Basics-5

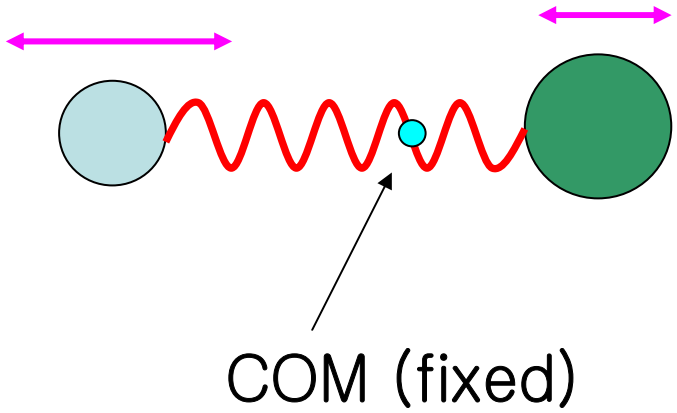
Vibrational Spectroscopy

Pure Vibrations

* Diatomics

"Harmonic oscillator approximation"

"one stretch mode"



$$\hat{H} = \hat{T}_n + V = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

$$\therefore\ E_v = h\nu\left(v + \frac{1}{2}\right),\quad v = 0, 1, 2, \ldots$$

$$\leftarrow \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\psi_v = \left(\frac{1}{2^v v!\pi^{1/2}}\right)^{1/2} H_v(y)\exp\left(-\frac{y^2}{2}\right),$$

$$\leftarrow\ H_v(y): \textit{Hermite Polynomial}$$

$$y = \left(\frac{4\pi^2\nu\mu}{h}\right)^{1/2}(x - x_e)$$

– Hermite polynomial $H_v(y)$

$$H_0(y)=1,\ H_1(y)=2y,\ H_2(y)=4y^2-2,\ldots$$

$$\rightarrow\quad H_v''(y)-2yH_v'(y)+2vH_v(y)=0$$

$$\rightarrow\quad \int_{-\infty}^{+\infty} H_{v'}(y)H_{v''}(y)e^{-y^2}dy=\begin{cases}0 & \text{if } v'\neq v'' \\ \pi^{1/2}2^v v! & \text{if } v'=v''\end{cases}$$

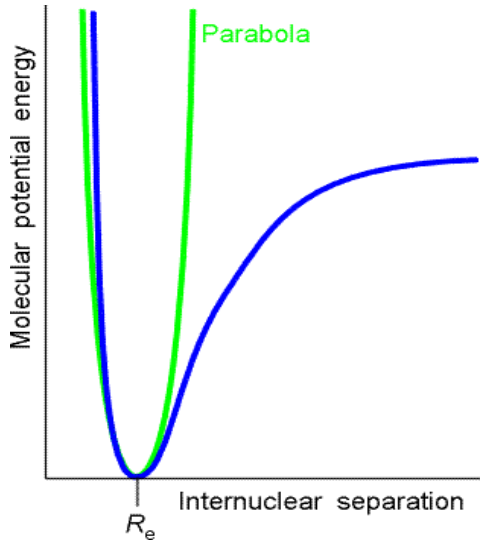
$$\textbf{(recursion relation)}\ 2yH_v(y)=H_{v+1}(y)+2vH_{v-1}(y)$$

– Anharmonicity in V(x)

$$V(x)=V(0)+\left.\frac{dV}{dx}\right|_{x=0}x+\frac{1}{2!}\left.\frac{d^2V}{dx^2}\right|_{x=0}x^2+\frac{1}{3!}\left.\frac{d^3V}{dx^3}\right|_{x=0}x^3+\ldots$$

$= k$

"anharmonicity (mechanical)"



Example: "Morse potential"

$$V(x)=D_e\left[1-e^{-ax}\right]^2,\ a=\sqrt{\frac{k}{2hcD_e}}$$

- Anharmonic expression of energy and wavefunction:

$$E_v = h\nu(v+\frac{1}{2}) - h\nu(v+\frac{1}{2})^2 x_e + h\nu(v+\frac{1}{2})^3 y_e + \ldots$$

$$\psi_{AHO} = \sum_i c_i \psi_{i,HO}$$

$$(Morse\ \ potential)\ E_v = h\nu(v+\frac{1}{2}) - h\nu(v+\frac{1}{2})^2 x_e \leftarrow x_e = \frac{a^2\hbar}{2\mu\omega}$$

$$v_{\max} < \frac{2D_e}{h\nu} - \frac{1}{2}, \quad ZPE = \frac{1}{2}h\nu(1-\frac{x_e}{2})$$

- Vibrational selection rule: "transition dipole moment"

$$M_{v'v} = \langle v' | \mu | v \rangle$$

anharmonicity (electrical)

$$\leftarrow \mu = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=0} x + \left.\frac{1}{2!}\frac{d^2\mu}{dx^2}\right|_{x=0} x^2 + \ldots$$

$$M_{v'v} = \mu_0 \langle v' | v \rangle + \left.\frac{d\mu}{dx}\right|_{x=0} \langle v' | x | v \rangle + \left.\frac{1}{2!}\frac{d^2\mu}{dx^2}\right|_{x=0} \langle v' | x^2 | v \rangle + \ldots$$

$$\leftarrow x|v\rangle = c_1 |v+1\rangle + c_2 |v-1\rangle$$

$$\therefore\ fundamental\ transition: \langle v' | x | v \rangle \neq 0 \leftrightarrow \Delta v = \pm 1$$

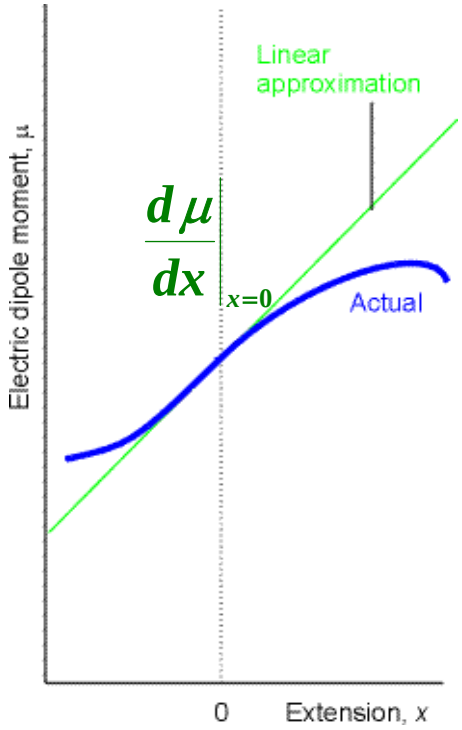
$$overtone\ transition: \langle v' | x^n | v \rangle \neq 0\ for\ n = 2,3,\ldots \leftrightarrow \Delta v = \pm 2, \pm 3, \ldots$$

– Vibrational intensity:

$$I_{fundamental} \propto |M_{10}|^2 N_0 \propto \left(\frac{d\mu}{dx}\bigg|_{x=0} \right)^2 N_0$$

$$I_{overtone} \propto |M_{n0}|^2 N_0 \propto \left(\frac{d^n\mu}{dx^n}\bigg|_{x=0} \right)^2 N_0$$

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



* Hot bands: $v_i > 0$, i.e. $v_i = 1, 2, \ldots$

– Vibrational transition energy (in cm^{-1}) :

$$G(v) = \bar{\nu}(v+\frac{1}{2}) - \bar{\nu}(v+\frac{1}{2})^2 x_e + \bar{\nu}(v+\frac{1}{2})^3 y_e + \ldots$$

$$\Delta G_{v+1/2} = G(v+1) - G(v)$$

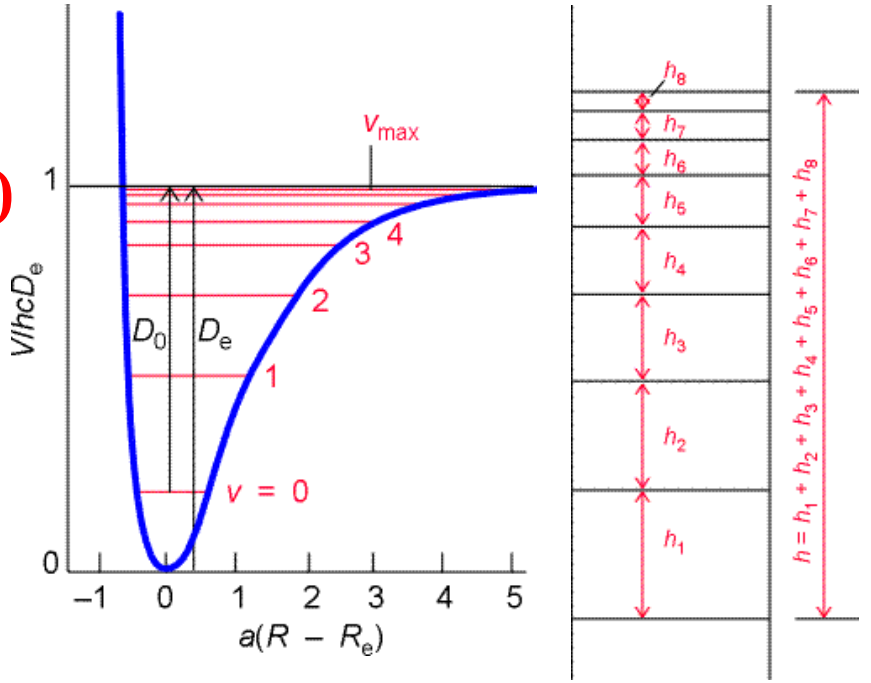
$$= \bar{\nu} - (2v+2)x_e\bar{\nu} + (3v^2+6v+13/4)x_e y_e + \ldots$$

– Dissociation energy D_e, D_0:

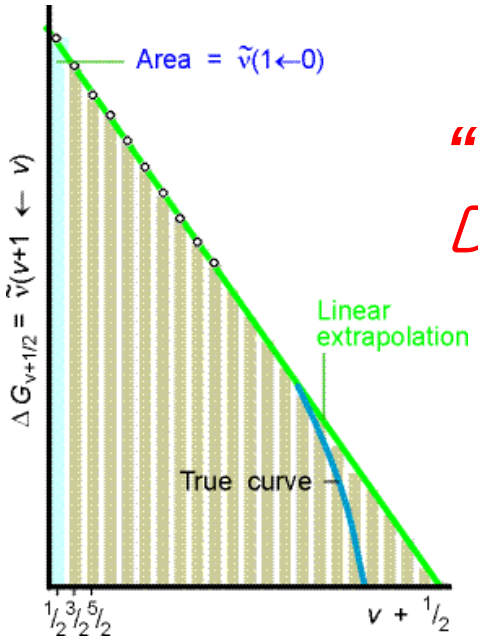
$$D_e \approx \frac{\bar{\nu}}{4x_e} \quad (exact: \ Morse \ \ potential)$$

$$D_0 = \sum_v \Delta G_{v+1/2}$$

* *D_e is unaffected by isotope exchange, but D_0 is affected*



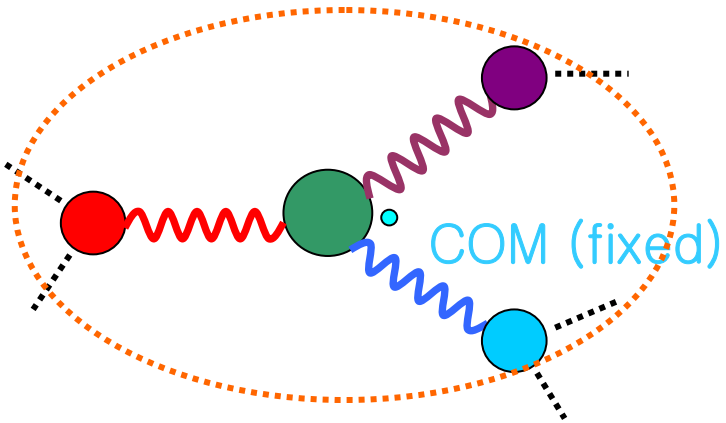
* Birge–Sponser extrapolation:



"assuming $\Delta G_{v+1/2}$ is linear function of v, D_0 is the area under $\Delta G_{v+1/2}$ vs v curve"

→ slightly overestimate the exact value

* Polyatomics



# of vibration modes (N atoms):
3N−6 (nonlinear)
3N−5 (linear)

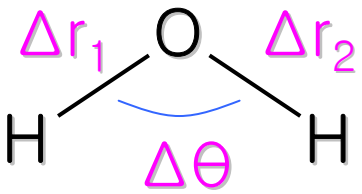
"…many atomic motions are coupled each other
→ need to get decoupled (*3N−6*) vibrational modes…"

easy to assign highly coupled		easy to visualize still coupled		decoupled difficult to visualize
Cartesian coordinate	⟺	Internal coordinate Symmetry coordinate	⟺	Normal coordinate
X_i, i=1,2,…3N (rot, trans: 6)		Δr_i, $\Delta\theta_i$, $\Delta\phi_i$ (3N−6) S_i, i=1,2,…3N−6		Q_i i=1,2,…3N−6

- Internal coordinate:

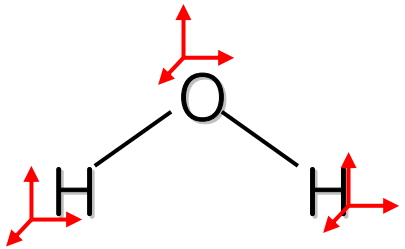
"bond length, bond angle, dihedral angle"

e.g) H_2O : # modes = 3x3−6=3



- Symmetry coordinate:

"... use character table to determine symmetries of vibrational modes, and apply symmetry projection operators to each internal coordinate..."



$2A_1 + B_2$

$$\hat{P}^{A_1} = 1\cdot\hat{O}_E + 1\cdot\hat{O}_{C_2} + 1\cdot\hat{O}_{\sigma_{xz}} + 1\cdot\hat{O}_{\sigma_{yz}}$$

$$\hat{P}^{B_2} = 1\cdot\hat{O}_E - 1\cdot\hat{O}_{C_2} - 1\cdot\hat{O}_{\sigma_{xz}} + 1\cdot\hat{O}_{\sigma_{yz}}$$

$$\hat{P}^{A_1}\Delta r_1 = \Delta r_1 + \Delta r_2 + \Delta r_2 + \Delta r_1 \rightarrow s_1(A_1) = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$$

$$\hat{P}^{A_1}\Delta\theta = \Delta\theta + \Delta\theta + \Delta\theta + \Delta\theta \rightarrow s_2(A_2) = r\Delta\theta$$

$$\hat{P}^{B_2}\Delta r_1 = \Delta r_1 - \Delta r_2 - \Delta r_2 + \Delta r_1 \rightarrow s_3(B_2) = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

– Normal modes (in harmonic approximation):

$$H = \frac{1}{2}\sum_i m_i \dot{x}_i^2 + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0 x_i x_j \quad \textit{in HO approx.}$$

$$\leftarrow k_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j}\right)_0, \quad q_i \equiv m_i^{1/2} x_i \ (\textit{mass-weighted coord.})$$

$$\therefore H = \frac{1}{2}\sum_i \dot{q}_i^2 + \frac{1}{2}\sum_{i,j} \underbrace{k_{ij}\frac{1}{(m_i m_j)^{1/2}}}_{=K_{ij}} q_i q_j = \frac{1}{2}\sum_i \dot{q}_i^2 + \frac{1}{2}\sum_{i,j} K_{ij} q_i q_j$$

$$= (\textit{matrix form})\ \frac{1}{2}\underset{\sim}{\dot{q}}^t \underset{\sim}{\dot{q}} + \frac{1}{2}\underset{\sim}{q}^t \underset{\approx}{K}\underset{\sim}{q}$$

$$\textit{Let } Q_k = \sum_j l_{kj} q_j \ (\textit{linear combi})$$

$$\underset{\sim}{Q} = \underset{\approx}{l}\underset{\sim}{q} \rightarrow \underset{\sim}{q} = \underset{\approx}{l}^t \underset{\sim}{Q} \quad (\underset{\approx}{l}^t = \underset{\approx}{l}^{-1} \ \because \textit{orthogonal matrix})$$

diagonal matrix $\{\lambda_i\}$

$$\therefore H = \frac{1}{2}\underset{\sim}{\dot{Q}}^t \underset{\approx}{l}\underset{\approx}{l}^t \underset{\sim}{\dot{Q}} + \frac{1}{2}\underset{\sim}{Q}^t \underset{\approx}{l}\underset{\approx}{K}\underset{\approx}{l}^t \underset{\sim}{Q} = \frac{1}{2}\underset{\sim}{\dot{Q}}^t \underset{\sim}{\dot{Q}} + \frac{1}{2}\underset{\sim}{Q}^t \underset{\approx}{\Lambda}\underset{\sim}{Q}$$

$$\Rightarrow \frac{1}{2}\sum_i \left(\dot{Q}_i^2 + \lambda_i Q_i^2\right) \qquad (3N-6)\ \lambda_i\text{'s} \neq 0$$

– Normal mode analysis (ab initio program):

Optimize geometries

Determine
force constant k_{ij}, K_{ij}

$$k_{ij} = \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_0 \qquad K_{ij} = k_{ij} \frac{1}{(m_i m_j)^{1/2}}$$

Diagonalize
K matrix to get λ_i's

Eigenvalues

Find normal modes
$\{Q_i\}$, i=1,2, 3N−6

$$\underset{\sim}{Q} = \underset{\approx}{l}\,\underset{\sim}{q}, \quad \underset{\approx}{l}\,\underset{\approx}{K}\,\underset{\approx}{l}^{t} = \underset{\approx}{\Lambda}$$

– Quantum description:

$$\hat{H}\psi = \sum_{i=1}^{3N-6}\left(-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\lambda_i Q_i^2\right)\psi = E\psi$$

$$\therefore \psi = \psi_{v_1}(Q_1)\cdots\psi_{v_{3N-6}}(Q_{3N-6}) = \prod_i \psi_{v_i}(Q_i)$$

$$\leftarrow \quad \psi_{v_i}(Q_i) = N_{v_i} H_{v_i}(y_i) e^{-y_i^2/2},\ y_i = \left(\frac{\omega_i}{\hbar}\right)^{1/2} Q_i$$

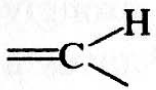
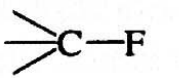
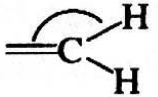
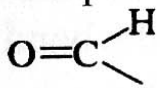
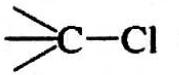
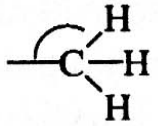
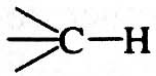
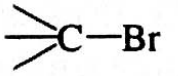
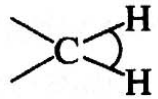
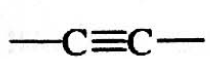
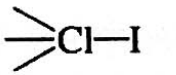
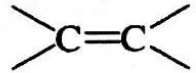
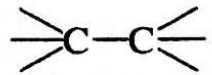
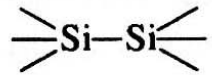
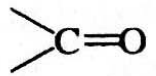
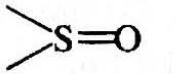
$$E = \sum_{i=1}^{3N-6}\left(v_i + \frac{1}{2}\right)\hbar\omega_i$$

(*Notation*) $|v_1 v_2 \ldots v_{3N-6}\rangle$ *e.g. ground state* $|0_1 0_2 \ldots 0_{3N-6}\rangle$

–Fundamental transition: $\Delta v_i = \pm 1,\ i = 1, 2, \ldots (3N-6)$

transition notation : $1_0^1,\ 2_0^1, \ldots . 3_1^2 \ldots .$

Table 6.3 Typical bond-stretching and angle-bending group vibration wavenumbers ω

Bond-stretching		Bond-stretching		Angle-bending	
Group	ω/cm^{-1}	Group	ω/cm^{-1}	Group	ω/cm^{-1}
	3300		2100		700
	3020		1100		1100
except: 	2800		650		1000
	2960		560		1450
	2050		500		300
	1650		3600[a]		
	900		3350		
	430		1295		
	1700		1310		

[a] May be reduced in a condensed phase by hydrogen bonding.

– Anharmonic transition:

Overtones: $\because \left.\frac{\partial^2 \mu}{\partial Q_i^{\,2}}\right|_0 \neq 0, \left.\frac{\partial^3 \mu}{\partial Q_i^{\,3}}\right|_0 \neq 0, \ldots.$ $\quad 1_0^2, 2_0^3, \ldots.$

$$\Delta v_i = \pm 2(1st), \pm 3(2nd), \ldots\ i = 1, 2, \ldots (3N-6)$$

Combination bands:

$$\because \left.\frac{\partial^2 \mu}{\partial Q_i \partial Q_j}\right|_0 \neq 0$$

$(v_i = v_j = 0) \rightarrow (v_i = 1, v_j = 1), \ldots.$ $\quad i_0^1 j_0^1$

$v_i = 1 \rightarrow v_j = 1, 2, \ldots$ $\quad i_1^0 j_0^1,\ i_1^0 j_0^2$

Fermi resonance: $\left.\frac{\partial^3 V}{\partial Q_i^2 \partial Q_j}\right|_0 \langle 2_i | Q_i^2 | 0_i \rangle \langle 0_j | Q_j | 1_j \rangle \neq 0$

"...if $|2_i 0_j\rangle$ and $|0_i 1_j\rangle$ have similar energies, same symmetries, and anharmonically coupled, two states mix resulting in changes of frequency and intensity..."

Vib-Rotations

* Diatomic molecules

$$E(v,J) = \hbar\omega(v+\frac{1}{2}) - \hbar\omega(v+\frac{1}{2})^2 x_e + \ldots$$

$$+ BJ(J+1) - D\left[J(J+1)\right]^2 + \ldots$$

$$\textit{selection rule}: \Delta v = \pm 1,\ \Delta J = \pm 1(P, R-\textit{branch}),$$

$$\Delta J = 0(Q-\textit{branch},\ \textit{weak})$$

"only for non-zero spin-orbital AM"

$$\nu_{R-branch}(v,J) = \nu_0 + 2B' + (3B' - B'')J + (B' - B'')J^2$$

$$\nu_{P-branch}(v,J) = \nu_0 - (B' + B'')J + (B' - B'')J^2$$

ν_0: band origin; B', B": excited, ground state constants

- Combination differences:

$$\nu_R(J-1) - \nu_P(J+1) = 4B''(J+\frac{1}{2})$$ "ground state constants"

$$\nu_R(J) - \nu_P(J) = 4B'(J+\frac{1}{2})$$ "excited state constants"

HCl: closed shell molecule ($^1\Sigma$ ground state): $\Delta J = \pm 1$

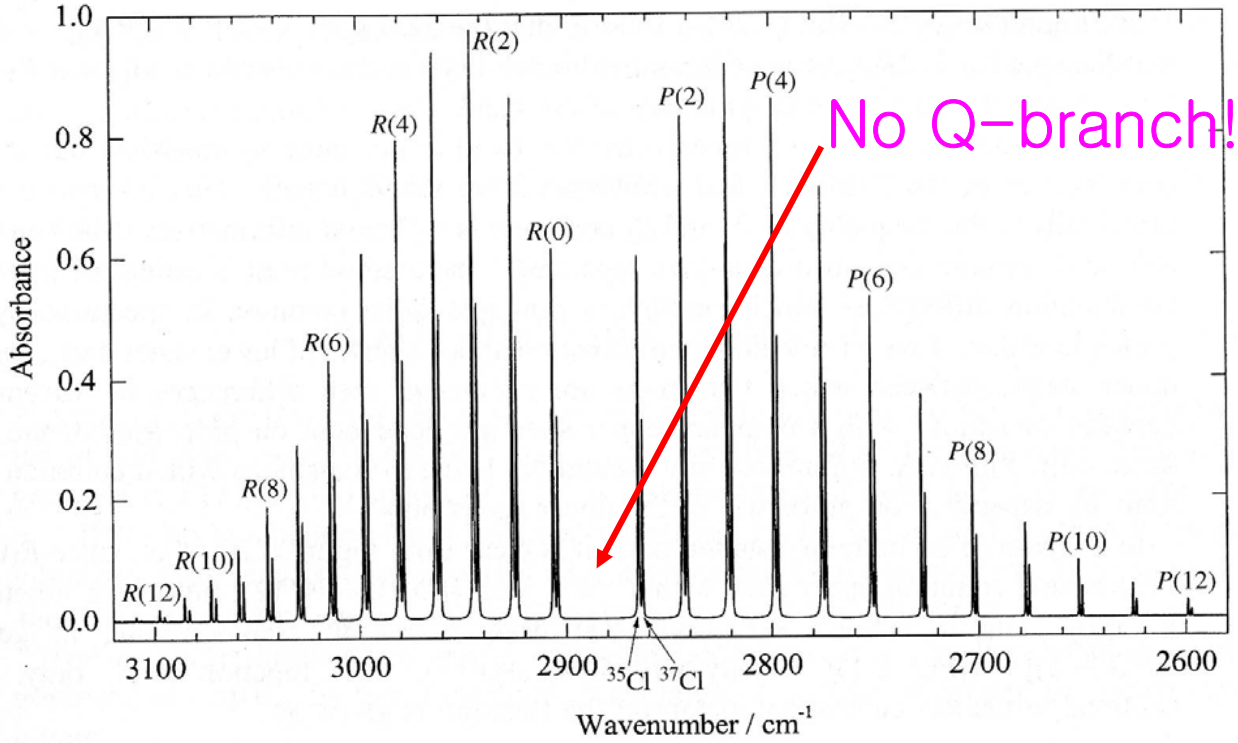


Figure 6.8 The $v = 1$–0 infrared spectrum of $^1H^{35}Cl$ and $^1H^{37}Cl$ showing the P- and R-branch rotational structure

From spectral analysis

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right)$$

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) $= 2885.9775\ \text{cm}^{-1}$	
$B_e = 10.593\,42\ \text{cm}^{-1}$	
$\alpha_e = 0.307\,18\ \text{cm}^{-1}$	

* Linear polyatomic molecules (N atoms)

Total 3N−5 modes: "(N−1) stretches and (N−2) deg bends"

$\Sigma \leftrightarrow \Sigma$ **" *parallel* " *transition* : $\Delta J = \pm 1$ (P, R – *branches*)**

$\Sigma \leftrightarrow \Pi$ **" *perpendicular* " *transition* : $\Delta J = 0, \pm 1$ (P, Q, R – *branches*)**

**** Π – states : l – type doubling – " spectral splittings "***

**** parity (e, f) selection rule – $P, R : e \leftrightarrow e$, $f \leftrightarrow f$; $Q : e \leftrightarrow f$***

**** nuclear spin statistics – " intensity alternations "***

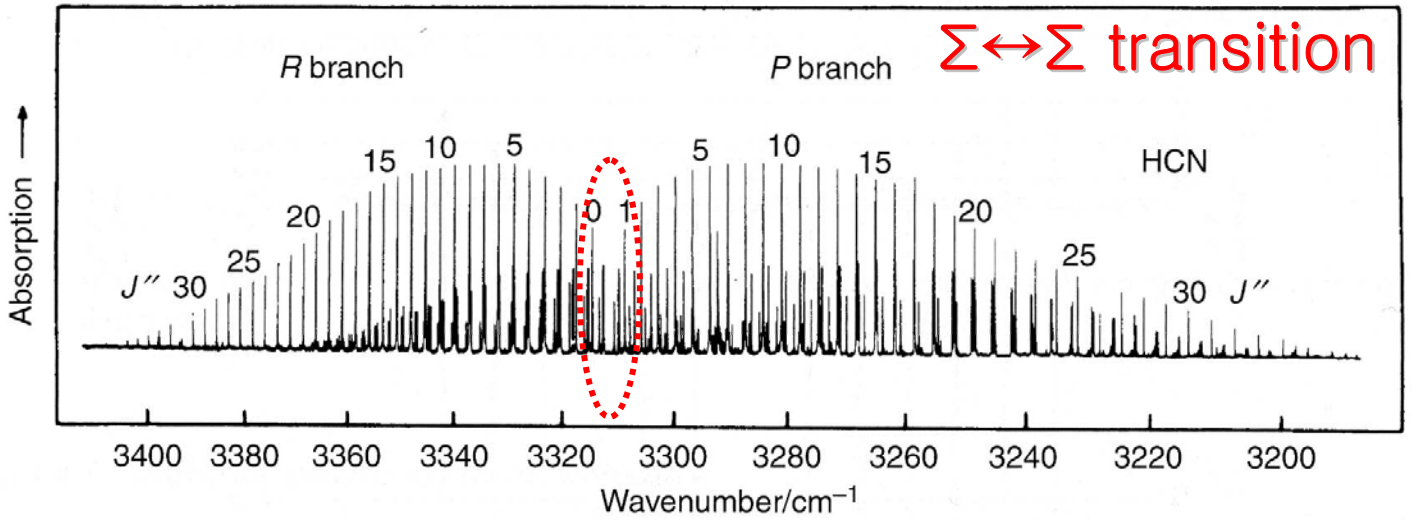


Figure 6.25 The 3_0^1, $\Sigma^+ - \Sigma^+$ infrared band of HCN and two weaker, overlapping bands. (Reproduced, with permission, from Cole, A. R. H., *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*, 2nd edn, p. 28. Copyright 1977 Pergamon Press, Oxford)

$\Sigma \leftrightarrow \Pi$ *transition* : $\Delta J = 0, \pm 1$

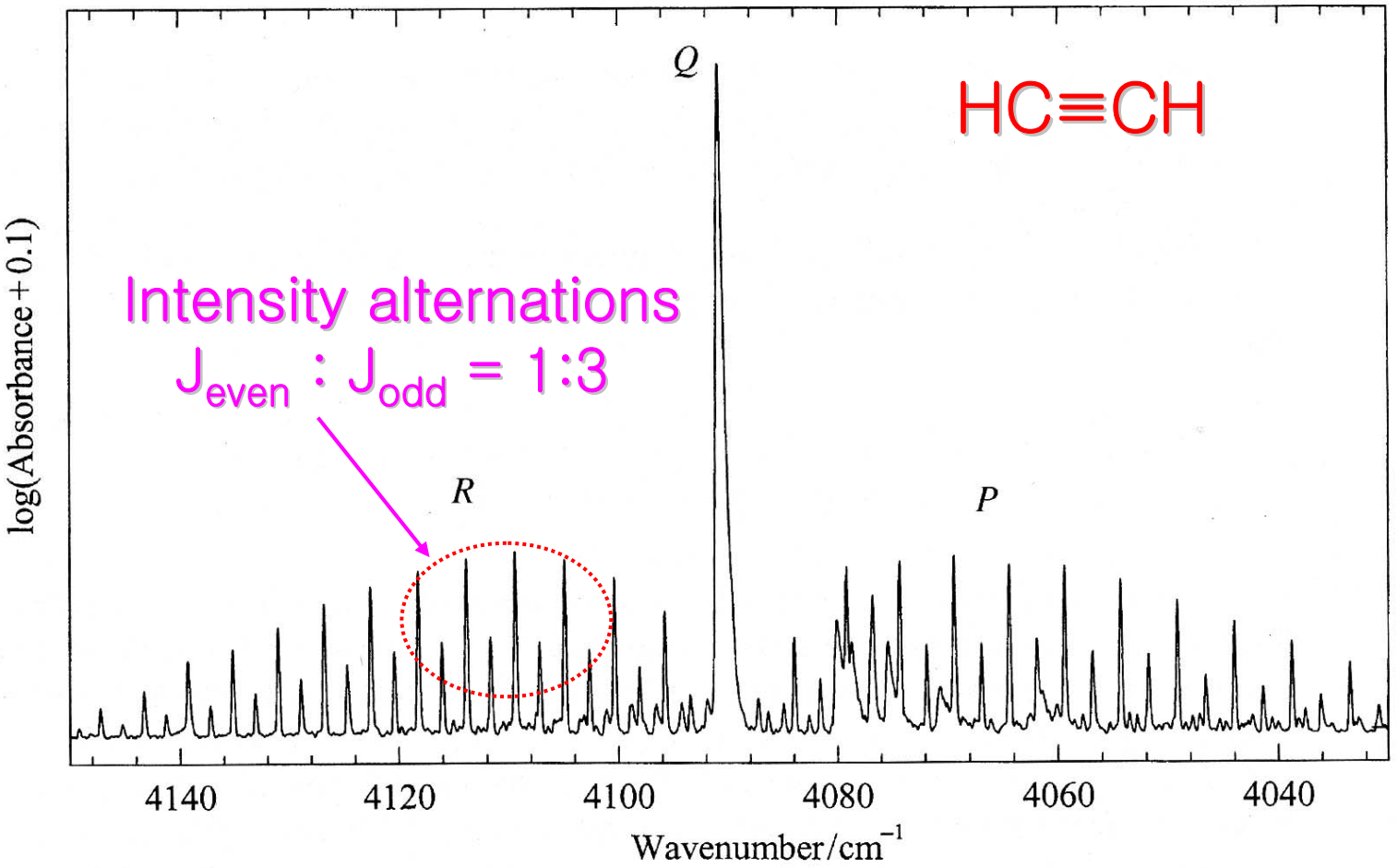


Figure 6.27 The $1_0^1 5_0^1$, $\Pi_u - \Sigma_g^+$ infrared band of acetylene. (The unusual vertical scale allows both the very intense Q branch and the weak P and R branches to be shown conveniently)

* Symmetry top molecules

Parallel transition : transition dipole moment $\vec{M} \,//\, \hat{z}$

$\rightarrow (K = 0)\ \Delta K = 0,\ \Delta J = \pm 1$

$(K \neq 0)\ \Delta K = 0,\ \Delta J = 0, \pm 1$

Perpendicular transition : $\vec{M} \perp \hat{z}$

$\rightarrow \Delta K = \pm 1,\ \Delta J = 0, \pm 1$

Parallel band

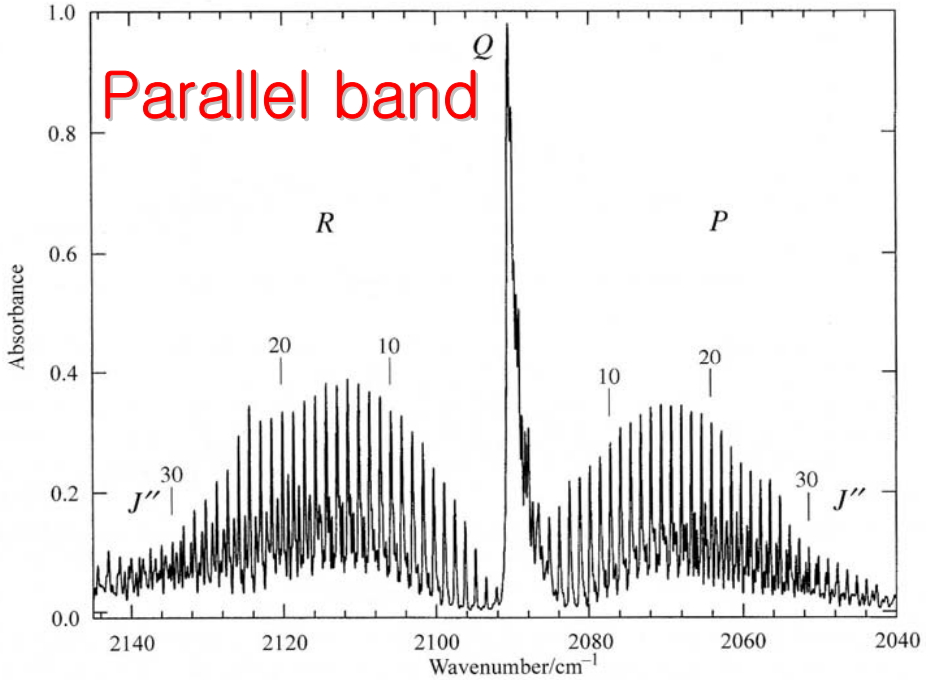


Figure 6.28 The 1_0^1, $A_1 - A_1$ infrared parallel band of C^2H_3F.

Perpendicular band

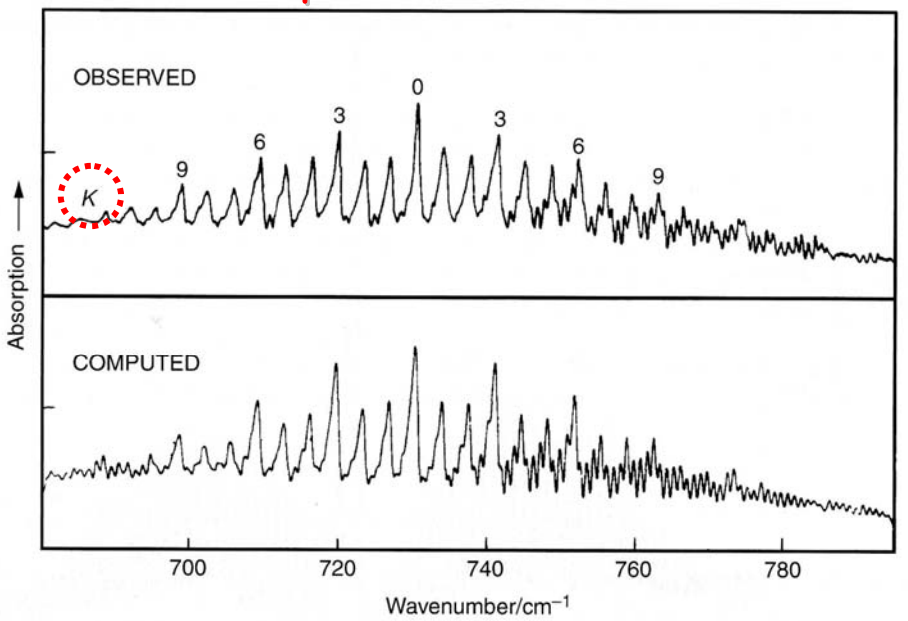


Figure 6.29 The 6_0^1, $E - A_1$ infrared perpendicular band of SiH_3F. (Reproduced, with permission, from Robiette, A. G., Cartwright, G. J., Hoy, A. R. and Mills, I. M., *Mol. Phys.*, **20**, 541, 1971)

* Asymmetry top molecules

$a-type\ transition:\ \vec{M} // \hat{a}$

$\rightarrow \Delta K_p = 0,\ \Delta K_o = \pm 1,\ \Delta J = 0, \pm 1\ (0\ for\ K_p \neq 0)$

$b-type\ transition:\ \vec{M} // \hat{b}$

$\rightarrow \Delta K_p = \pm 1,\ \Delta K_o = \pm 1,\ \Delta J = 0, \pm 1$

$c-type\ transition:\ \vec{M} // \hat{c}$

$\rightarrow \Delta K_p = \pm 1,\ \Delta K_o = 0,\ \Delta J = 0, \pm 1\ (0\ for\ K_o \neq 0)$

$H_2C=CH_2$

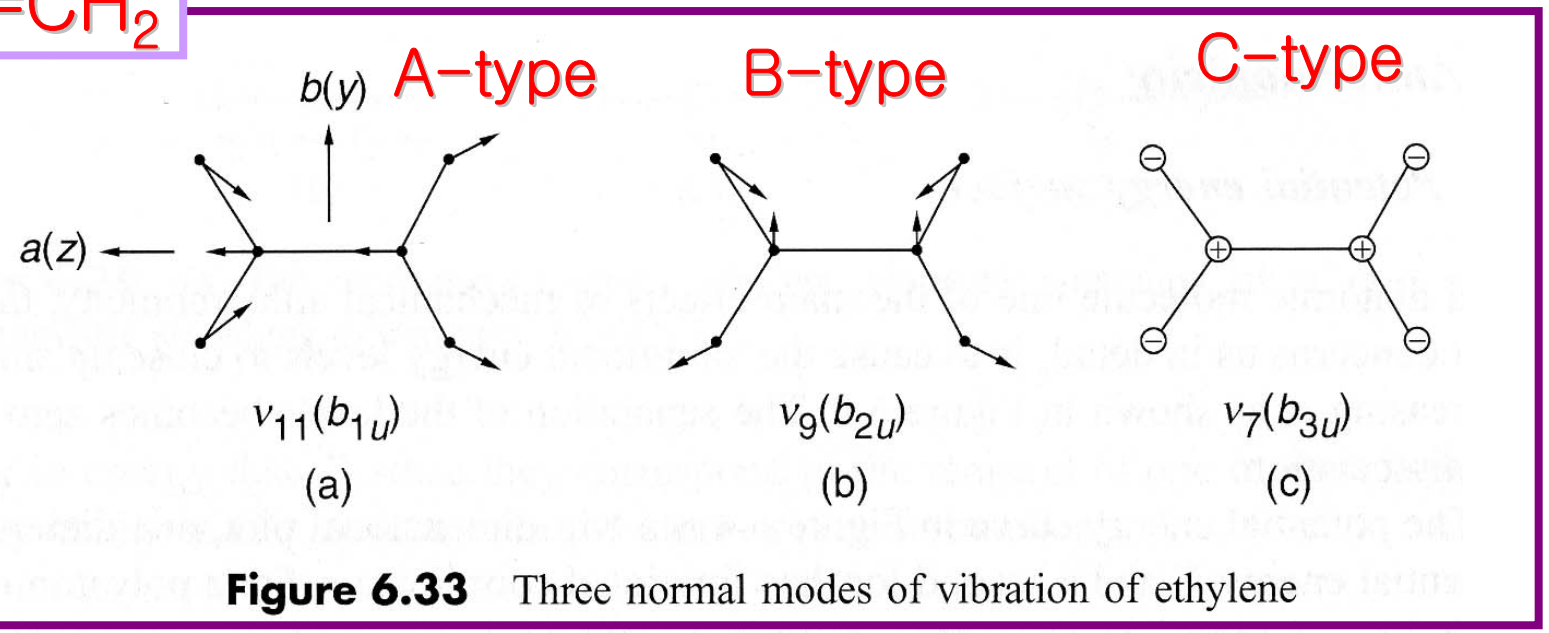


Figure 6.33 Three normal modes of vibration of ethylene

$H_2C=CH_2$

A–type

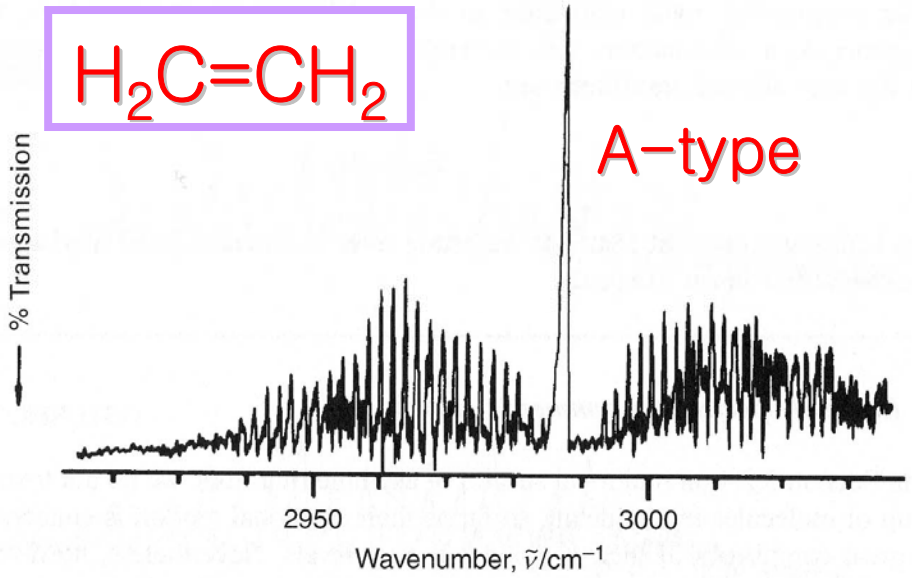


Figure 6.30 The 11_0^1 type *A* band of ethylene

B–type

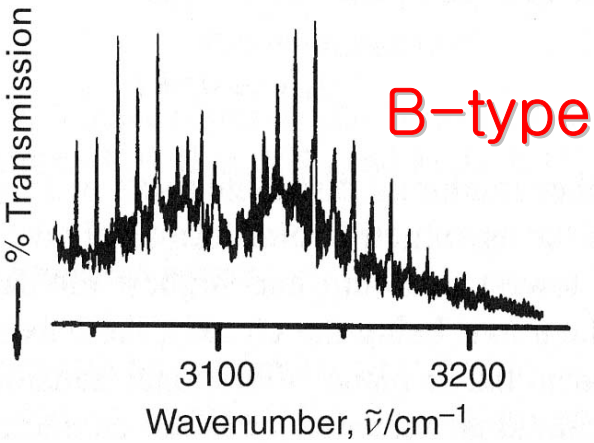


Figure 6.31 The 9_0^1 type *B* band of ethylene

C–type

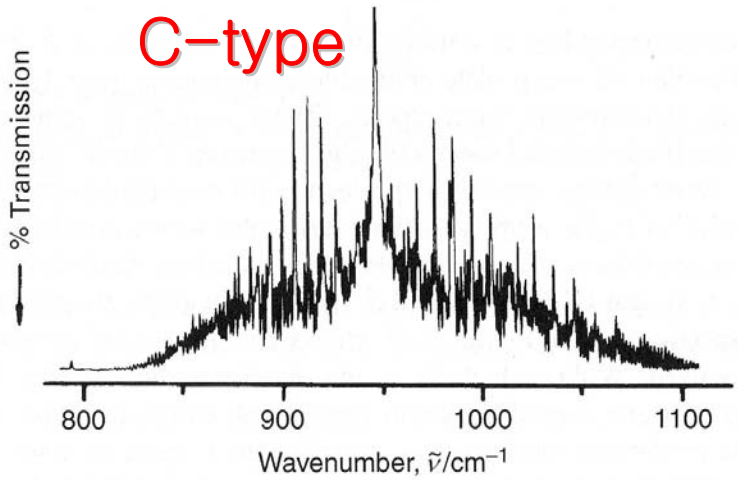


Figure 6.32 The 7_0^1 type *C* band of ethylene

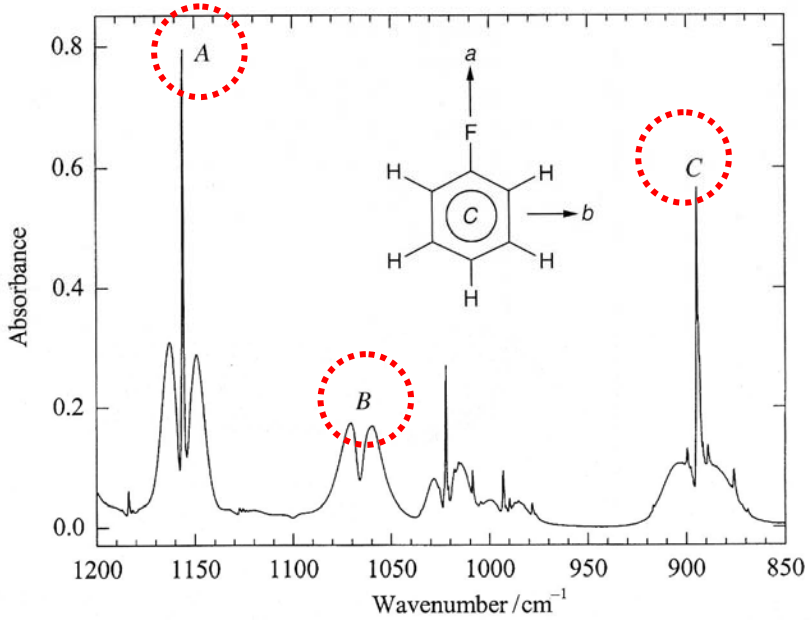


Figure 6.34 Part of the infrared spectrum of fluorobenzene showing typical type *A*, *B* and *C* bands

Fluxional Molecules

* Inversion: Example – NH_3

Reaction coordinate: Umbrella motion

"doubling"

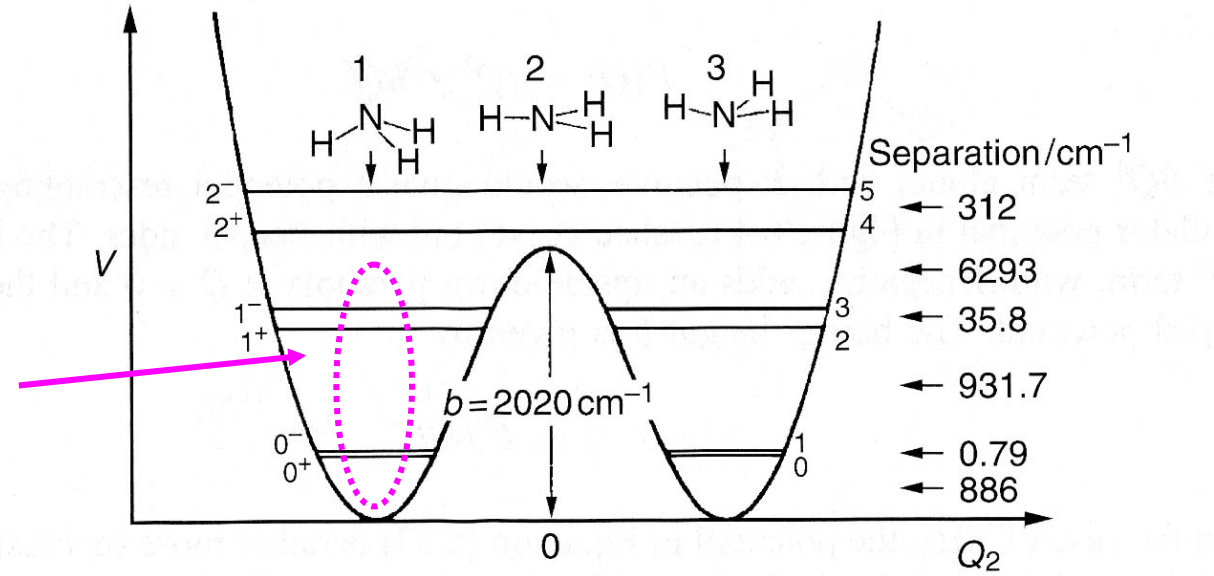


Figure 6.40 Potential energy curve for the inversion vibration v_2 of NH_3

$$\textit{Tunneling time } (L \rightarrow R)\ \tau = \frac{1}{2\Delta\nu}$$

Spectral splitting vs inversion potential barrier

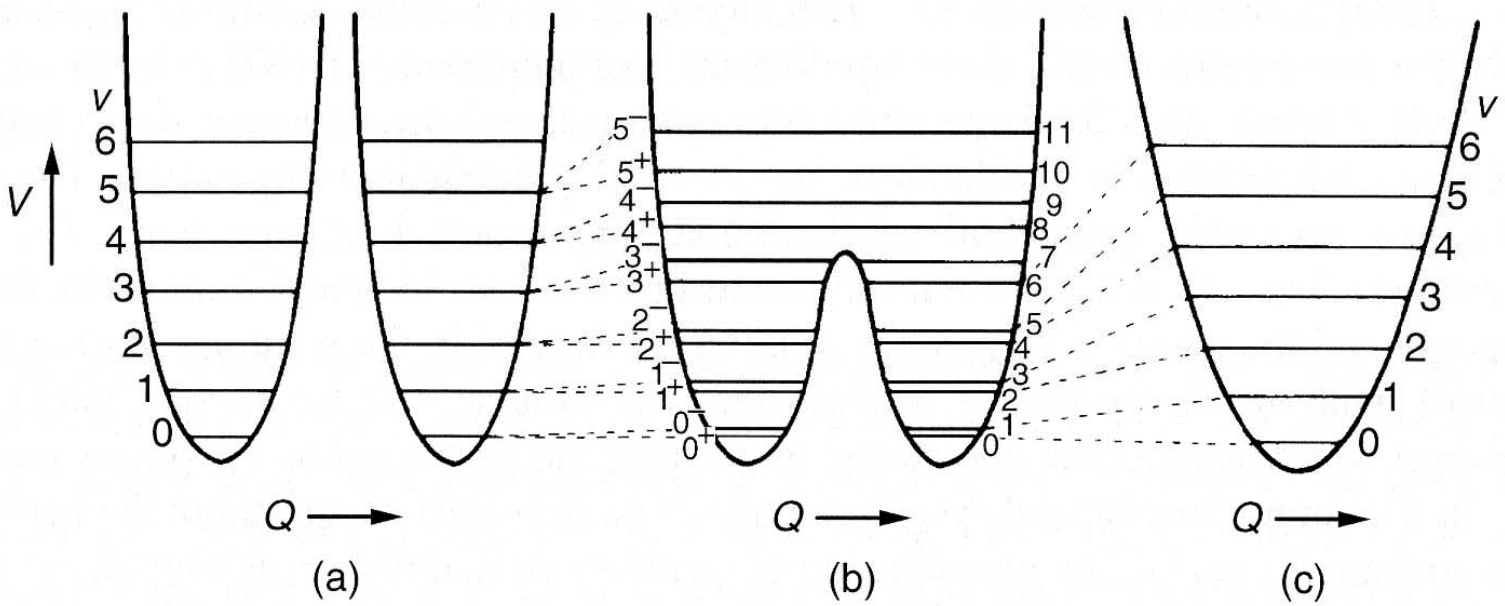


Figure 6.41 Potential energy curves and vibrational energy levels for an inversion vibration when the barrier to planarity is (a) infinite, (b) moderately low and (c) zero

* Ring-puckering: Example - cyclopentene

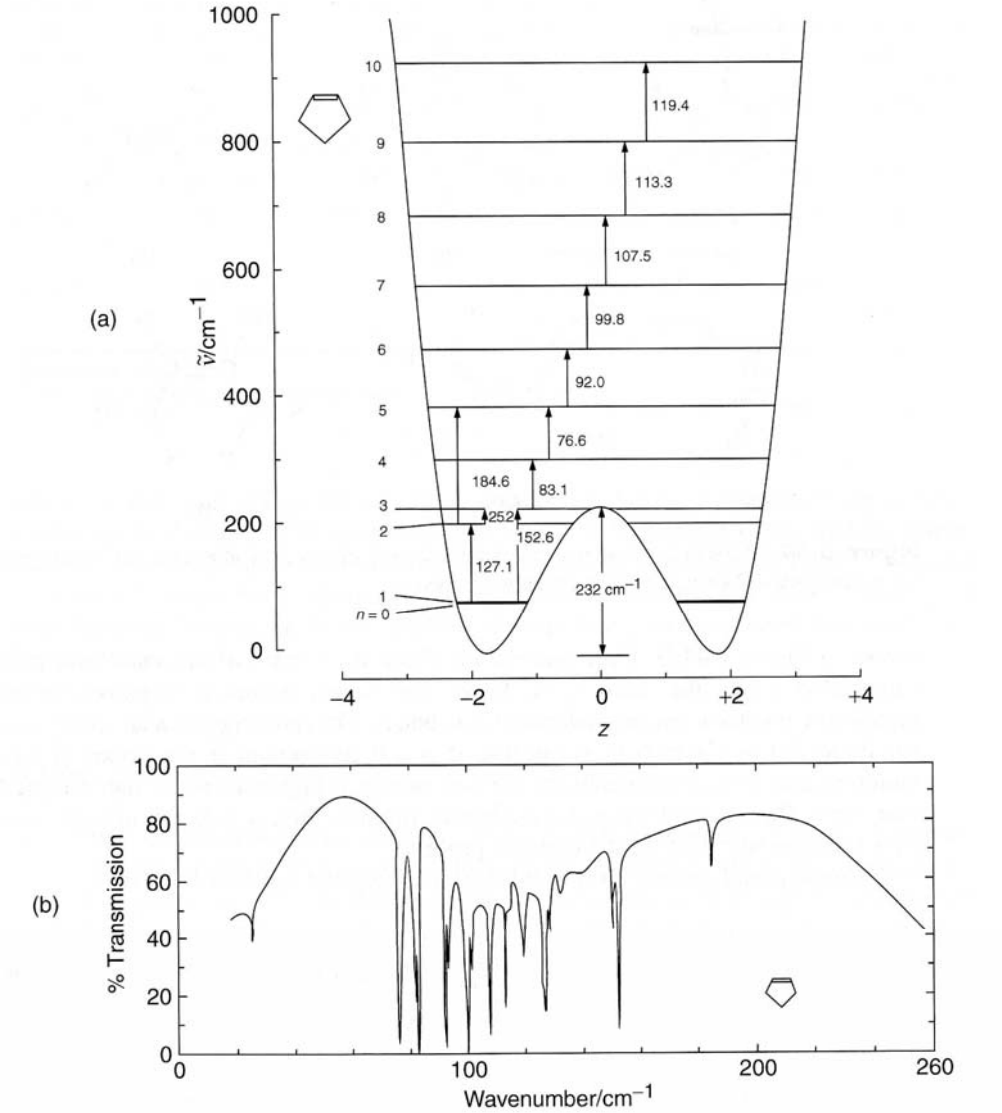


Figure 6.43 (a) Ring-puckering potential function for cyclopentene. The reduced coordinate z is proportional to the normal coordinate. (b) Far-infrared absorption spectrum of cyclopentene vapour. (Reproduced, with permission, from Laane, J. and Lord, R. C., *J. Chem. Phys.*, **47**, 4941, 1967)

* Internal rotation: Example

"... Internal rotations w/ n-fold barriers (i.e. 2π/n repetitions): n-fold splittings…"

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

V_2: two-fold barrier

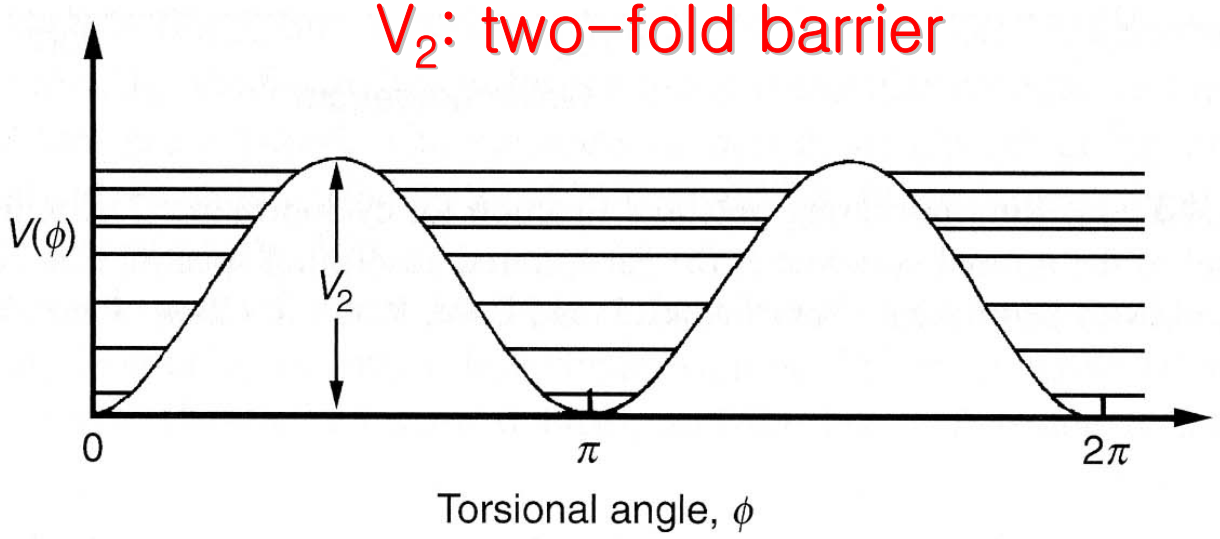


Figure 6.45 Torsional potential function, $V(\phi)$, showing a two-fold barrier

Raman Spectroscopy

"...interaction of light field E with molecular polarizability α induces dipole moment $\mu_{ind} = \alpha E$ (in linear approximation)…"

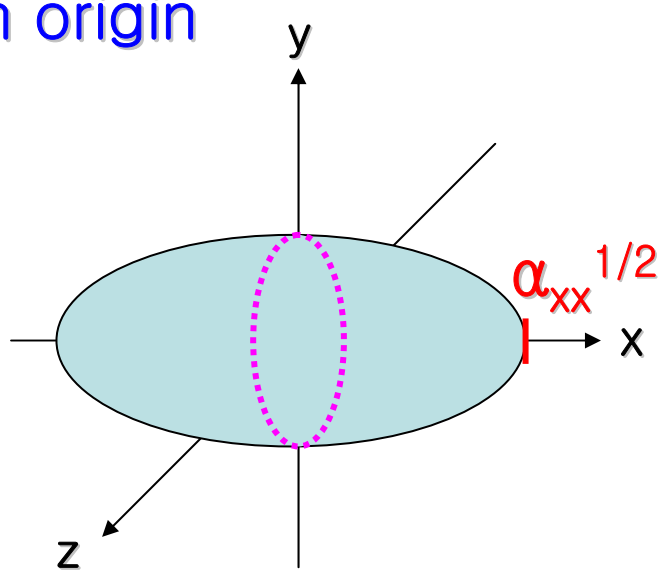
* Molecular polariability α:

  – measure of electron displacement from nuclei (tensor)

"polarizability ellipsoid": Surfaces of $\alpha^{1/2}$ distances in each direction from origin

$$\vec{\alpha} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

Real symmetric matrix



* Interaction of light field with polariability α:

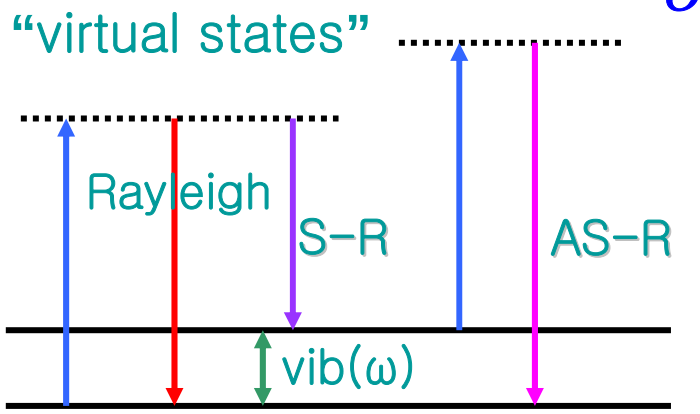
$$\alpha = \alpha_0 + \alpha_1 \cos\omega t \leftarrow \omega : \textit{molecular frequencies}$$

"static or average" "dynamic"

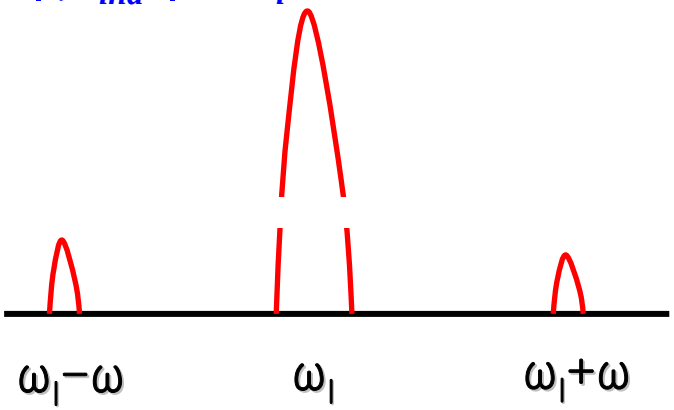
$$\therefore \quad \mu_{ind} = \alpha E = (\alpha_0 + \alpha_1 \cos\omega t) E_0 \cos\omega_I t$$

$$= \alpha_0 E_0 \cos\omega_I t + \alpha_1 E_0 \cos\omega t \cos\omega_I t$$

$$= \underbrace{\alpha_0 E_0 \cos\omega_I t}_{\text{"Rayleigh"}} + \underbrace{\alpha_1 E_0 \frac{\cos(\omega_I + \omega)t}{2}}_{\text{"anti-Stokes Raman"}} + \underbrace{\alpha_1 E_0 \frac{\cos(\omega_I - \omega)t}{2}}_{\text{"Stokes Raman"}}$$



$$\sigma_{scattering} \propto \omega^4 |\mu_{ind}|^2 N_i$$



* Vib-rotation Raman spectra

Selection rule : $\Delta v = \pm 1,\ \Delta J = 0, \pm 2\ \ (O, Q, S - branches)$

"double rotations of polarizability ellipsoid per turn"

Assuming B'=B"=B $\bar{\nu}[S(J)] = \bar{\nu}_0 + 4BJ + 6B,\ \bar{\nu}[Q(J)] = \bar{\nu}_0$

$\bar{\nu}[O(J)] = \bar{\nu}_0 - 4BJ + 2B$

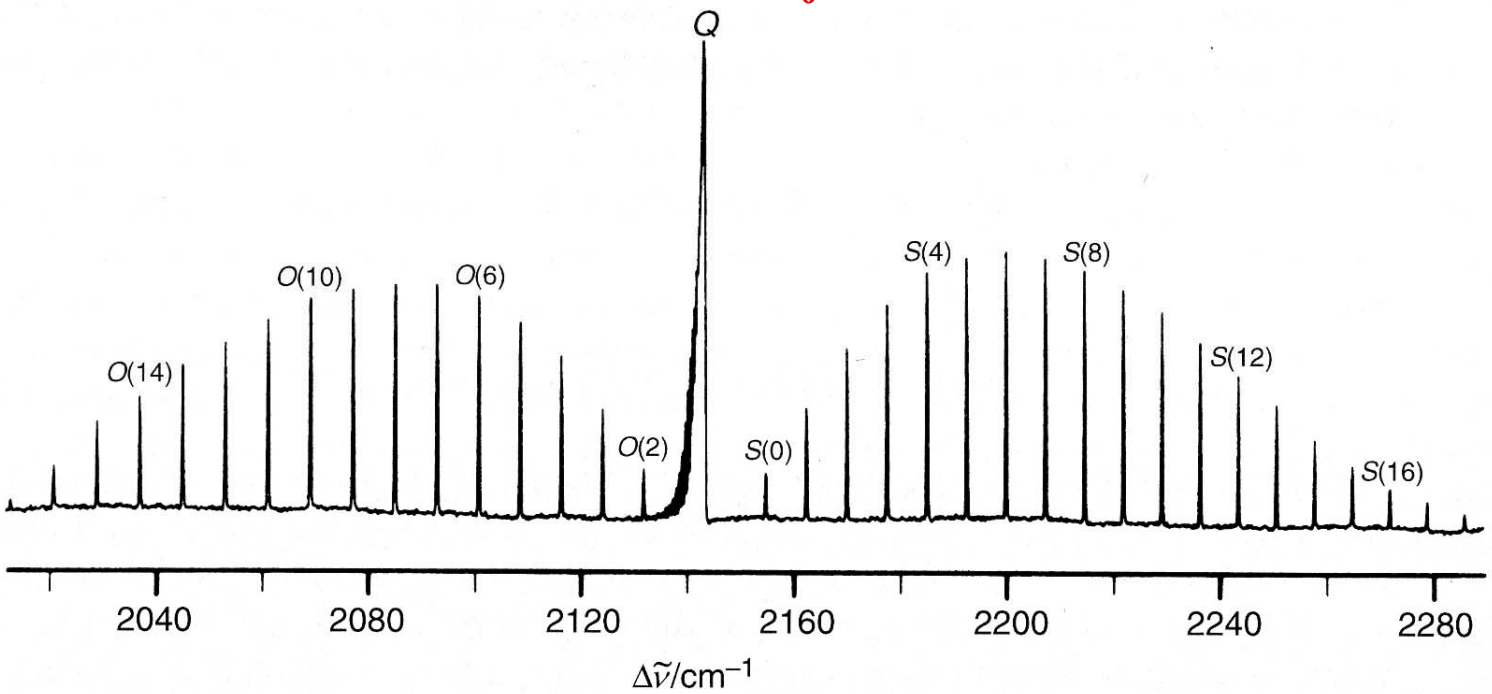


Figure 6.9 The 1–0 Stokes vibrational Raman spectrum of CO showing the *O*-, *Q*-, and *S*-branch rotational structure

* Group theoretical approach for IR and Raman activity

$$IR: \langle \psi_f | \mu_{x,y,z} | \psi_i \rangle \neq 0$$

$$Raman: \langle \psi_f | \alpha_{xx,xy,\ldots} | \psi_i \rangle \neq 0$$

$$\therefore\ IR: \Gamma(\psi_f) \times \Gamma(x,y,z) \times \Gamma(\psi_i) \ni A_1(totally\ symmetric)$$

$$Raman: \Gamma(\psi_f) \times \Gamma(x^2, xy, \ldots) \times \Gamma(\psi_i) \ni A_1(totally\ symmetric)$$

H_2O: $2A_1+B_2$ “all IR and Raman active”
CH_4: A_1+E+2T_2 “all IR and Raman active”

Molecules with center of symmetry: only IR or Raman active