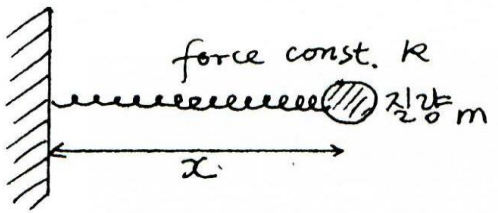
6. Vibrational Spectroscopy

6.1 Diatomic Molecules

6.1.0 Harmonic Oscillator



classically

$$m\ddot{x} = -kx$$

$$\ddot{x} + \omega^2 x = 0 \qquad \omega = \left(\frac{k}{m}\right)^{1/2}$$

Quantum Mechanically

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}k\hat{x}^2 = \frac{1}{2m}\hat{p}^2 + \frac{1}{2}m\omega^2\hat{x}^2 = \frac{1}{2m}(\hat{p}^2 + m^2\omega^2\hat{x}^2)$$

$$= \frac{1}{2m}(\hat{p} + im\omega\hat{x})(\hat{p} - im\omega\hat{x}) + \frac{i\omega}{2}[\hat{p}, \hat{x}]$$

$$= \hbar\omega\,\hat{\eta}_+\hat{\eta}_- + \frac{\hbar\omega}{2}$$

where $\hat{\eta}_\pm = \dfrac{1}{\sqrt{2m\hbar\omega}}(\hat{p} \pm im\omega\hat{x})$ $\rightarrow$

$$\begin{cases} \hat{x} = -i\sqrt{\dfrac{\hbar}{2m\omega}}(\hat{\eta}_+ - \hat{\eta}_-) \\ \hat{p} = \sqrt{\dfrac{m\hbar\omega}{2}}(\hat{\eta}_+ + \hat{\eta}_-) \end{cases}$$

$$\hat{\eta}_-\hat{\eta}_+ = \frac{1}{2m\hbar\omega}\left\{\hat{p}^2 + m^2\omega^2\hat{x}^2 + i\omega m[\hat{p}, \hat{x}]\right\} = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$$

$$\hat{\eta}_+\hat{\eta}_- = \frac{1}{2m\hbar\omega}\left\{\hat{p}^2 + m^2\omega^2\hat{x}^2 - i\omega m[\hat{p}, \hat{x}]\right\} = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}$$

Thus we have $[\hat{\eta}_-, \hat{\eta}_+] = 1$ (1)

$$\hat{H} = \hbar\omega(\hat{\eta}_-\hat{\eta}_+ - \tfrac{1}{2}) = \hbar\omega(\hat{\eta}_+\hat{\eta}_- + \tfrac{1}{2}) \quad (2)$$

From (2) we have $[\hat{H}, \hat{\eta}_+] = \hbar\omega\hat{\eta}_+$ (3)

$$[\hat{H}, \hat{\eta}_-] = -\hbar\omega\hat{\eta}_- \quad (4)$$

$$\begin{pmatrix} \hat{\eta}_+^* = \hat{\eta}_- \\ \hat{\eta}_-^* = \hat{\eta}_+ \end{pmatrix}$$

$\hat{H}$ 의 고유함수를 $|v\rangle$, 고유치를 E_v 라하면 $\hat{H}|v\rangle = E_v|v\rangle$

$$\hat{H}\{\hat{\eta}_-|v\rangle\} = \{[\hat{H}, \hat{\eta}_-] + \hat{\eta}_-\hat{H}\}|v\rangle = \{\hat{\eta}_-\hat{H} - \hbar\omega\hat{\eta}_-\}|v\rangle$$

$$= (E_v - \hbar\omega)\{\hat{\eta}_-|v\rangle\}$$

$\therefore$ $\hat{\eta}_-|v\rangle$ 는 고유치 $E_v - \hbar\omega$ 를 갖는 $\hat{H}$ 의 고유함수

$\hat{\eta}_-^2|v\rangle$ 는 고유치 $E_v - 2\hbar\omega$ 〃 〃

$\vdots$ $\vdots$

$$\hat{H}\{\hat{\eta}_+|v\rangle\} = \{[\hat{H}, \hat{\eta}_+] - \hat{\eta}_-\hat{H}\}|v\rangle = \{\hat{\eta}_+\hat{H} + \hbar\omega\hat{\eta}_+\}|v\rangle$$

$$= (E_v + \hbar\omega)\{\hat{\eta}_+|v\rangle\}$$

$\therefore$ $\hat{\eta}_+|v\rangle$ 는 고유치 $E_v + \hbar\omega$ 를 갖는 $\hat{H}$ 의 고유함수

$\hat{\eta}_+^2|v\rangle$ 는 〃 $E_v + 2\hbar\omega$ 〃 〃

$\vdots$ $\vdots$ $\vdots$ $\vdots$

$\hat{\eta}_+$: raising operator

$\hat{\eta}_-$: lowering operator

} ladder operators

a) Ground state를 $|0\rangle$라 하면

$$\hat{\eta}_- |0\rangle = 0$$

$$\hat{H}|0\rangle = \hbar\omega\left(\hat{\eta}_+\hat{\eta}_- + \frac{1}{2}\right)|0\rangle = \frac{1}{2}\hbar\omega|0\rangle$$

$$\therefore E_0 = \frac{1}{2}\hbar\omega$$

$$\hat{H}\hat{\eta}_+|0\rangle = (E_0 + \hbar\omega)\hat{\eta}_+|0\rangle = \frac{3}{2}\hbar\omega\,\hat{\eta}_+|0\rangle$$

$$\vdots$$

$$\hat{H}\hat{\eta}_+^{\upsilon}|0\rangle = (E_0 + \upsilon\hbar\omega)\hat{\eta}_+^{\upsilon}|0\rangle = \left(\upsilon + \frac{1}{2}\right)\hbar\omega\,\hat{\eta}_+^{\upsilon}|0\rangle$$

$$\therefore \underbrace{E_\upsilon = \left(\upsilon + \frac{1}{2}\right)\hbar\omega}$$

$$|\upsilon\rangle = \text{const.}\,\hat{\eta}_+^{\upsilon}|0\rangle$$

$$= C_\upsilon\,\hat{\eta}^{\upsilon}|0\rangle$$

b) C_v ?

$$|v\rangle = C_v \hat{\eta}_+^v |0\rangle, \quad |v-1\rangle = C_{v-1} \hat{\eta}_+^{v-1} |0\rangle$$

$$\hat{\eta}_+ |v-1\rangle = C_{v-1} \eta_+^v |0\rangle = \frac{C_{v-1}}{C_v} |v\rangle$$

$$\therefore \quad |v\rangle = \frac{C_v}{C_{v-1}} \hat{\eta}_+ |v-1\rangle \qquad \langle v| = \frac{C_v^*}{C_{v-1}^*} \langle v-1| \hat{\eta}_-$$

$$1 = \langle v|v\rangle = \left|\frac{C_v}{C_{v-1}}\right|^2 \langle v-1| \hat{\eta}_- \hat{\eta}_+ |v-1\rangle$$

$$= \left|\frac{C_v}{C_{v-1}}\right|^2 \langle v-1| \frac{\hat{H}}{\hbar\omega} + \frac{1}{2} |v-1\rangle = \left|\frac{C_v}{C_{v-1}}\right|^2 \left\{(v-\tfrac{1}{2}) + \tfrac{1}{2}\right\} = \left|\frac{C_v}{C_{v-1}}\right|^2 v$$

$$\therefore \quad C_v = \frac{1}{\sqrt{v}} C_{v-1} = \frac{1}{\sqrt{v(v-1)}} C_{v-2} = \cdots = \frac{1}{\sqrt{v!}} C_0$$

$$\therefore \quad |v\rangle = \frac{1}{\sqrt{v!}} \hat{\eta}_+^v |0\rangle, \qquad \begin{cases} \hat{\eta}_+ |v\rangle = \sqrt{v+1}\, |v+1\rangle \\ \hat{\eta}_- |v\rangle = \sqrt{v}\, |v-1\rangle \end{cases}$$

c) $|0\rangle$? $\hat{\eta}_- |0\rangle = 0$

$$\frac{1}{\sqrt{2m\hbar\omega}} \left(\hat{p} - i m\omega \hat{x} \right) |0\rangle = 0$$

$$\frac{\hbar}{i}\frac{d}{dx}|0\rangle - i m\omega \hat{x}|0\rangle = 0 \qquad \frac{d}{dx}|0\rangle = -\frac{m\omega}{\hbar} x |0\rangle$$

$$|0\rangle = a_0 e^{-\frac{m\omega}{2\hbar}x^2}$$

$$1 = \langle 0|0\rangle = a_0^2 \int_{-\infty}^{\infty} e^{-\frac{m\omega}{\hbar^2}x^2} dx = a_0^2 \int_{-\infty}^{\infty} \sqrt{\frac{\hbar}{m\omega}} e^{-y^2} dy = a_0^2 \sqrt{\frac{\pi\hbar}{m\omega}}$$

$$a_0 = \sqrt[4]{\frac{m\omega}{\pi\hbar}}$$

$$\therefore |0\rangle = \sqrt[4]{\frac{m\omega}{\pi\hbar}} e^{-\frac{m\omega}{2\hbar^2}x^2} \equiv N_0 e^{-\frac{y^2}{2}} H_0(y), \qquad y \equiv \sqrt{\frac{m\omega}{\hbar^2}}\, x$$

d) $|v\rangle = ?$

$$|v\rangle = \frac{1}{\sqrt{v!}} \hat{\eta}_+^v |0\rangle = \frac{1}{\sqrt{v!}} \left(\frac{1}{2m\hbar\omega} \right)^{\frac{v}{2}} \left(\hat{p} + i m\omega \hat{x} \right)^v |0\rangle$$

$$= \frac{1}{\sqrt{v!}} \left(\frac{1}{2m\hbar\omega} \right)^{v/2} \left(\frac{\hbar}{i}\frac{\partial}{\partial x} + i m\omega \hat{x} \right)^v |0\rangle$$

$$= \frac{1}{\sqrt{v!}}\left(\frac{1}{2}\right)^{\frac{v}{2}}\left(y - \frac{\partial}{\partial y}\right)^{v}|0\rangle$$

$$\left(y - \frac{\partial}{\partial y}\right)f = -e^{\frac{y^2}{2}}\frac{\partial}{\partial y}\left(e^{-\frac{y^2}{2}}f\right)$$

$$\left(y - \frac{\partial}{\partial y}\right)^2 f = -e^{-y^2/2}\frac{\partial}{\partial y}\left\{e^{-\frac{y^2}{2}}\left[\left(y - \frac{\partial}{\partial y}\right)f\right]\right\}$$

$$= (-1)^2 e^{\frac{y^2}{2}}\left(\frac{\partial}{\partial y}\right)^2 e^{-y^2/2} f$$

$$\vdots \qquad\qquad \vdots$$

$$\left(y - \frac{\partial}{\partial y}\right)^v f = (-1)^v e^{y^2/2}\left(\frac{\partial}{\partial y}\right)^v e^{-y^2/2} f$$

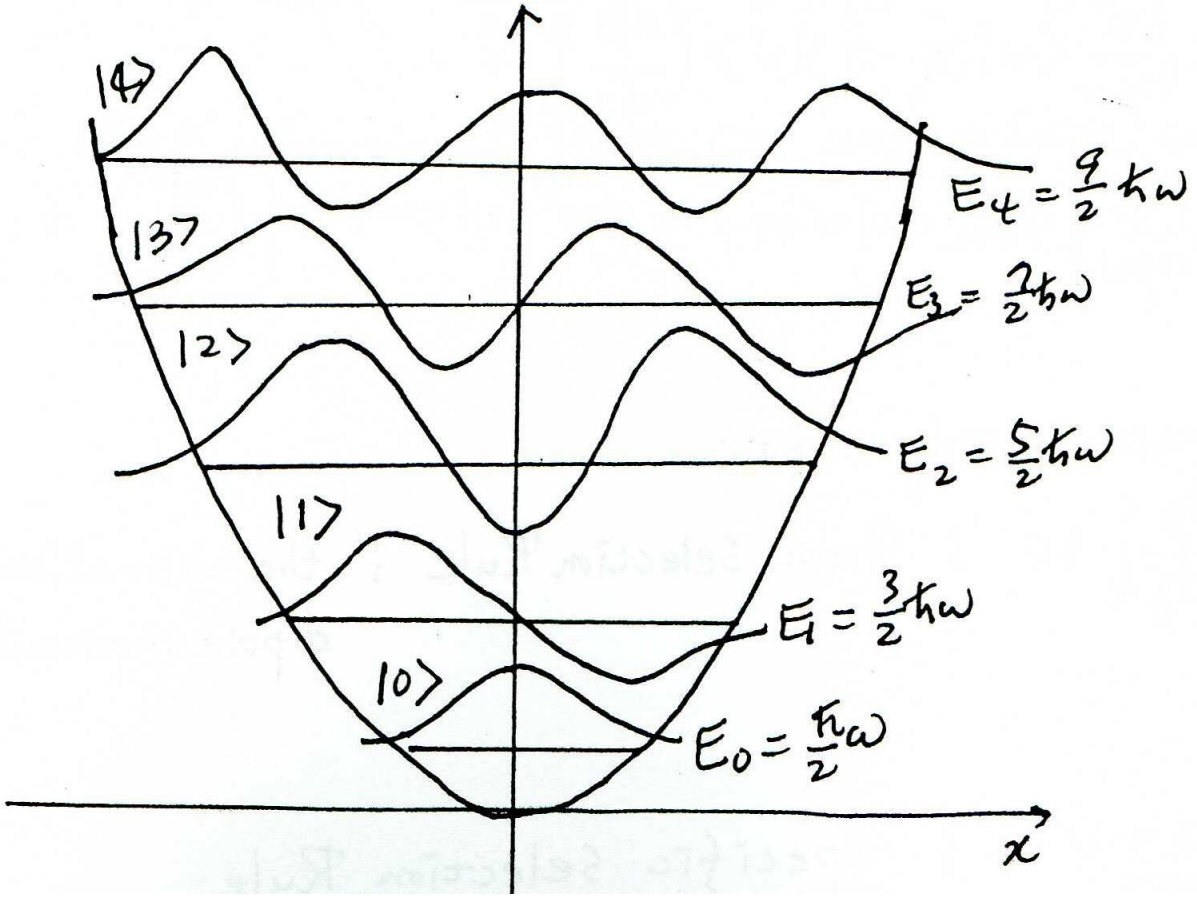
$$|v\rangle = \frac{1}{\sqrt{v!\,2^v}}(-1)^v e^{y^2/2}\left(\frac{\partial}{\partial y}\right)^v e^{-y^2/2}|0\rangle \longrightarrow N_0 e^{-y^2/2}$$

$$= \frac{N_0}{\sqrt{v!\,2^v}}(-1)^v e^{y^2/2}\left(\frac{\partial}{\partial y}\right)^v e^{-y^2} = \frac{N_0}{\sqrt{v!\,2^v}} e^{-y^2/2}\underbrace{(-1)^v e^{y^2}\left(\frac{\partial}{\partial y}\right)^v e^{-y^2}}_{H_v(y)\ ;\ \text{Hermite Polynomia}}$$

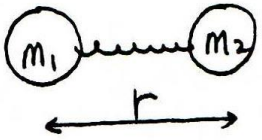
$$= \sqrt[4]{\frac{m\omega}{\pi\hbar}}\frac{1}{\sqrt{2^v v!}} e^{-\frac{m\omega}{2\hbar}x^2} H_v\left(\sqrt{\frac{m\omega}{\hbar}}x\right)$$

$$= \sqrt[4]{\frac{m\omega}{\pi\hbar}}\frac{1}{\sqrt{2^v v!}} e^{-y^2/2} H_v(y) = N_v e^{-y^2/2} H_v(y).$$

($H_0(y) = 1$, $H_1(y) = 2y$, $H_2(y) = 4y^2 - 2$, $H_3(y) = 8y^3 - 12y$
$H_4(y) = 16y^4 - 48y^2 + 12$, $H_5(y) = 32y^5 - 160y^3 + 120y$, . . .)



< Diatomic Molecules >



$$\mu = \frac{m_1 m_2}{m_1 + m_2}, \qquad V(r) = \frac{1}{2} k(r-r_e)^2 \text{ assuming harmonic potential}$$

$$\hat{H} = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}k(r-r_e)^2 = \frac{\hat{p}^2}{2\mu} + \frac{1}{2}kq^2, \qquad q \equiv r - r_e$$

$$\Rightarrow \begin{cases} E_v = \hbar\omega\left(v + \frac{1}{2}\right), & \omega = \sqrt{\frac{k}{\mu}} \\ |v\rangle = N_v e^{-y^2/2} H_v(y), & y = \sqrt{\frac{\mu\omega}{\hbar^2}}(r - r_e) \end{cases}$$

6.1.1. Infrared Spectra

$$\mu_{if} = \langle v|\mu|v'\rangle = \langle v|\mu_e|v'\rangle + \left(\frac{d\mu}{dq}\right)_e \langle v|q|v'\rangle + \text{higher order}$$

$(q = r - r_e)$

$$= \left(\frac{d\mu}{dq}\right)_e \langle v|q|v'\rangle + \cdots$$

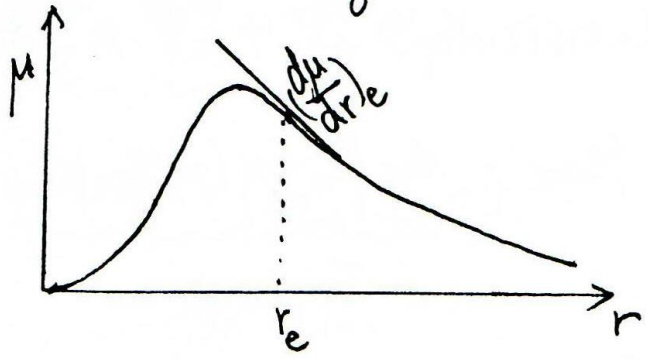
$$= -i\sqrt{\frac{\hbar}{2\mu\omega}} \langle v|(\hat{\eta}_+ - \hat{\eta}_-)|v'\rangle \left(\frac{d\mu}{dq}\right)_e + \cdots$$

$$= -i\sqrt{\frac{\hbar}{2\mu\omega}} \left\{\sqrt{v'+1}\,\langle v|v'+1\rangle - \sqrt{v'}\,\langle v|v'-1\rangle\right\} \left(\frac{d\mu}{dq}\right)_e + \cdots$$

$\Rightarrow$ nonzero only when.

- $\left(\frac{d\mu}{dq}\right)_e \neq 0$; Gross Selection Rule ; the vibration should induce dipole moment change
- $v = v' \pm 1$; Specific Selection Rule

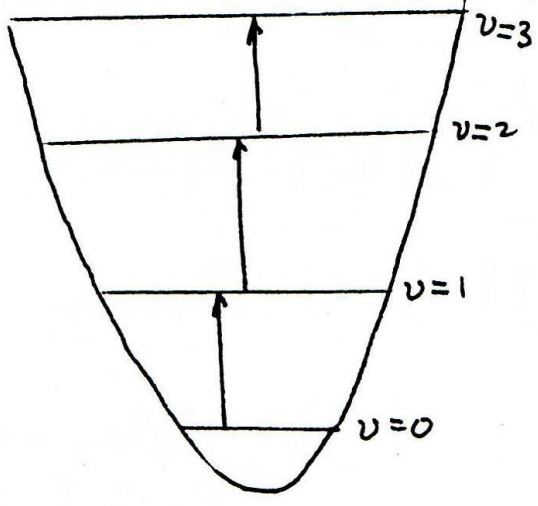
For homonuclear diatomic molecules, $\mu_e = \left(\frac{d\mu}{dq}\right)_e = 0$

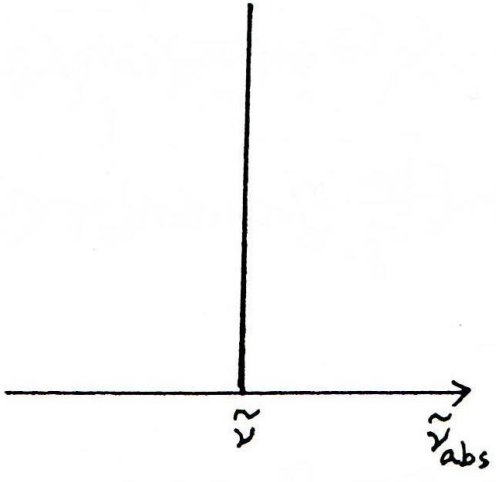


For heteronuclear diatomic molecules

<Spectrum>

$$\tilde{\nu}_{abs} = \frac{E_{v+1} - E_v}{hc} = \frac{2\pi h\nu\{v + 3/2 - (v+\frac{1}{2})\}}{hc} = \tilde{\nu}$$





<Population>

$$\frac{N_v}{N_0} = \exp\left(-\frac{E_v}{kT}\right)$$

$$\Rightarrow \exp\left[-\frac{1000}{207}\right] \sim 8 \times 10^{-3} \quad \text{for } 1000\ cm^{-1} \text{ vibration}$$

$\therefore$ Most vibrational states are unpopulated except at $v = 0$

6.1.2. Raman Spectra

<Classically>

$$\mu_{ind} = \underbrace{\alpha_e \mathcal{E}_0 \cos(2\pi \nu_{ex} t)}_{\text{Rayleigh}} + \frac{\mathcal{E}_0}{2}\left(\frac{\partial \alpha}{\partial q}\right)_e q_0 \Big[\underbrace{\cos 2\pi(\nu_{ex}+\nu)t}_{\text{Stokes-Raman}} + \underbrace{\cos 2\pi(\nu_{ex}-\nu)t}_{\text{Anti-stokes Raman.}}$$

<Partial Quantum Mechanical Treatment>

$$[\mu_{ind}]_{if} = \langle v | \alpha \mathcal{E} | v' \rangle = \langle v | \left(\alpha_e + \left(\frac{\partial \alpha}{\partial q}\right)_e q + \cdots\right)(\mathcal{E}_0 \cos 2\pi \nu_{ex} t) | v' \rangle$$

$$= \alpha_e \mathcal{E}_0 \cos 2\pi \nu_{ex} t \langle v | v' \rangle \quad ; \text{ Rayleigh}$$

$$+ \left(\frac{\partial \alpha}{\partial q}\right)_e \mathcal{E}_0 \cos 2\pi \nu_{ex} t \langle v | q | v' \rangle \quad ; \text{ Raman}$$

$$+ \quad \cdots \quad ; \text{ higher orders.}$$

The Raman term is nonzero only when

$\left(\frac{\partial \alpha}{\partial q}\right)_e \neq 0$; Gross selection Rule ; Vibration should induce anisotropic polarizability change

$v' = v \pm 1$; specific selection Rule.

< Time-dependent perturbation Treatment >

"Oh polished perturbation! Golden care!
That keepst the ports of slumber open wide
To many a watchful night!" – William Shakespeare –

Reference ; D. A. Long, "Raman Spectroscopy", 5장.

When the system is perturbed, the time dependent wave function Ψ_i' may be expressed as $\Psi_i' = \Psi_i^{(0)} + \Psi_i^{(1)} + \Psi_i^{(2)} + \cdots$

$$\left[\mu_{ind}\right]_{fi} = \langle \Psi_f' | \mu_{ind} | \Psi_i' \rangle = \langle \Psi_f^{(0)} + \Psi_f^{(1)} + \Psi_f^{(2)} + \cdots | \mu_{ind} | \Psi_i^{(0)} + \Psi_i^{(1)} + \Psi_i^{(2)} + \cdots \rangle$$

$$= \langle \Psi_f^{(0)} | \mu_{ind} | \Psi_i^{(0)} \rangle$$ — out of consideration

$$+ \langle \Psi_f^{(1)} | \mu_{ind} | \Psi_i^{(0)} \rangle + \langle \Psi_f^{(0)} | \mu_{ind} | \Psi_i^{(1)} \rangle$$ → responsible for Rayleigh and Raman

$$+ \langle \Psi_f^{(1)} | \mu_{ind} | \Psi_i^{(1)} \rangle + \langle \Psi_f^{(2)} | \mu_{ind} | \Psi_i^{(0)} \rangle + \langle \Psi_f^{(0)} | \mu_{ind} | \Psi_i^{(2)} \rangle$$ → responsible for Hyper Raman

$$+ \cdots$$

$$\Psi_i^{(1)} = \sum_r a_{ir} \Psi_r^{(0)}$$

$\Psi_r^{(0)}$ ← zeroth order wave function.

$$\Psi_f^{(1)} = \sum_r a_{fr} \Psi_r^{(0)}$$

$$\dot{a}_{ir} = -\frac{i}{\hbar} \langle \Psi_r^{(0)} | H' | \Psi_i^{(0)} \rangle$$

For Raman transition $H' = -\mu_{ind} \cdot \mathcal{E}$

$$\mathcal{E} = \mathcal{E}_0 \exp(-i\omega t) + \mathcal{E}_0^* \exp(i\omega t)$$

$$a_{ir} = \frac{1}{\hbar} (\mu_{ind})_{ir} \cdot \left[\frac{\mathcal{E}_0^* \exp\{i(\omega_{ri} + \omega)t\}}{\omega_{ri} + \omega} + \frac{\mathcal{E}_0 \exp\{i(\omega_{ri} - \omega)t\}}{\omega_{ri} - \omega} \right]$$

$$a_{fr}^* = \frac{1}{\hbar} (\mu_{ind})_{fr} \cdot \left[\frac{\mathcal{E}_0 \exp\{-i(\omega_{rf} + \omega)t\}}{\omega_{rf} + \omega} + \frac{\mathcal{E}_0^* \exp\{-i(\omega_{rf} - \omega)t\}}{\omega_{rf} - \omega} \right]$$

$$\langle \psi_f^{(1)} | \mu_{ind} | \psi_i^{(0)} \rangle + \langle \psi_f^{(0)} | \mu_{ind} | \psi_i^{(1)} \rangle$$

$$= \frac{1}{\hbar} \sum_r \left[\frac{([\mu_{ind}]_{fr} \cdot \mathcal{E}_0)[\mu_{ind}]_{ri}}{\omega_{rf} + \omega} + \frac{[\mu_{ind}]_{fr}([\mu_{ind}]_{ri} \cdot \mathcal{E}_0)}{\omega_{ri} - \omega} \right] \exp\{-i(\omega - \omega_{fi})t\}$$

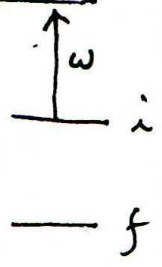
$$+ \frac{1}{\hbar} \sum_r \left[\frac{([\mu_{ind}]_{fi} \cdot \mathcal{E}_0^*)[\mu_{ind}]_{ri}}{\omega_{rf} + \omega} + \frac{[\mu_{ind}]_{fr}([\mu_{ind}]_{ri} \cdot \mathcal{E}_0^*)}{\omega_{ri} - \omega} \right] \exp\{i(\omega + \omega_{fi})t\} \quad \cdots ①$$

The second term of ① will have corresponding real transition moment if $\omega + \omega_{fi} < 0$. That is $\omega < \omega_i - \omega_f$ This means that transition does not take place $\Rightarrow$ Out of Consideration.

The first term of ① will have corresponding real transition moment if $\omega - \omega_{fi} > 0$. That is $\omega > \omega_{fi}$ ... (2)

This is because $\mathrm{Re}\{\mu_{me}\exp\{-i\omega_{em}t\}\} = \mu_{me}\exp(-i\omega_{em}t)$ $+\mu^{*}_{me}\exp(i\omega_{em}t)$ only if $\omega_{em} > 0$

If ω_{fi} is negative, $\omega > \omega_{fi}$ always



ω_{fi} is zero, $\omega > \omega_{fi}$ always

ω_{fi} is positive, then ω must be greater than ω_{fi}

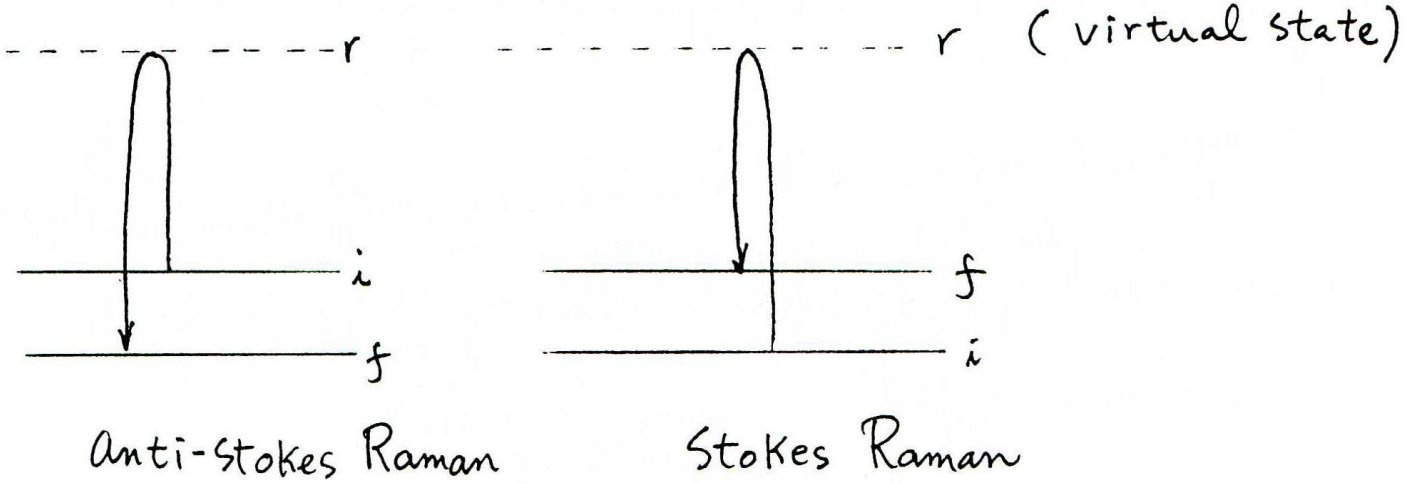
$$\left\{ \langle \Psi_f^{(1)} | \mu_{ind} | \Psi_i^{(0)} \rangle + \langle \Psi_f^{(0)} | \mu_{ind} | \Psi_i^{(1)} \rangle \right\}$$

$$= \left[\mu_{ind}^{(0)}\right]_{fi} \exp\{-i(\omega - \omega_{fi})t\} + \text{complex conjugate}$$

where $$\left[\mu_{ind}^{(0)}\right]_{fi} = \frac{1}{\hbar} \sum_r \left\{ \frac{([\mu_{ind}]_{fr} \cdot \mathcal{E}_0)[\mu_{ind}]_{ri}}{\omega_{rf} + \omega} + \frac{[\mu_{ind}]_{fr}([\mu_{ind}]_{ri} \cdot \mathcal{E}_0)}{\omega_{ri} - \omega} \right\}$$

going down transition

going up transition



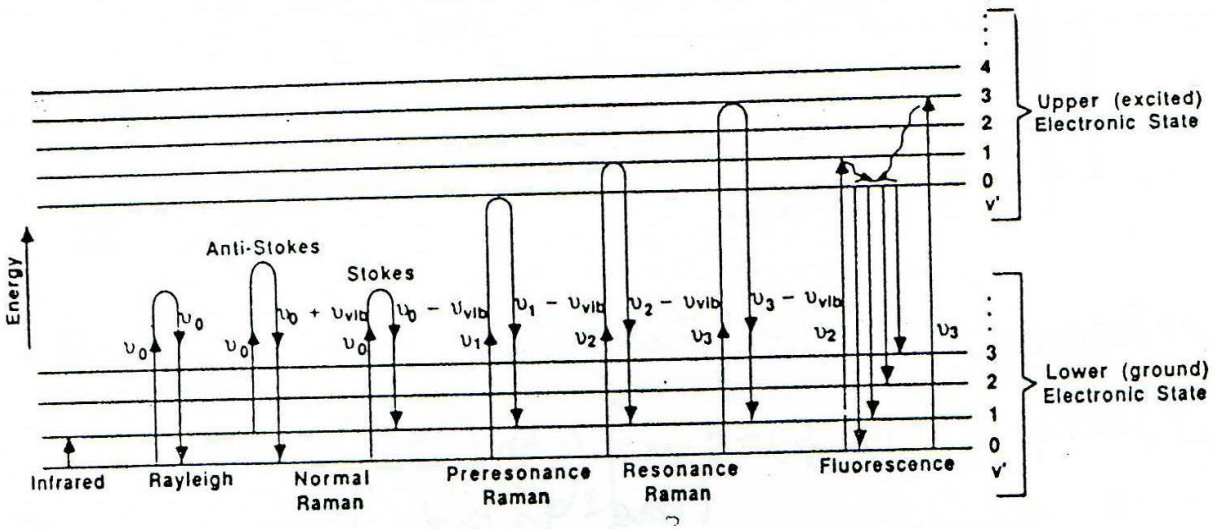
(virtual state)

Anti-Stokes Raman

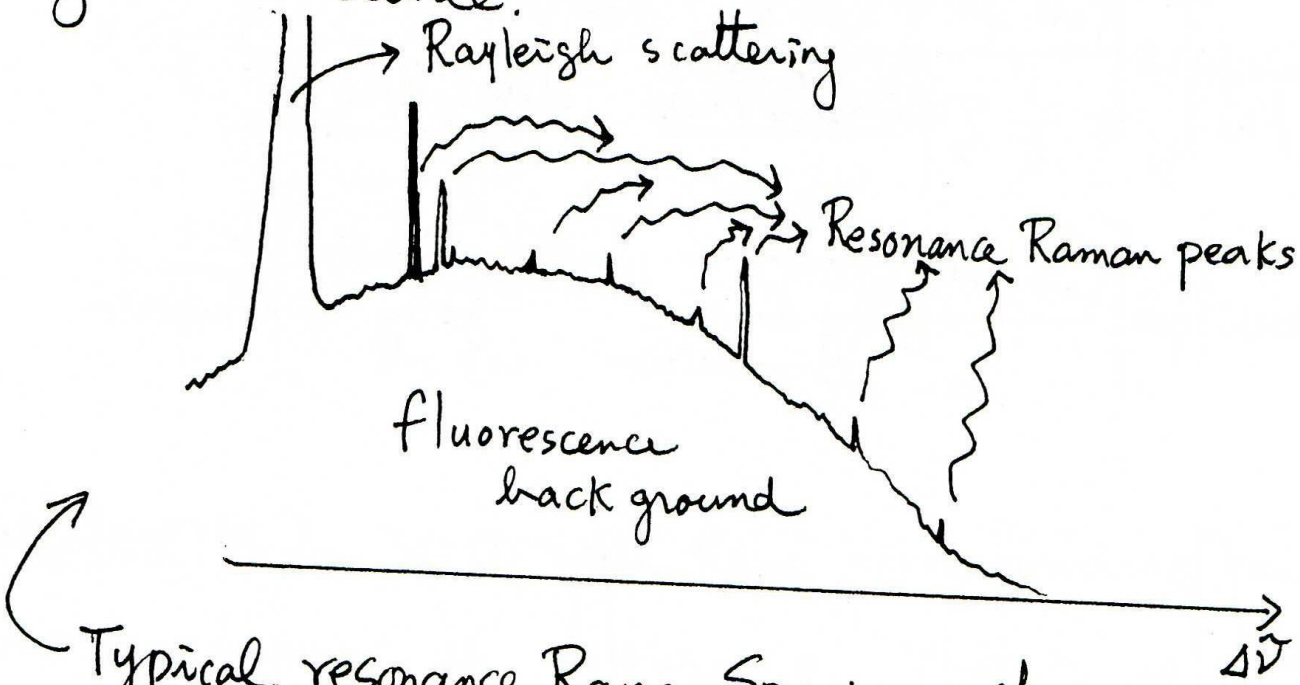
Stokes Raman

If the virtual state is a real state

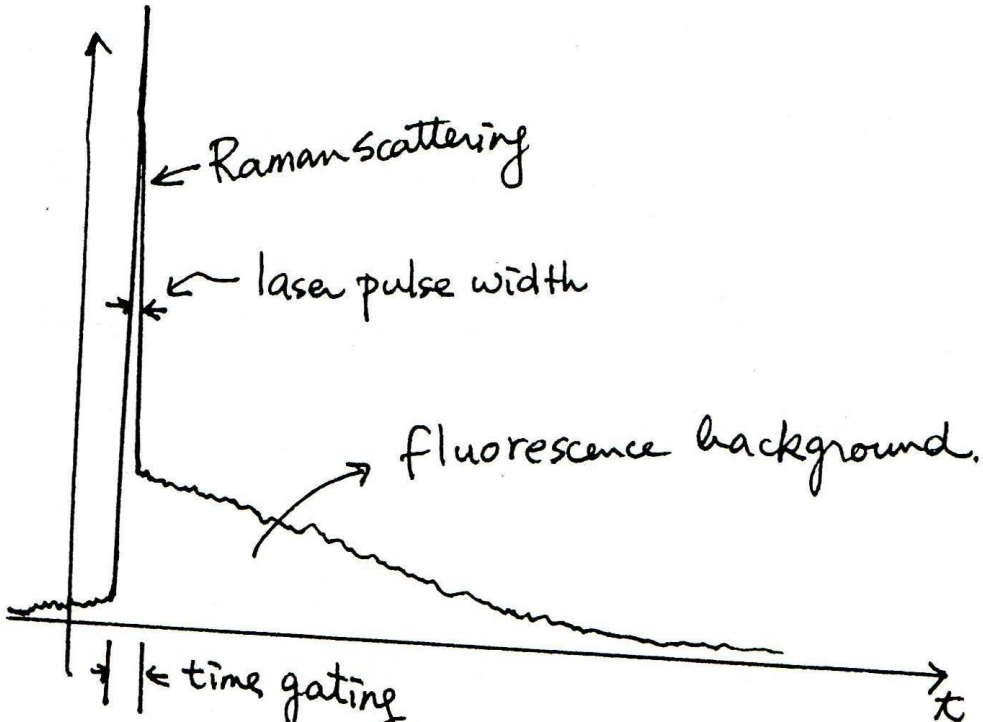
$\Rightarrow$ resonance Raman

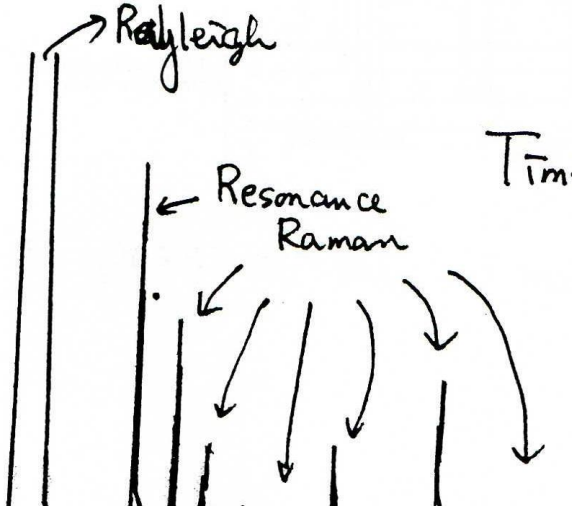


Resonance Raman Scattering almost always accompanies strong fluorescence.



Typical resonance Raman Spectrum of solution phase sample (No timing gating)





Time-gated Resonance Spectrum of solution phase sample.

6.1.3. Anharmonicity

6.1.3.1 Electrical anharmonicity

For Absorption

$$\mu_{if} = \underbrace{\left(\frac{d\mu}{dx}\right)_e \langle v|x|v'\rangle}_{\text{first order term}} + \underbrace{\frac{1}{2}\left(\frac{d^2\mu}{dx}\right)_e \langle v|x^2|v'\rangle + \cdots}_{\text{higher order term}}$$

Second order term $\Rightarrow$ $v = v' \pm 2$ for specific selection Rul

third order term $\Rightarrow$ $v = v' \pm 3$ for specific selection Ru

$\vdots$

For Raman scattering

$$\alpha = \alpha_0 + \underbrace{\left(\frac{\partial \alpha}{\partial x}\right)_e x \cos(2\pi\nu t + \phi)}_{\text{first order term}} + \underbrace{\frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial x^2}\right)_e x^2 \cos^2(2\pi\nu t + \phi) + \cdots}_{\text{higher order term}}$$

$$\mu_{ind}$$

$$= \alpha_0 \mathcal{E}_0 \cos(2\pi \nu_{ex} t) + \frac{\mathcal{E}_0}{2}\left(\frac{\partial \alpha}{\partial x}\right)_e x \left[\cos 2\pi(\nu_{ex}+\nu)t + \cos 2\pi(\nu_{ex}-\nu)t\right]$$

$$+ \frac{1}{2}\mathcal{E}_0\left(\frac{\partial^2 \alpha}{\partial x^2}\right)_e x^2 \left[\frac{\cos 2\pi(\nu_{ex}+2\nu)t + \cos 2\pi(\nu_{ex}-2\nu)t}{4} + \cos 2\pi(\nu_{ex}t)\right]$$

$$+ \ldots$$

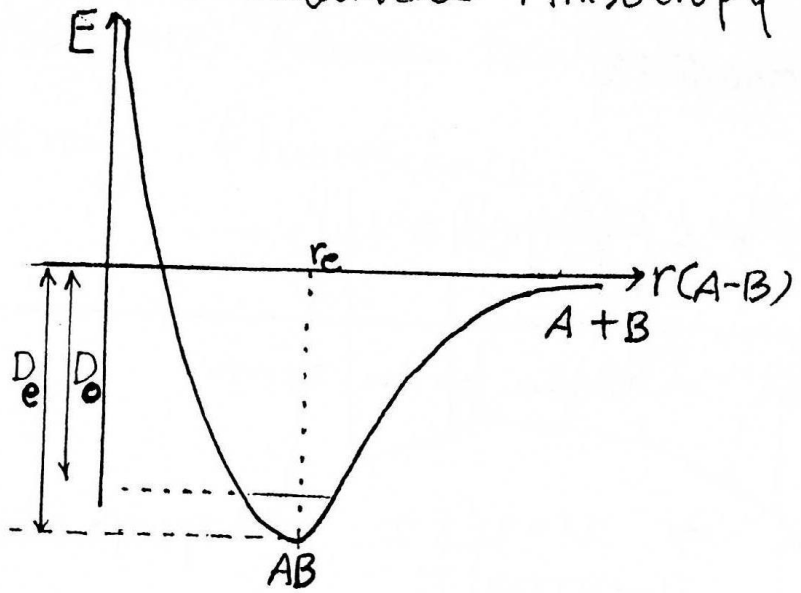
$$\left[\mu_{ind}\right]_{if} = \alpha_0 \mathcal{E}_0 \cos(2\pi \nu_{ex} t)\langle v|v'\rangle$$

$$+ \frac{\mathcal{E}_0}{2}\left(\frac{\partial \alpha}{\partial x}\right)_e \left[\cos 2\pi(\nu_{ex}+\nu)t + \cos 2\pi(\nu_{ex}-\nu)t\right]\langle v|x|v'\rangle$$

$$+ \frac{1}{2}\mathcal{E}_0\left(\frac{\partial^2 \alpha}{\partial x^2}\right)_e \left[\frac{\cos 2\pi(\nu_{ex}+2\nu)t + \cos 2\pi(\nu_{ex}-2\nu)t}{4} + \cos 2\pi(\nu_{ex}t)\right]$$

$$\times \langle v|x^2|v'\rangle,$$

6.1.3.2. Mechanical Anisotropy



$$E = \frac{J + K}{1 + S^2}$$

$$J = \langle \psi_A(1)\psi_B(2) | H | \psi_A(1)\psi_B(2) \rangle$$

$$K = \langle \psi_A(1)\psi_B(2) | H | \psi_A(2)\psi_B(1) \rangle$$

$$S = \langle \psi_A(1) | \psi_B(2) \rangle$$

Ab initio potential ; $V(r) = E + E_{min}$

Semi-empirical potential $V(r) = D_e [1 - e^{-a(r - r_e)}]^2$

(Morse potential)

$$V(r) = V(\xi) = D_e\left[1 - \left(1 - a\xi + \frac{a^2}{2}\xi^2 - \frac{a^3}{6}\xi^3 + \cdots\right)\right]^2$$

$$= D_e a^2 \xi^2 \left\{1 + \frac{a}{2}\xi - \frac{a^2}{6}\xi^2 + \cdots\right\}^2$$

$$\doteq D_e a^2 \xi^2 \left(1 + a\xi - \frac{a^2}{3}\xi^2 + \cdots\right) \qquad \leftarrow \ (1+x)^2 \doteq 1 + 2x \text{ for } x \ll 1$$

$$= D_e a^2 \xi^2 + D_e a^3 \xi^3 - \frac{a^4}{3} D_e \xi^4 + \cdots$$

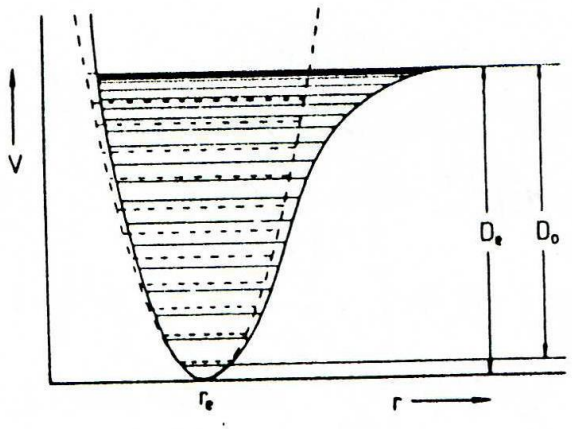
$$= \frac{1}{2} k \xi^2 + D_e a^3 \xi^3 - \frac{a^4}{3} D_e \xi^4 + \cdots$$

(where $k = 2 D_e a^2$)

$$E_v = \left(v + \frac{1}{2}\right)\hbar\omega_e + D_e a^3 \langle v|\xi^3|v\rangle - \frac{a^4}{3} D_e \langle v|\xi^4|v\rangle$$

(where $\omega_e = \sqrt{\frac{k}{\mu}} = \sqrt{\frac{2D_e}{\mu}}\, a$)

$$= \left(v + \frac{1}{2}\right)\hbar\omega_e - \left(v + \frac{1}{2}\right)^2 x_e \hbar \cdots \qquad \left(x_e = \frac{a^2\hbar}{2\mu\omega_e}\right)$$



$$G(v) = \frac{E_v}{hc} = \tilde{\nu}_e\left[(v+\tfrac{1}{2}) - \chi_e(v+\tfrac{1}{2})^2 + y_e(v+\tfrac{1}{2})^3 + \ldots\right]$$

For example, $^1H^{35}Cl$

$\tilde{\nu}_e = 2990.946\ cm^{-1}$, $\chi_e\tilde{\nu}_e = 52.8186\ cm^{-1}$

$y_e\tilde{\nu}_e = 0.2244\ cm^{-1}$ etc.

$$D_e = \frac{k}{2a^2} = \frac{\hbar}{4\chi_e\mu\omega_e}(\mu\omega_e^2) = \frac{\omega_e^2\hbar}{4\chi_e\omega_e} = \frac{\tilde{\nu}_e^2}{4\chi_e\tilde{\nu}_e}(hc)$$

$$= \frac{(2990.9\ cm^{-1})^2}{52.819\ cm^{-1}\times 4}(hc) = (42314\ cm^{-1})\,hc \doteq 5.25\ eV \doteq \frac{hc}{236\ nm}$$

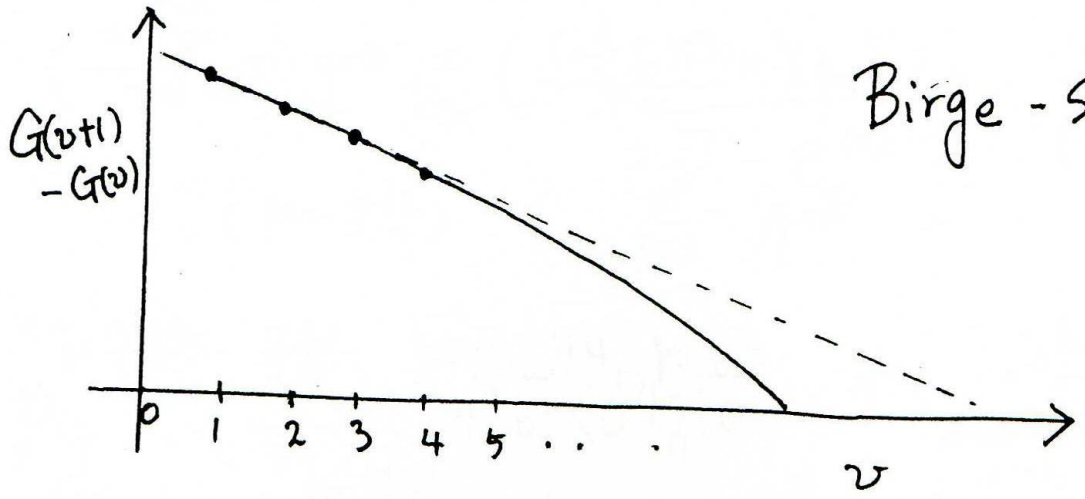
$$\doteq 121\ Kcal/mol$$

Experimentally,

$$D_0 = D_e - G(0)hc$$

$$= \left[\{G(1) - G(0)\} + \{G(2) - G(1)\} + \cdots + \{G(v+1) - G(v)\} + \cdots \right] hc$$

$$= \sum_{v=0}^{\infty} \{G(v+1) - G(v)\} hc$$

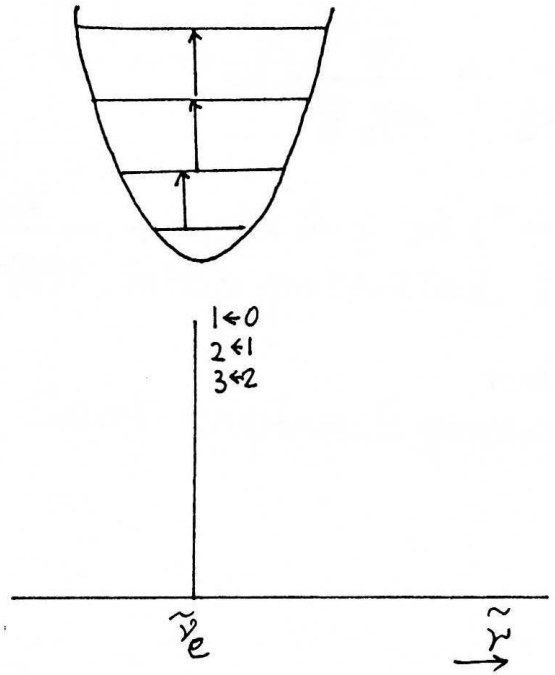


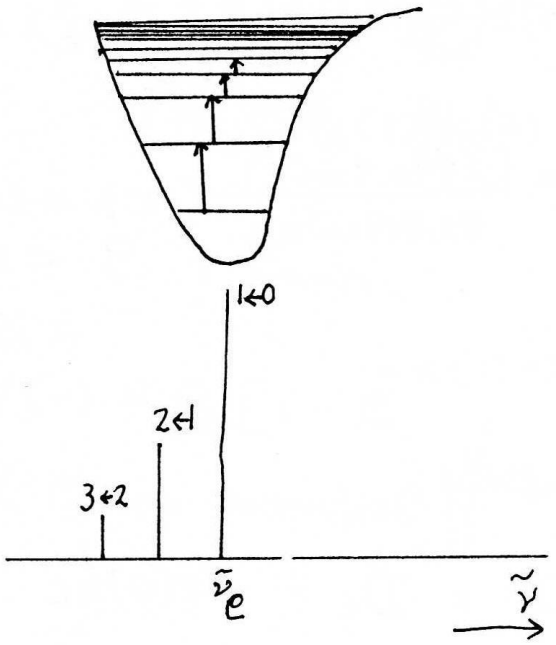
Birge - Sponer extrapolation

< Spectrum에 나타나는 anharmonicity의 영향 >

① Hot band structure가 분리되어 나타날 수 있다.

harmonic potential에서는 $1 \leftarrow 0$, $2 \leftarrow 1$, ..., $v \leftarrow v-1$의 모든 transition이 같은 $\tilde{\nu}$에서 일어나지만 anharmonic potential에서는 이들 transition frequency가 각각 다르다.





즉 Morse potential을 갖는 vibration을 예로들면 $1 \leftarrow 0$ 은 $\tilde{\nu}_e$ 에서 $2 \leftarrow 1$ 는 $\tilde{\nu}_e(1-2\chi_e)$ 에서, $\cdots$, $v \leftarrow v-1$ 은 $\tilde{\nu}_e(1-2v\chi_e)$ 에서 일어난다. 이들의 상온에서의 상대적 intensity는

$$\frac{I(2\leftarrow 1)}{I(1\leftarrow 0)} = \exp\left(-\frac{(E_1 - E_0)}{kT}\right) \simeq \exp\left(-\frac{\tilde{\nu}_e hc}{kT}\right)$$

$$= \exp\left(-\frac{\tilde{\nu}_e}{207\,cm^{-1}}\right) \quad (\text{상온에서})$$

$\therefore$ $\frac{\text{hot band}}{\text{fundamental band}}$ 는 온도에 민감하며 낮은 진동수의 vibration 일수록 hot band의 상대적 크기가 크다.

② Appearance of overtone peaks.

$\mu_{if} = \left(\frac{\partial \mu}{\partial q}\right)_e \langle v' | q | v \rangle$; vibrational transition between different v and v'

$\Rightarrow \left(\frac{\partial \mu}{\partial q}\right)_e \langle v'^{(0)} | q | v^{(0)} \rangle$ in case of harmonic potential.

where $|v^{(0)}\rangle$ represents (unperturbed) vibrational wavefunction of the harmonic potential.

μ_{if} is nonzero only when $v' = v \pm 1$

However, for anharmonic potential,

$$|v\rangle = a_0|0^{(0)}\rangle + a_1|1^{(0)}\rangle + \cdots + a_k|k^{(0)}\rangle + \cdots + |v^{(0)}\rangle$$

where $a_k = \dfrac{\langle k^{(0)}|\hat{H}'|v^{(0)}\rangle}{E_v^{(0)} - E_k^{(0)}}$, $\quad \hat{H}' = De\,a^3 q^3 - \frac{a^4}{3} De\, q^4$ if Morse potential

$(k \neq v)$

$$|v'\rangle = b_0|0^{(0)}\rangle + b_1|1^{(0)}\rangle + \cdots + b_k|k^{(0)}\rangle + \cdots + |v'^{(0)}\rangle$$

where $b_{k'} = \dfrac{\langle k'^{(0)}|\hat{H}'|v'^{(0)}\rangle}{E_{v'}^{(0)} - E_k^{(0)}}$

Then

$$\mu_{if} = \left(\frac{\partial \mu}{\partial q}\right)_e \Big[a_0^* b_0 \langle 0^{(0)}|q|0^{(0)}\rangle + a_1^* b_0 \langle 1^{(0)}|q|0^{(0)}\rangle + a_0^* b_1 \langle 0^{(0)}|q|1^{(0)}\rangle + \cdots + a_k^* b_{k'} \langle k^{*(0)}|q|k'^{(0)}\rangle + \cdots + \langle v^{(0)}|q|v'^{(0)}\rangle$$

$\therefore v' = v \pm 1$ selection rule is relaxed and

$v' = v \pm 2$, (2nd overtone)

$v \pm 3$ (3rd overtone) etc. are observable

6.1.4. Vibration-Rotation Spectroscopy

6.1.4.1 Infrared Spectra

$$S(v, J) = G(v) + F_v(J)$$

$$= \tilde{\nu}_e\left(v+\tfrac{1}{2}\right) - \tilde{\nu}_e x_e\left(v+\tfrac{1}{2}\right)^2 + \cdots + B_v J(J+1) - D_v J^2(J+1)$$

Vibrational selection Rule: $\Delta v = \pm 1$

rotational selection Rule; $\Delta J = +1$ (R branch)

-1 (O branch)

$\Delta J = 0$ (pure vibrational transition) is forbidden because $\Delta J = 0$ is not an allowed selection rule for diatomic molecule. Exceptions to this selection rule are molecules such as NO, which have an electronic angular momentum in the ground state.

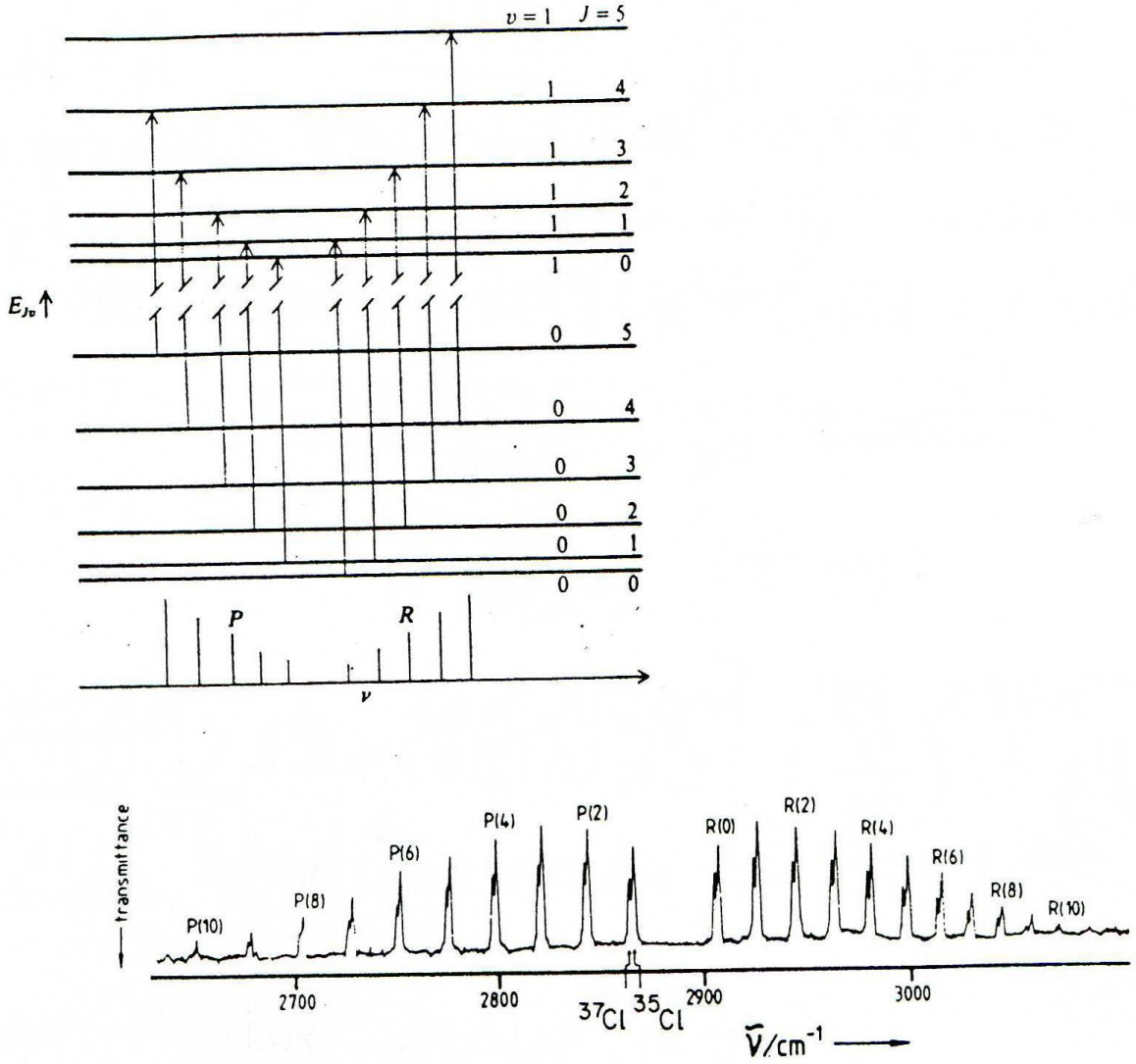


Figure 6.8 The $v = 1$–0 infrared spectrum of $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$ showing the *P*- and *R*-branch rotational structure.

Consider Only $\Delta v = +1$ transition and neglect centrifugal distortion,

$$S(0, J) = \tilde{\nu}_e \cdot \frac{1}{2} - \tilde{\nu}_e \frac{x_e}{4} + B_0 J(J+1)$$

$$S(1, J) = \tilde{\nu}_e \frac{3}{2} - \tilde{\nu}_e \frac{x_e}{9} + B_1 J(J+1)$$

assuming $B_1 = B_0 = B$, (in fact $B_1 = B_0 - \frac{1}{2}\alpha_e$)

$$\tilde{\nu}[R(J)] = S(1, J+1) - S(0, J) = \tilde{\nu}_e \left(1 + \frac{5}{36} x_e\right) + 2B(J+1)$$

$$= \tilde{\nu}_0 + 2B(J+1) \qquad J = 0, 1, 2, \cdots$$

$$\tilde{\nu}[P(J)] = S(1, J-1) - S(0, J) = \tilde{\nu}_e \left(1 + \frac{5}{36} x_e\right) - 2BJ$$

$$= \tilde{\nu}_0 - 2BJ \qquad J = 1, 2, 3, \cdots$$

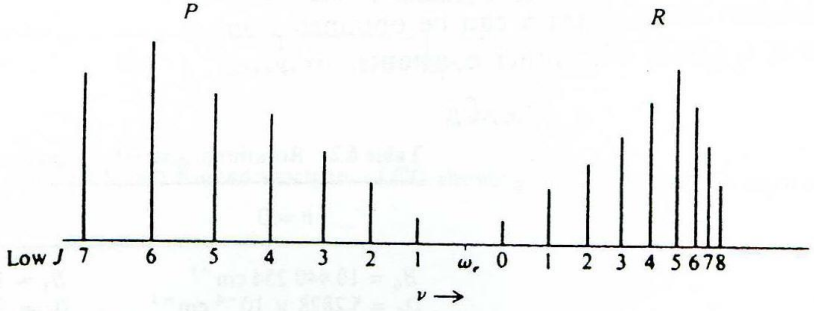
However, when α_e is not neglected,

$$\tilde{\nu}[R(J)] = \tilde{\nu}_0 + 2B_0 \cdot (J+1) - \frac{1}{2}\alpha_e (J+1)(J+2),$$

$$= \tilde{\nu}_0 + \left[2B_0 - \frac{1}{2}\alpha_e (J+2)\right](J+1) \qquad J = 0, 1, 2, \cdots$$

$$\tilde{\nu}[P(J)] = \tilde{\nu}_0 - 2B_0 J - \frac{1}{2}\alpha_e J(J-1)$$

$$= \tilde{\nu}_0 - \left[2B_0 + \frac{1}{2}\alpha_e \cdot (J-1)\right] J \qquad J = 1, 2, 3, \cdots$$



In general cases of $(v+1, J'') \leftarrow (v, J')$ transition,

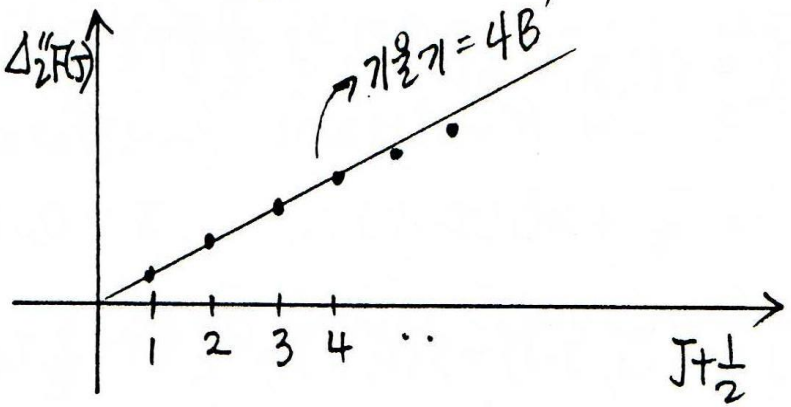
$R(J-1)$ and $P(J+1)$ have a common upper state

and $\tilde{\nu}[R(J-1)] - \tilde{\nu}[P(J+1)]$ is a function of B''

$$\Delta_2'' F(J) = \tilde{\nu}[R(J-1)] - \tilde{\nu}[P(J+1)]$$

$$= \tilde{\nu}_0 + B'J(J+1) - B''(J-1)J - [\tilde{\nu}_0 + B'J(J+1) - B''(J+1)(J+2)]$$

$$= 4B''(J+\tfrac{1}{2})$$



Similarly, since all pairs of transitions $R(J)$ and $P(J)$ have common lower states, $\tilde{\nu}[R(J)] - \tilde{\nu}[P(J)]$ is a function of B' only and we have

$$\begin{aligned}\Delta_2' F(J) &= \tilde{\nu}[R(J)] - \tilde{\nu}[P(J)] \\ &= \tilde{\nu}_0 + B'(J+1)(J+2) - B''J(J+1) \\ &\quad - [\tilde{\nu}_0 + B'(J-1)J - B''J(J+1)] \\ &= 4B'(J+\tfrac{1}{2})\end{aligned}$$

and a graph of $\Delta_2' F(J)$ versus $(J + \frac{1}{2})$ is a straight line of slope $4B'$.

Any effects of centrifugal distortion will show up as slight curvature of the $\Delta_2 F(J)$ versus $(J + \frac{1}{2})$ graphs. If the term $-DJ^2(J+1)^2$ is included, as in equation (6.24), in the rotational term value expression we get

$$\Delta_2'' F(J) = (4B'' - 6D'')(J+\tfrac{1}{2}) - 8D''(J+\tfrac{1}{2})^3$$

and

$$\Delta_2' F(J) = (4B' - 6D')(J+\tfrac{1}{2}) - 8D'(J+\tfrac{1}{2})^3$$

A graph of $\Delta_2'' F(J)/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ is a straight line of slope $8D''$ and intercept $4B''$ (or, strictly, $(4B'' - 6D'')$, but $6D''$ may be too small to affect the intercept). Similarly a graph of $\Delta_2' F(J)/(J+\frac{1}{2})$ versus $(J+\frac{1}{2})^2$ is a straight line of slope $8D'$ and intercept $4B'$.

If B_v can be obtained for at least two vibrational levels, say B_0 and B_1, then B_e and the vibrational–rotation interaction constant α can be obtained from equation (5.25). Values for B_e and α, together with other constants, are given for $^1H^{35}Cl$ in Table 6.2.

Table 6.2 Rotational and vibrational constants for $^1H^{35}Cl$.

$v = 0$	$v = 1$
$B_0 = 10.440\,254\ \text{cm}^{-1}$	$B_1 = 10.136\,228\ \text{cm}^{-1}$
$D_0 = 5.2828 \times 10^{-4}\ \text{cm}^{-1}$	$D_1 = 5.2157 \times 10^{-4}\ \text{cm}^{-1}$
ω_0 (for $v = 1$–0 transition) $= 2885.9775\ \text{cm}^{-1}$	
$B_e = 10.593\,42\ \text{cm}^{-1}$	
$\alpha_e = 0.307\,18\ \text{cm}^{-1}$	

6.1.4.2. Raman Spectra

Vibrational selection Rule

$$\begin{cases} \Delta v = 0 & ; \text{ Rayleigh} \\ \Delta v = -1 & ; \text{ Stokes Raman} \\ \Delta v = +1 & ; \text{ Anti-Stokes Raman} \end{cases}$$

Rotational selection Rule

$$\begin{cases} \Delta J = 0 & ; \quad Q\text{-branch} \\ \Delta J = -2 & ; \quad O\text{-branch} \\ \Delta J = +2 & ; \quad S\text{-branch} \end{cases}$$

Assuming $B_1 = B_0 = B$

$$\tilde{\nu}[S(J)] = \tilde{\nu}_0 + 4B\left(J + \frac{3}{2}\right)$$

$$\tilde{\nu}[O(J)] = \tilde{\nu}_0 - 4B\left(J - \frac{1}{2}\right)$$

$$\tilde{\nu}[Q(J)] = \tilde{\nu}_0$$

where $\tilde{\nu}_0$ can be any Rayleigh, Anti-Stokes Raman, Stokes Raman wave number.

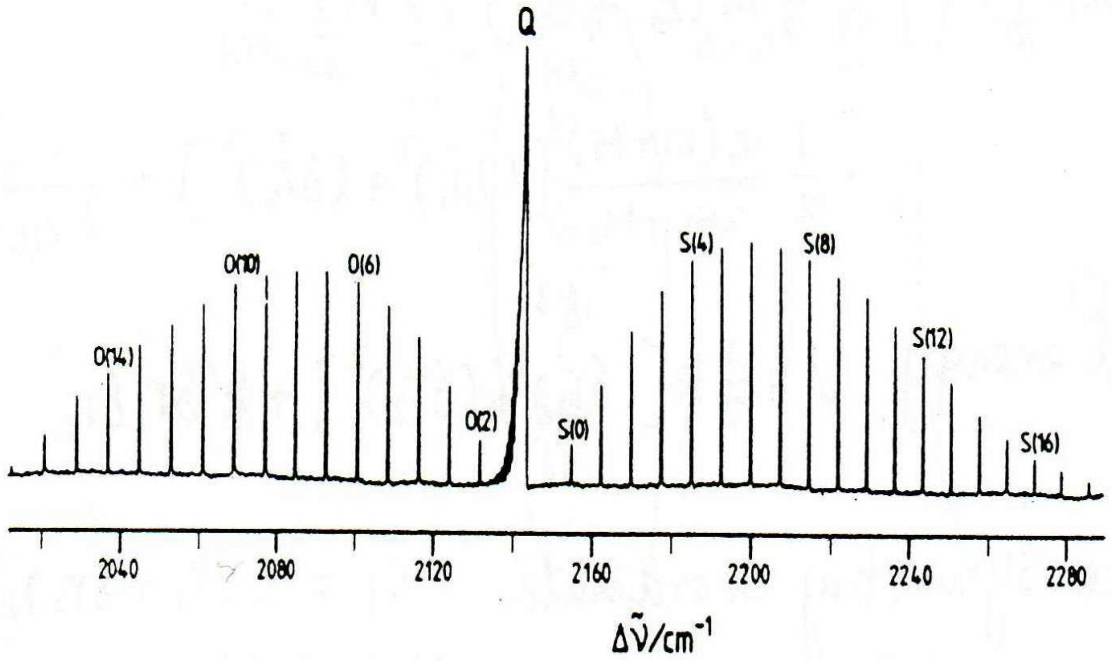


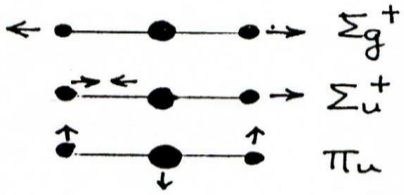
Figure 6.9 The 1–0 Stokes Raman spectrum of CO showing the *O*-, *Q*-, and *S*-branch rotational structure.

6.2 Polyatomic Molecules

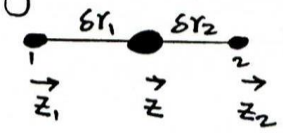
6.2.1 Normal Mode of Vibrations

a) Simple case

; Linear symmetric triatomic molecule (ex ; CO_2).



(Stretching vibration)



For conservation of center of mass

$$m(\dot{z}_1 + \dot{z}_2) + M\dot{z} = 0 \quad \cdots\cdots (1)$$

$z - z_1 = \delta r_1$, $z - z_2 = -\delta r_2$, these together with (1) give:

$$\begin{cases} z_1 = -\dfrac{m+M}{2m+M}\delta r_1 - \dfrac{m}{2m+M}\delta r_2 \\ z_2 = \dfrac{m}{2m+M}\delta r_1 + \dfrac{m+M}{2m+M}\delta r_2 \\ z = \dfrac{m}{2m+M}(\delta r_1 - \delta r_2) \end{cases}$$

Kinetic energy $T = \frac{1}{2}m(\dot{z}_1^2 + \dot{z}_2^2) + \frac{1}{2}M\dot{z}^2$

$$= \frac{1}{2}\frac{m(m+M)}{2m+M}\left[(\delta\dot{r}_1)^2 + (\delta\dot{r}_2)^2\right] + \frac{m^2}{(2m+M)}\delta\dot{r}_1\delta\dot{r}_2$$

Potential energy $V = \frac{1}{2}k\left[(\delta r_1)^2 + (\delta r_2)^2\right] + k'\delta r_1\delta r_2$

Introduce symmetry coordinate $S_1 = (\delta r_1 + \delta r_2)/\sqrt{2}$

$S_3 = (\delta r_1 - \delta r_2)/\sqrt{2}$

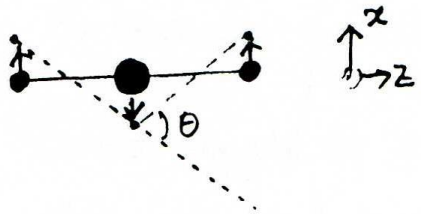
$$T = \frac{1}{2}m\dot{S}_1^2 + \frac{1}{2}\frac{mM}{2m+M}\dot{S}_3^2$$

$$V = \frac{1}{2}(k+k')S_1^2 + \frac{1}{2}(k-k')S_3^2$$

$\omega_1 = \sqrt{\frac{k+k'}{m}}$

$\sqrt{\frac{2m+M}{(k-k')}}$

(bending vibration)



$$\left.\begin{aligned} m(x_1+x_2)+Mx &= 0 \\ x_1 &= x_2 \\ l\theta &= (x-x_1)+(x-x_2) \end{aligned}\right\} \text{ these give } x = \frac{m}{2m+M} l\theta$$

$$x_1 = x_2 = -\frac{1}{2}\frac{M}{2m+M} l\theta$$

$$\therefore T = \frac{m}{2}(\dot{x}_1^2+\dot{x}_2^2)+\frac{M}{2}\dot{x}^2 = \frac{mM}{4(2m+M)} l^2\dot{\theta}^2$$

$$V = \frac{1}{2}k_\theta\theta^2 \qquad \therefore \omega_2 = \sqrt{\frac{2(2m+M)\,k_\theta}{mM\quad l^2}}$$

CO_2의 경우 $\tilde{\nu}_1 = 1337\,cm^{-1}$, $\tilde{\nu}_2 = 667\,cm^{-1}$, $\tilde{\nu}_3 = 2349\,cm^{-1}$

b) General cases

① Cartesian displacement coordinate

Kinetic energy : $2T = \sum_{\alpha=1}^{N} m_\alpha [(\delta\dot{x}_\alpha)^2 + (\delta\dot{y}_\alpha)^2 + (\delta\dot{z}_\alpha)^2]$

$$= \underset{\sim}{\dot{X}}' \underset{\approx}{M} \underset{\sim}{\dot{X}}$$

where $\underset{\sim}{X} = \begin{pmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \\ \vdots \\ \delta x_N \\ \delta y_1 \\ \vdots \\ \delta y_N \\ \delta z_1 \\ \vdots \\ \delta z_N \end{pmatrix}$ and $\underset{\approx}{M} = \begin{pmatrix} m_1 & & & & & & & & & \\ & m_2 & & & & & & & & \\ & & \ddots & & & & & & & \\ & & & m_N & & & & & & \\ & & & & m_1 & & & & & \\ & & & & & \ddots & & & & \\ & & & & & & m_N & & & \\ & & & & & & & m_1 & & \\ & & & & & & & & \ddots & \\ & & & & & & & & & m_N \end{pmatrix}$

mass-weighted cartesian coordinate를 정의하면

즉 $x_1 = (m_1)^{1/2}\delta x_1$, $x_2 = (m_1)^{1/2}\delta y_1$, $x_3 = (m_1)^{1/2}\delta z_1$, ...

$x_4 = (m_2)^{1/2}\delta x_2$, etc.

$$2T = \sum_{i=1}^{3N} \dot{x}_i^2 = \underset{\sim}{\dot{x}}' \underset{\sim}{\dot{x}} \qquad \text{where } \underset{\sim}{x} = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ \vdots \\ x_{3N} \end{pmatrix}$$

Potential energy ;

$$2V = 2V_0 + 2\sum_{i=1}^{3N} \left(\frac{\partial V}{\partial x_i}\right)_0 x_i + \sum_{i}^{3N}\sum_{j}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right) x_i x_j + \cdots$$

Harmonic 진동자의 경우만을 고려하고 $V_0 = 0$ 라 하면,

$$2V = \sum_{i}^{3N}\sum_{j}^{3N} \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right) x_i x_j = \sum_{i}^{3N}\sum_{j}^{3N} f_{ij}\, x_i x_j$$

f_{ij} 는 x 좌표에서 일반화시킨 force constant

Lagrange Equation $\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{x}_j}\right) + \frac{\partial V}{\partial x_j} = 0$ 을 만족하려면

$$\ddot{x}_j + \sum_{i}^{3N} f_{ij}\, x_i = 0 \qquad j = 1, \cdots, 3N$$

이 식은 $x_j = a_j \cos(\omega t + \phi)$ 형태의 근을 갖는다.

($\omega = 2\pi\nu$; frequency parameter
ϕ ; phase)

$$\sum_{i}^{3N} (f_{ij} - \delta_{ij}\omega^2) a_j = 0, \quad j = 1, \cdots, 3N$$

matrix 식으로 쓰면 $(\underset{\approx}{f} - \omega^2 \underset{\approx}{I})\underset{\sim}{a} = 0$

위 matrix가 nonzero solution을 갖을 수 있으려면

$$\det(\underset{\approx}{f} - \omega^2 \underset{\approx}{I}) = 0$$

즉,
$$\begin{bmatrix} f_{11}-\omega^2 & f_{12} & f_{13} & \cdots & f_{1,3N} \\ f_{21} & f_{22}-\omega^2 & f_{23} & \cdots & f_{2,3N} \\ \vdots & & \ddots & & \\ & & & & \\ (& & & & \omega^{2} \end{bmatrix} = 0$$

3N 개의 ω^2가 존재한다
그중 3개는 0 (translation)
3개는 0 (rotation)
3N-6개는 (vibration) nonzero

② Internal coordinate

Bond length와 angle의 증가를 좌표로 사용해서 나타내 보자.
이를 internal coordinate $r_1, r_2, \cdots, r_{3N-6}$ 라 하자.

$$2V = \sum_{i}^{3N-6}\sum_{j}^{3N-6}\left(\frac{\partial^2 V}{\partial r_i \partial r_j}\right)_0 r_i r_j = \sum_{i}^{3N-6}\sum_{j}^{3N-6} f_{ij}\, r_i r_j$$

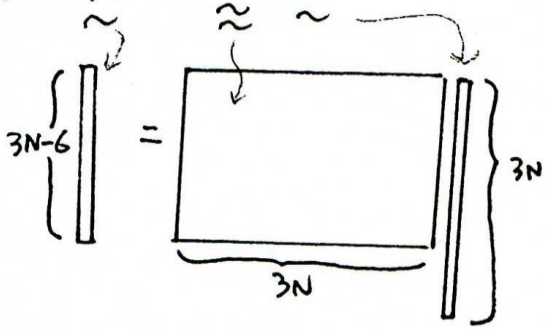
f_{ij} 는 r 좌표에서 일반화시킨 force constant

or $2V = \underset{\sim}{R}'\,\underset{\approx}{F}\,\underset{\sim}{R}$, where $\underset{\sim}{R} = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_{3N-6} \end{pmatrix} = \begin{pmatrix} \delta r_1 \\ \delta r_2 \\ \vdots \\ \delta\theta_1 \\ \delta\theta_2 \\ \vdots \\ \delta\phi_1 \\ \vdots \end{pmatrix}$

r_i 는 cartesian displacement 좌표로 부터 얻어 진다.

즉 $r_i = \sum_{k}^{3N} b_{ik} X_k$ or $\underset{\sim}{R} = \underset{\approx}{B}\,\underset{\sim}{X}$

$(i = 1, \cdots, 3N-6)$



$$2T = \dot{\underset{\sim}{X}}' \underset{\approx}{M} \dot{\underset{\sim}{X}}$$

The relation $\underset{\sim}{R} = \underset{\approx}{B}\,\underset{\sim}{X}$ can be inverted if Eckart's Condition is added

Eckart's condition

$$\sum_i m_i \delta r_i = 0, \quad \sum_i m_i \delta x_i = \sum_i m_i \delta y_i = \sum_i m_i \delta z_i = 0$$

$$\sum_i m_i \underset{\sim}{r}_{i0} \times \delta \underset{\sim}{r}_i = 0 \qquad \sum_i m_i (y_{i0}\delta z_i - z_{i0}\delta y_i)$$

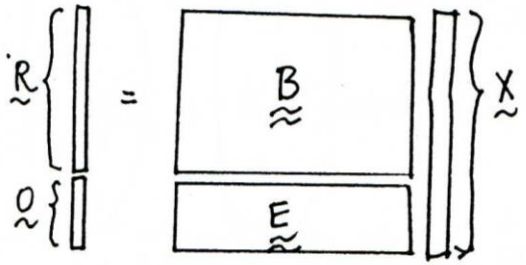
$$= \sum_i m_i (z_{i0}\delta x_i - x_{i0}\delta z_i)$$

$$= \sum_i m_i (x_{i0}\delta y_i - y_{i0}\delta x_i) = 0$$

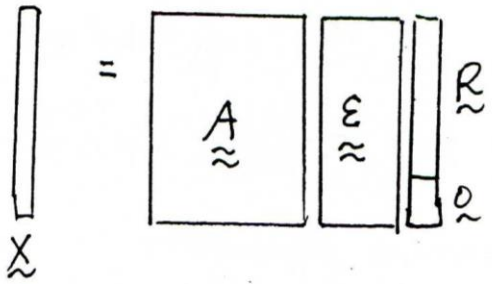
Eckart Matrix

$$\underset{\approx}{E} = \begin{bmatrix}
m_1 & m_2 & m_3 & \cdots & m_N & 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 \\
0 & 0 & 0 & \cdots & 0 & m_1 & m_2 & \cdots & m_N & 0 & 0 & \cdots & 0 \\
0 & 0 & 0 & \cdots & 0 & 0 & 0 & \cdots & 0 & m_1 & m_2 & \cdots & m_N \\
0 & 0 & 0 & \cdots & 0 & -m_1 z_{10} & -m_2 z_{20} & \cdots & -m_N z_{N0} & m_1 y_{10} & m_2 y_{20} & \cdots & m_N y_{N0} \\
m_1 z_{10} & m_2 z_{20} & \cdots & & m_N z_{N0} & 0 & 0 & \cdots & 0 & -m_1 x_{10} & -m_2 x_{20} & \cdots & -m_N x_{N0} \\
-m_1 y_{10} & -m_2 y_{20} & \cdots & & -m_N y_{N0} & m_1 x_{10} & m_2 x_{20} & \cdots & m_N x_{N0} & 0 & 0 & \cdots & 0
\end{bmatrix}$$

$$\underset{\approx}{E}\,\underset{\sim}{X} = \underset{\sim}{0}$$



If inverted,



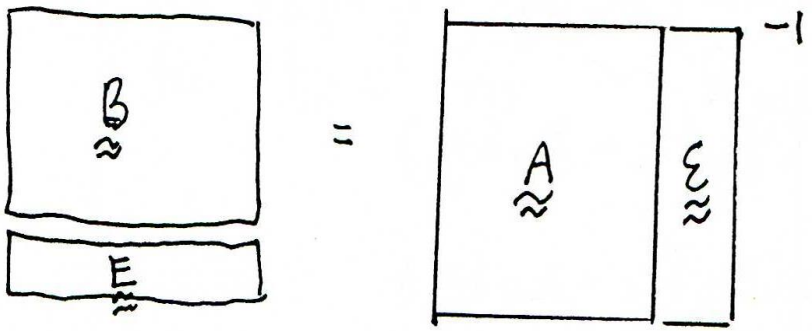
$$\underset{\sim}{X} = \underset{\approx}{A}\,\underset{\sim}{R}$$

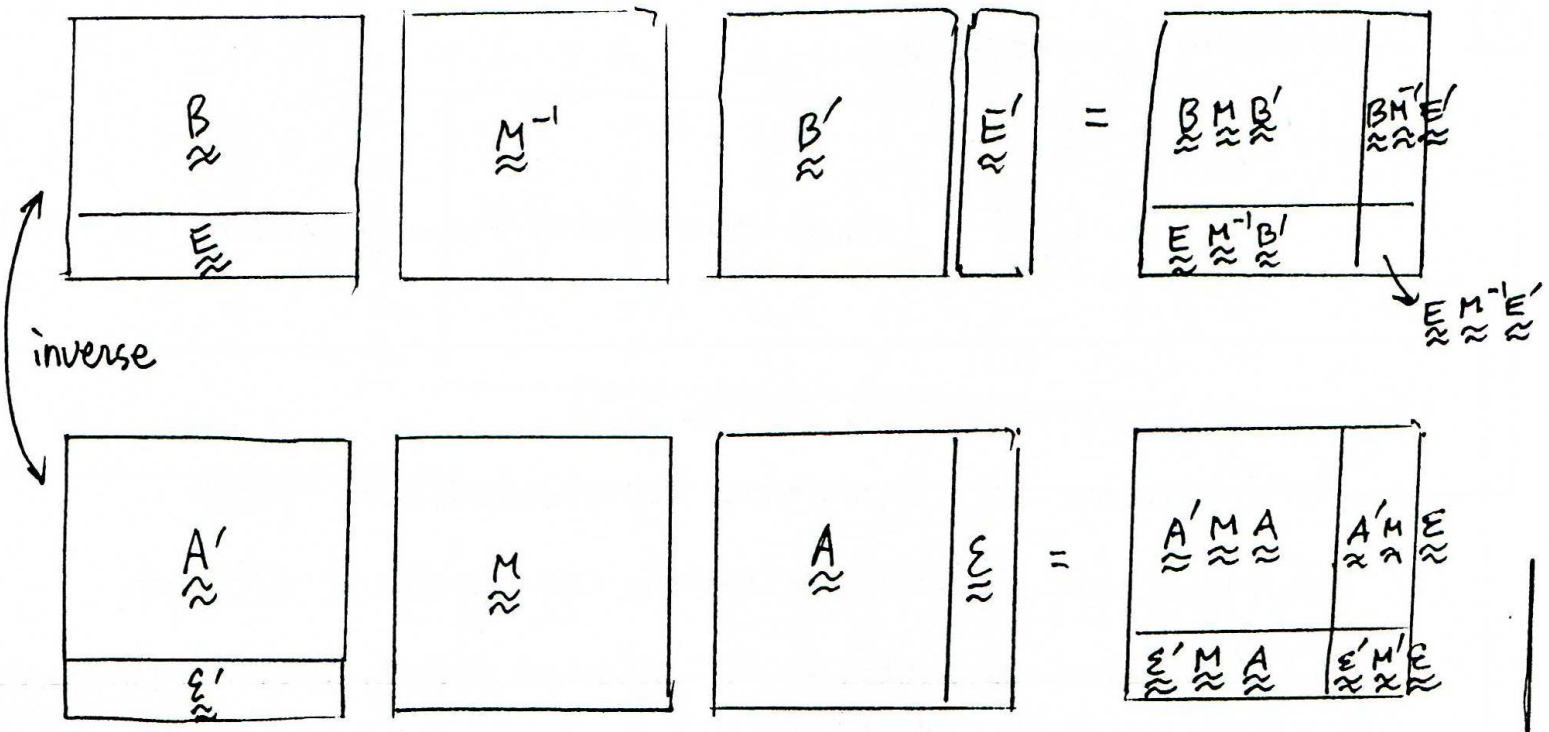
Then $T = \frac{1}{2}\dot{\underset{\sim}{R}}'\,\underset{\approx}{A}'\,\underset{\approx}{M}\,\underset{\approx}{A}\,\dot{\underset{\sim}{R}}$, $\quad V = \frac{1}{2}\underset{\sim}{R}'\,\underset{\approx}{F}\,\underset{\sim}{R}$

Wilson's Discovery $(\underset{\approx}{A}'\underset{\approx}{M}\underset{\approx}{A})^{-1} = (\underset{\approx}{B}\,\underset{\approx}{M}\,\underset{\approx}{B}') \equiv \underset{\approx}{G}$ (G-matrix)

A proof of Wilson's relation

ref; Wilson Decius, Cross, Molecular Vibrations (McGraw Hill, New York, 1955) Appendix.





$$\therefore (A' M A)^{-1} = (B M B')$$

$$2T = \dot{\underset{\sim}{R}}' \underset{\approx}{G}^{-1} \dot{\underset{\sim}{R}} = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \dot{r}_i \, g_{ij}^{-1} \, \dot{r}_j$$

$$2V = \underset{\sim}{R}' \underset{\approx}{F} \underset{\sim}{R} = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} r_i \, f_{ij} \, r_j$$

Lagrange's Equation $\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{r}_j}\right) + \frac{\partial V}{\partial r_j} = 0$ 를 만족하려면

$$\sum_{i=1}^{3N-6} \left(g_{ij}^{-1} \ddot{r}_j + f_{ij} r_i \right) = 0 \qquad j = 1, 2, \cdots, 3N-6$$

or $$\sum_{i=1}^{3N-6} \left(\ddot{r}_j + f_{ij} g_{ij} r_i \right) = 0$$

$r_j = a_j \cos(\omega t + \phi)$ 형태의 근을 갖는다.

$$\sum_{i=1}^{3N-6} \left(f_{ij} g_{ij} - \delta_{ij} \omega^2 \right) a_j = 0 \qquad j = 1, 2, \cdots, 3N-6$$

Matrix 식으로 쓰면 $\underset{\approx}{F}\underset{\approx}{G} - \omega^2 \underset{\approx}{I} = 0$

nonzero solution이 존재하려면

$$\det\left(\underset{\approx}{F}\underset{\approx}{G} - \omega^2 \underset{\approx}{I} \right) = 0$$

3N-6 의 근 → vibrational frequency

③ Symmetry Coordinate

$$\underset{\sim}{S} = \underset{\approx}{U}\,\underset{\sim}{R}$$

$$\underset{\sim}{R} = \underset{\approx}{U}'\underset{\sim}{S} \quad \text{since symmetry transformation is unitary}$$

Symmetry coordinate를 구하는 방법.

(1) Vibration 의 Symmetry representation을 구한다.

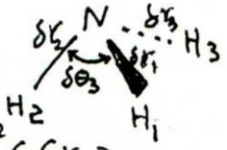
(2) δr_i 와 $\delta\theta_j$ 를 써서 internal coordinate를 설정한다.

(3) Projection operator를 각 internal 좌표에 걸어 각 symmetry 로 project되는 좌표를 구한다.

$$P(\Gamma) = \frac{1}{h}\sum_R \chi(R)\,R$$

(4) Normalization and linear combination

예) NH_3 의 경우



$$\Gamma_{vib} = 2A_1 + 2E$$

$$P(A_1)\,\delta r_1 = (1)E(\delta r_1) + (1)C_3(\delta r_1) + (1)C_3^2(\delta r_1)$$

$$= \delta r_1 + \delta r_2 + \delta r_3$$

$$P(A_1)\delta\theta_1 = (1)E(\delta\theta_1) + (1)C_3(\delta\theta_1) + (1)C_3^2(\delta\theta_1)$$
$$= \delta\theta_1 + \delta\theta_2 + \delta\theta_3$$
$$P(E_1)\delta r_1 = (1)E(\delta r_1) + \varepsilon C_3(\delta r_1) + \varepsilon^* C_3^2(\delta r_1)$$
$$= \delta r_1 + \varepsilon\delta r_2 + \varepsilon^*\delta r_3 \qquad \varepsilon = \exp\left(\frac{2\pi i}{3}\right)$$
$$P(E_2)\delta r_1 = (1)E(\delta r_1) + \varepsilon^* C_3(\delta r_1) + \varepsilon C_3^2(\delta r_1)$$
$$= \delta r_1 + \varepsilon^*\delta r_2 + \varepsilon\delta r_3$$
$$P(E_1)\delta\theta_1 = \delta\theta_1 + \varepsilon\delta\theta_2 + \varepsilon^*\delta\theta_3$$
$$P(E_2)\delta\theta_2 = \delta\theta_1 + \varepsilon^*\delta\theta_2 + \varepsilon\delta\theta_3$$

$$S_1 = \frac{1}{\sqrt{3}}(\delta r_1 + \delta r_2 + \delta r_3)$$
$$S_2 = \frac{1}{\sqrt{3}}(\delta\theta_1 + \delta\theta_2 + \delta\theta_3) \quad \Big] : A_1$$

$$S_{3a} = \frac{1}{\sqrt{6}}(2\delta r_1 - \delta r_2 - \delta r_3)$$
$$S_{3b} = \frac{1}{\sqrt{2}}(\delta r_2 - \delta r_3) \quad \Big] : E$$

$$S_{4a} = \frac{1}{\sqrt{6}}(2\delta\theta_1 - \delta\theta_2 - \delta\theta_3)$$
$$S_{4b} = \frac{1}{\sqrt{2}}(\delta\theta_1 - \delta\theta_3) \quad \Big] : E$$

$\underset{\approx}{U} =$

	δr_1	δr_2	δr_3	$\delta\theta_1$	$\delta\theta_2$	$\delta\theta_3$
S_1	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$	0	0	0
S_2	0	0	0	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
S_{3a}	$2/\sqrt{6}$	$-1/\sqrt{6}$	$-1/\sqrt{6}$	0	0	0
S_{4a}	0	0	0	$2/\sqrt{6}$	$-1/\sqrt{6}$	$-1/\sqrt{6}$
S_{3b}	0	$1/\sqrt{2}$	$-1/\sqrt{2}$	0	0	0
S_{4b}	0	0	0	0	$1/\sqrt{2}$	$-1/\sqrt{2}$

$$2T = \underset{\sim}{R}'\underset{\approx}{G}^{-1}\underset{\sim}{R} = \underset{\sim}{S}'\underset{\approx}{U}\,\underset{\approx}{G}^{-1}\underset{\sim}{U}'\underset{\sim}{S} \equiv \underset{\sim}{S}'\underset{\approx}{\mathcal{G}}^{-1}\underset{\sim}{S}$$

$$2V = \underset{\sim}{R}'\underset{\approx}{F}\underset{\sim}{R} = \underset{\sim}{S}'\underset{\approx}{U}\,\underset{\approx}{F}\,\underset{\sim}{U}'\underset{\sim}{S} \equiv \underset{\sim}{S}'\underset{\approx}{\tilde{F}}\underset{\sim}{S}$$

where $\underset{\approx}{\mathcal{G}} = \underset{\approx}{U}'\underset{\approx}{G}\underset{\approx}{U}$, $\underset{\approx}{\tilde{F}} = \underset{\approx}{U}\underset{\approx}{F}\underset{\approx}{U}'$

Then the secular determinant takes the form,

$$\det\left(\underset{\approx}{\mathcal{G}}\,\underset{\approx}{\tilde{F}} - \omega^2\underset{\approx}{I}\right) = 0$$

적용 앞의 NH_3의 경우에 적용할 때

$$\underset{\approx}{F} =$$

	Δr_1	Δr_2	Δr_3	$\Delta\theta_1$	$\Delta\theta_2$	$\Delta\theta_3$
Δr_1	f_r	$f_{rr'}$	$f_{rr'}$	0	$f_{r\theta}$	$f_{r\theta}$
Δr_2	$f_{rr'}$	f_r	$f_{rr'}$	$f_{r\theta}$	0	$f_{r\theta}$
Δr_3	$f_{rr'}$	$f_{rr'}$	f_r	$f_{r\theta}$	$f_{r\theta}$	0
$\Delta\theta_1$	0	$f_{r\theta}$	$f_{r\theta}$	f_θ	0	0
$\Delta\theta_2$	$f_{r\theta}$	0	$f_{r\theta}$	0	f_θ	0
$\Delta\theta_3$	$f_{r\theta}$	$f_{r\theta}$	0	0	0	f_θ

$$\underset{\approx}{f} = \underset{\approx}{U}\underset{\approx}{F}\underset{\approx}{U}' =$$

$$\begin{bmatrix} f_r + 2f_{rr'} & 2f_{r\theta} & 0 & 0 & 0 & 0 \\ 2f_{r\theta} & f_\theta & 0 & 0 & 0 & 0 \\ 0 & 0 & f_r - f_{rr'} & -f_{r\theta} & 0 & 0 \\ 0 & 0 & -f_{r\theta} & f_\theta & 0 & 0 \\ 0 & 0 & 0 & 0 & f_r - f_{rr'} & -f_{r\theta} \\ 0 & 0 & 0 & 0 & -f_{r\theta} & f_\theta \end{bmatrix}$$

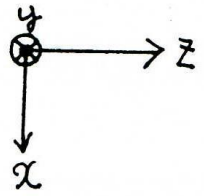
$\underset{\approx}{G}$ =

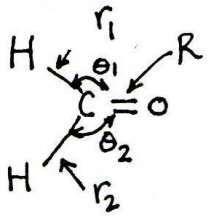
	δr_1	δr_2	δr_3	$\delta\theta_1$	$\delta\theta_2$	$\delta\theta_3$
δr_1	g^2_{rr}	$g^1_{rr'}$	$g^1_{rr'}$	$g^1_{r\theta}(2)$	$g^2_{r\theta}$	$g^2_{r\theta}$
δr_2		g^2_{rr}	$g^1_{rr'}$	$g^2_{r\theta}$	$g^1_{r\theta}(2)$	$g^2_{r\theta}$
δr_3			g^2_{rr}	$g^2_{r\theta}$	$g^2_{r\theta}$	$g^1_{r\theta}(2)$
$\delta\theta_1$				$g^3_{\theta\theta}$	$g^2_{\theta\theta'}(1)$	$g^2_{\theta\theta'}(1)$
$\delta\theta_2$					$g^3_{\theta\theta}$	$g^2_{\theta\theta'}(1)$
$\delta\theta_3$						$g^3_{\theta\theta}$

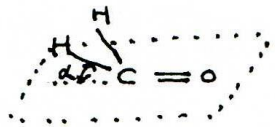
$$\underset{\approx}{g} = \underset{\approx}{u}'\underset{\approx}{G}\underset{\approx}{u} = \begin{bmatrix} g^2_{rr} + 2g^1_{rr'} & g^1_{r\theta}(2) + 2g^2_{r\theta} & 0 & 0 & 0 & 0 \\ g^1_{r\theta}(2) + 2g^2_{r\theta} & g^3_{\theta\theta} + 2g^2_{\theta\theta'}(1) & 0 & 0 & 0 & 0 \\ 0 & 0 & g^2_{rr} - g^1_{rr'} & g^1_{r\theta}(2) - 2g^2_{r\theta} & 0 & 0 \\ 0 & 0 & g^1_{r\theta}(2) - 2g^2_{r\theta} & g^3_{\theta\theta} - 2g^2_{\theta\theta'}(1) & 0 & 0 \\ 0 & 0 & 0 & 0 & g^2_{rr} - g^1_{rr'} & g^1_{r\theta}(2) - 2g^2_{r\theta} \\ 0 & 0 & 0 & 0 & g^1_{r\theta}(2) - 2g^2_{r\theta} & g^3_{\theta\theta} - 2g^2_{\theta\theta'}(1) \end{bmatrix}$$

적용 예

$H_2C{=}O$ 분자.







α: out of plane angle

$$\underset{\approx}{B} =$$

	δx_c	δx_0	δx_1	δx_2	δz_c	δz_0	δz_1	δz_2	δy_c	δy_0	δy_1	δy_2
δR	0	0	0	0	-1	1	0	0	0	0	0	0
δr_1	$\sin\theta$	0	$-\sin\theta$	0	$-\cos\theta$	0	$\cos\theta$	0	0	0	0	0
δr_2	$-\sin\theta$	0	0	$\sin\theta$	$-\cos\theta$	0	0	$\cos\theta$	0	0	0	0
$\delta\theta_1$	$-\frac{1}{R}+\frac{\cos\theta}{r}$	$\frac{1}{R}$	$-\frac{\cos\theta}{r}$	0	$\frac{\sin\theta}{r}$	0	$-\frac{\sin\theta}{r}$	0	0	0	0	0
$\delta\theta_2$	$\frac{1}{R}-\frac{\cos\theta}{r}$	$-\frac{1}{R}$	0	$\frac{\cos\theta}{r}$	$\frac{\sin\theta}{r}$	0	0	$-\frac{\sin\theta}{r}$	0	0	0	0
$\delta\alpha$	0	0	0	0	0	0	0	0	$\frac{R-r\cos\theta}{Rr\cos\theta}$	$\frac{1}{R}$	$-\frac{1}{2r\cos\theta}$	$-\frac{1}{2r\cos\theta}$

$$\underset{\approx}{U} =$$

	δR	δr_1	δr_2	$\delta\theta_1$	$\delta\theta_2$	$\delta\alpha$	
S_1	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	0	0	0	A_1 Symmetry
S_2	1	0	0	0	0	0	
S_3	0	0	0	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$		
S_4	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	0	0	B_1 Symmetry
S_5	0	0	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	
S_6	0	0	0	0	0	1	B_2 Symmetry

$$\underset{\approx}{Q} = \underset{\approx}{U}\underset{\approx}{G}\underset{\approx}{U}' = \underset{\approx}{U}\underset{\approx}{B}\underset{\approx}{M}^{-1}\underset{\approx}{B}'\underset{\approx}{U}' = \cdots$$

$$= \begin{array}{c|ccc:ccc}
 & S_1 (=\frac{\delta r_1+\delta r_2}{\sqrt{2}}) & S_2 (=\delta R) & S_3 (=\frac{\delta\theta_1+\delta\theta_2}{\sqrt{2}}) & S_4 (=\frac{\delta r_1-\delta r_2}{\sqrt{2}}) & S_5 (=\frac{\delta\theta_1-\delta\theta_2}{\sqrt{2}}) & S_6 (=\delta\alpha) \\
\hline
 & \frac{1}{m_H}+\frac{1}{m_C}(1+\cos 2\theta) & \frac{\sqrt{2}}{m_C}\cos\theta & -\frac{\sqrt{3}}{m_C}\frac{\sin 2\theta}{r} & 0 & 0 & 0 \\
 & \frac{\sqrt{2}}{m_C}\cos\theta & \frac{1}{m_C}+\frac{1}{m_O} & -\frac{\sqrt{6}}{m_C}\frac{\sin\theta}{r} & 0 & 0 & 0 \\
 & -\frac{\sqrt{3}}{m_C}\frac{\sin 2\theta}{r} & -\frac{\sqrt{3}}{m_C}\frac{\sin 2\theta}{r} & 3\left(\frac{1}{m_H}+\frac{1}{m_C}\right)\frac{1}{r^2}-\frac{3}{m_C}\frac{\cos 2\theta}{r^2} & 0 & 0 & 0 \\
\hdashline
 & 0 & 0 & 0 & \frac{1}{m_H}+\frac{1}{m_C}(1-\cos 2\theta) & -\frac{2}{m_C}\left(\frac{\sin\theta}{R}+\frac{\cos\theta}{r}\right) & 0 \\
 & 0 & 0 & 0 & -\frac{2}{m_C}\left(\frac{\sin\theta}{R}+\frac{\cos\theta}{r}\right) & \frac{2}{R^2}\left(\frac{1}{m_C}+\frac{1}{m_O}\right)+\left(\frac{1}{m_H}+\frac{1+\cos 2\theta}{m_C}\right)\frac{1}{r^2}-\frac{4\cos 2\theta}{m_C Rr} & 0 \\
 & 0 & 0 & 0 & 0 & 0 & \left[\frac{r^2}{m_O}\cos^2\theta+\frac{(R-r\cos\theta)^2}{m_C}+\frac{R^2}{2m_H}\right]/R^2r^2\cos^2\phi
\end{array}$$

$$\underset{\approx}{\tilde{f}} = \underset{\approx}{U}' \underset{\approx}{F} \underset{\approx}{U} =$$

$$\begin{pmatrix}
k_{rr} + k_{rr'} & \sqrt{2}k_{Rr} & \sqrt{3}(k_{\theta r} + k_{\theta r'}) & 0 & 0 & 0 \\
\sqrt{2}k_{Rr} & k_R & \sqrt{6}\,k_{\theta R} & 0 & 0 & 0 \\
\sqrt{3}(k_{\theta r} + k_{\theta r'}) & \sqrt{6}\,k_{\theta R} & 3(k_{\theta\theta} + k_{\theta\theta'}) & 0 & 0 & 0 \\
0 & 0 & 0 & k_{rr} - k_{rr'} & k_{\theta r} - k_{\theta r'} & 0 \\
0 & 0 & 0 & k_{\theta r} - k_{\theta r'} & k_{\theta\theta} - k_{\theta\theta'} & 0 \\
0 & 0 & 0 & 0 & 0 & k_{\alpha\alpha}
\end{pmatrix}$$

For tricky way of getting $\underset{\approx}{g}$, refer to "F. Albert Cotton, Chemical Applications of Group Theory, Appendix IV.

or "Wilson, Decius, Cross, Molecular Vibrations.

④ Normal Coordinate

Find $\underset{\approx}{L}$ that diagonalizes $\underset{\approx}{gF}$.

How?

$$\begin{vmatrix} (gF)_{11} - \omega^2 & (gF)_{12} & (gF)_{13} & \cdots \\ (gF)_{21} & (gF)_{22} - \omega^2 & \cdots & \\ \vdots & & & \end{vmatrix} = 0$$

는 $3N-6$ 개의 solution 존재

$\Rightarrow \omega_1^2, \omega_2^2, \cdots, \omega_{3N-6}^2$ 라 하면

$$\begin{pmatrix} (gF)_{11} - \omega_1^2 & (gF)_{12} & \cdots \\ (gF)_{21} & (gF)_{22} - \omega_2^2 & \\ \vdots & & \ddots \end{pmatrix} \begin{pmatrix} l_{11} \\ l_{12} \\ \vdots \\ l_{1,3N-6} \end{pmatrix} = 0$$

and Normalization condition

$$\sum_j l_{1j}^2 = 1$$

gives. $\underset{\approx}{L} = \begin{pmatrix} l_{11} & l_{12} & \cdots & l_{1\,3N-6} \\ \times & \times & & \times \\ \times & & \ddots & \\ & & & \\ \ddots & & & \end{pmatrix}$

$$\begin{pmatrix} (gF)_{11} - \omega_2^2 & (gF)_{12} & \cdots \\ (gF)_{21} & (gF)_{22} - \omega_2^2 & \cdots \\ & \vdots & \end{pmatrix} \begin{pmatrix} l_{21} \\ l_{22} \\ \vdots \\ l_{2,3N-6} \end{pmatrix} = 0$$ and normalization condition $\sum_j l_{2j}^2 = 1$

gives $\underset{\approx}{L} = \begin{pmatrix} \times & \times & \times & \times & \times & \times \\ l_{21} & l_{22} & \cdot & \cdot & \cdot & l_{2,3N-6} \\ \times & \times & & & & \\ \times & & \times & & & \\ \times & & & \times & & \\ \times & & & & \cdot & \\ \times & & & & & \times \end{pmatrix}$

In this way $\underset{\approx}{L} = \begin{pmatrix} l_{11} & l_{12} & \cdots & l_{3N-6} \\ l_{21} & l_{22} & \cdots & \vdots \\ \vdots & & \ddots & \vdots \\ l_{3N-6} & \cdots & & l_{3N-6,3N-6} \end{pmatrix}$ can be determined.

Note that $\underset{\approx}{L}$ is block-diagonalized according to its symmetry.

The fact that $\underset{\approx}{g}\underset{\approx}{F}$ is diagonalized by $\underset{\approx}{L}$ means that

$$\underset{\approx}{L}'(\underset{\approx}{g}\underset{\approx}{F})\underset{\approx}{L} = \begin{pmatrix} w_1^2 & 0 & \cdots & 0 \\ 0 & w_2^2 & & \\ \vdots & & \ddots & \\ 0 & & & w_{3N-6}^2 \\ 0 & & & \end{pmatrix}$$

$$\underset{\approx}{L}'(\underset{\approx}{g}\underset{\approx}{F})\underset{\approx}{L} = (\underset{\approx}{L}'\underset{\approx}{g}\underset{\approx}{L})(\underset{\approx}{L}'\underset{\approx}{F}\underset{\approx}{L})$$

If we adjust the amplitude of $\underset{\approx}{L}$, we can let

$$\underset{\approx}{L}'\underset{\approx}{g}\underset{\approx}{L} = \underset{\approx}{I}, \quad \underset{\approx}{L}'\underset{\approx}{F}\underset{\approx}{L} = \begin{pmatrix} w_1^2 & & & 0 \\ & w_2^2 & & \\ & & \ddots & \\ 0 & & & w_{3N-6}^2 \end{pmatrix} \equiv \underset{\approx}{W}\cdot\underset{\approx}{\ell}$$

Now consider the new coordinate, $\underset{\sim}{Q} = \underset{\approx}{L}\,\underset{\sim}{S}$.

Then $T = \frac{1}{2}\dot{\underset{\approx}{R}}'\underset{\approx}{G}^{-1}\dot{\underset{\approx}{R}} = \frac{1}{2}\dot{\underset{\approx}{S}}'\underset{\approx}{\mathcal{G}}^{-1}\dot{\underset{\approx}{S}} = \frac{1}{2}\dot{\underset{\sim}{Q}}'\underset{\approx}{L}'\underset{\approx}{\mathcal{G}}^{-1}\underset{\approx}{L}\dot{\underset{\sim}{Q}} = \frac{1}{2}\dot{\underset{\sim}{Q}}'\dot{\underset{\sim}{Q}}$

$$= \frac{1}{2}\sum_j \dot{q}_j^2$$

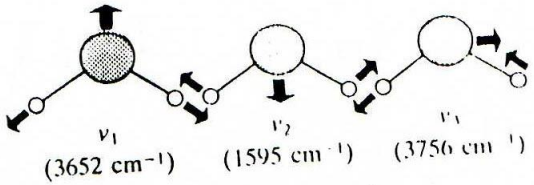
$V = \frac{1}{2}\underset{\approx}{R}'\underset{\approx}{E}\underset{\approx}{R} = \frac{1}{2}\underset{\approx}{S}'\underset{\approx}{\mathcal{F}}\underset{\approx}{S} = \frac{1}{2}\underset{\sim}{Q}'\underset{\approx}{L}'\underset{\approx}{\mathcal{F}}\underset{\approx}{L}\underset{\sim}{Q} = \frac{1}{2}\underset{\sim}{Q}'\underset{\approx}{W}\cdot\underset{\approx}{W}($

$$= \frac{1}{2}\sum_j \omega_j^2 q_j^2$$

$\underset{\sim}{Q}$ is called normal coordinate,
since $\underset{\sim}{Q}$ is the block-diagonalized transformation of $\underset{\sim}{\xi}$,
the symmetry of q_j takes the symmetry of S_i

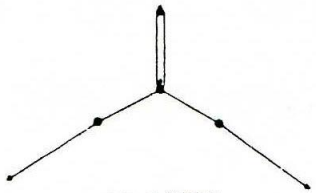
H_2O

$3N-6=3$



H_2CO

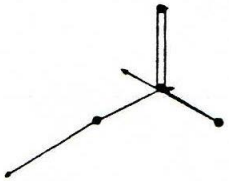
$3N-6=6$



$\omega_1 = 2766$
CH_2(SYM) STRETCH

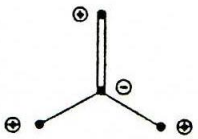
$\omega_2 = 1746$
C=O STRETCH

$\omega_3 = 1501$
CH_2 DEFORMATION

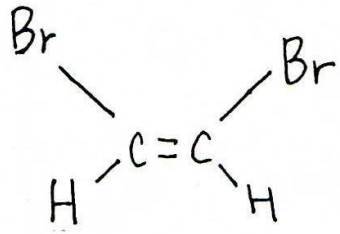


$\omega_4 = 2843$
CH_2(ASYM) STRETCH

$\omega_5 = 1247$
CH_2 ROCK



$\omega_6 = 1164$
CH_2 WAG



$3N-6 = 12$

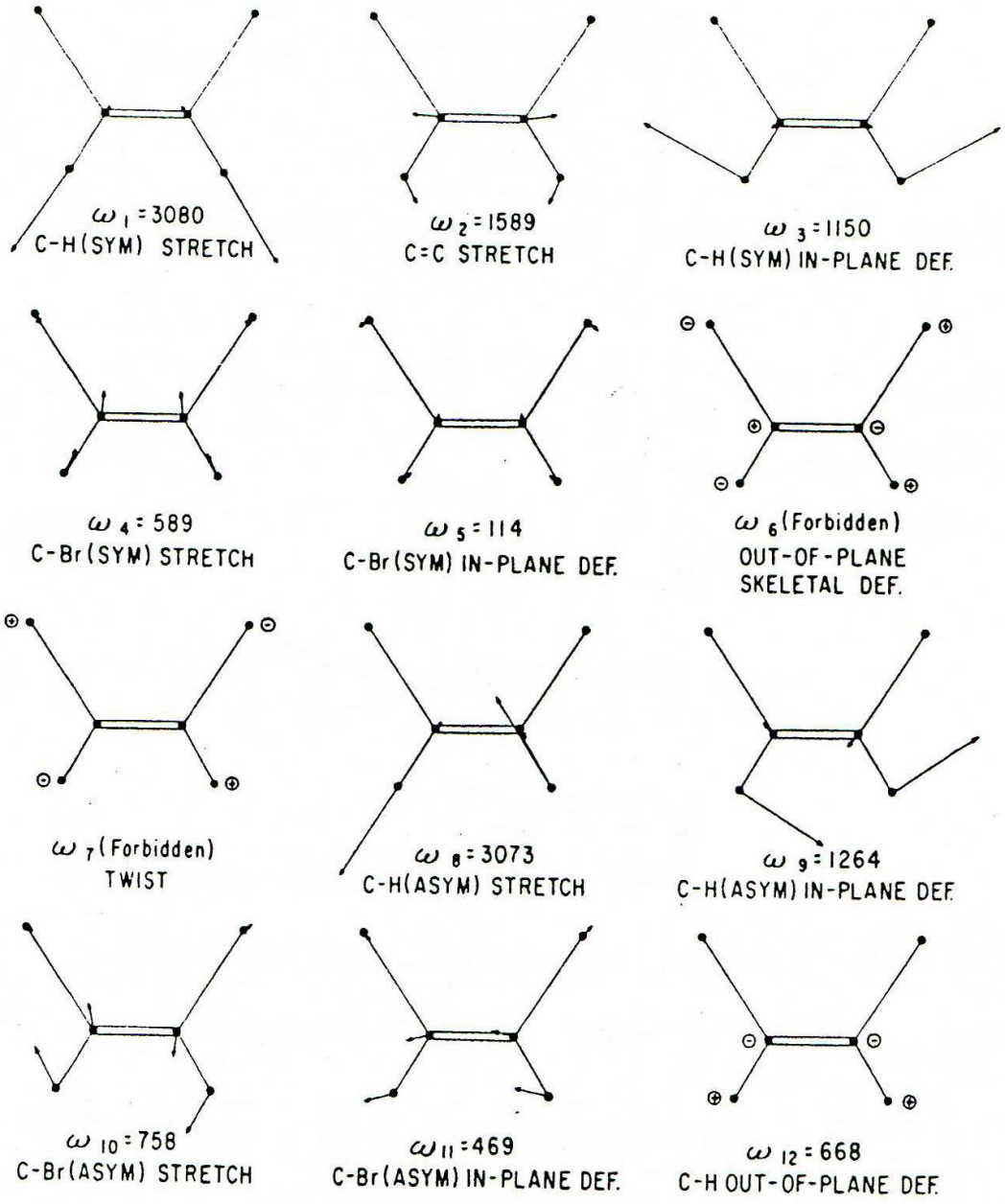


FIGURE 8-1c ***The normal modes of cis-dibromo ethylene.*** ***(Data from J. Scherer and J. Overend, J. Chem. Phys. 33, (1960)).***

$$\hat{H} = T + V = \sum_j \left(\frac{1}{2} \dot{q}_j^2 + \frac{1}{2} \omega_j^2 q_j^2 \right) = \sum_j \left(\frac{p_j^2}{2} + \frac{\omega_j^2}{2} q_j^2 \right)$$

$$E(v_1, v_2, \cdots, v_j \cdots) = \sum_j \hbar \omega_j \left(v_j + \frac{1}{2} \right)$$

$$\psi(v_1, v_2, \cdots, v_j, \cdots) = \prod_j \psi_{v_j}(q_j) = \prod_j \sqrt[4]{\frac{\omega_j}{\pi \hbar}} \frac{1}{\sqrt{2^{v_j} v_j!}} e^{-\frac{\omega_j}{2\hbar} q_j^2} H_{v_j}\left(\sqrt{\frac{\omega_j}{\hbar}} q_j \right)$$

Determination of force constants

As previously discussed, it is in general not possible to determine the force constants (F matrix) from the experimentally determined fundamental frequencies, because the secular equation yields only $3N - 6$ equations in $\frac{1}{2}(3N - 6)(3N - 6 + 1)$ unknowns. This is unfortunate, for both frequencies and force constants must be known before the L matrix can be found, a visual geometric picture of the normal vibrations obtained, and some understanding of the vibrations gained. Fortunately, means do exist by which force constants may be obtained. The most important methods of approach are (*a*) use of frequencies from isotopically substituted molecules, (*b*) use of symmetry operations to factor the secular equation, and (*c*) simplifying approximations about the nature of the force field.

If one or more atoms in a molecule are substituted by isotopic atoms, presumably the electronic structure of the molecule, hence all force constants, is altered only to negligible degree. However, because the atomic masses differ, the G matrix elements (inverse kinetic energy) and normal vibration frequencies will be different. This will be most pronounced when hydrogen is replaced by deuterium, for in this case the factor of mass change is largest. If a molecule with several isotopic changes is available, enough of the elements of the G matrix will be altered so that several *additional* equations in the $\frac{1}{2}(3N - 6)(3N - 6 + 1)$ force constants will result from the experimental frequencies of this isotopic molecule. If a multiplicity of isotopically substituted molecules is available, then in some cases it is actually possible to have many more independent equations than unknowns, and the force constants may not only be determined but checked independently. Unfortunately, isotopic substitutions other than D for H often do not help much in practice, for only little change is made in the G-matrix elements by replacing, say, mass 16 (of O^{16}) by 18, and this is likely to result in only a small change in the normal coordinates. But substitution of D for H, where applicable, represents a powerful method of obtaining accurate force constants (within the framework of a general quadratic potential function) so that accurate normal coordinates may be obtained.

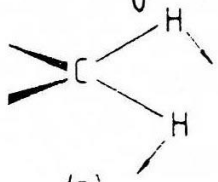
‹Typical vibrational frequencies›

Table 6.3 Typical bond-stretching and angle-bending group vibration wavenumbers $\tilde{\nu}$.

Bond-stretching		Bond-stretching	
Group	$\tilde{\nu}$/cm^{-1}	Group	$\tilde{\nu}$/cm^{-1}
$\equiv C-H$	3300	$-O-H$	3600†
$=C<^{H}$	3020	$>N-H$	3350
except $O=C<^{H}$	2800	$\geq P=O$	1295
$\geq C-H$	2960	$>S=O$	1310
$-C\equiv C-$	2050	Angle-bending	
$>C=C<$	1650	$\equiv C-H$	700
$\geq C-C\leq$	900	$=C<^{H}_{H}$	1100
$\geq Si-Si\leq$	430	$-C<^{H}_{H}-H$	1000
$>C=O$	1700	$>C<^{H}_{H}$	1450
$-C\equiv N$	2100		
$\geq C-F$	1100	$C\equiv C-C$	300
$\geq C-Cl$	650		
$\geq C-Br$	560		
$\geq Cl-I$	500		

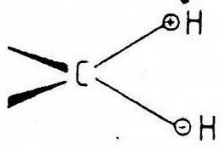
< Other terms of vibrational modes >

Rocking



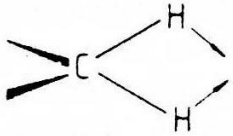
(a)

Twisting



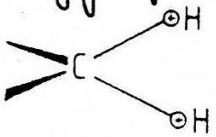
(b)

Scisso ring



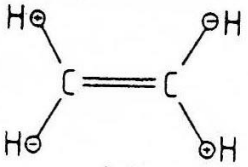
(c)

Wagging



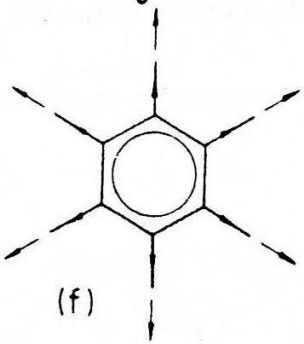
(d)

torsion



(e)

Ring breathing



(f)

(g)

inversion or umbrella motion

6.2.2. Vibrational Selection Rules

< Specific Selection Rule >

$$\mu = \mu_e + \sum_i \left(\frac{\partial \mu}{\partial q_i}\right)_e q_i + \text{higher orders}$$

For $|v_1', v_2', \cdots, v_k' \cdots\rangle \leftarrow |v_1, v_2, \cdots, v_k, \cdots\rangle$ transition,

$$\mu_{if} = \underbrace{\mu_e \langle v_1', v_2', \cdots, v_k', \cdots | v_1, v_2, \cdots, v_k, \cdots\rangle}_{\text{zero or no transition}} + \sum_i \left(\frac{\partial \mu}{\partial q_i}\right)_e \langle v_1', v_i', \cdots, v_k' | q_i | v_1, v_2, \cdots v_k$$

$$= \sum_i \left(\frac{\partial \mu}{\partial q_i}\right)_e \langle v_i' | q_i | v_i \rangle \prod_{k \neq i} \prod_{k' \neq i} \langle v_k | v_{k'} \rangle$$

$$= \sum_i \left(\frac{\partial \mu}{\partial q_i}\right)_e \left(-i\sqrt{\frac{\hbar}{2\omega}}\right) \left\{ \sqrt{v_i+1}\, \langle v_i' | v_i+1 \rangle - \sqrt{v_i}\, \langle v_i' | v_i - 1 \rangle \right\} \prod_{k \neq i} \prod_{k' \neq i} \delta_{v_k v_{k'}}$$

In order for $\prod_{k=i} \prod_{k' \neq i} \delta_{v_k v_{k'}}$ to be non zero, $v_k = v_{k'}$ for $k \neq$

Then

$\langle v_i' | v_i \rangle$ term becomes no transition term.

In order for $\langle v_i' | v_i + 1 \rangle$ to be non zero, $v_i' = v_i \pm 1$

This implies only one mode of vibration can be excited by $\Delta v = \pm 1$ while other modes are not excited.

No combination bands occur.

<Gross selection Rule - Symmetry Consideration>

For absorption (or emission) transition between $|0\rangle \leftrightarrow |1\rangle$

$$\mu_{if} = \langle 1|\mu|0\rangle = e\langle 1|r|0\rangle$$

where $|0\rangle \propto \exp\left(-\frac{\omega_i}{2\hbar} q_i^2\right)$, totally symmetric

$|1\rangle \propto q_i \exp\left(-\frac{\omega_i}{2\hbar} q_i^2\right)$, spans as q_i

$\therefore$ If q_i spans as $r = (x, y, z)$, $\mu_{if} \neq 0$

$\therefore$ IR active

For Raman scattering transition between $|0\rangle \Leftrightarrow |1\rangle$

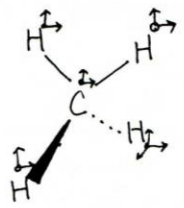
$(\mu_{ind})_{if} \propto \langle 1|\alpha|0\rangle$

α spans as $(x^2, y^2, z^2, xy, yz, zx)$

$\therefore$ If g_i spans as $(x^2, y^2, z^2, xy, yz, zx)$, $(\mu_{ind})_{if} \neq 0$

$\therefore$ Raman Active

예제 CH_4 in T_d



T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	$h=24$
Γ	15	0	-1	-1	3	

$\Gamma = A_1 + E + T_1 + 3T_2$

(x, y, z) spans as $T_2 \Rightarrow$ Translational

(R_x, R_y, R_z) " $T_1 \Rightarrow$ Rotational

$\therefore \Gamma_{vib} = A_1 + E + 2T_2$

(xy, yz, zx) spans as T_2

$\Gamma(x^2, y^2, z^2) = a A_1 + b E$

$\therefore$ A_1 is Raman active, IR inactive.

E is Raman active, IR inative

T_2 is IR active, Raman active.

Exclusion Rule,

In centrosymmetric molecule, Raman active mode is IR inactive, IR active mode is Raman inactive.

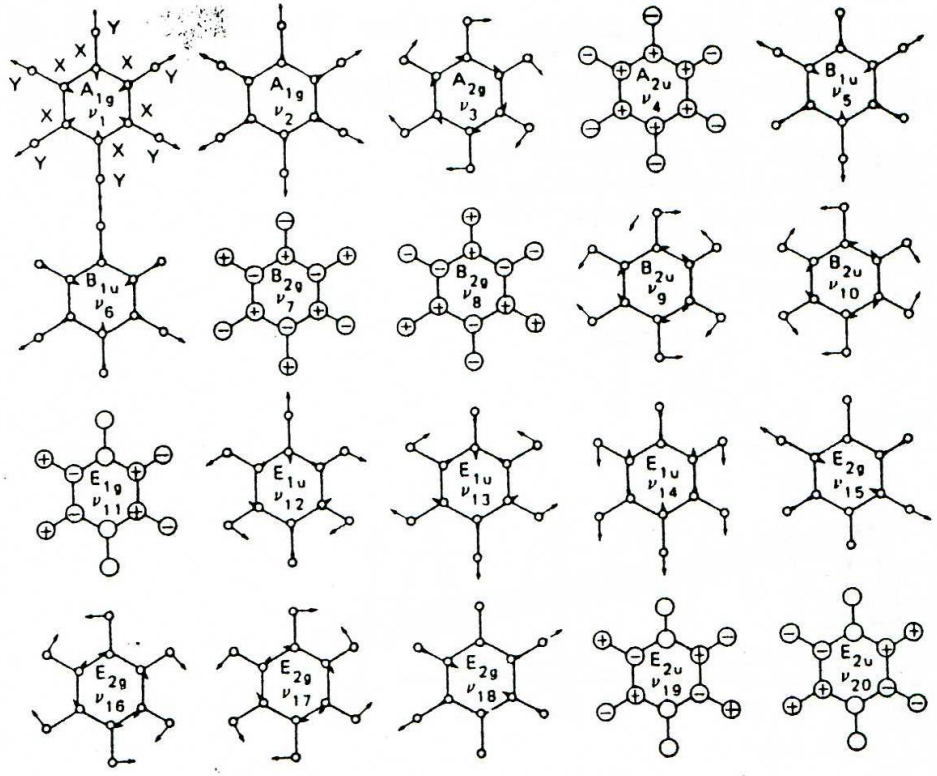
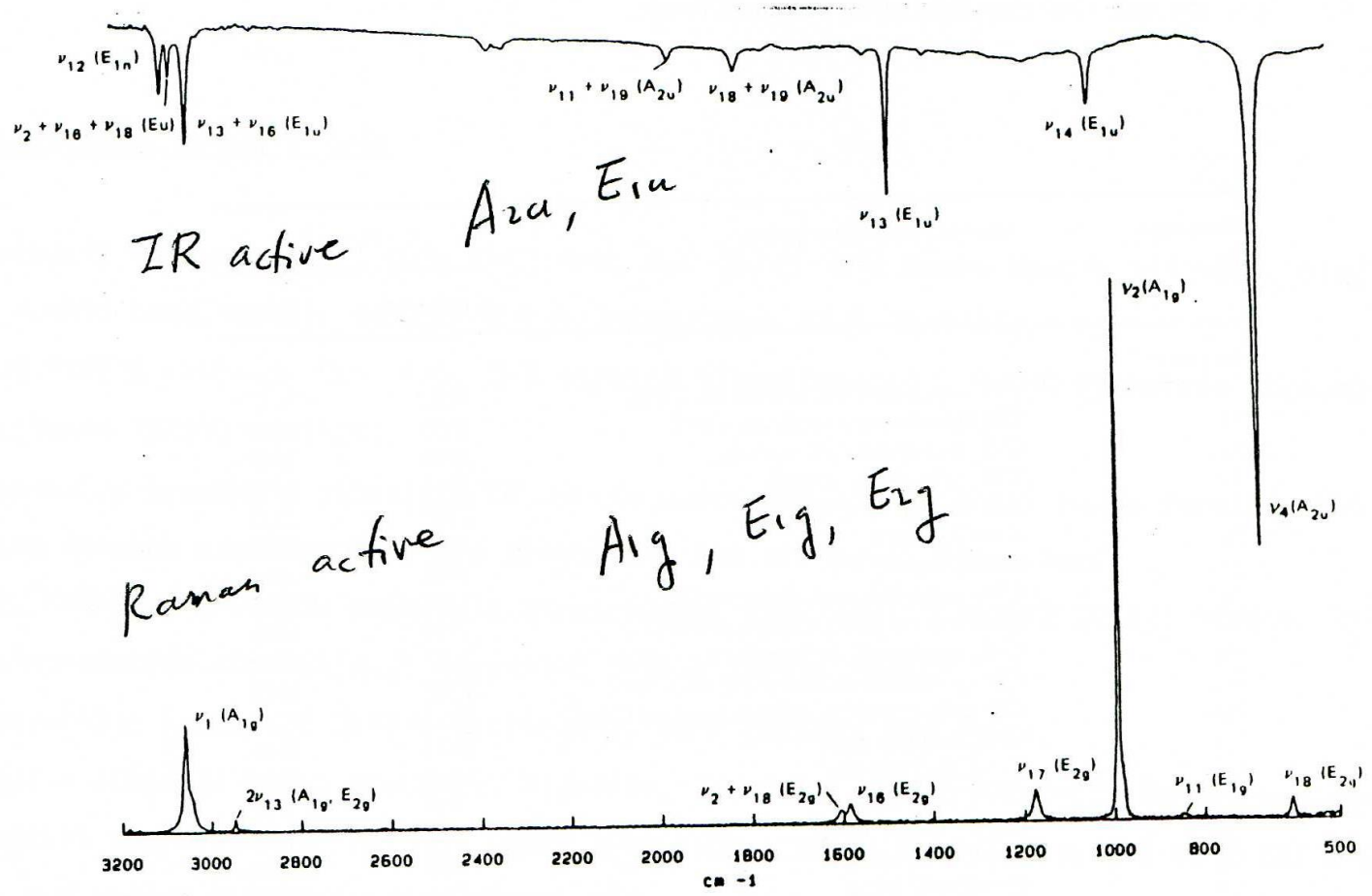


Fig. 2.20 — The fundamental vibrational modes of benzene.

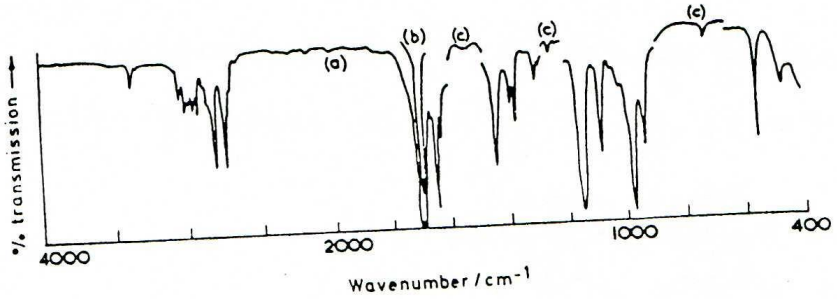


IR active A_{2u}, E_{1u}

Raman active A_{1g}, E_{1g}, E_{2g}

153-

< IR absorption vs Raman >



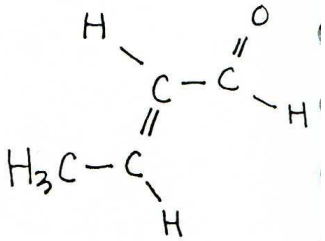


Figure 6.15 The infrared vibrational spectrum of crotonaldehyde. The parts marked (a), (b), and (c) refer to a 10 per cent (by volume) solution in CCl_4, a 1 per cent solution in CCl_4, and a thin liquid film respectively. (Reproduced, with permission, from Bowles, A. J., George, W. O., and Maddams, W. F., *J. Chem. Soc.* (*B*), 810, 1969.)

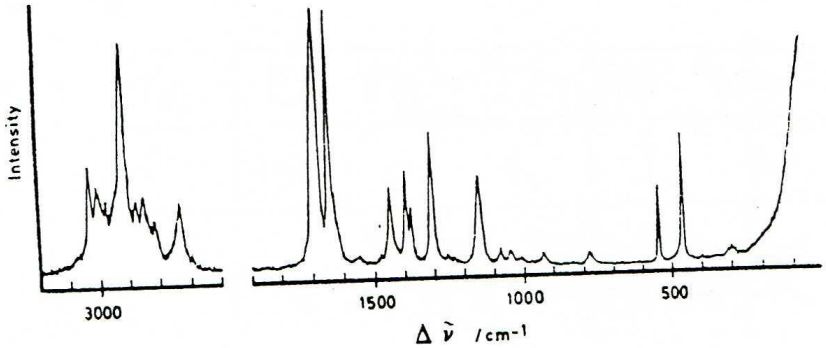


Figure 6.17 The laser Raman vibrational spectrum of liquid crotonaldehyde. (Reproduced, with permission, from Durig, J. R., Brown, S. C., Kalasinsky, V. F., and George, W. O., *Spectrochim. Acta*, **32A**, 807, 1976. Copyright (1976) Pergamon Press.)

Vibration[a]	Approximate description	$\tilde{\nu}$/cm^{-1}	
		Infrared	Raman
In plane			
ν_1	CH antisymmetric stretch on C=C	3042	3032
ν_2	CH symmetric stretch on C=C	3002	3006
ν_3	CH_3 antisymmetric stretch	2944	2949
ν_4	CH_3 symmetric stretch	2916	2918
ν_5	CH stretch on CHO	2727	2732
ν_6	C=O stretch	1693	1682
ν_7	C=C stretch	1641	1641
ν_8	CH_3 antisymmetric deformation	1444	1445
ν_9	CH rock (in-plane bend) on CHO	1389	1393
ν_{10}	CH_3 symmetric deformation	1375	1380
ν_{11}	CH symmetric deformation on C=C	1305	1306
ν_{12}	CH antisymmetric deformation on C=C	1253	1252
ν_{13}	CH_3 in-plane rock	1075	1080
ν_{14}	C—CHO stretch	1042	1046
ν_{15}	C—CH_3 stretch	931	931
ν_{16}	CH_3—C=C bend	542	545
ν_{17}	C=C—C bend	459	464
ν_{18}	C—C=O bend	216	230
Out-of-plane			
ν_{19}	CH_3 antisymmetric stretch	2982	2976
ν_{20}	CH_3 antisymmetric deformation	1444	1445
ν_{21}	CH_3 rock	1146	1149
ν_{22}	CH antisymmetric deformation on C=C	966	—
ν_{23}	CH symmetric deformation on C=C	—	780
ν_{24}	CH wag (out-of-plane bend) on CHO	727	—
ν_{25}	CH_3 bend	297	300
ν_{26}	CH_3 torsion	173	—
ν_{27}	CHO torsion	121	—

Raman이 IR 보다 나은 점

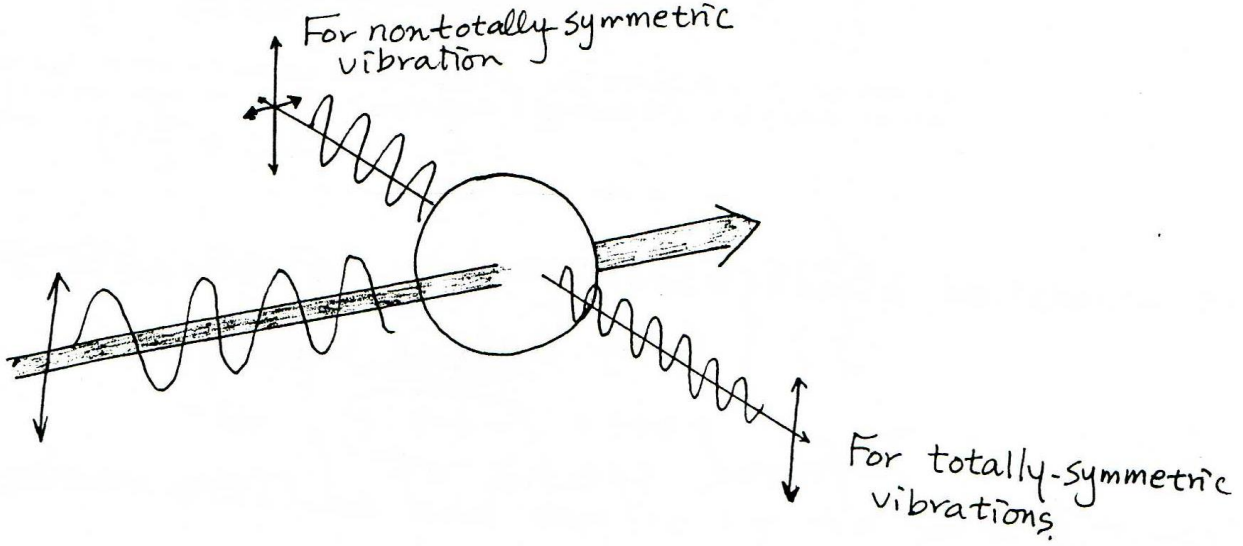
① low frequency vibrations (40 -400 cm^{-1})을 쉽게 얻는다.

② glass가 visible에서 완전히 투명하기 때문에 capillary tube나 bottle등의 sample의 Raman을 쉽게 얻는다.

③ 물의 Raman band는 매우 약하므로 용매로서 사용할 수 있다.

④ 고체 물질의 경우 mull이나 disk로서 만들 필요가 없다.

⑤ Depolarization 실험에 의해 vibration의 symmetry을 알 수 있다.



Raman Spectrum의 일반적인 경향

① Symmetric한 Vibration(예 : S-S, C=C, N=N, C≡C 등)은 강한 Raman Band를 나타낸다. single bond에서 double bond, triple bond로 갈수록 intensity는 더욱 강해진다.

② IR에서 약하게 나타나는 C≡N, C=S, S-H stretch vibration이나 C-O-O-C symmetric stretch vibration이 강하게 나타난다.

③ The symmetry breathing vibration of cyclic compounds in which all bonds forming the cyclic skeleton stretch simutaneously are frequently the strongest Raman band.

④ X=Y=Z, C=N=C, O=C=O$^-$등의 symmetric stretching은 Raman에서 강하지만 IR에서 약하다. 반면 이들의 anti-symmetric stretching은 Raman에서 약하고 IR에서 강하다.

⑤ C-C stretch는 Raman에서 강하게 나타나지만, 매우 coupled 되어 있다.

⑥ alcohol과 alkane의 Raman spectra는 비슷하다. 그 이유는 (1) C-O와 C-C의 force constant와 bond strength가 비슷하기 때문 (2) OH 그룹의 질량이 CH_3 그룹의 질량이 비슷하기 때문 (3) O-H band는 C-H나 N-H band에 비해 Raman에서 약하기 때문.

6.2.3. Vibration-Rotation Spectroscopy

$$S(v_1, v_2, \cdots, v_i, \cdots ; J, K) = \underbrace{F_{v_1, \cdots v_i \cdots}(J, K)}_{\text{rotation term}} + \underbrace{G(v_1, v_2, \cdots ; v_i \cdots)}_{\text{vibration term}}$$

$$G(v_1, v_2, \cdots, v_i, \cdots) = \sum_{i=1}^{3N-6} \tilde{\nu}_i \left(v_i + \tfrac{1}{2}\right)$$

$$= \sum_{j=1}^{f} \tilde{\nu}_j \left(v_j + \tfrac{1}{2}\right) d_j$$

$$= \sum_{i=1}^{f} \hat{\nu}_i \left(v_i + \frac{d_i}{2}\right)$$

d_i ; degeneracy of vibration i

f ; # of unique vibrational modes

6.2.3.1 Infrared spectra of linear molecules

For $D_{\infty h}$ molecules (O=C=O, HC≡CH, etc).

(x, y) spans as Π_u, z spans as Σ_u^+

Therefore, transitions of the type $\Sigma_u^+ \leftrightarrow \Sigma_g^+$ and $\Pi_u \leftrightarrow \Sigma_g^+$ are active.

For $C_{\infty v}$ molecules (HCN, OCS, etc)

(x, y) spans as Π, z spans as Σ^+

Therefore, transitions of the type $\Sigma^+ \leftrightarrow \Sigma^+$ and $\Pi \leftrightarrow \Sigma^+$ are active.

1) For all types of Σ vibrational levels,

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2$$

and $\Delta J = \pm 1$ for rotational transition

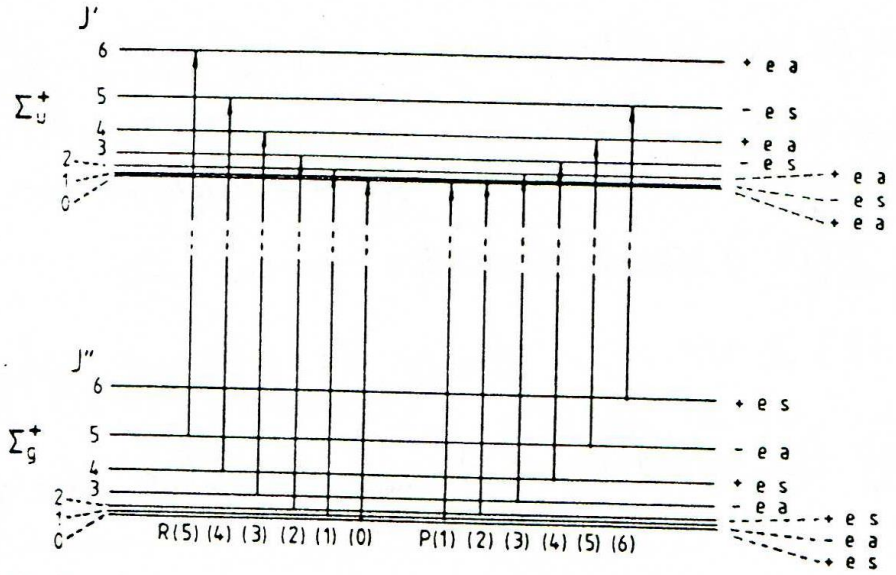


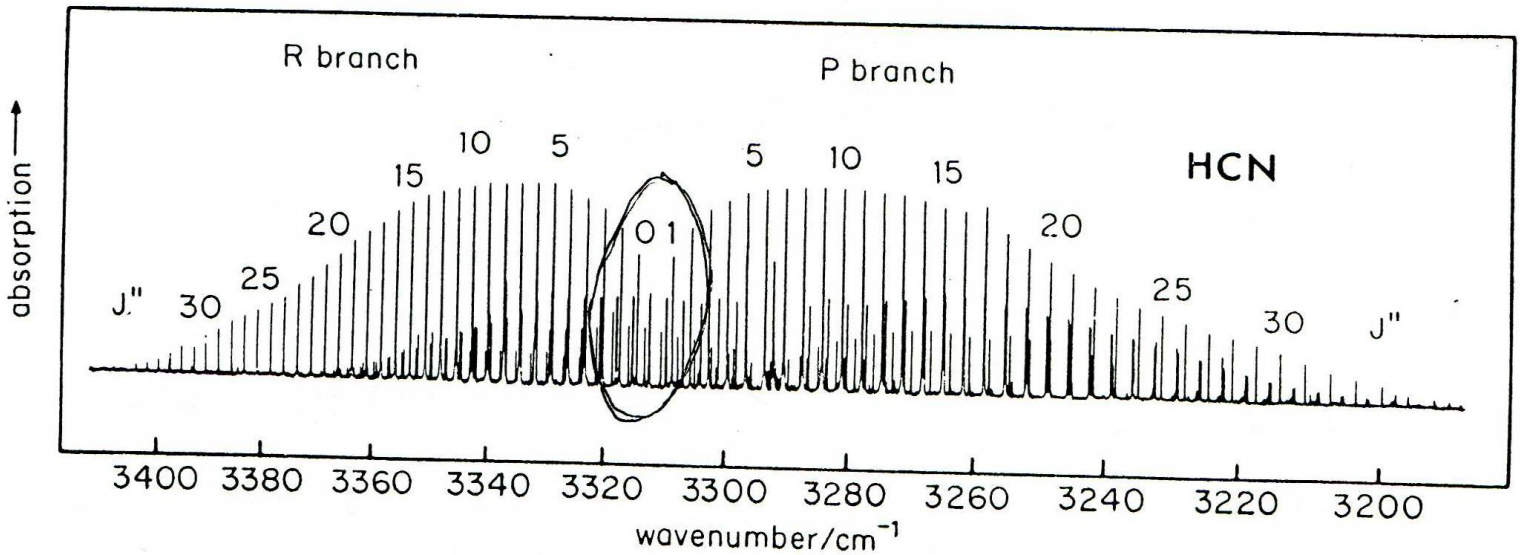
Figure 6.22 Rotational transitions accompanying a $\Sigma_u^+ - \Sigma_g^+$ infrared vibrational transition in a $D_{\infty h}$ linear polyatomic molecule. For $C_{\infty v}$ the g and u subscripts and s and a labels should be dropped.

For Dosh molecules, { nuclear spin statistics } should be taken account
{ parity condition }

$- \leftrightarrow -$, $+ \leftrightarrow -$, $+ \leftrightarrow +$

But these are superfluous and can be ignored for Σ-Σ transition type

For Cosh molecules, the above condition is absent.



igure 6.23 The 3_0^1, $\Sigma^+ - \Sigma^+$ infrared band of HCN and two weaker, overlapping bands. (Reproduced, with permission, from Cole, A. R. H., *Tables f Wavenumbers for the Calibration of Infrared Spectrometers*, 2nd ed., p. 28. Copyright (1977) Pergamon Press, Oxford.)

Notice two vibrational-rotation bands (3_0^1 (3292 cm^{-1}), 2_0^2 (3290 cm^{-1})) are overlapped.

2) For $^1\Pi_u$ ($D_{\infty h}$ molecule) and $^1\Pi$ ($C_{\infty v}$ molecule),

l type coupling (vibrational angular momentum about the internuclear axis) and Coriolis force $\Rightarrow$

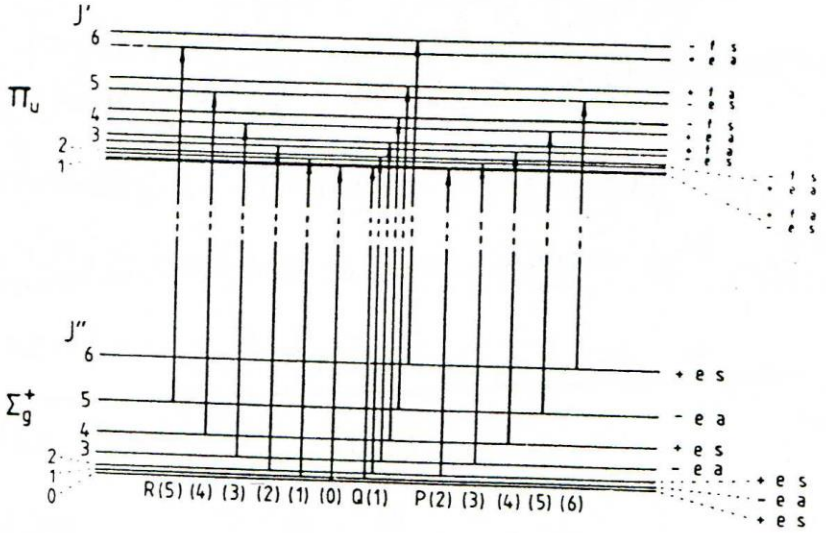
① $J \geq |l| \geq v$ $\therefore$ $J=0$ is absent when $v=1$

② Each of the rotational level is split, the splitting increasing with J.

③ $F_v(J) = B_v J(J+1) - B_v \pm \frac{q_i}{2} J(J+1)$ for $v=1$

(q_i is a parameter which determines the magnitude of the splitting.)

④ $\Delta J = 0, \pm 1$, a Central Q-branch ($\Delta J=0$) appears!



6.24 Rotational transitions accompanying a $\Pi_u - \Sigma_g^+$ infrared vibrational transition in linear polyatomic molecule. For $C_{\infty v}$ the g and u subscripts and s and a labels should be dropped.

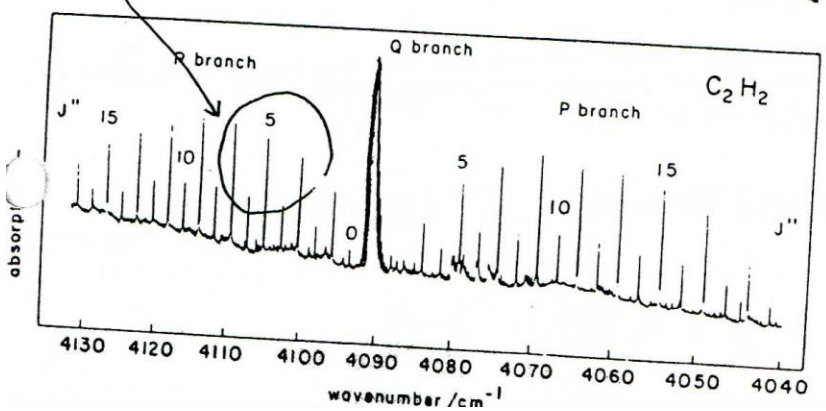
⑤ For Dosh molecule, $+ \longleftrightarrow -$, $+ \nleftrightarrow +$, $- \nleftrightarrow -$

Intensity alternations $J_{even} : J_{odd} = 1:3$ or

$e \longleftrightarrow f$, $e \nleftrightarrow e$, $f \nleftrightarrow f$ for $\Delta J = 0$

$e \nleftrightarrow f$, $e \longleftrightarrow e$, $f \longleftrightarrow f$ for $\Delta J = \pm 1$

and Nuclear spin statistics



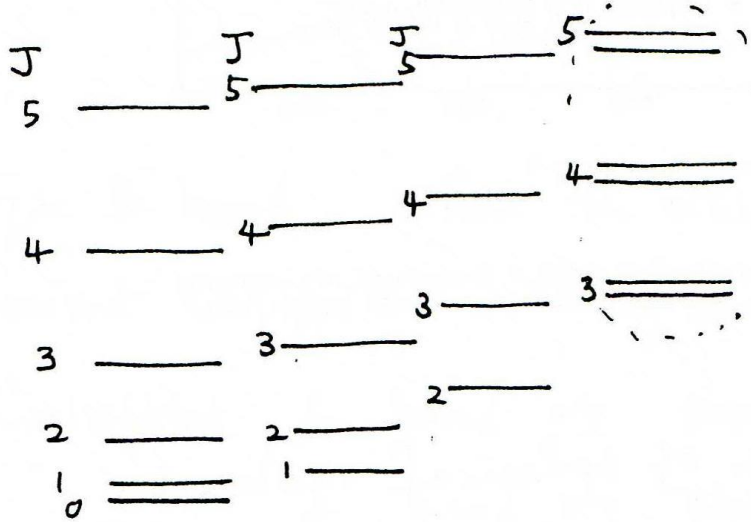
The $1_0^1 5_0^1$, $\Pi_u - \Sigma_g^+$ infrared band of acetylene.

6.2.3.2. Infrared spectra of symmetric rotors.

For C_{3v} (NH_3, CH_3Cl, etc) molecules, (x, y) spans as E
z spans as A_1, Therefore $A_1 \leftrightarrow A_1$, $E \leftrightarrow A_1$ vibrations are active.

$A_1 \leftrightarrow A_1$ → parallel band
$E \leftrightarrow A_1$ → perpendicular band

1) For parallel $A_1 \leftrightarrow A_1$ band, when $K=0$, $\Delta K=0$ and $\Delta J=\pm 1$
when $K\neq 0$, $\Delta K=0$ and $\Delta J=0,\pm 1$
Q-branch appears



→ slight splitting of all the levels with $K = 3n$, where $n=1,2,3,\ldots$

Parallel band

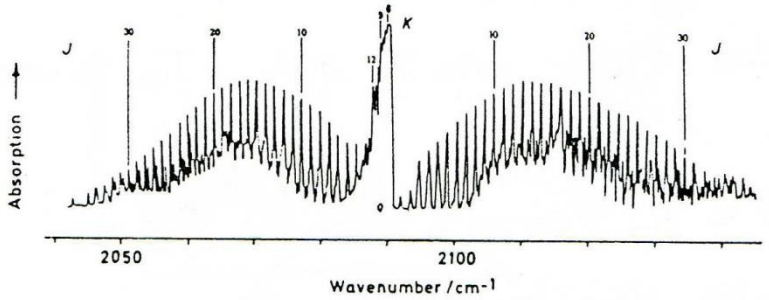
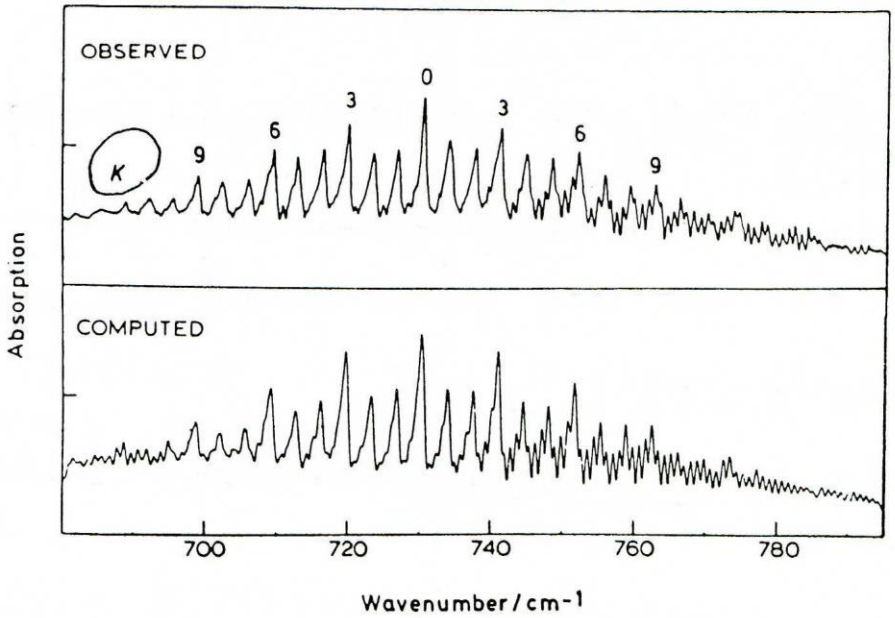


Figure 6.26 The 1_0^1, A_1–A_1 infrared parallel band of C^2H_3F. (Reproduced, with permission, from Jones, E. W., Popplewell, R. J., and Thompson, H. W., *Proc. R. Soc.*, **A290**, 490, 1966.)

3) For perpendicular $E \leftrightarrow A_1$ band.

Perpendicular band



Spread-out Q-banch !!

Figure 6.27 The 6_0^1, E–A_1 infrared perpendicular band of SiH_3F. (Reproduced, with permission, from Robiette, A. G., Cartwright, G. J., Hoy, A. R., and Mills, I. M., *Mol. Phys.*, **20**, 541, 1971.)

6.2.3.3. Infrared spectra of spherical molecules.

For Td molecules (CH_4, etc), only $T_2 \leftrightarrow A_1$ vibration is active.

For Oh molecules (SF_6, etc), only $T_{1u} \leftrightarrow A_{1g}$ vibration is active.

$$F_v(J) = B_v J(J+1), \quad \Delta J = 0, \pm 1$$

The band looks similar to $\Pi - \Sigma$ type band in a linear molecule.

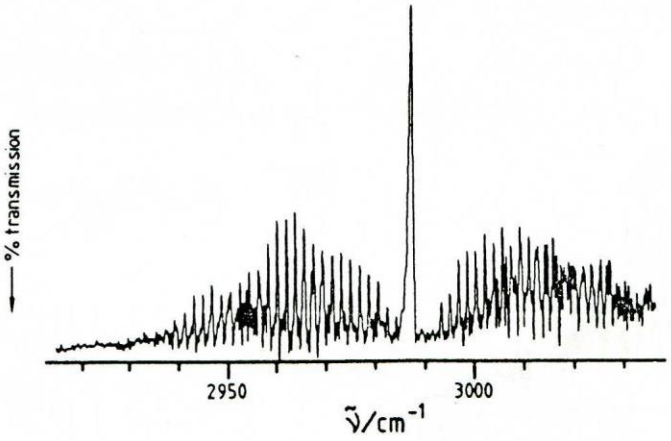
6.2.3.4. Infrared spectra of asymmetric rotors

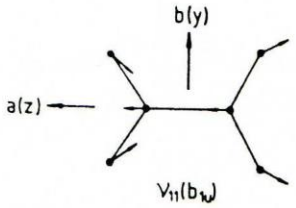
1) Type A band : When the vibrational transition dipole moment $\langle v' | \mu | v \rangle$ is along the a-axis of the molecule.

Correlates $\parallel$ band of prolate symmetric rotor.
or $\perp$ band of oblate symmetric rotor.

$\vec{M} \parallel \hat{a}$ $\Delta K_a = 0$ $\Delta K = \pm 1$ $\Delta J = 0, \pm 1$ ($J \neq 0$ for $K = 0$)

ex) The 11_0^1 band of ethylene





A-type

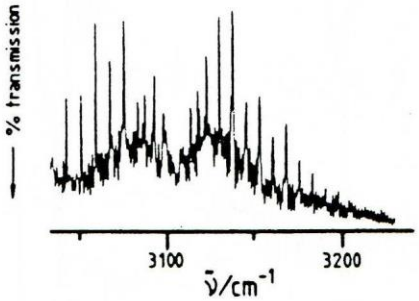
2) Type B band: When the vibrational transition dipole moment $\langle v'|\mu|v\rangle$ is along the b-axis of the molecule.

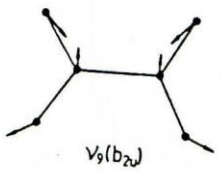
Correlates $\perp$ band of prolate symmetric rotor.

or $\perp$ band of oblate symmetric rotor.

$\vec{M} \parallel \hat{b}$ $\Delta K_p = \pm 1$, $\Delta K_o = \pm 1$, $\Delta J = 0, \pm 1$

ex). The 9_0^1 band of ethylene.





B-type

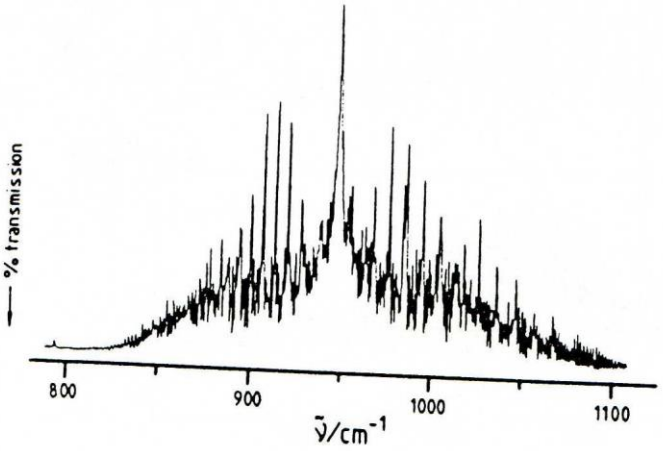
3) Type C band: When the vibrational transition dipole moment $\langle v'|\mu|v\rangle$ is along the c-axis of the molecule.

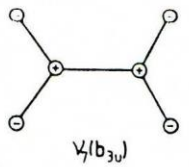
Correlates $\perp$ band of prolate symmetric rotor.

or $\parallel$ band of oblate symmetric rotor.

$\vec{M} \parallel \vec{c}$ $\quad \Delta K_p = \pm 1, \ \Delta K_o = 0, \ \Delta J = 0, \pm 1$ (0 for $K_o \neq 0$)

Ex) The 7_0^1 band of ethylene





C-type

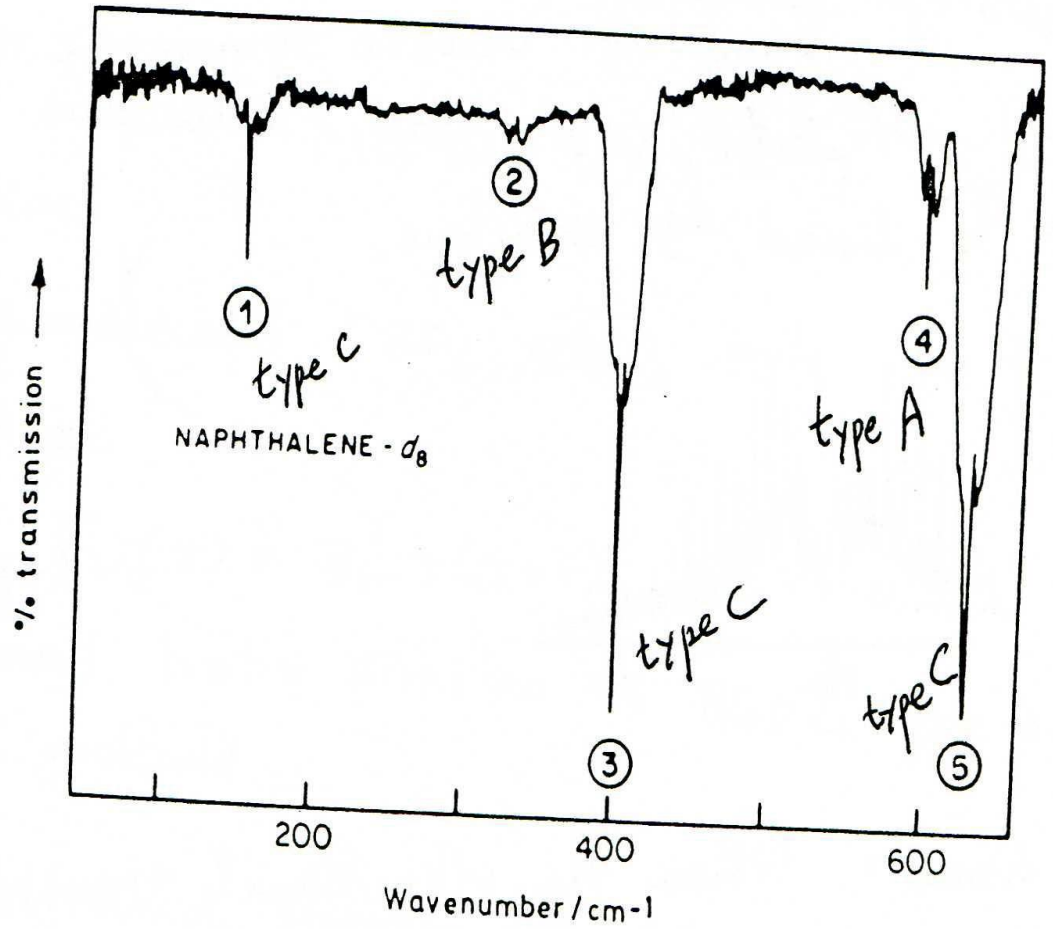
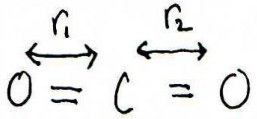


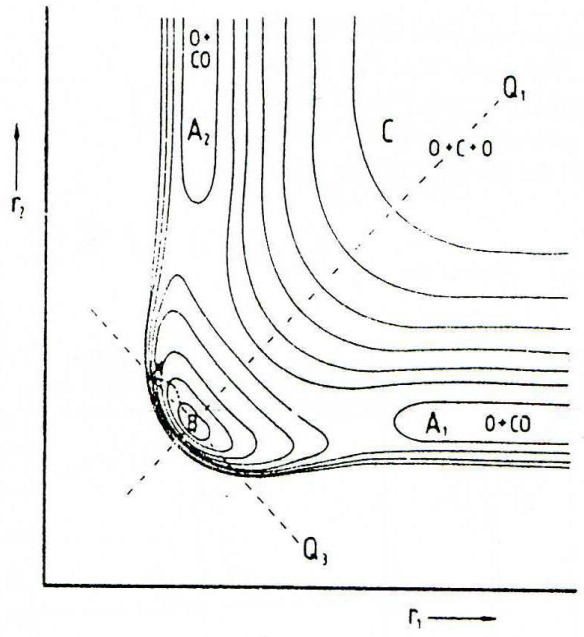
Figure 6.32 Part of the far-infrared spectrum of perdeuteronaphthalene. Band 4 is type *A*, band 2 type *B*, and bands 1, 3, and 5 type *C*. (Reproduced, with permission, from Duckett, J. A., Smithson, T. L., and Wieser, H., *J. Mol. Struct.*, **44**, 97, 1978.)

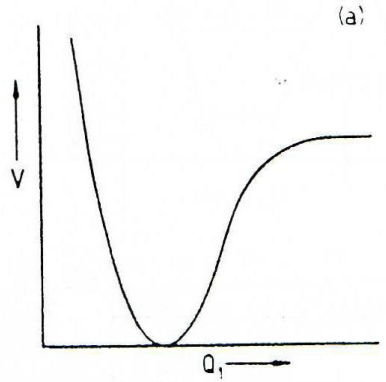
6.2.4 Anharmonicity

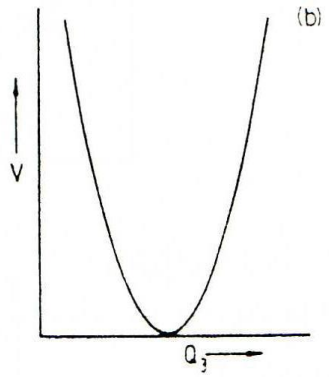
6.2.4.1 Potential Energy Surfaces

CO_2의 경우









6.2.4.2. Vibrational Term Values

$$G(v_1, \cdots, v_j, \cdots) = \sum_i G(v_i) = \sum_i^{3N-6} \tilde{\nu}_i \left(v_i + \frac{1}{2}\right) + \sum_{i \le j}^{3N-6} \chi_{ij} \left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right)$$

$$\text{or} \quad = \sum_i^f \tilde{\nu}_i \left(v_i + \frac{d_i}{2}\right) + \sum_{i \le j}^f \chi_{ij} \left(v_i + \frac{d_i}{2}\right)\left(v_j + \frac{d_j}{2}\right) + \sum_{i \le j} g_{ij} l_i l_j$$

f: # of unique vibrational modes.

d_i ; degree of freedom of vibration i

$g_{ij} l_i l_j$; an additional anharmonic term

6.2.4.3 Anharmonicity 의 결과

① Hot Band가 나타남.

② Overtone peak, combination peak 가 나타남

③ Fermi Resonance 가 나타남

④ Intensity of Vibrational Bands

6.2.4.4 Vibrational Potential functions with more than one minimum

a) Inversion vibrations

the inversion vibration ν_2 of NH_3

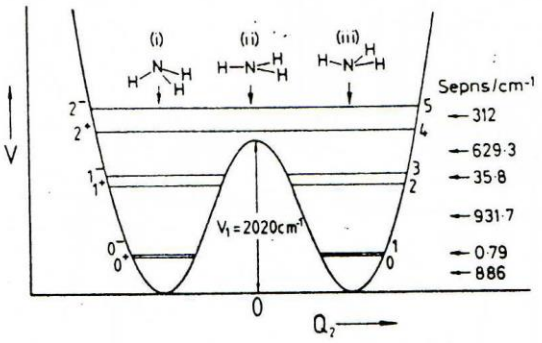


Figure 5.64 Potential energy curve for the inversion vibration ν_2 of the NH_3 molecule. The equilibrium configuration, (i) or (iii), is pyramidal and, classically, it requires a potential energy V_1, the height of the barrier, to go to the planar configuration (ii)

an energy barrier of height b at Q=0

$$V(Q) = \frac{1}{2}aQ^2 + b\exp(-cQ^2)$$ suggested by Swalen & Ibe

an ordinary harmonic oscillator potential

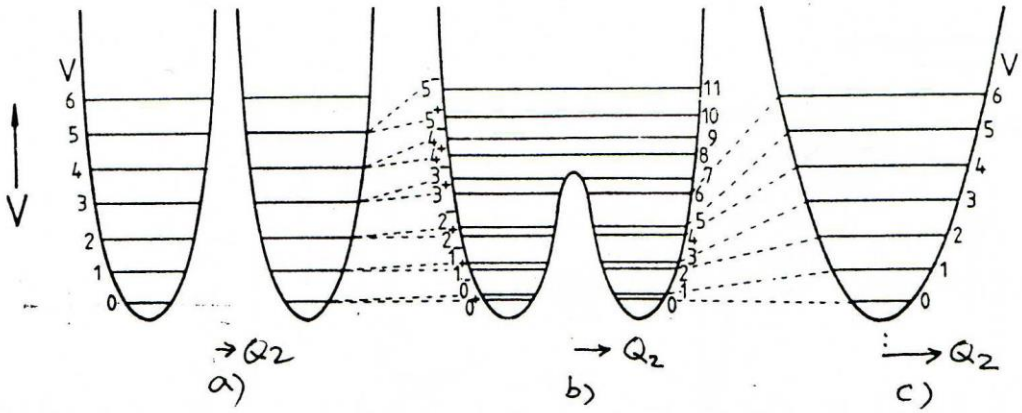


Figure 5.65 Potential energy curves and energy levels for the inversion vibration ν_2 when the barrier to planarity is (a) infinite, (b) moderately low and (c) zero

< Tunneling Interaction >

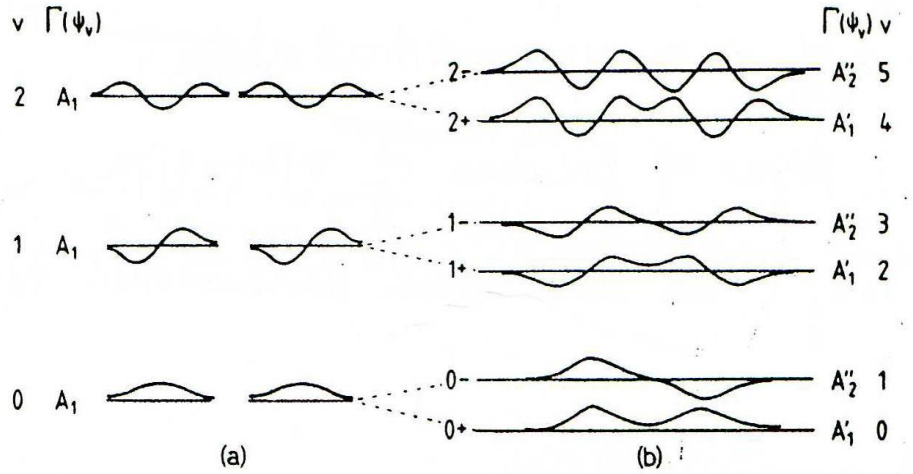


Figure 5.66 The forms of the vibrational wave functions for an inversion vibration when the barrier to planarity is (a) infinite, and (b) moderately low

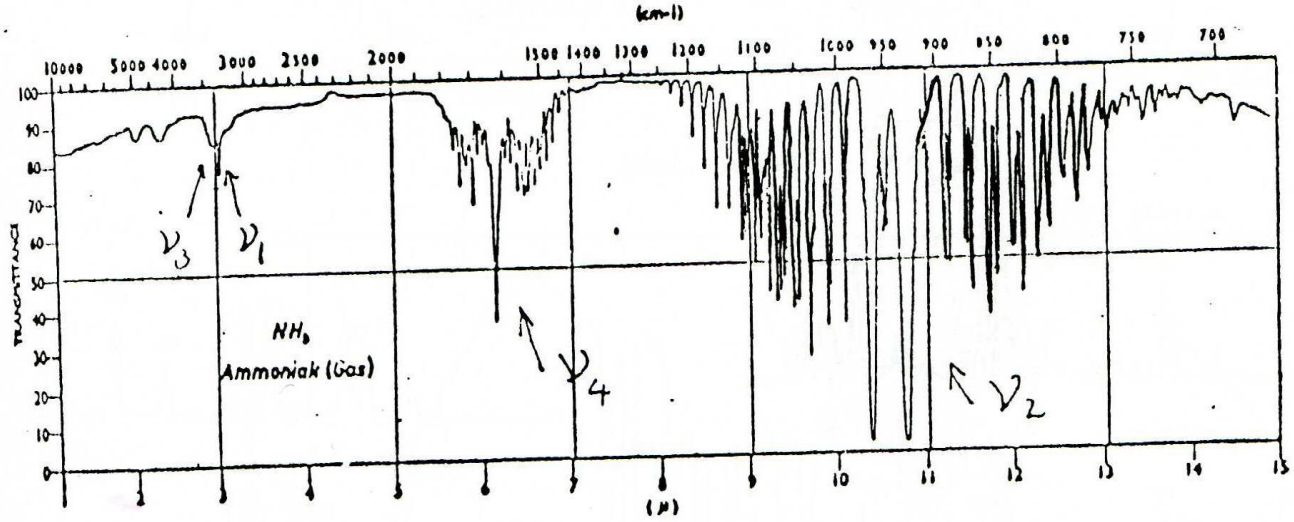
$$\psi_v^+ = \psi_v(Q_2) + \psi_v(-Q_2)$$

$$\psi_v^- = \psi_v(Q_2) - \psi_v(-Q_2)$$

The time for inversion is $\tau = (2\Delta\nu)^{-1}$, where $\Delta\nu$ is the frequency separation of the vibrational level

$\Delta\nu$ for $0^+, 0^-$ separation	$^{14}NH_3$ 23.786 GHz	$^{15}NH_3$ 22.705 GHz	$^{14}ND_3$ 1.600 GHz
τ "	21 ps	22 ps	310 ps

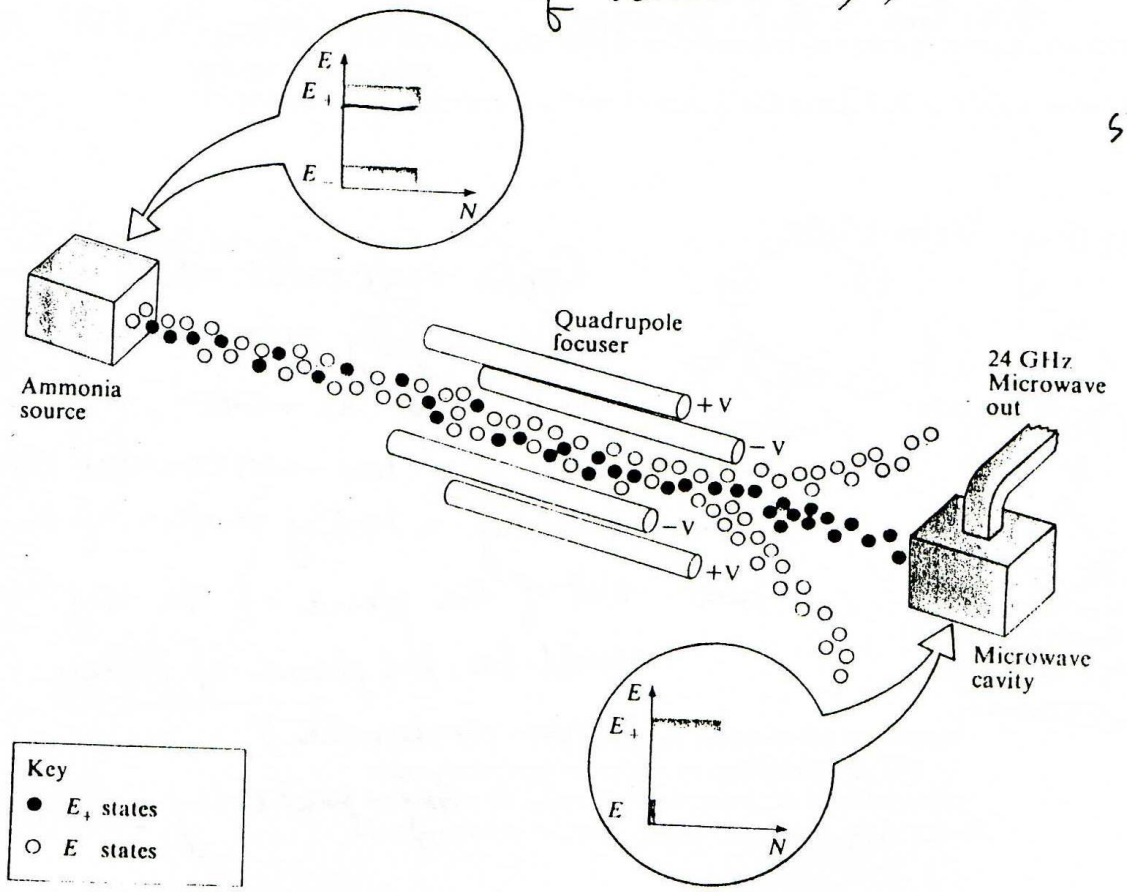
For symmetry reason, only $+ \leftrightarrow +$, $- \leftrightarrow -$ transitions are allowed.

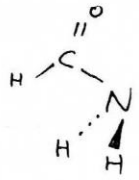


Infrared Spectrum of NH_3

< Invention of Maser (Microwave Amplication of Stimulated Emission of Radiation) >

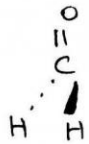
see Gordon, Zeiger and Townes, Phys. Rev. 95 2822 (1954).

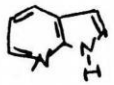


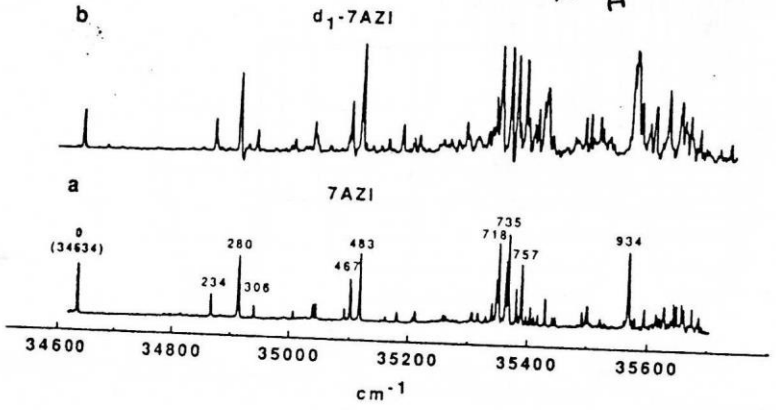
Other examples,  (foramide, barrier ~ 370 cm^{-1})

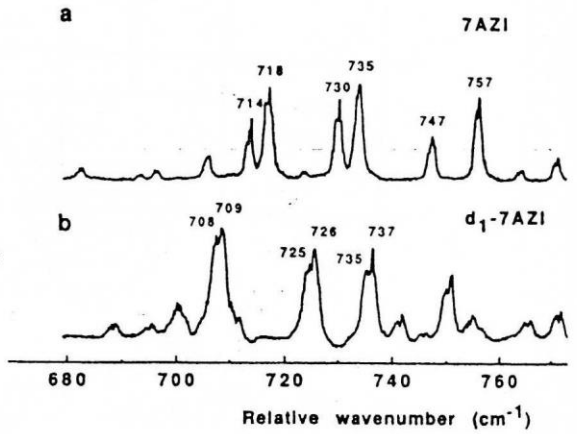
(aniline, barrier ~450cm^{-1})

(planar in the ground excited state)

 (pyramidal in S_1 (barrier ~ 350cm^{-1}) and in T_1 (barrier ~ 783cm^{-1})

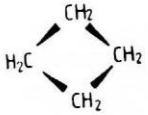
 7-azaindole

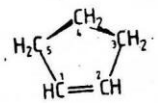


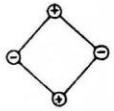


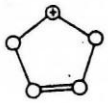
S.K. Kim & E.R. Bernstein, J. Phys. Chem, 94, 3531 (1990).

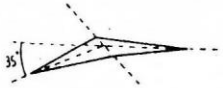
b) Ring-Puckering Vibrations











Cyclic molecules which are at least partially saturated and contain such groups as $-CH_2-$, $-O-$ or $-S-$ have low-wavenumber vibrations involving a bending motion of the group out of the plane of the ring (or what would be the plane if it were a planar molecule)

"a ring-puckering vibration"

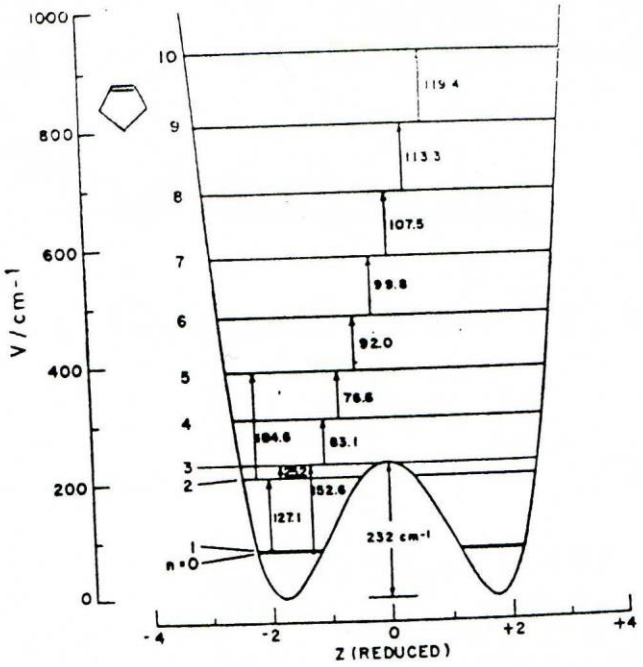


Figure 5.68 Puckering potential function for cyclopentene. Potential energy V is in cm^{-1} and is plotted against a reduced coordinate z which is proportional to the normal coordinate but takes into account the reduced mass for the puckering motion
(Reproduced, with permission, from Laane, J. and Lord, R. C. (1967). *J. chem. Phys.*, **47**, 4941)

a: positive
a potential resembling the harmonic oscillator potential

$$V = aQ^4 + bQ^2$$

barrier height: $b^2/4a$

b: negative
an upside-down parabola at $Q = 0$

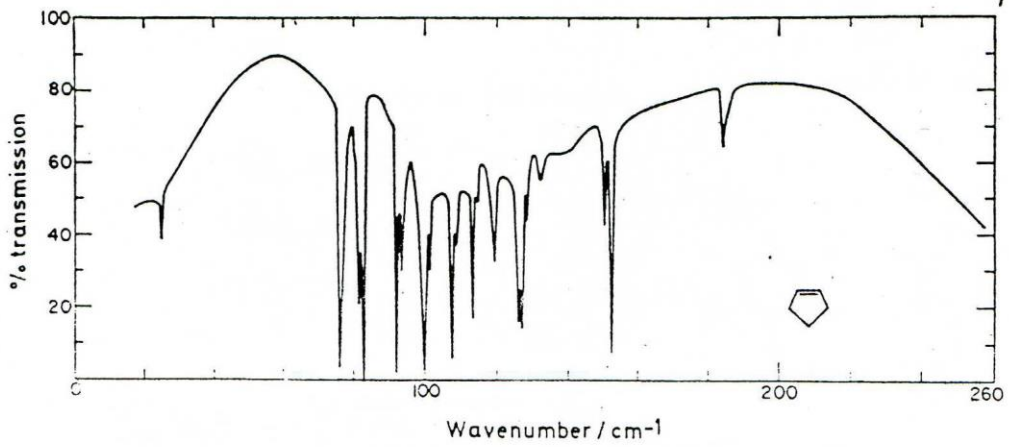
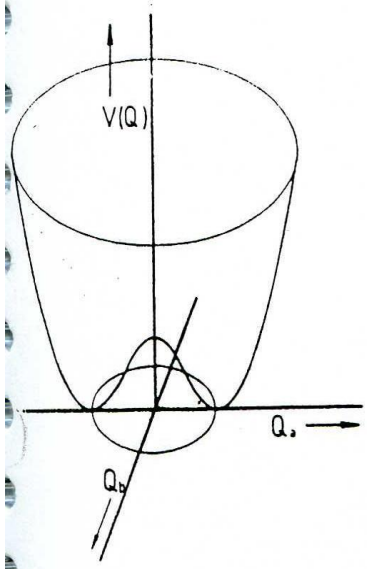
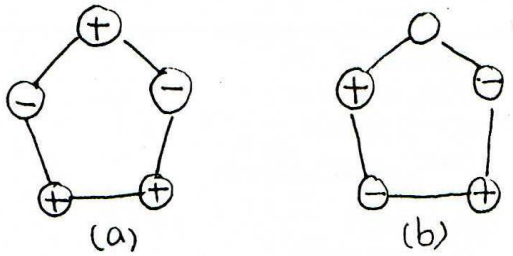


Figure 5.69 Far infrared spectrum of cyclopentene in which percentage transmission is plotted against wavenumber
(Reproduced, with permission, from Laane, J. and Lord, R. C. (1967). *J. chem. Phys.*, **47**, 4941)

Cyclopentane





(degenerate)

Figure 5.71 The potential function for the degenerate puckering vibration in cyclopentane. The barrier to pseudorotation around the circular valley is assumed to be zero but not quite zero.

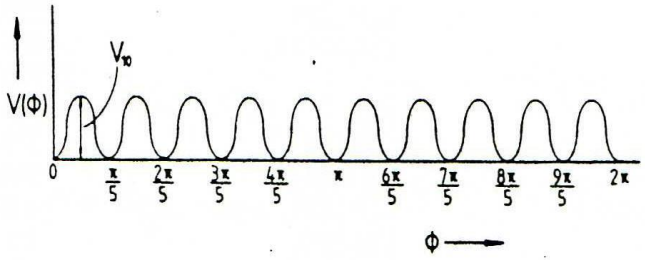
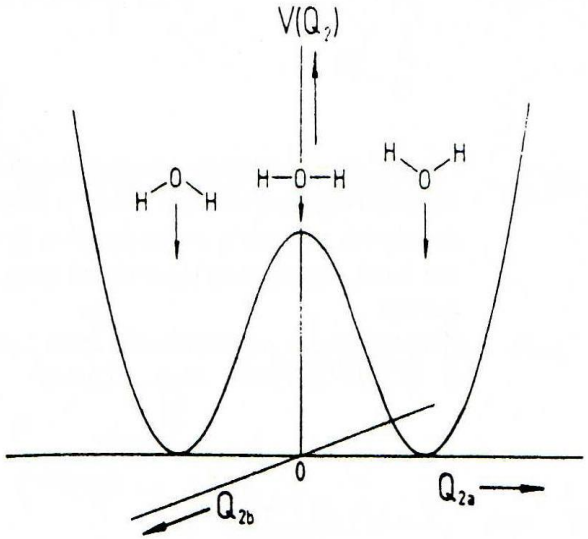


Figure 5.72 The ten maxima and minima in the potential function for cyclopentane representing motion around the circular valley in *Figure 5.71* and assuming a small barrier to pseudorotation

c) Bending vibrations in nonlinear triatomic molecules

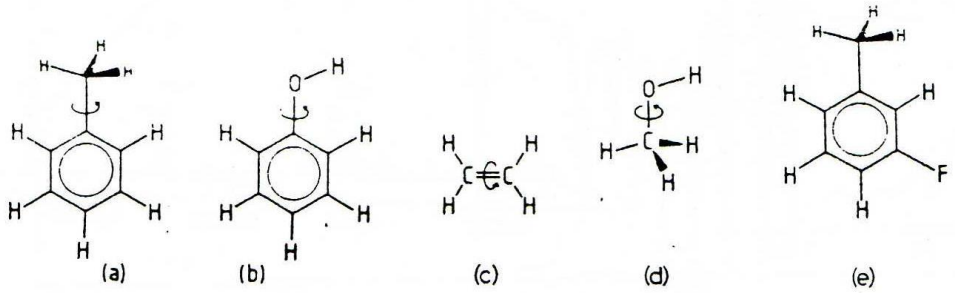


$$V(Q_2) = \frac{1}{2} a Q^2 + b e^{-c Q_2^2}$$

No humps in the circular valley, between Q_{2a} and Q_{2b}.

$\Rightarrow$ No splitting of levels due to tunneling.

d) Torsional vibrations.



$$V(\phi) = \frac{1}{2} \sum_n V_n (1 - \cos n\phi)$$

Table 5.20 Barrier heights (V) in some non-rigid molecules

Molecule	V/cm^{-1}	
NH_3	2020	(inversion)
$C_6H_5NH_2$	450	(NH_2 inversion)
C_6H_5OH	1207	(C—O torsion)
$CH_2{=}CH_2$	14000	(calc.) (C=C torsion)
	22750	(expt.)
H_2O	10400	(bending)
CH_3OH	375	(C—O torsion)
CH_3CH_3	960	(C—C torsion)
$C_6H_5CH_3$	4.9	(C—CH_3 torsion)
CH_3NO_2	2.1	(C—N torsion)
$(CH_3)_3CNO_2$	71	(C—N torsion)
$(CHO)_2$	1771	(C—C torsion) s-*trans* → s-*cis*
$CH_2{=}CH{-}CH{=}CH_2$	2660	(C—C torsion) s-*trans* → s-*cis*