(r)\psi_v(r)}_{\text{Potential energy}}=E_v\psi_v(r)$$

Small amplitude motion

$\Delta r=r-r_e$ r_e : eqilibtium nuclear position



$$E_e(r) = \underset{\substack{\big\downarrow \\ \text{constant}}}{E_0^0} + \underset{\substack{\big\downarrow \\ 0}}{\left(\frac{dE_e(r)}{dr}\right)_{r=r_r}} \Delta r + \frac{1}{2}\left(\frac{d^2E_e(r)}{dr^2}\right)_{r=r_e} \Delta r^2 + \cdots$$

$$\sim \frac{1}{2}k\Delta r^2 \qquad k = \left(\frac{d^2E_e(r)}{dr^2}\right)_{r=r_e} \quad \text{force constant}$$

$$dr \to d(\Delta r)$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_v(\Delta r)}{d\Delta r^2} + \frac{1}{2}k\Delta r^2\psi_v(\Delta r) = E_v\psi_v(\Delta r)$$

Schrödinger equation for vibration

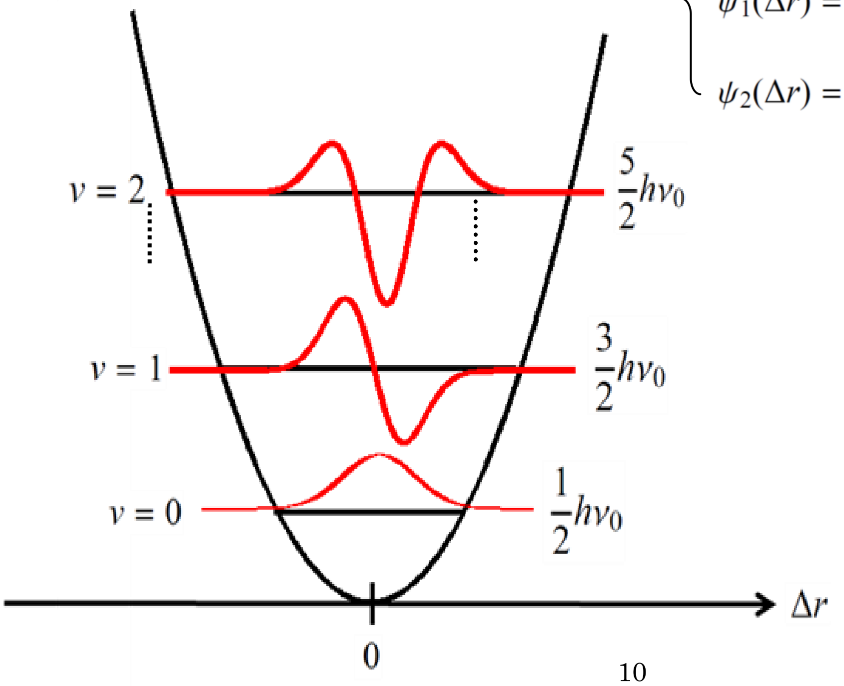
Eigen energy

$$E_v = h\nu_0(v + \frac{1}{2}) \qquad v: \text{vibrational quantum number}$$

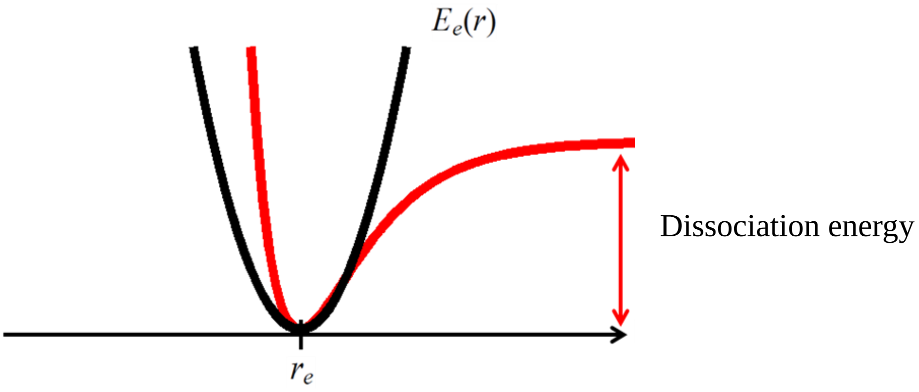
$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{Eigen frequency (= classical frequency)}$$

Eigen functions

$$\left\{\begin{array}{l} \psi_0(\Delta r) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \exp\left(-\frac{\alpha\Delta r^2}{2}\right) \\ \psi_1(\Delta r) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} (2\alpha)^{\frac{1}{2}}\Delta r \exp\left(-\frac{\alpha\Delta r^2}{2}\right) \\ \psi_2(\Delta r) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} \frac{1}{\sqrt{2}}(2\alpha\Delta r^2 - 1) \exp\left(-\frac{\alpha\Delta r^2}{2}\right) \end{array}\right.$$



2) Anharmonic Oscillator 非諧振子



Morse potential $V_M(\Delta r)$

$$V_M(\Delta r) = D_e(1 - \exp(-a\Delta r))^2$$

$$\Delta r \to \infty \quad V_M \to D_e$$

$$\Delta r \to 0 \quad V_M = 0$$

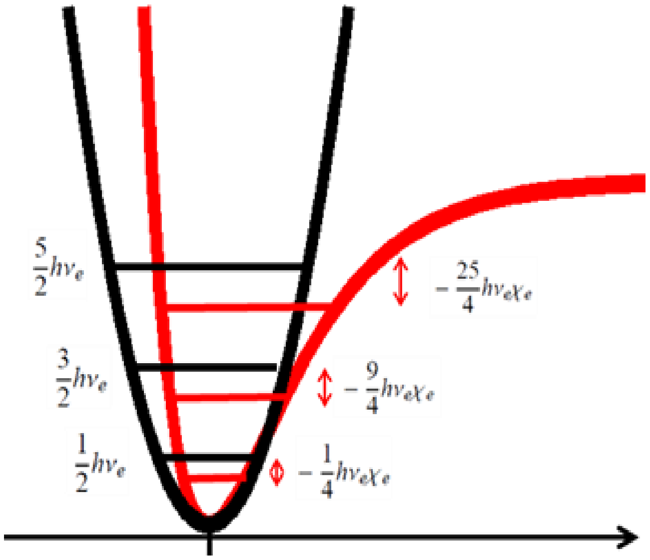
$$V_M(\Delta r) = \underbrace{a^2 D_e \Delta r^2}_{\text{harmonic}} - \underbrace{a^3 D_e \Delta r^3}_{\text{anharmonic}} + \cdots$$

$$\begin{cases} \frac{1}{2}k = a^2 D_e \\ k = 2a^2 D_e \end{cases}$$

$$-\frac{\hbar^2}{2\mu}\frac{d^2}{d\Delta r^2}\psi_v(\Delta r) + V_M(\Delta r)\psi_v(\Delta r) = E_v\psi_v(\Delta r)$$

$$E_v = h\nu_e(v + \frac{1}{2}) - h\nu_e\chi_e(v + \frac{1}{2})^2$$

$$\begin{cases} \nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} & \text{: harmonic frequency} \\ \chi_e = \frac{h\nu_e}{4D_e} & \text{: anharmonic constant} \end{cases}$$



3) Selection rules

a) infrared absorption

$$I \propto \left| \int \psi_f^* \mu \psi_i d\tau \right|^2 \qquad \mu : \mu_x, \mu_y, \mu_z$$

$\psi_i = \psi_{v_i}(\Delta r)$ $\quad v_i$: vibrational quantum number of the initial state

$\psi_f = \psi_{v_f}(\Delta r)$ $\quad v_f$: vibrational quantum number of the final state

$$\begin{aligned}\mu &= \mu(\Delta r)\\ &= \mu_0 + \left(\frac{d\mu}{d\Delta r}\right)_{\Delta r=0} \Delta r + \underbrace{\frac{1}{2}\left(\frac{d^2\mu}{d(\Delta r)^2}\right)}_{\text{neglect}}{}_{\Delta r=0} \Delta r^2 + \cdots\end{aligned}$$

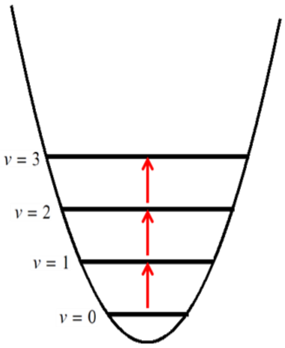
Harmonic oscillator wavefunctions

$$\int \psi_{v_f}^* \psi_{v_i} d\Delta r = \delta_{v_f, v_i}$$

$$\int \psi_{v_f}^* \Delta r \psi_{v_i} d\Delta r = \begin{cases} 0 & v_f \neq v_i + 1 \\ \sqrt{\dfrac{(v_i + 1)h}{8\pi^2 \nu_0 \mu}} & v_f = v_i + 1 \end{cases}$$

$$\begin{aligned} I &\propto \left| \int \psi_f^* \mu \psi_i d\tau \right|^2 \\ &= \left| \mu_0 \int \psi_f(\Delta r)^* \psi_i(\Delta r) d\Delta r + \left(\frac{d\mu}{d\Delta r}\right)_{\Delta r=0} \int \psi_f(\Delta r)^* \Delta r \psi_i(\Delta r) d\Delta r \right|^2 \\ &= \begin{cases} 0 & v_f \neq v_i + 1 \\ \left(\dfrac{d\mu}{d\Delta r}\right)^2_{\Delta r=0} \dfrac{(v_i + 1)h}{8\pi^2 \nu_0 \mu} & v_f = v_i + 1 \end{cases} \end{aligned}$$

Harmonic selection rules



$$\begin{cases} \Delta v = 1 \\ \left(\dfrac{d\mu}{d\Delta r}\right)_{\Delta r=0} \neq 0 \end{cases}$$

Fundamental tone and hot bands

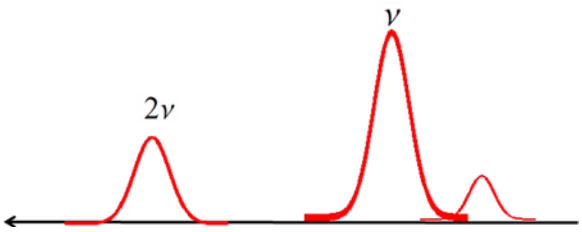
$$v = 0 \rightarrow v = 1 \quad \text{Fundamental tone}$$
$$v = v_i \rightarrow v = v_i + 1 \ \ (v_i \neq 0) \qquad \text{Hot bands}$$

$$\frac{I_{1\rightarrow 2}}{I_{0\rightarrow 1}} = e^{-\frac{h\nu_0}{kT}}$$

$$T = 300\text{K} \quad kT \sim 200\text{cm}^{-1}$$

$$\text{CO} \ \ \nu_0 = 2143\text{cm}^{-1} \qquad \frac{I_{1\rightarrow 2}}{I_{0\rightarrow 1}} = 3.4\times 10^{-5}$$

$$\text{ICl} \ \ \nu_0 = 381\text{cm}^{-1} \qquad 0.161$$



Overtones

v=0 ⟶ v=2 first overtone

v=0 ⟶ v=3 second overtone

v=0 ⟶ v=4, 5,6…….

anharmonicity

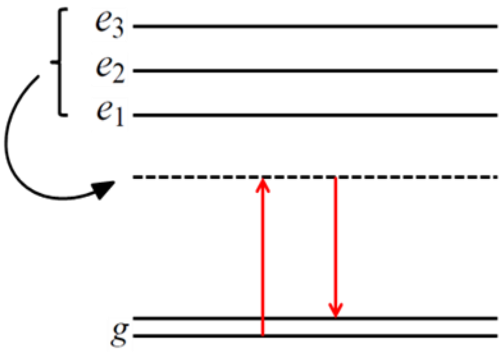
mechanical anharmonicity $\chi_e \neq 0$

electrical anharmonicity $\left(\frac{d^2\mu}{d(\Delta r)^2}\right)_{\Delta r=0} \neq 0$ overtone

$$\mu = \mu(\Delta r)$$
$$= \mu_0 + \left(\frac{d\mu}{d\Delta r}\right)_{\Delta r=0} \Delta r + \frac{1}{2}\left(\frac{d^2\mu}{d(\Delta r)^2}\right)_{\Delta r=0} \Delta r^2 + \cdots$$

b) Raman scattering

Placzek polarizability theory



$$I \propto \left|\int \psi_f^* \alpha \psi_i d\tau\right|^2$$

$$\alpha = \alpha_{xz}, \alpha_{xy}, \cdots$$

$$\alpha = \alpha_0 + \left(\frac{d\alpha}{d\Delta r}\right)_{\Delta r=0}\Delta r + \underbrace{\frac{1}{2}\cdots}_{\text{neglect}}$$

$$I = \left|\int \psi_{v_f}(\Delta r)\alpha\psi_{v_i}(\Delta r)d\Delta r\right|^2$$

$$= 0 \qquad\qquad v_f \neq v_i + 1$$

$$\begin{cases} \left(\dfrac{d\alpha}{d\Delta r}\right)^2_{\Delta r=0} \dfrac{(v_i+1)h}{8\pi^2 \nu_0 \mu} & v_f = v_i + 1 \\ \left(\dfrac{d\alpha}{d\Delta r}\right)^2_{\Delta r=0} \dfrac{v_i h}{8\pi^2 \nu_0 \mu} & v_f = v_i - 1 \end{cases}$$

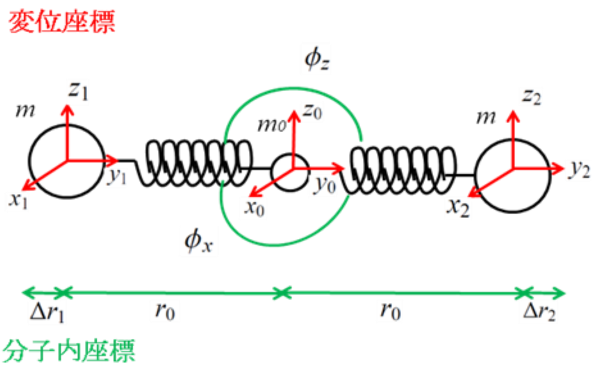
Harmonic selection rule

$$\begin{cases} \Delta v = \pm 1 \\ \left(\dfrac{d\alpha}{d\Delta r}\right)_{\Delta r=0} \neq 0 \end{cases}$$

6.3 Vibrational spectra of polyatomic molecules

1) Normal coordinates of vibration

XY_2 : CO_2 , CS_2



Total kinetic energy T_t

$$T_t = \frac{1}{2}m(\dot{x}_1{}^2 + \dot{y}_1{}^2 + \dot{z}_1{}^2) + \frac{1}{2}m_0(\dot{x}_0{}^2 + \dot{y}_0{}^2 + \dot{z}_0{}^2) + \frac{1}{2}m(\dot{x}_2{}^2 + \dot{y}_2{}^2 + \dot{z}_2{}^2)$$

$$= \frac{1}{2}(m_0 + 2m)\left\{\left(\frac{m(\dot{x}_1 + \dot{x}_2) + m_0\dot{x}_0}{m_0 + 2m}\right)^2 + \left(\frac{m(\dot{y}_1 + \dot{y}_2) + m_0\dot{y}_0}{m_0 + 2m}\right)^2 + \left(\frac{m(\dot{z}_1 + \dot{z}_2) + m_0\dot{z}_0}{m_0 + 2m}\right)^2\right\}$$

↑translation→
（motion of center of mass）

$$+ \frac{1}{2}m\left(\frac{\dot{x}_2 - \dot{x}_1}{\sqrt{2}}\right)^2 + \frac{1}{2}m\left(\frac{\dot{y}_2 - \dot{y}_1}{\sqrt{2}}\right)^2 + \frac{1}{2}m\left(\frac{\dot{z}_2 - \dot{z}_1}{\sqrt{2}}\right)^2$$

↑rotation

$$+ \frac{1}{2}\mu\left(\frac{2\dot{x}_0 - \dot{x}_1 - \dot{x}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{2\dot{y}_0 - \dot{y}_1 - \dot{y}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{2\dot{z}_0 - \dot{z}_1 - \dot{z}_2}{\sqrt{2}}\right)^2$$

↑vibration

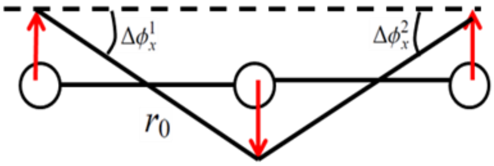
$$\frac{1}{\mu} = \frac{2}{m_0} + \frac{1}{m}$$

$$T_v = \frac{1}{2}m\left(\frac{\dot{y}_2 - \dot{y}_1}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{2\dot{x}_0 - \dot{x}_1 - \dot{x}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{2\dot{y}_0 - \dot{y}_1 - \dot{y}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{2\dot{z}_0 - \dot{z}_1 - \dot{z}_2}{\sqrt{2}}\right)^2$$

$\Downarrow$ Intramolecular coordinates

$$\begin{cases} \Delta r_1 = y_0 - y_1 \\ \Delta r_2 = y_2 - y_0 \\ r_0\Delta\phi_x = x_1 + x_2 - 2x_0 \\ r_0\Delta\phi_z = z_1 + z_2 - 2z_0 \end{cases}$$

$r_0 \sin(\Delta\phi_x^1) \sim r_0\Delta\phi_x^1$ $\quad$ $\Delta\phi_x^1 + \Delta\phi_x^2 = \Delta\phi_x$



$$\left.\begin{aligned} r_0\Delta\phi_x^1 &= x_1 - x_0 \\ r_0\Delta\phi_x^2 &= x_2 - x_0 \end{aligned}\right\} r_0\Delta\phi_x = x_1 + x_2 - 2x_0$$

$\Downarrow$

$$T_v = \frac{1}{2}m\left(\frac{\Delta\dot{r}_1 + \Delta\dot{r}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{\Delta\dot{r}_1 - \Delta\dot{r}_2}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{r_0\Delta\dot{\phi}_x}{\sqrt{2}}\right)^2 + \frac{1}{2}\mu\left(\frac{r_0\Delta\dot{\phi}_z}{\sqrt{2}}\right)^2$$

$$\Longrightarrow T = \frac{1}{2}(\dot{Q}_1^2 + \dot{Q}_2^2 + \dot{Q}_3^2 + \dot{Q}_4^2)$$

Normal coordinates

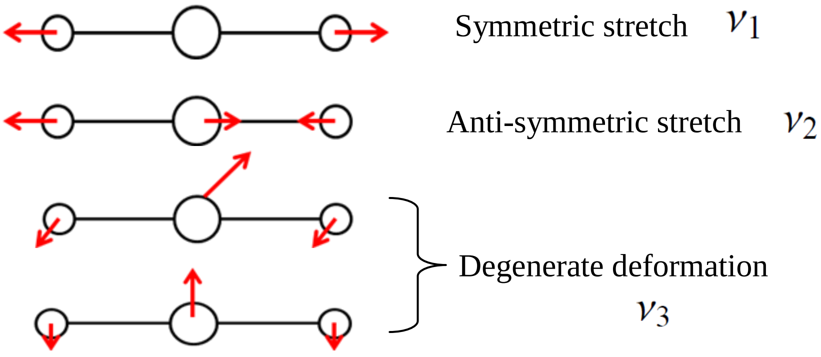
Kinetic energy in normal coordinates

$$Q_1 = \frac{\sqrt{m}(\Delta r_1 + \Delta r_2)}{\sqrt{2}}$$

$$Q_2 = \frac{\sqrt{\mu}(\Delta r_1 - \Delta r_2)}{\sqrt{2}}$$

$$Q_3 = \frac{\sqrt{\mu}r_0\Delta\phi_x}{\sqrt{2}}$$

$$Q_4 = \frac{\sqrt{\mu}r_0\Delta\phi_z}{\sqrt{2}}$$



2) Molecular force field: Potential energy　分子力場

Cartesian coordinates

$$V = V(x_0, y_0, z_0, x_1, y_1, z_1, x_2, y_2, z_2)$$

Intramolecular coordinates

$$\begin{aligned} V = \frac{1}{2}K(\Delta r_1)^2 + \frac{1}{2}K(\Delta r_2)^2 + k\Delta r_1 \Delta r_2 \\ + \frac{1}{2}H(r_0\Delta\phi_x)^2 + \frac{1}{2}H(r_0\Delta\phi_z)^2 \end{aligned}$$

$$\left\{ \begin{array}{l} K: \text{ force constant for stretch} \\ H: \text{ force constant for bend} \\ k: \text{ coupling constant between two stretches} \end{array} \right.$$

Normal coordinates

$$\begin{aligned} V = \frac{1}{2}\frac{K+k}{m}Q_1^2 + \frac{1}{2}\frac{K-k}{\mu}Q_2^2 \\ + \frac{H}{\mu}Q_3^2 + \frac{H}{\mu}Q_4^2 \end{aligned}$$

$$T = \frac{1}{2}(\dot{Q}_1^2 + \dot{Q}_2^2 + \dot{Q}_3^2 + \dot{Q}_4^2)$$

3) Energy levels and selection rules

$$\begin{aligned} H &= T + V \\ &= \frac{1}{2}\dot{Q}_1{}^2 + \frac{1}{2}\dot{Q}_2{}^2 + \frac{1}{2}\dot{Q}_3{}^2 + \frac{1}{2}\dot{Q}_4{}^2 \\ &+ \frac{1}{2}\frac{K+k}{m}Q_1^2 + \frac{1}{2}\frac{K-k}{\mu}Q_2^2 + \frac{H}{\mu}Q_3^2 + \frac{H}{\mu}Q_4^2 \\ &= H_1 + H_2 + H_3 + H_4 \end{aligned}$$

$$H\psi = E\psi$$

$$\begin{cases} \psi = \psi_1(Q_1)\psi_2(Q_2)\psi_3(Q_3)\psi_4(Q_4) \\ E = E_1 + E_2 + E_3 + E_4 \end{cases}$$

$$\psi = \psi_{v_1}(Q_1)\psi_{v_2}(Q_2)\psi_{v_3}(Q_3)\psi_{v_4}(Q_4)$$

$$E = h\nu_1(v_1 + \frac{1}{2}) + h\nu_2(v_2 + \frac{1}{2}) + h\nu_3(v_3 + v_4 + 1)$$

a) infrared absorption

$$\begin{aligned} \mu &= \mu(Q_1, Q_2, Q_3, Q_4) \\ &= \mu_0 + \sum_i \left(\frac{\partial\mu}{\partial Q_i}\right)Q_i + \frac{1}{2}\cdots \end{aligned}$$

Selection rules for vibrational quantum numbers

Fundamental tone　基本音

(0,0,0,0) → (1,0,0,0)　$\nu_1$fundamenat;
(0,0,0,0) → (0,1,0,0)　$\nu_2$fundamental
(0,0,0,0) → (0,0,1,0)　$\nu_3$fundamental
(0,0,0,0) → (0,0,0,1)

Hot bands

(1,0,0,0) → (2,0,0,0)
(1,0,0,0) → (1,1,0,0)

Combination tones (anharmonicity) 結合音

(0,0,0,0) → (1,1,0,0)
(0,0,0,0) → (1,0 ,1,0)
………

Intermolecular combination band

$(CD_3)_2C=O$	1706 cm^{-1}	
$CHCl_3$	3019 cm^{-1}	
	4725 cm^{-1}	Observed: 4718 cm^{-1} (observed only for mixtures)

Selection rule for vibrational mode

$$\left(\frac{\partial \mu}{\partial Q_i}\right) \neq 0$$

b) Raman scattering

$$\begin{aligned}\alpha &= \alpha(Q_1, Q_2, Q_3, Q_4)\\ &= \alpha_0 + \sum_i \left(\frac{\partial \alpha}{\partial Q_i}\right) Q_i + \cdots\end{aligned}$$

Selection rule for vibrational mode

$$\left(\frac{\partial \alpha}{\partial Q_i}\right) \neq 0$$

c) Vibrational selection rules and molecular symmetry

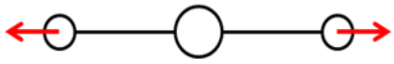
Parity

$$x, y, z \xrightarrow{i} -x, -y, -z$$

odd u $\quad \mu_j \xrightarrow{i} -\mu_j \quad (j = x, y, z)$

even g $\quad \alpha_{mn} \xrightarrow{i} \alpha_{mn} \quad (m, n = x, y, z)$

Raman active g

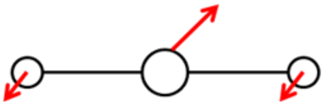


ν_1

Infrared active u

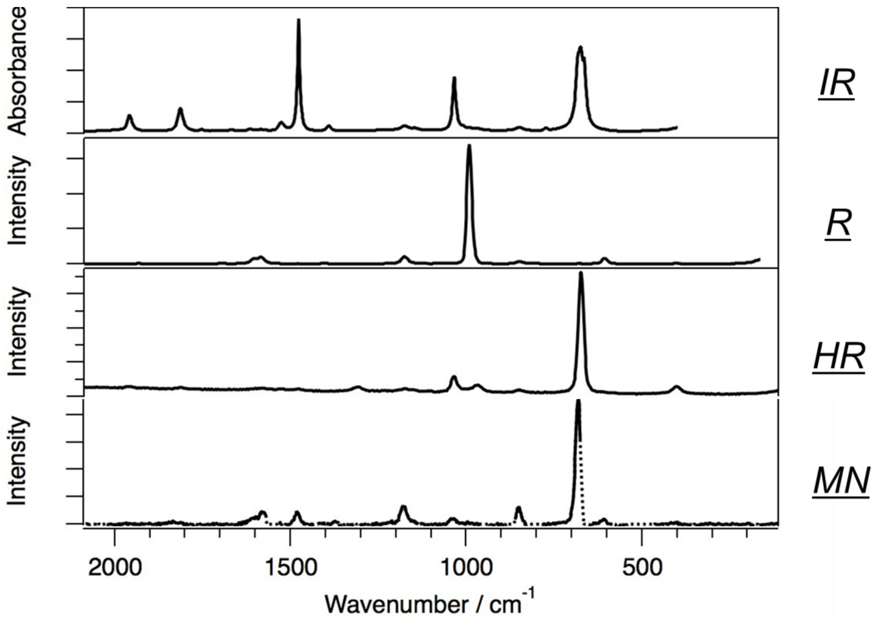
ν_2

Infrared active u

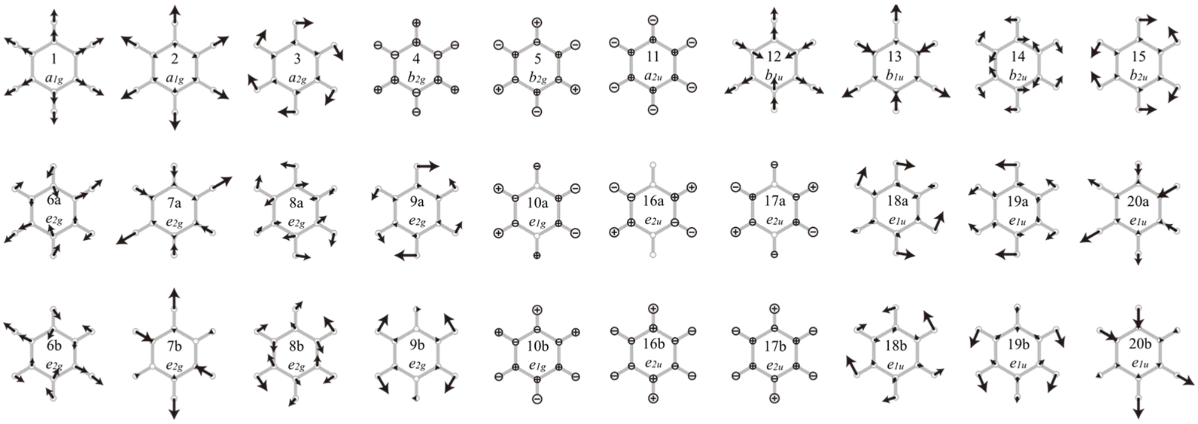


ν_3

Mutual exclusion principle holds for molecules with inversion symmetry.



Vibrational spectra of benzene


1 a_{1g}
2 a_{1g}
3 a_{2g}
4 b_{2g}
5 b_{2g}
11 a_{2u}
12 b_{1u}
13 b_{1u}
14 b_{2u}
15 b_{2u}
6a e_{2g}
7a e_{2g}
8a e_{2g}
9a e_{2g}
10a e_{1g}
16a e_{2u}
17a e_{2u}
18a e_{1u}
19a e_{1u}
20a e_{1u}
6b e_{2g}
7b e_{2g}
8b e_{2g}
9b e_{2g}
10b e_{1g}
16b e_{2u}
17b e_{2u}
18b e_{1u}
19b e_{1u}
20b e_{1u}