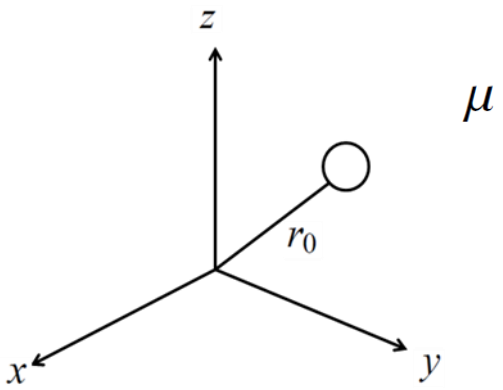
5. Rotational Spectroscopy　旋轉光譜　（回轉光譜）

5.1 Rotational spectra of diatomic molecules

a) Quantum theory of a point mass rotor

- Born-Oppenheimer approximation
- Rigid body approximation



$$-\frac{\hbar^2}{2\mu r_0^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\phi_r(\theta,\phi)=E_r(r_0)\phi_r(\theta,\phi)$$

$$\frac{\tilde{L}^2}{2I}\phi_r(\theta,\phi)=E_r\phi_r(\theta,\phi)$$

$I=\mu r_0^2$　Moment of inertia

Rotational eigen functions and energy levels

$$\phi_r(\theta,\phi)=Y_l^m(\theta,\phi)$$

$Y_l^m(\theta,\phi)$：球諧函数

$$\begin{cases}\tilde{L}^2Y_l^m(\theta,\phi)=l(l+1)\hbar^2Y_l^m(\theta,\phi)\\ L_zY_l^m(\theta,\phi)=m\hbar Y_l^m(\theta,\phi)\end{cases}$$

$$E_r = \frac{l(l+1)\hbar^2}{2I} = Bl(l+1)$$

$$B = \frac{\hbar^2}{2I}$$ Rotational constant

b) Rotational energy levels and selection rules

absorption

absorption intensity ∝ absorption cross section ∝ B coefficient

$$B = \frac{2\pi^2}{3\varepsilon_0 h^2}\left|\int \phi_f^*(\theta,\phi)\mu(\theta,\phi)\phi_i(\theta,\phi)\sin\theta d\theta d\phi\right|^2$$

$\phi_i(\theta,\phi)$: initial rotational state
$\phi_f(\theta,\phi)$: final rotational state
$\mu(\theta,\phi)$: electric dipole moment

Selection rule : $\int \phi_f^* \mu \phi_i d\tau \neq 0$

$\mu(\theta,\phi) = (0,0,\mu)$ Molecule fixed coordinate

$\mu(\theta,\phi) = (\mu_x,\mu_y,\mu_z)$ Space fixed coordinate

$$\begin{cases} \mu_x = \mu\sin\theta\cos\phi \\ \mu_y = \mu\sin\theta\sin\phi \\ \mu_z = \mu\cos\theta \end{cases} \longrightarrow \begin{cases} \mu_1 = \mu\sin\theta e^{i\phi} \sim Y_1^1 \\ \mu_0 = \mu\cos\theta \sim Y_1^0 \\ \mu_{-1} = \mu\sin\theta e^{-i\phi} \sim Y_1^{-1} \end{cases}$$

$$\phi_i = Y_{l_i}^{m_i}(\theta,\phi), \phi_f = Y_{l_f}^{m_f}(\theta,\phi)$$

$$\int \phi_f^* \mu(\theta,\phi)\phi_i d\tau \propto \mu \int Y_{l_f}^{-m_f} Y_1^m Y_{l_i}^{m_i} d\tau$$

For l

$$l = l_i \text{ and } l = 1$$

$$l_f = l_i \pm 1 \quad \begin{cases} l_f = l_i + 1 \\ l_f = l_i - 1 \end{cases}$$

For m (note that $Y_l^m \sim e^{im\phi}$)

$$m_i + m - m_f = 0$$

Absorption selection rules

$$\begin{cases} l_f = l_i + 1 \\ -m_f + m + m_i = 0 \\ \mu \neq 0 \end{cases}$$

Raman scattering

$$\int \phi_f^* \alpha \phi_i d\tau \neq 0$$

$$\begin{cases} \Delta l = 2 \\ \Delta m = 0 \end{cases}$$

$$\begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

$$\alpha = \alpha^{(0)} + \alpha^{(2)}$$

$$\alpha^{(0)} = \frac{1}{\sqrt{3}}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})Y_0^0$$

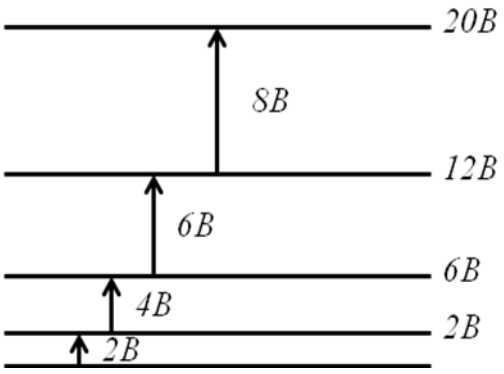
$$\alpha^{(2)} = \frac{1}{\sqrt{6}}(2\alpha_{zz} - \alpha_{xx} - \alpha_{yy})Y_2^0$$

c) Rotational absorption spectra of diatomic molecules

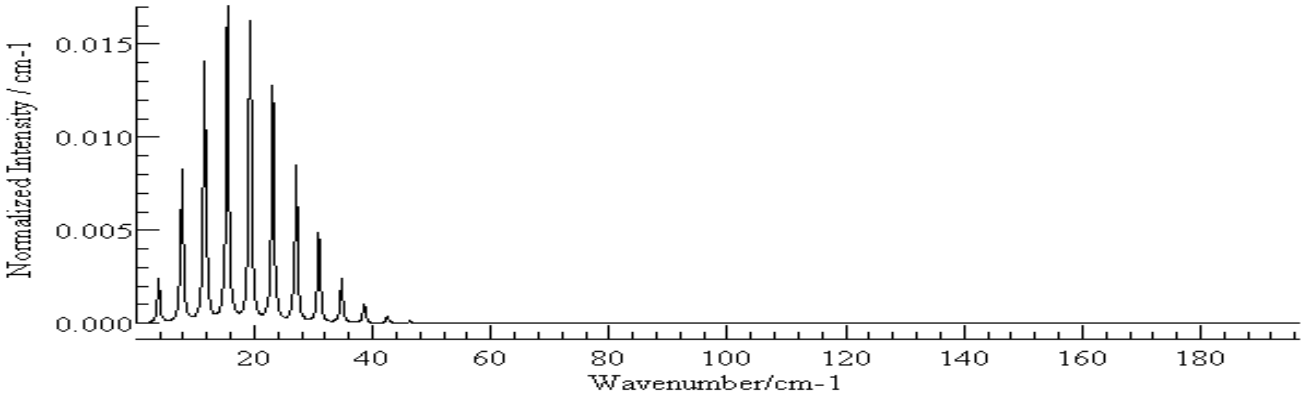
$$\begin{cases} \mu \neq 0 \\ \Delta l = +1 \end{cases}$$

$$E_r = Bl(l+1)$$

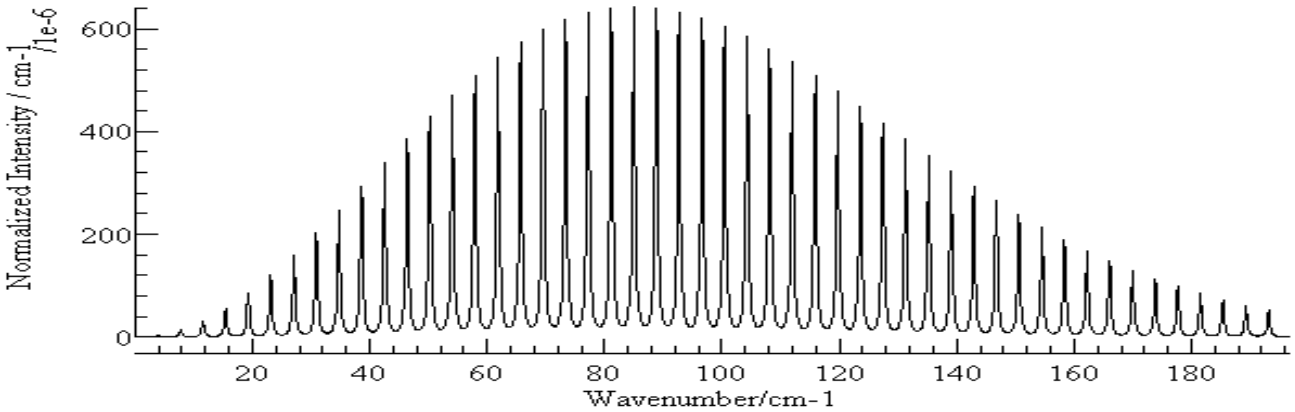
$$\text{Intensity} \propto \underbrace{(l+1)}\, \underbrace{e^{-\frac{Bl(l+1)}{kT}}} \int \phi_f^* \mu \phi_i d\tau$$



Rotational spectrum of CO at 50 K



Rotational spectrum of CO at 1350 K



http://www.galaxyzooforum.org/index.php?topic=279339.0

CO rotational spectrum: line spacing 3.8cm^{-1}

$$2B = 3.8\text{cm}^{-1} = 8.0 \times 10^{-23}\text{J} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$I = \frac{\hbar^2}{2B} = 1.4 \times 10^{-46}\text{kg m}^2 \qquad = 1.1 \times 10^{-26}\text{kg}$$

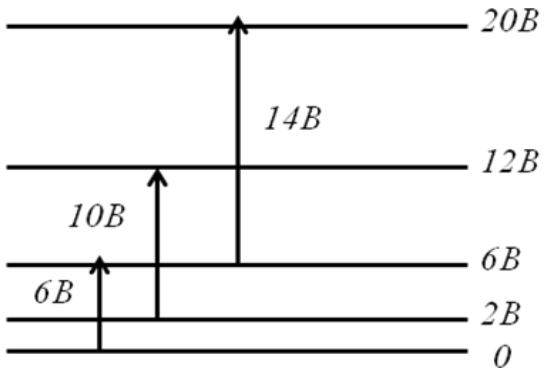
$$= \mu r_0^2$$

$$r_0^2 = \frac{I}{\mu} = 1.27 \times 10^{-20}\text{m}^2$$

$$r_0 = 1.1 \times 10^{-10}\text{m} = 1.1\text{Å}$$

d) Rotational Raman spectra of homonuclear diatomic molecules and the nuclear spin weight

$$\begin{cases} \mu = 0 \\ E_r = Bl(l+1) \\ \Delta l = 2 \end{cases}$$



Intensity $\propto \dfrac{3(l+1)(l+2)}{2(2l+1)} e^{-\frac{Bl(l+1)}{2(2l+1)}}$

Nuclear spin weight

$$\begin{cases} \text{Bose particle} & \text{Nuclear spin } I & I\text{: integer} & {}^{2}\text{H},\ {}^{14}\text{N} \\ \text{Fermi particle} & & I\text{: half integer} & {}^{1}\text{H},\ {}^{15}\text{N} \end{cases}$$

Exchange of nuclei

$$|\psi|^2 \xrightarrow[\text{Exchange}]{} |\psi|^2$$

$$\psi \longrightarrow \begin{cases} +\psi & \text{Bose particle} \\ -\psi & \text{Fermi particle} \end{cases}$$

$^{1}H_2$ molecule ($I = 1/2$)

$$\psi = \psi_r \psi_N$$

$$\psi_r \xrightarrow[\theta \to \theta + \pi]{\text{exchange}} \begin{cases} + & \text{even } l & \times 1 & \text{para} \\ - & \text{odd } l & \times 3 & \text{ortho} \end{cases}$$

$$\psi_N \qquad \alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$$

$$S = 0 \quad \alpha\beta - \beta\alpha \qquad\qquad S = 1 \quad \begin{cases} \alpha\alpha \\ \alpha\beta + \beta\alpha \\ \beta\beta \end{cases}$$

$^2H_2$ (D_2) molecule ($I = 1$)

$$\psi = \psi_r \psi_N$$

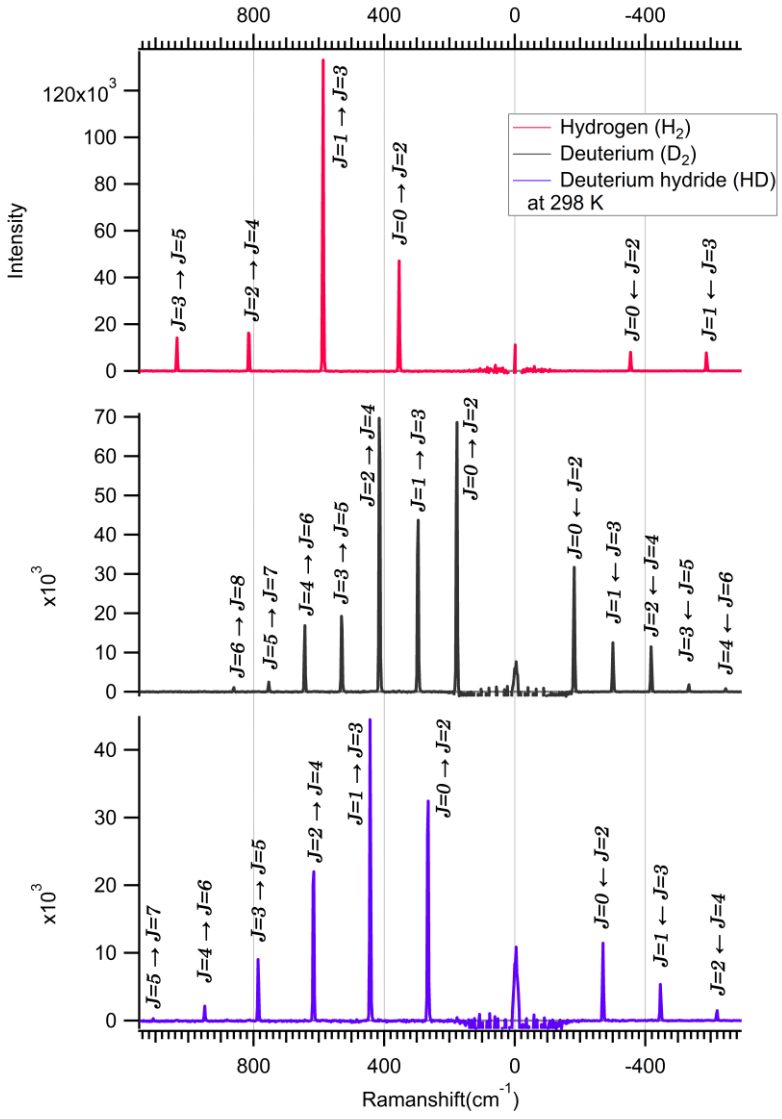
$$\psi_r \xrightarrow[\theta \to \theta + \pi]{\text{exchange}} \begin{cases} + & \text{even } l & \times 6 \\ - & \text{odd } l & \times 3 \end{cases}$$

ψ_N |1,1>, |1,0>, |1,-1>, |0,1>, |0,0>, |0,-1>, |-1,1>. |-1,0>, |-1,-1>

S=0 |1,-1> + |0,0> + |-1,1> (1 fold)

S=1 |1,0> - |0,1>; |1,-1> - |-1,1>; |-1,0> - |-1,0> (3 fold)

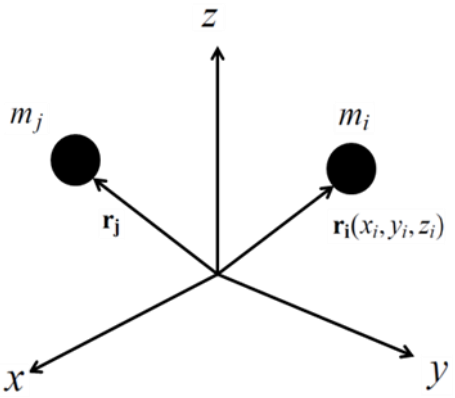
S=1 |1,1>; |1,0> + |0,1>; |0,0>; |-1,0> + |0,-1>; |-1,-1> (5 fold)



Rotational Raman spectra of H2, D2 and HD

5.2 Rotational spectra of polyatomic molecules （多原子分子）

a) Quantum theory of a rigid rotor 剛体旋轉子的量子論



Inertia tensor $\boldsymbol{I}$

$$\boldsymbol{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix}$$

$$\begin{cases} I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \\ I_{xy} = -\sum_i m_i x_i y_i \end{cases}$$

Angular velocity $\boldsymbol{\omega}$

$$\boldsymbol{\omega} = \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

Angular momentum $\boldsymbol{L}$

$$\boldsymbol{L} = \begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix}$$

Rotational kinetic energy T

$$T = \frac{1}{2}\boldsymbol{\omega}^t \boldsymbol{I} \boldsymbol{\omega} \qquad \boldsymbol{\omega}^t = (\omega_x, \omega_y, \omega_z)$$

$$= \frac{1}{2}\boldsymbol{L}^t \boldsymbol{I}^{-1} \boldsymbol{L}$$

Conversion to inertial system

$$x, y, z \rightarrow A, B, C$$

$$\mathbf{I} = \begin{pmatrix} I_A & 0 & 0 \\ 0 & I_B & 0 \\ 0 & 0 & I_C \end{pmatrix} \qquad I_A \leq I_B \leq I_C$$

Principal moments of inertia

$$\boldsymbol{\omega} = \begin{pmatrix} \omega_A \\ \omega_B \\ \omega_C \end{pmatrix} \qquad \boldsymbol{L} = \begin{pmatrix} L_A \\ L_B \\ L_C \end{pmatrix}$$

$$T = \frac{1}{2}\boldsymbol{L}^t \boldsymbol{I}^{-1} \boldsymbol{L}$$
$$= \frac{1}{2}\left(\frac{L_A^2}{I_A} + \frac{L_B^2}{I_B} + \frac{L_C^2}{I_C}\right)$$

b) Spherical molecules $I_A = I_B = I_C = I$

$$T = \frac{1}{2I}(L_A^2 + L_B^2 + L_C^2)$$
$$= \frac{L^2}{2I} \xrightarrow{\text{quantization}} T = \frac{\hat{L}^2}{2I}$$

Energy levels

$$E_r = \frac{l(l+1)\hbar^2}{2I} = Bl(l+1) \qquad B = \frac{\hbar^2}{2I}$$

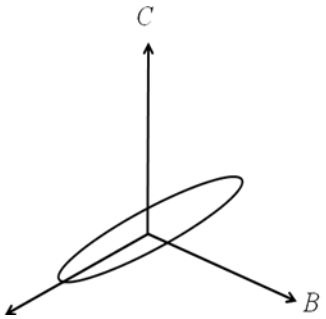
Selection rules

Absorption $\mu = 0$ → inactive

Raman scattering

$$\alpha = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \sim Y_0^0 \quad \rightarrow \text{ inactive}$$

c) Linear molecules $I_A = 0 \quad I_B = I_C = I$



$$\frac{L_A^2}{I_A} \to 0$$

$I_A \to 0$, $L_A \to 0$

L_A approaches to zero faster

$$T = \frac{1}{2}\left(\frac{L_A^2}{I_A} + \frac{L_B^2}{I_B} + \frac{L_C^2}{I_C}\right)$$

$$= \frac{L^2}{2I} \qquad (L^2 \equiv L_B^2 + L_C^2)$$

$$\tilde{T} = \frac{\tilde{L}^2}{2I}$$: same as diatomic molecules

Selection rules

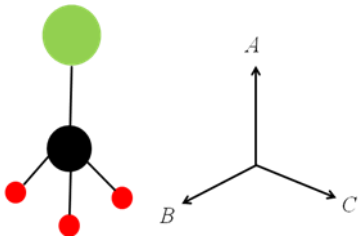
Absorption $\mu \neq 0 \quad \Delta l = 1$

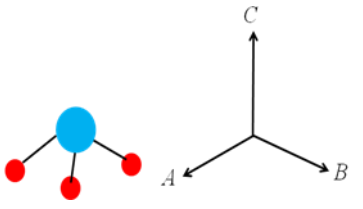
Raman scattering $\Delta l = \pm 2$

d) Symmetric top molecules

Symmetric top

- prolate（偏重） $I_A < I_B = I_C$ CH_3Cl
- Oblate（偏平） $I_A = I_B < I_C$ NH_3



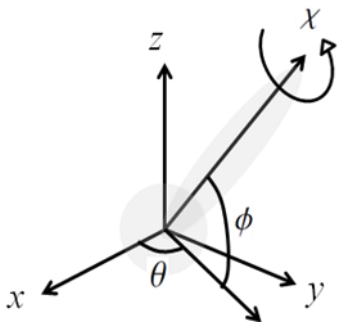


Prolate symmetric top

$$I_A < I_B = I_C$$

$$\begin{aligned} T &= \frac{1}{2}\left(\frac{L_A^2}{I_A} + \frac{L_B^2}{I_B} + \frac{L_C^2}{I_C}\right) \\ &= \frac{1}{2}\left(\frac{L_A^2}{I_A} + \frac{L_B^2 + L_C^2}{I_B}\right) \\ &= \frac{1}{2}\frac{L^2}{I_B} + \frac{1}{2}\left(\frac{1}{I_A} - \frac{1}{I_B}\right)L_A^2 \\ \tilde{T} &= \frac{1}{2}\frac{\tilde{L}^2}{I_B} + \frac{1}{2}\left(\frac{1}{I_A} - \frac{1}{I_B}\right)\tilde{L}_A^2 \end{aligned}$$

Eigen functions $\phi_r^{lkm}(\theta, \phi, \chi)$



Euler angle

$\theta \quad \phi \quad \chi$

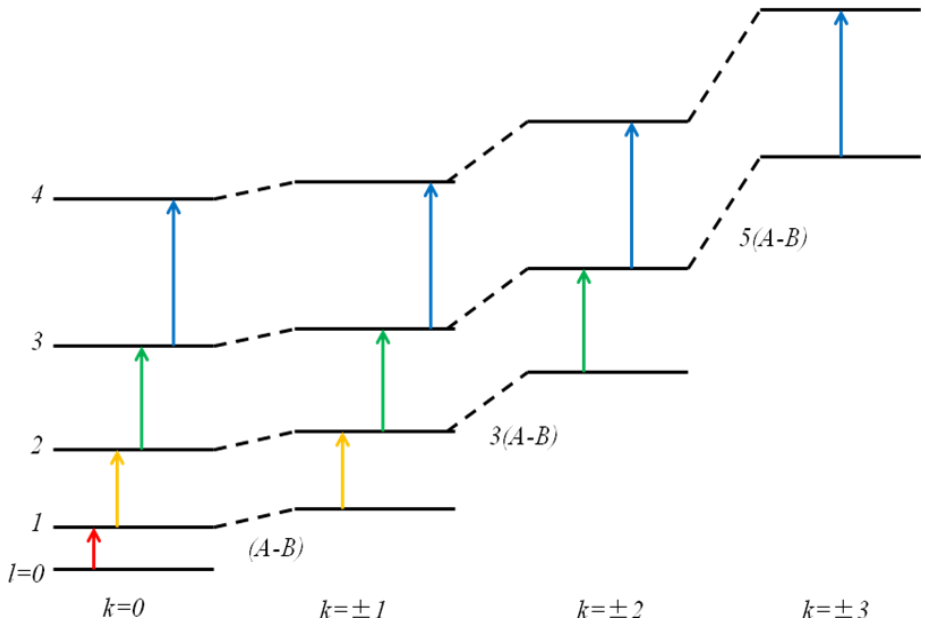
$$\phi_r^{lkm}(\theta, \phi, \chi) = \Theta_{lkm}(\theta) e^{ik\chi} e^{im\phi}$$

$$\begin{cases} \tilde{L}^2 \phi_r^{lkm} = l(l+1)\hbar^2 \phi_r^{lkm} & l = 0, 1, 2, \cdots \\ \tilde{L}_z \phi_r^{lkm} = m\hbar \phi_r^{lkm} & m = -l, -l+1, \cdots, -1, 0, 1, \cdots, l-1, l \\ \tilde{L}_A \phi_r^{lkm} = k\hbar \phi_r^{lkm} & k = -l, -l+1, \cdots, -1, 0, 1, \cdots, l-1, l \end{cases}$$

Energy levels

$$\begin{aligned} E_r^{lkm} &= \frac{1}{2}\frac{l(l+1)\hbar^2}{I_B} + \frac{1}{2}\left(\frac{1}{I_A} - \frac{1}{I_B}\right)k^2\hbar^2 \\ &= Bl(l+1) + (A - B)k^2 \end{aligned}$$

$$B = \frac{\hbar^2}{2I_B} \quad A = \frac{\hbar^2}{2I_A}$$



Selection rules

Absorption

$$\mu \neq 0$$

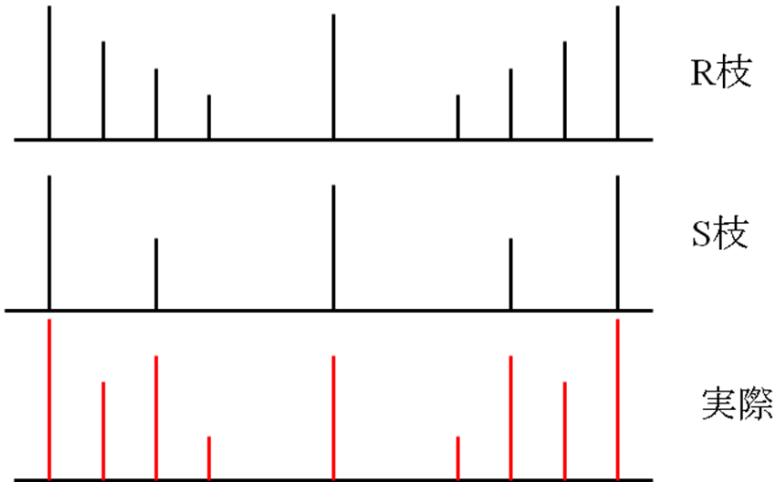
$$\Delta l = 1 \quad \Delta k = 0$$

Raman scattering

$$\begin{cases} \Delta l = \pm 1 \quad (k \neq 0) \quad \pm 2 \\ \Delta k = 0 \end{cases}$$

$\Delta l = \pm 1 \quad 4B, 6B, 8B, \cdots,$ R-branch

$\Delta l = \pm 2 \quad 6B, 10B, 14B, \cdots,$ S-branch



Benzene

B.P. Stoicheff　Can. J. Phys 32, 339(1954)

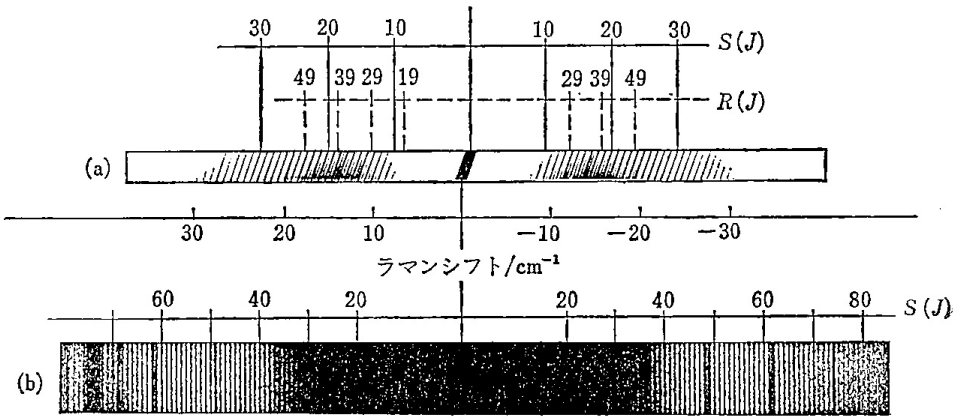


図 4.2.1　ベンゼンの回転ラマンスペクトル[1,3]．(a)圧力 70 mmHg，温度 288 K，488.0 nm 励起．(b)圧力 380 mmHg，温度 333 K，435.8 nm 励起．

Line spacings of S branch

C_6H_6　0.7584 cm^{-1}　B_H=0.1896 cm^{-1}

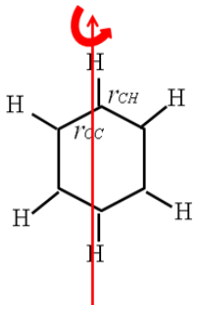
C_6D_6　0.6272 cm^{-1}　B_D=0.1568 cm^{-1}

$$B = \frac{\hbar^2}{2I_B}$$

$$\begin{cases} I_B(C_6H_6) = 1.476 \times 10^{-45}\,\mathrm{kg\,m^2} \\ I_B(C_6D_6) = 1.785 \times 10^{-45}\,\mathrm{kg\,m^2} \end{cases}$$

$$I_B = 2\left\{2m_C\left(r_{CC}\times\frac{\sqrt{3}}{2}\right)^2 + 2m_H\left(r_{CC}\times\frac{\sqrt{3}}{2} + r_{CH}\times\frac{\sqrt{3}}{2}\right)^2\right\}$$

$$= 3\left(m_C r_{CC}^2 + m_H(r_{CC}+r_{CH})^2\right)$$



$$\begin{cases} r_{CC} = 1.397\text{Å} \\ r_{CH} = 1.084\text{Å} \end{cases}$$