

22. Vibrational Spectroscopy of Polyatomic Molecules

A. Classical Motion + Normal Modes



Even if we assume chemical bonds to be simple harmonic oscillators, the overall vibrational motions are complex. Let's first consider the motion classically in Cartesian coordinates.

ξ_i $i = 1, 3N$ Cartesian coordinates of displacement from equilibrium position.

$$2T = \sum_i m_i \dot{\xi}_i^2 \quad V = \underbrace{V_e}_{\substack{\text{can be set} \\ \text{to zero}}} + \sum_i \underbrace{\left(\frac{\partial V}{\partial \xi_i}\right)_e}_0 \xi_i + \frac{1}{2} \sum_{i,j} \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\right)_e \xi_i \xi_j + \dots$$

$$2V = \sum_{i,j} b'_{ij} \xi_i \xi_j$$

Switching to mass-weighted coordinates:

$$\eta_i = \sqrt{m_i} \xi_i \quad \xi_i = m_i^{-1/2} \eta_i$$

$$\therefore 2T = \sum_i \dot{\eta}_i^2 \quad 2V = \sum_{i,j} b_{ij} \eta_i \eta_j \quad b_{ij} = b_{ji}$$

$\mathcal{L} = T - V$; Lagrangian formulation $\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{\eta}_k} - \frac{\partial \mathcal{L}}{\partial \eta_k} = 0 \quad k = 1, 2, 3, \dots, 3N$

$$\frac{\partial \mathcal{L}}{\partial \dot{\eta}_k} = \frac{\partial T}{\partial \dot{\eta}_k} = \dot{\eta}_k \quad \frac{\partial \mathcal{L}}{\partial \eta_k} = -\frac{\partial V}{\partial \eta_k} = -\sum_j b_{kj} \eta_j$$

$$\ddot{\eta}_k + \sum_j b_{kj} \eta_j = 0 \quad k = 1, 2, 3, \dots, 3N$$

Attempt a harmonic solution $\eta_k = \eta_k^0 \sin(\sqrt{\lambda} t + \delta)$

in which all atoms move with same frequency $\omega = \sqrt{\lambda}$ and phase δ .

$$\ddot{\eta}_k = -\lambda \eta_k \quad \therefore -\lambda \eta_k + b_{kk} \eta_k + \sum_{j \neq k} b_{kj} \eta_j = 0$$

Cancelling out the sin terms:

$$-\lambda \eta_k + b_{kk} \eta_k + \sum_{j \neq k} b_{kj} \eta_j = 0$$

$$\sim (b_{kk} - \lambda) \eta_k + \sum_{j \neq k} b_{kj} \eta_j = 0$$

To avoid the trivial solution ($\eta_i = 0$) we set the secular determinant equal to zero:

$$\begin{vmatrix} b_{11} - \lambda & b_{12} & b_{13} & \dots \\ b_{21} & b_{22} - \lambda & & \\ \vdots & & b_{33} - \lambda & \\ & & & \ddots \end{vmatrix} = 0$$

Solution of $|b_{kj} - \lambda \delta_{kj}| = 0$ yields $3N$ roots for λ
 $\sqrt{\lambda} = \omega = 2\pi\nu$ "normal frequencies of vibrations".

They need not be distinct and will be zero for non-vibrational modes. The classical motion is a linear combination of the motions in all modes. It depends on the initial conditions. To obtain the relationships among the η_k in any one mode, substitute the λ into the linear equations.

e.g. $\lambda = \lambda_m$

$$(b_{11} - \lambda_m) \eta_1 + b_{12} \eta_2 + \dots + b_{1,3N} \eta_{3N} = 0$$

$$\vdots$$

$$b_{3N,1} \eta_1 + b_{3N,2} \eta_2 + \dots + (b_{3N,3N} - \lambda_m) \eta_{3N} = 0$$

only $3N-1$ eq. are independent. They lead to ratios of the η_i^0 rather than to absolute values. One can use normalization to obtain a full set.

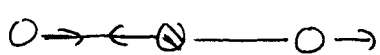
For $\lambda = \lambda_m$, label the η_i^0 as $\eta_{1m}^0, \eta_{2m}^0, \dots, \eta_{3N,m}^0$

Let $l_{km} = N_m \eta_{km}^0 \quad \sum_k l_{km}^2 = 1$

The l_{km} for each mode can be represented by column vectors; e.g.:

$m=1$	$\begin{pmatrix} l_{11} \\ l_{21} \\ l_{31} \\ \vdots \\ l_{3N,1} \end{pmatrix}$	$m=2$	$\begin{pmatrix} l_{12} \\ l_{22} \\ \vdots \\ l_{3N,2} \end{pmatrix}$
$\lambda_1 = \omega_1^2$		$\lambda_2 = \omega_2^2$	
from unitary matrix			

which themselves are often represented by displacement arrows:



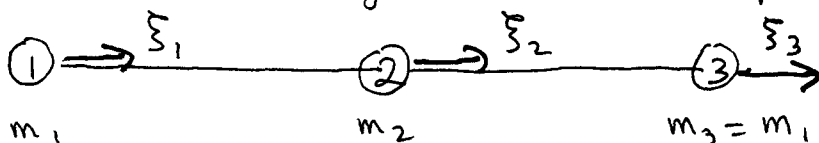
We refer to the collective modes as "normal modes".

The overall motion is $\eta_i = \sum_m A_m \eta_{im}$
i = atomic coordinate

$\eta_i = \sum_m A_m \eta_{im}^0 \sin(\sqrt{\lambda_m} t + \delta_m)$
modes

A Simple Example: the Linear B-A-B Molecule

- 3 coordinates only if motion confined to 1-dimension



displacement from equilibrium

$$2V = k(\xi_2 - \xi_1)^2 + k(\xi_3 - \xi_2)^2$$

$$= k(\xi_1^2 - 2\xi_1\xi_2 + \xi_2^2) + k(\xi_2^2 - 2\xi_2\xi_3 + \xi_3^2)$$

$$2V = k(\xi_1^2 + 2\xi_2^2 + \xi_3^2 - 2\xi_1\xi_2 - 2\xi_2\xi_3)$$

$$2T = m_1 \dot{\xi}_1^2 + m_2 \dot{\xi}_2^2 + m_1 \dot{\xi}_3^2 \quad \eta_i = \sqrt{m_i} \dot{\xi}_i$$

$$2T = \dot{\eta}_1^2 + \dot{\eta}_2^2 + \dot{\eta}_3^2$$

$$2V = \sum_{i,j} b_{ij} \eta_i \eta_j = k \left\{ \frac{\eta_1^2}{m_1} + \frac{2\eta_2^2}{m_2} + \frac{\eta_3^2}{m_1} - \frac{2\eta_1\eta_2}{\sqrt{m_1 m_2}} - \frac{2\eta_2\eta_3}{\sqrt{m_1 m_2}} \right\}$$

$$b_{11} = \frac{k}{m_1} \quad b_{22} = \frac{2k}{m_2} \quad b_{33} = \frac{k}{m_1} \quad b_{13} = b_{31} = 0$$

$$b_{12} = b_{21} = -\frac{k}{\sqrt{m_1 m_2}} = b_{23} = b_{32}$$

$$|b_{ij} - \lambda \delta_{ij}| = 0 = \begin{vmatrix} \frac{k}{m_1} - \lambda & -k/\sqrt{m_1 m_2} & 0 \\ -k/\sqrt{m_1 m_2} & \frac{2k}{m_2} - \lambda & -k/\sqrt{m_1 m_2} \\ 0 & -k/\sqrt{m_1 m_2} & \frac{k}{m_1} - \lambda \end{vmatrix}$$

$$\left(\frac{k}{m_1} - \lambda\right)^2 \left(\frac{2k}{m_2} - \lambda\right) - 2 \left(\frac{k}{m_1} - \lambda\right) \frac{k^2}{m_1 m_2} = 0$$

$$\left(\frac{k}{m_1} - \lambda\right) \left\{ \left(\frac{2k}{m_2} - \lambda\right) \left(\frac{k}{m_1} - \lambda\right) - 2 \frac{k^2}{m_1 m_2} \right\} = 0$$

$$\lambda_1 = \frac{k}{m_1} \quad \left[\lambda^2 - \lambda \left(\frac{k}{m_1} + \frac{2k}{m_2} \right) \right] = 0$$

$$\lambda_3 = 0 \text{ (translation)} \quad \lambda_2 = k \left(\frac{1}{m_1} + \frac{2}{m_2} \right)$$

$$\omega_1 = \sqrt{k/m_1} = 2\pi\nu_1 \quad \omega_2 = \sqrt{k(1/m_1 + 1/m_2)} = 2\pi\nu_2 > \omega_1$$

$$\omega_3 = 0$$

The Motion of The Modes

$$(b_{11} - \lambda) \eta_1^0 + b_{12} \eta_2^0 + b_{13} \eta_3^0 = 0$$

$$b_{12} \eta_1^0 + (b_{22} - \lambda) \eta_2^0 + b_{23} \eta_3^0 = 0$$

$$b_{13} \eta_1^0 + b_{23} \eta_2^0 + (b_{33} - \lambda) \eta_3^0 = 0$$

OR

$$(k/m_1 - \lambda) \eta_1^0 - k/\sqrt{m_1 m_2} \eta_2^0 = 0 \quad (1)$$

$$-k/\sqrt{m_1 m_2} \eta_1^0 + \left(\frac{2k}{m_2} - \lambda\right) \eta_2^0 - \frac{k}{\sqrt{m_1 m_2}} \eta_3^0 = 0 \quad (2)$$

$$-k/\sqrt{m_1 m_2} \eta_2^0 + \left(\frac{k}{m_1} - \lambda\right) \eta_3^0 = 0 \quad (3)$$

$$a) \lambda_3 = 0 \quad (1) \Rightarrow \frac{k}{m_1} \eta_1^0 = \frac{k}{\sqrt{m_1 m_2}} \eta_2^0$$

$$\therefore \eta_1^0 = \eta_3^0$$

$$(3) \Rightarrow \frac{k}{m_1} \eta_3^0 = \frac{k}{\sqrt{m_1 m_2}} \eta_2^0$$

$$\eta_2^0 = \frac{\sqrt{m_1 m_2}}{m_1} \eta_1^0 = \sqrt{m_2/m_1} \eta_1^0$$

$$\eta_i = \sqrt{m_i} \xi_i \quad \xi_1^0 = \xi_3^0; \sqrt{m_2} \xi_2^0 = \sqrt{\frac{m_2}{m_1}} \sqrt{m_1} \xi_1^0 = \xi_2^0$$

$$\xi_1^0 = \xi_2^0 = \xi_3^0 \quad \text{all equal} \quad \xi_i = \xi_i^0 \sin \delta \quad \text{all equal}$$

O \longrightarrow O \longrightarrow O \longrightarrow translation

(CAN SHOW THAT A SPECIFIC SOLN TO EQ'S: ALL $\xi_i = A \pm$)

23. Vibrational Spectroscopy (cont.)

In column vector format, mode 3 = $\frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \approx N \begin{pmatrix} 1 \\ \sqrt{m_1/m_2} \\ 1 \end{pmatrix}$
 (ξ_i : representative) η_i : represent.

b) $\lambda_1 = \frac{k}{m_1}$ (1) $\Rightarrow \eta_2^0 = 0$ (as does (3))
 (2) $\Rightarrow \eta_3^0 = -\eta_1^0$

O_2 , $\xi_2^0 = 0$ $\xi_3^0 = -\xi_1^0$ $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ $\leftarrow \begin{matrix} 0 & \text{---} & \text{---} & 0 \end{matrix} \rightarrow$
 $\rightarrow \quad \leftarrow$
 "symmetric stretch"

c) $\lambda_2 = k \left(\frac{1}{m_1} + \frac{2}{m_2} \right)$

(1) $\Rightarrow -\frac{k \cdot 2}{m_2} \eta_1^0 - \frac{k}{\sqrt{m_1 m_2}} \eta_2^0 = 0$
 (3) $\Rightarrow -\frac{k}{\sqrt{m_1 m_2}} \eta_2^0 - \frac{2k}{m_2} \eta_3^0 = 0$ $\left. \vphantom{\begin{matrix} (1) \\ (3) \end{matrix}} \right\} \eta_1^0 = \eta_3^0$

(1) $\Rightarrow \eta_2^0 = -\frac{2k}{m_2} \frac{\sqrt{m_1 m_2}}{k} \eta_1^0 = -2 \sqrt{m_1/m_2} \eta_1^0$

In terms of ξ_i^0 : $\xi_1^0 = \xi_3^0$ $\sqrt{m_2} \xi_2^0 = -2 \sqrt{\frac{m_1}{m_2}} \sqrt{m_1} \xi_1^0$
 $\therefore \xi_2^0 = -2 \frac{m_1}{m_2} \xi_1^0$

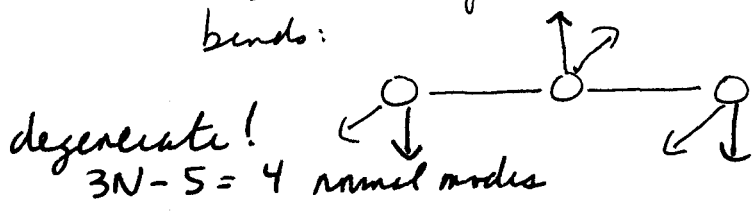
Note that $m_1 \xi_1^0 + m_2 \xi_2^0 + m_1 \xi_3^0 = 2m_1 \xi_1^0 + m_2 \left(\frac{-2m_1}{m_2} \right) \xi_1^0$

$= 0$
 \therefore center of mass invariant (true for all vibrations)

$O \rightarrow \leftarrow \textcircled{\otimes} \rightarrow \leftarrow O \rightarrow$ "asymmetric stretch"

5: representation:
$$N \begin{pmatrix} 1 \\ -2m_1/m_2 \\ 1 \end{pmatrix}$$

In the full 3-D solution, there are also two bends:

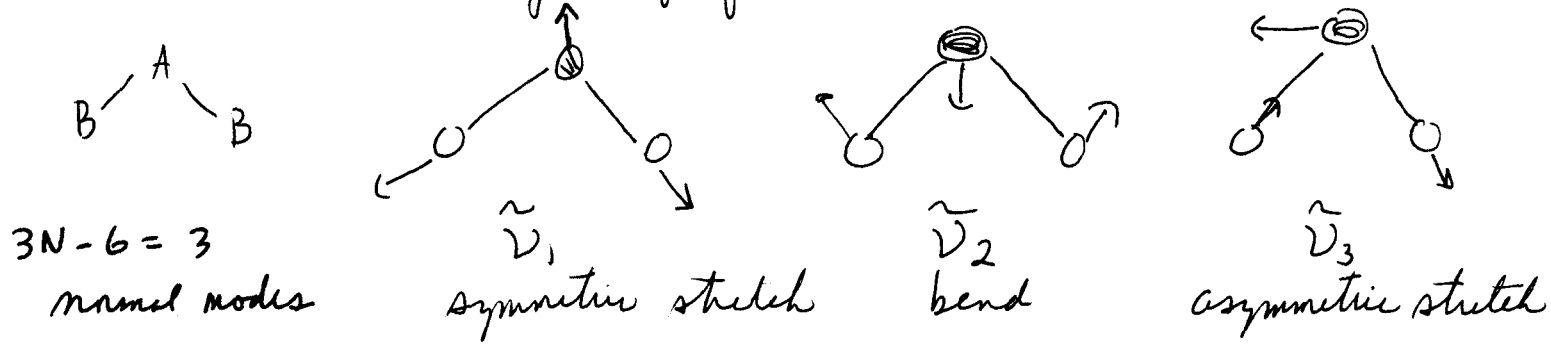


which preserve the center of mass.

degenerate!
 $3N - 5 = 4$ normal modes

There are also two additional translations + 2 rotations.

For a bent triatomic, there are only 3 normal modes + 3 rotational degrees of freedom:



For H_2O , $\hat{\nu}_1 = 3657 \text{ cm}^{-1}$ $\tilde{\nu}_2 = 1595 \text{ cm}^{-1}$, $\hat{\nu}_3 = 3756 \text{ cm}^{-1}$

Normal Coordinates Q_k (See WDC)

- these are linear combinations of mass-weighted η_k coordinates such that no cross terms appear in the kinetic and potential energy terms.

unitary \rightarrow
$$Q_k = \sum_l a_{kl} \eta_l \text{ such that } 2T = \sum_k \dot{Q}_k^2$$

$$+ 2V = \sum_k \lambda_k Q_k^2 \quad (\lambda_k = \omega_k^2)$$

$$- \mathcal{L} = T - V \quad \frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{Q}_k} - \frac{\partial \mathcal{L}}{\partial Q_k} = 0 \Rightarrow \ddot{Q}_k + \lambda_k Q_k = 0$$

$$Q_k = Q_k^0 \sin(\sqrt{\lambda_k} t + \delta_k)$$

It can be shown that $Q_k = \sum_{\ell} \eta_{\ell} \ell_{\ell k}$
 where η_{ℓ} are *nuclear coordinates* and $\ell_{\ell k}$ are *column vectors of normalized normal mode amplitudes in η space*.

Example: Simple Triatomic

$$\lambda_1 = \frac{k}{m_1} \quad \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \quad Q_1 = \frac{1}{\sqrt{2}} (\eta_1 - \eta_3)$$

$$\lambda_2 = k \left(\frac{1}{m_1} + \frac{2}{m_2} \right) \quad Q_2 = \frac{1}{\sqrt{2M}} \begin{pmatrix} \sqrt{m_2} \eta_1 - 2\sqrt{m_1} \eta_2 \\ + \sqrt{m_2} \eta_3 \end{pmatrix}$$

$$\lambda_3 = 0 \quad Q_3 = \frac{1}{\sqrt{M}} (\sqrt{m_1} \eta_1 + \sqrt{m_2} \eta_2 + \sqrt{m_1} \eta_3)$$

Quantum Mechanics

Normal coordinates are exceedingly important because the Hamiltonian is separable:

$$\hat{H} = \sum_k \hat{H}_k(Q_k) \quad \hat{H}_k = \frac{1}{2} \dot{Q}_k^2 + \frac{1}{2} \lambda_k Q_k^2$$

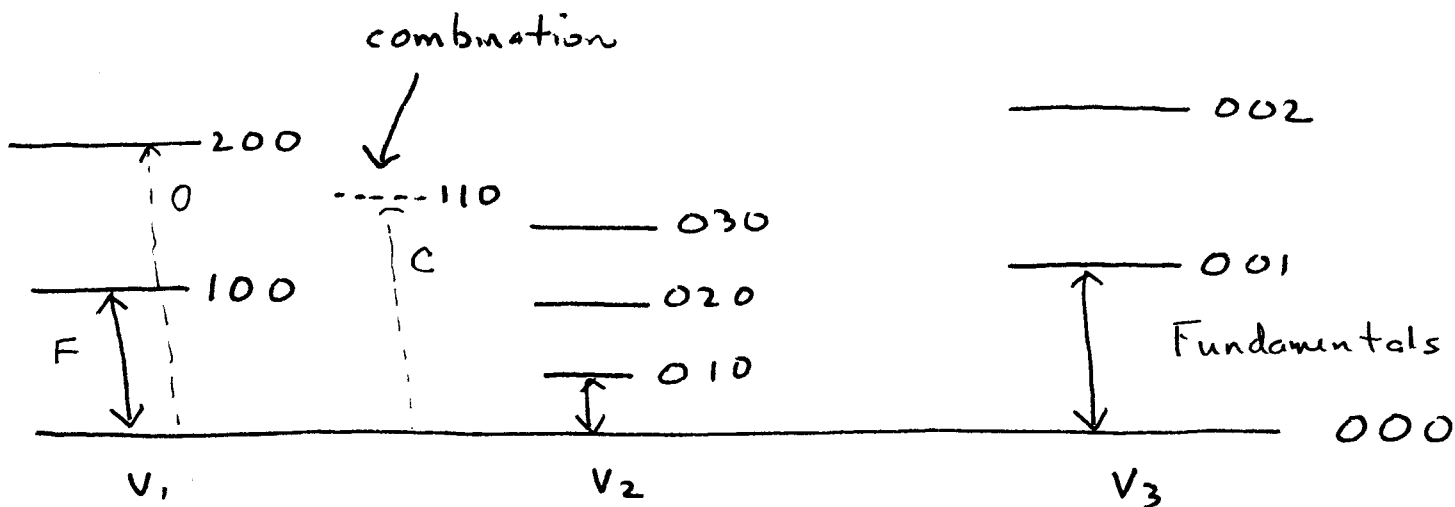
$$\Psi = \prod_k \psi_k(Q_k) \quad E = \sum_k E_k$$

$$\omega_k = \sqrt{\lambda_k} \quad E_k = h\nu_k \left(\nu_k + \frac{1}{2} \right)$$

$$\nu_k = \frac{1}{2\pi} \sqrt{\lambda_k} \quad \psi_{\nu_k} = N_{\nu_k} H_{\nu_k} \left(\frac{Q_k \lambda_k^{1/4}}{\sqrt{h}} \right) e^{-\lambda_k^{1/2} \frac{Q_k^2}{2h}}$$

Levels characterized by sets of quantum numbers $v_1, v_2, v_3, \dots, v_{3N-6}$.

Example: H₂O



Selection Rules

A mode is "IR-active" iff $\left(\frac{\partial \mu_j}{\partial Q_i}\right)_e \neq 0$ $j = x, y, z$

$$\langle \Psi_{v_i'} | \mu_j | \Psi_{v_i} \rangle = \mu_{je} \langle \Psi_{v_i'} | \Psi_{v_i} \rangle + \left(\frac{\partial \mu_j}{\partial Q_i}\right)_e \langle \Psi_{v_i'} | Q_i | \Psi_{v_i} \rangle + \dots$$

p.m. rotation

can use group theory

$$+ \left(\frac{\partial \mu_j}{\partial Q_i}\right)_e \langle \Psi_{v_i'} | Q_i | \Psi_{v_i} \rangle + \dots$$

$\neq 0$ $\Delta v_i = \pm 1$ (e.g. 100-000)

weaker transitions: overtones, combinations
(200-000) (110-000)

Overtone: $\frac{1}{2} \left(\frac{\partial^2 \mu_j}{\partial Q_i^2}\right)_e \langle \Psi_{v_i'} | Q_i^2 | \Psi_{v_i} \rangle$

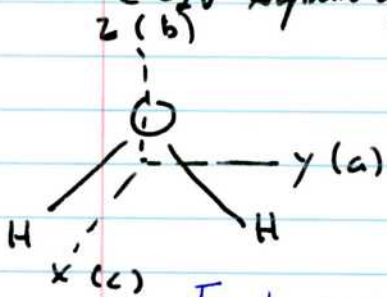
$\Delta v_i = \pm 2$

24. The Symmetry of Normal Modes

Theorem Each normal mode is a basis for an irreducible representation of the point group of the molecule.

[energy invariance $\Rightarrow R \Psi_{\nu_k}$ eigenfunction with eigenvalue E_{ν_k}]

Consider, as an example, the vibrations of the H_2O molecule (C_{2v} symmetry)

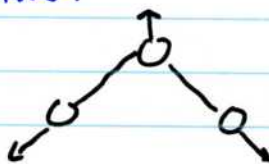


C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

z $\mu_z(b)$
x $\mu_x(c)$
y $\mu_y(a)$

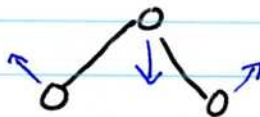
First consider symmetry of modes:

1. Symmetric Stretch



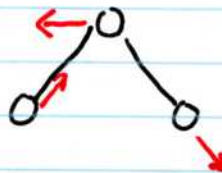
coordinates transform as A_1

2. Bend



coordinates transform as A_1

3. Asymmetric Stretch



coordinates transform as B_2

(antisymmetric to C_2, σ_{xz})

1-D Representations

To determine the symmetry of the actual wave functions $\Psi_{\nu_k}(Q_k)$ we must look only at the Hermite polynomials since the exponentials are always symmetric ($\exp[-\alpha Q_k^2]$)

H_{ν_k} is either symmetric (ν_k even) or transforms as the coordinate (ν_k odd)

Example: ν_3 (asymmetric stretch)

ψ_0, ψ_2, ψ_4 transform as A_1

ψ_1, ψ_3, ψ_5 transform as B_2

Now consider $\langle \psi_{v_i'} | \mu_{a,b,c} | \psi_{v_0} \rangle \neq 0$ iff $\chi(\psi_{v_i'} \otimes \mu_i \otimes \psi_{v_0})$ contains totally symmetric representation.

$\langle \psi_i | \mu_{a,b,c} | \psi_0 \rangle$ fundamental
 ↗ transforms as Q_i ↖ transforms as A_1

Theorem: The fundamental of a mode is IR-active if the mode transforms as a component of the dipole operator

Symmetric Stretch & Bend (A_1)

$A_1 - A_1$ allowed via $\mu_z(b)$ $A_1 \times A_1 \times A_1 = A_1$
 (b-type // rotations)

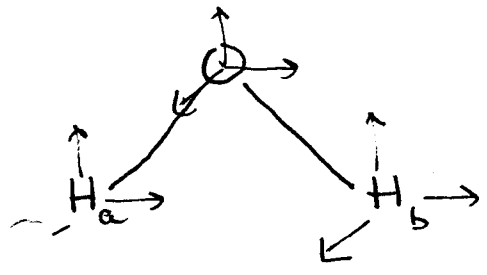
Asymmetric Stretch (B_2)

$B_2 - A_1$ allowed via $\mu_y(c)$ $B_2 \times B_2 \times A_1 = A_1$
 (a-type \perp rotations)

But how determine which are allowed in a large molecule with unknown Q_i ?

A General Method To Determine Normal Mode Representations

- use vectors to determine $3N$ -fold reducible representation & reduce it!



9 basis vectors } to be decomposed into
 3 translations (CM)
 3 rotations
 3 vibrations

- x_0
- y_0
- z_0
- x_{Ha}
- y_{Ha}
- z_{Ha}
- x_{Hb}
- y_{Hb}
- z_{Hb}

To determine the trace of the matrix for each symmetry operation, we need only focus on the diagonal elements:

C_{2v} Elements

E $\begin{pmatrix} 1 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & 1 \end{pmatrix}$ $\chi(E) = 9$

C₂ H_a ↔ H_b nm. diagonal $\begin{matrix} 0 & z \rightarrow z \\ & x \rightarrow -x \\ & y \rightarrow y \end{matrix}$ $\begin{pmatrix} -1 & & \\ & -1 & \\ & & 1 \end{pmatrix} \rightarrow \chi(C_2) = -1$

σ_{xz} H_a ↔ H_b nm. diagonal $\begin{matrix} 0 & z \rightarrow z \\ & x \rightarrow x \\ & y \rightarrow -y \end{matrix}$ $\begin{pmatrix} 1 & & \\ & -1 & \\ & & 1 \end{pmatrix} \rightarrow \chi(\sigma_{xz}) = +1$

σ_{yz} F_n each atom $\begin{matrix} z \rightarrow z \\ x \rightarrow -x \\ y \rightarrow y \end{matrix}$ $3 \times \begin{pmatrix} -1 & & \\ & -1 & \\ & & 1 \end{pmatrix} \Rightarrow \chi(\sigma_{yz}) = +3$

C _{2v}	E	C ₂	σ _{xz}	σ _{yz}		
A ₁	1	1	1	1	z	Q ₁ , Q ₂
A ₂	1	1	-1	-1	R _z	
B ₁	1	-1	1	-1	x, R _y	
B ₂	1	-1	-1	1	y, R _x	Q ₃

$\chi(\Gamma_g) \quad 9 \quad -1 \quad 1 \quad 3 \quad 9$ - dimensional

Via reduction theorem n times + even:

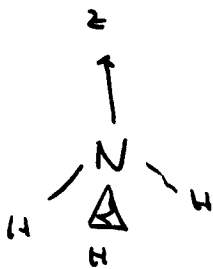
$\chi(\Gamma_g) = 3\chi(A_1) + \chi(A_2) + 2\chi(B_1) + 3\chi(B_2)$

Translation (C of Mass) X, Y, Z : A₁ + B₁ + B₂

Rotation (3 axes) R_x, R_y, R_z : A₂ + B₁ + B₂

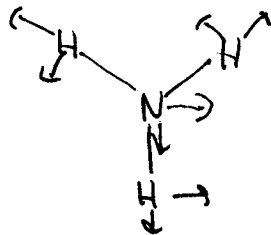
∴ Vibration 2A₁ + B₂ Fundamentals : A₁ allowed by μ_z, B₂ by μ_y.

Example II



C_{3v}

(symmetric top)



C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	(x,y) (R_x, R_y)

$3N - 6 = 6$

vibrational modes

$\Gamma_{12} = 12 \quad 0 \quad 2$

Consider for each atom: Γ_{12} .

For Γ_{12} : $\chi(E) = 12$

σ_v : 2 H's completely exchange. For remaining atoms:

N: $z \rightarrow z$ One H: $z \rightarrow z$
 $x \rightarrow x$ $x \rightarrow x$
 $y \rightarrow -y$ $y \rightarrow -y$

$\chi(\sigma_v) = +2$

(choose simplest plane since x invariant)

C_3 : H vectors all change

N: $z \rightarrow z$

$x \rightarrow \cos \theta x + \dots = \cos 120^\circ x = -\frac{1}{2} x$

$y \rightarrow \dots + \cos \theta y = -\frac{1}{2} y$

$\chi(C_3) = 0$

$h=6 \quad s=3$

$\chi(\Gamma_{12}) = 3\chi(A_1) + \chi(A_2) + 4\chi(E)$

- translation: $\chi(A_1) \quad \chi(E)$
 - rotation: $\chi(A_2) \quad + \chi(E)$

Vibrations $2\chi(A_1) + 2\chi(E)$

2 doubly degenerate pairs

A_1 modes IR active due to $\mu_z (A_1)$ || bands
 $\langle \psi_1 | \mu_z | \psi_0 \rangle$ goes as A_1

Let's consider a degenerate pair.

$$E_1 = h\nu(\nu_1 + 1/2) \quad E_2 = h\nu(\nu_2 + 1/2)$$

$$E = h\nu(\nu_1 + \nu_2 + 1)$$

$$\Psi_{\nu_1, \nu_2} = H_{\nu_1}(Q_1) H_{\nu_2}(Q_2) e^{-\frac{1}{2}(Q_1^2 + Q_2^2)} \dots$$

Think of Q_1 as x and Q_2 as y for simplicity

$$\Psi_{0,0} = N e^{-\underbrace{(x^2 + y^2)}_{\text{goes as } A_1}} \quad \boxed{\text{no degeneracy}}$$

$$\Psi_{1,0} = N x e^{-(x^2 + y^2)} \quad \Psi_{0,1} = N y e^{-(x^2 + y^2)}$$

generally $\Psi = a \Psi_{1,0} + b \Psi_{0,1}$ goes as E

$\mu = c \mu_x + d \mu_y$ goes as E

$$\langle \Psi | \mu | \Psi_{0,0} \rangle \neq 0 ?$$

$$\begin{array}{ccc} | & \setminus & \setminus \\ E & E & A_1 \end{array}$$

$$E \times E = E + A_1 + A_2$$

$$\therefore \langle \Psi | \mu | \Psi_{0,0} \rangle \text{ contains } A_1$$

\therefore can extend simple rules to degenerate set.

All modes IR active

E : 1 bands

Reduction of Reducible Representations

$$N_j = \frac{1}{h} \sum_{i=1}^s N_i \chi_{red}(R_i) \chi_j(R_i)$$

I.

$$h = s = 4$$

$$C_{2v} \quad N_j(\Gamma_4) = \frac{1}{4} \{ 9(\quad) + (-1)(\quad) + 1(\quad) + 3(\quad) \}$$

$$A_1 \quad N_{A_1} = \frac{1}{4} \{ 4 - 1 + 1 + 3 \} = 3$$

$$A_2 \quad N_{A_2} = \frac{1}{4} \{ 9 - 1 - 1 - 3 \} = 1$$

$$B_1 \quad N_{B_1} = \frac{1}{4} \{ 4 + 1 + 1 - 3 \} = 2$$

$$B_2 \quad N_{B_2} = \frac{1}{4} \{ 4 + 1 - 1 + 3 \} = 3$$

$$\chi(\Gamma_4) = 3\chi(A_1) + \chi(A_2) + 2\chi(B_1) + 3\chi(B_2)$$

II. C_{3v}

$$h = 6$$

$$s = 3$$

$$N_j = \frac{1}{6} \left[(1)(12)(\quad) + 2(0)(\quad) + 3(2)(\quad) \right]$$

$$N(A_1) = \frac{1}{6} [12 + 6] = 3$$

$$N(A_2) = \frac{1}{6} [12 - 6] = 1$$

$$N(E) = \frac{1}{6} [24] = 4$$

$$\chi(\Gamma_{12}) = 3\chi(A_1) + \chi(A_2) + 4\chi(E)$$

