13-9 The Vibrations of Polyatomic Molecules are Represented by Normal Coordinates.

A molecule consisting of N atoms has $3N$ degree of freedom:
- 3 translational
- 3 rotational (2 for linear molecule)
- $3N$-6 vibrational ($3N$-5 for linear molecule)

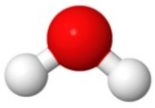
$$V(q_1, q_2, \cdots q_{3N-6}) = V(0,0,\cdots 0) + \underbrace{\frac{1}{2}\sum_i \sum_j \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right) q_i q_j} + \cdots$$

$$\Rightarrow \frac{1}{2}\sum_i \sum_j f_{ij} q_i q_j$$

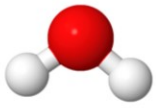
$$= \frac{1}{2}\sum_j F_j Q_j^{\,2} \qquad \{Q_j\} \text{ normal mode coordinate}$$

$$\left.\begin{aligned} \hat{H}_{\text{vib}} &= -\sum_j \frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + \frac{1}{2}\sum_j F_j Q_j^{\,2} \\ &= \sum_j \left(-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}Q^2} + \frac{1}{2}F_j Q_j^{\,2}\right) \equiv \sum_j \hat{H}_{\text{vib},j} \\ \psi_{\text{vib}}(Q_1, Q_2, \cdots Q_{3N-6}) &= \psi_{\text{vib},1}(Q_1)\psi_{\text{vib},2}(Q_2)\cdots\psi_{\text{vib},3N-6}(Q_{3N-6}) \end{aligned}\right\} \Rightarrow E = \sum_j h\nu_j\left(\upsilon_j + \frac{1}{2}\right)$$

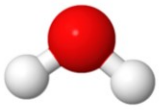
Normal modes of H_2O



A_1 3650 cm^{-1}



B_2 3760 cm^{-1}



A_1 1600 cm^{-1}

Selection rule: $\Delta\upsilon = +1$, $\Delta J = \pm 1$ — Dipole moment is parallel to bond axis.

$\Delta\upsilon = +1$, $\Delta J = 0, \pm 1$ — Dipole moment is perpendicular to bond axis.

Equation of motion for coupled oscillator

$$F_{ix} = m_i \frac{d^2}{dt^2} x_i$$

$$= \sum_j \frac{d^2\phi}{dx_i dx_j}(x_j - x_i) \equiv \sum_j k_{ij}(x_j - x_i)$$

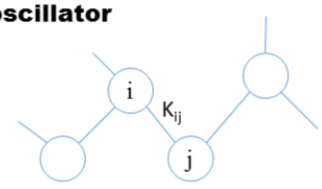
$$\left.\begin{aligned} K_{ij} &= -k_{ij} \\ K_{ii} &= \sum_j k_{ij} \end{aligned}\right\} \Rightarrow F_{ix} = -\sum_j K_{ij} x_j$$

$$x_i = x_{0i} \exp(-i\omega t)$$

$$\Rightarrow F_{ix} = -m_i \omega^2 x_i$$

$$\sum_j K_{ij} x_j = m_i \omega^2 x_i \Rightarrow Kx = Mx\omega^2$$

$$V = \frac{1}{2} x^t K x = \frac{1}{2} x^t M x \omega^2$$



φ: two-body potential
When a force proportional to displacement is taken into account, it is called harmonic approximation.

K: stiffness matrix

Oscillating x is assumed as a solution.

Simultaneous equations for all the particles.
→ An equation of matrix

V: Vibrational energy

Hessian method

$$M^{-1}Kx = x\omega^2$$

$$M = \begin{pmatrix} m_1 & & & & & & \\ & m_1 & & & & 0 & \\ & & m_1 & & & & \\ & & & \ddots & & & \\ & & & & m_N & & \\ & 0 & & & & m_N & \\ & & & & & & m_N \end{pmatrix}, \quad K = \begin{pmatrix} \frac{\partial^2 U}{\partial x_1^2} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & \frac{\partial^2 U}{\partial x_1 \partial y_1} & & & \\ \frac{\partial^2 U}{\partial y_1 \partial x_1} & \frac{\partial^2 U}{\partial y_1^2} & \frac{\partial^2 U}{\partial y_1 \partial z_1} & \cdots & & \cdots \\ \frac{\partial^2 U}{\partial z_1 \partial x_1} & \frac{\partial^2 U}{\partial z_1 \partial y_1} & \frac{\partial^2 U}{\partial z_1^2} & & & \\ & \vdots & & \ddots & & \\ & & & & \frac{\partial^2 U}{\partial x_N^2} & \frac{\partial^2 U}{\partial x_N \partial y_N} & \frac{\partial^2 U}{\partial x_N \partial z_N} \\ & \vdots & & & \frac{\partial^2 U}{\partial y_N \partial x_N} & \frac{\partial^2 U}{\partial y_N^2} & \frac{\partial^2 U}{\partial y_N \partial z_N} \\ & & & & \frac{\partial^2 U}{\partial z_N \partial x_N} & \frac{\partial^2 U}{\partial z_N \partial y_N} & \frac{\partial^2 U}{\partial z_N^2} \end{pmatrix}$$

$$M^{-1} = \begin{pmatrix} \mu_1 & & & & & & \\ & \mu_1 & & & & 0 & \\ & & \mu_1 & & & & \\ & & & \ddots & & & \\ & & & & \mu_N & & \\ & 0 & & & & \mu_N & \\ & & & & & & \mu_N \end{pmatrix}, \quad x = \begin{pmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ x_N \\ y_N \\ z_N \end{pmatrix}$$

x is an eigenvector of $M^{-1}K$.
→ You have to find a set of x that diagonalizes $M^{-1}K$.

GF method

A variation of Hessian method, where the coordinate system is transformed so that the variables represents molecular parameters (such as bond length, bond angle, etc.).

$$\begin{cases} M^{-1}Kx = x\omega^2 \\ x' = U^t x \end{cases}$$

$$\Rightarrow U^t M^{-1} U U^t K U x' = U^t U x' \omega^2$$

$$\begin{cases} U^t M^{-1} U \equiv G \\ U^t K U \equiv F \end{cases}$$

$$\Rightarrow GFx' = x'\omega^2$$

U transforms the Cartesian coordinate into internal molecular coordinate.

F is a set of parameters such as stretching, biting, etc., intuitionally understandable.

x' is an eigenvector of GF.

→ You have to find a set of *x*' that diagonalizes GF matrix.

Natural oscillation of a diatomic molecule

$$\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}\omega^2$$

Hesseian Method

$$\begin{pmatrix} \mu_1 K - \omega^2 & -\mu_1 K \\ -\mu_2 K & \mu_2 K - \omega^2 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = 0$$

when $\omega^2 = 0$

$$x_1 = \frac{1}{\sqrt{2}},\ x_2 = \frac{1}{\sqrt{2}}$$

when $\omega^2 = (\mu_1 + \mu_2)K$

$$x_1 = \frac{\mu_1}{\sqrt{\mu_1^2 + \mu_2^2}},\ x_2 = -\frac{\mu_2}{\sqrt{\mu_1^2 + \mu_2^2}}$$

GF method

$$x' = U^t x = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \frac{1}{\sqrt{2}}\begin{pmatrix} x_1 + x_2 \\ x_1 - x_2 \end{pmatrix}$$

$$G = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} \mu_1 & 0 \\ 0 & \mu_2 \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \frac{1}{2}\begin{pmatrix} \mu_1 + \mu_2 & \mu_1 - \mu_2 \\ \mu_1 - \mu_2 & \mu_1 + \mu_2 \end{pmatrix}$$

$$F = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} K & -K \\ -K & K \end{pmatrix}\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} 0 & 0 \\ 0 & 2K \end{pmatrix}$$

$$GF = \begin{pmatrix} 0 & (\mu_1 - \mu_2)K \\ 0 & (\mu_1 + \mu_2)K \end{pmatrix}$$

$$\begin{pmatrix} -\omega^2 & (\mu_1 - \mu_2)K \\ 0 & (\mu_1 + \mu_2)K - \omega^2 \end{pmatrix}\begin{pmatrix} x_1' \\ x_2' \end{pmatrix} = 0$$

Mass-weighted Hessian method

$$M^{-1}Kx = x\omega^2$$

$M^{-1}K$ is not a symmetric matrix.
→x's are not diagonalized with each other.
→ω is not necessarily real.

$$M^{-1/2}KM^{-1/2}M^{1/2}x = M^{1/2}x\omega^2$$

$$M^{1/2} = \begin{pmatrix} \sqrt{m_1} & & & & & \\ & \sqrt{m_1} & & & 0 & \\ & & \sqrt{m_1} & & & \\ & & & \ddots & & \\ & & & & \sqrt{m_N} & \\ & 0 & & & & \sqrt{m_N} \\ & & & & & & \sqrt{m_N} \end{pmatrix}$$

When we multiply $M^{1/2}$ on the both hands of the equation.

M is a diagonal matrix.
→$M^{1/2}$ is easily obtained.

$$\left.\begin{aligned} M^{-1/2}KM^{-1/2} &\equiv D \\ M^{1/2}x &\equiv w \end{aligned}\right\} \Rightarrow Dw = w\omega^2 \qquad D_{ij} = \sqrt{\mu_i}\sqrt{\mu_j}K_{ij}$$

D is diagonal matrix.
→so-called dynamical matrix

Natural oscillation of a diatomic molecule

$$\begin{pmatrix} \mu_1 K & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = \begin{pmatrix} w_1 \\ w_2 \end{pmatrix}\omega^2$$

$$\begin{pmatrix} \mu_1 K-\omega^2 & -\sqrt{\mu_1\mu_2}K \\ -\sqrt{\mu_1\mu_2}K & \mu_2 K-\omega^2 \end{pmatrix}\begin{pmatrix} w_1 \\ w_2 \end{pmatrix} = 0$$

when $\omega^2 = 0$

$$w_1 = \sqrt{\frac{\mu_2}{\mu_1+\mu_2}},\quad w_2 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}}$$

when $\omega^2 = (\mu_1+\mu_2)K$

$$w_1 = \sqrt{\frac{\mu_1}{\mu_1+\mu_2}},\quad w_2 = -\sqrt{\frac{\mu_2}{\mu_1+\mu_2}}$$

Compared with GFmethod

$$GFx' = x'\omega^2$$

$$G^{1/2}FG^{1/2}G^{-1/2}x'$$

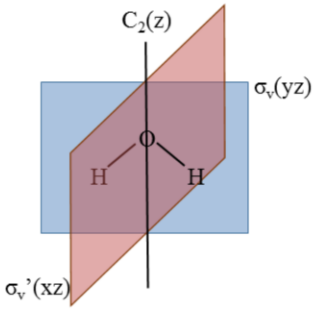
$$\begin{cases} G^{1/2}FG^{1/2} \equiv D' \\ G^{-1/2}x' \equiv w' \end{cases}$$

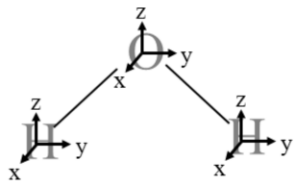
$$\Rightarrow D'w' = w'\omega^2$$

$$\begin{cases} w' = G^{-1/2}x' \\ \quad = U^t M^{1/2}UU^t M^{-1/2}w = U^t w \\ D' = G^{1/2}FG^{1/2} \\ \quad = U^t M^{-1/2}UU^t KUU^t M^{-1/2}U \\ \quad = U^t DU \end{cases}$$

Orthonormalize GF matrix
→D and D' are transformed to each other using U.

13-10 Normal Coordinates Belong to Irreducible Representation of Molecular Point Groups.





C_{2v}	E	C_2	$\sigma_v'(xz)$	$\sigma_v(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

C_{2v}	E	C_2	$\sigma_v'(xz)$	$\sigma_v(yz)$
Γ_{3N}	9	-1	1	3

$\Gamma_{3N} = 3A_1 + A_2 + 2B_1 + 3B_2$

$T_x, T_y, T_z \Rightarrow B_1, B_2, A_1$
$R_x, R_y, R_z \Rightarrow B_2, B_1, A_2$
振動 $\Rightarrow A_1, A_1, B_2$

13-11 Selection Rules are Derived from Time-dependent Perturbation Theory.

Time-dependent Schrödinger equation: $\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$, $\Psi_n(r,t) = \psi_n(r)\exp\left[-i\frac{E_n t}{\hbar}\right]$

Perturbation from electromagnetic field: $E = E_0\cos 2\pi\nu t$

$$\hat{H}^{(1)} = -\mu\cdot E = -\mu\cdot E_0\cos 2\pi\nu t$$

Two-state Model: $\Psi_1(t) = \psi_1\exp\left[-i\frac{E_1 t}{\hbar}\right]$, $\Psi_2(t) = \psi_2\exp\left[-i\frac{E_2 t}{\hbar}\right]$

By substituting $\Psi = a_1(t)\Psi_1 + a_2(t)\Psi_2$ into $\hat{H} + \hat{H}^{(1)}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$, we obtain

$$\hat{H}^{(1)}\left(a_1\exp\left[-i\frac{E_1}{\hbar}t\right]\psi_1 + a_2\exp\left[-i\frac{E_2}{\hbar}t\right]\psi_2\right)$$
$$= i\hbar\left(\frac{\partial a_1}{\partial t}\right)\exp\left[-i\frac{E_1}{\hbar}t\right]\psi_1 + i\hbar\left(\frac{\partial a_2}{\partial t}\right)\exp\left[-i\frac{E_2}{\hbar}t\right]\psi_2$$

13-11 Selection Rules are Derived from Time-dependent Perturbation Theory. (cont.)

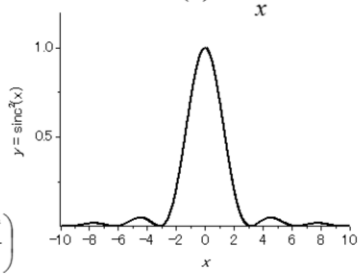
Multiply ψ_2^* and integrate over the space. Then, assuming $a_1(0) = 1$, $a_2(0) = 0$, we obtain :

$$\frac{\partial a_2}{\partial t} = -\frac{i}{\hbar}\exp\left[i\frac{(E_2 - E_1)}{\hbar}t\right]\int \psi_2^* \hat{H}^{(1)}\psi_1 \,\mathrm{d}\tau$$

$$a_2(t) = -\frac{i}{2\hbar}(\mu_z)_{12}E_{0z}\int_0^t \left\{\exp\left[i\frac{(E_2 - E_1 + h\nu)t'}{\hbar}\right] + \exp\left[i\frac{(E_2 - E_1 - h\nu)t'}{\hbar}\right]\right\}\mathrm{d}t'$$

$$= \frac{1}{2}(\mu_z)_{12}E_{0z}\left\{\frac{1 - \exp\left[-i\dfrac{(E_2 - E_1 - h\nu)t}{\hbar}\right]}{E_2 - E_1 - h\nu}\right\}$$

$$\mathrm{sinc}(x) = \frac{\sin x}{x}$$



Here, the transition dipole moment,

$$(\mu_z)_{12} = \int \psi_2^* \mu_z \psi_1 \,\mathrm{d}\tau$$

was defied.

$$a_2^*(t)a_2(t) = \frac{|(\mu_z)_{12}|^2 {E_{0z}}^2 t^2}{4\hbar^2}\mathrm{sinc}^2\left(\frac{(E_2 - E_1 - h\nu)t}{2\hbar}\right)$$

13-12 The selection rule in the Rigid Rotator Approximation is $\Delta J = \pm 1$.

$$(\mu_z)_{J,M;J',M'} = \int\int Y_J^M(\theta,\phi)\,\hat{\mu}_z\,Y_{J'}^{M'}(\theta,\phi)\sin\theta\;\mathrm{d}\theta\mathrm{d}\phi$$

$$\hat{\mu}_z = \mu\cos\theta$$

$$\Rightarrow \quad M' = M,\; J' = J+1 \text{ or } J-1$$

$$\Rightarrow \quad \Delta M = 0,\; \Delta J = \pm 1$$

13-13 The Harmonic Oscillator Selection Rule is $\Delta v = \pm 1$.

$$(\mu_z)_{\upsilon,\upsilon'} = \int N_\upsilon N_{\upsilon'}\,H_{\upsilon'}(\alpha^{1/2}q)e^{-\alpha q^2/2}\hat{\mu}_z\,H_\upsilon(\alpha^{1/2}q)e^{-\alpha q^2/2}\;\mathrm{d}q$$

$$\mu_z = eq$$

$$\Rightarrow \quad \upsilon' = \upsilon+1,\; \upsilon-1$$

$$\Rightarrow \quad \Delta\upsilon = \pm 1$$

13-14 Group Theory is Used to Determine the Infrared Activity of Normal Coordinate Vibrations Problems

$$I_{0\to1} = \int \psi_0(Q_1, Q_2, \cdots Q_{3N-6}) \hat{\mu}_z \psi_1(Q_1, Q_2, \cdots Q_{3N-6})\, dQ_1 dQ_2 \cdots dQ_{3N-6}$$

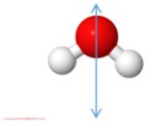
Ground state (totally symmetric) A_1

Excited state (Symmetry depends on normal mode)

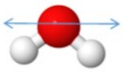
$\mu_x,\ \mu_y,\ \mu_z \Rightarrow B_1, B_2, A_1$

For water case:

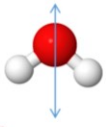
	A_1 (sym. Stretch)	A_1 (bend)	B_2 (asym. Stretch)
B_1 (μ_x)	B_1	B_1	A_2
B_2 (μ_y)	B_2	B_2	A_1
A_1 (μ_z)	A_1	A_1	B_2



A_1 3650 cm^{-1}



B_2 3760 cm^{-1}



A_1 1600 cm^{-1}