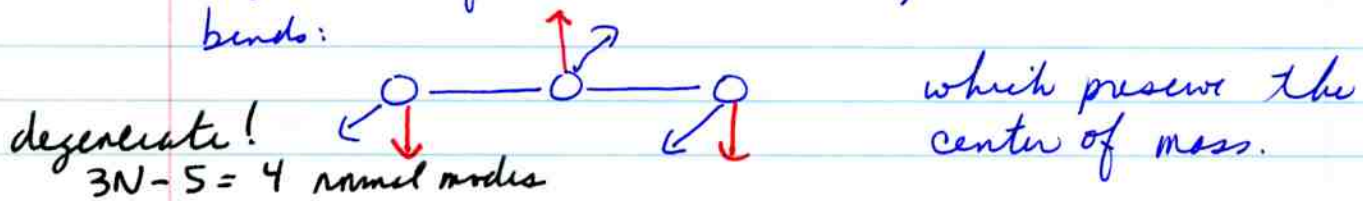


$\leftarrow \text{O} \rightarrow \quad \leftarrow \text{O} \rightarrow \quad \leftarrow \text{O} \rightarrow$ "asymmetric stretch"

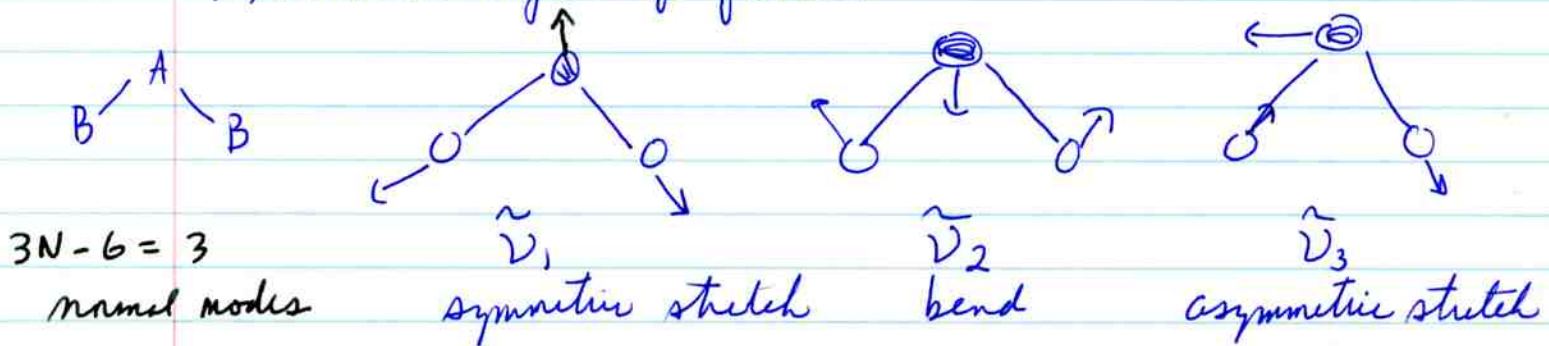
3rd representation:
$$N \begin{pmatrix} 1 \\ -2m_1/m_2 \\ 1 \end{pmatrix}$$

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



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

Normal Coordinates Q_k (see WDC)

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

$Q_k = \sum_l r_l b_{lk}$ such that $2T = \sum_k \dot{Q}_k^2$

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

Sum of HO's
($m=1$)

unitary

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

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

It can be shown that $Q_k = \sum_{\ell} \eta_{\ell} \ell_{\ell k}$
 nuclear coordinates \downarrow
 column vector 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:

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

$$\Psi = \prod_k \psi_k(Q_k) \quad E = \sum_k E_k \quad \text{" } P_k^2$$

$$\omega_k = \sqrt{\lambda_k}$$

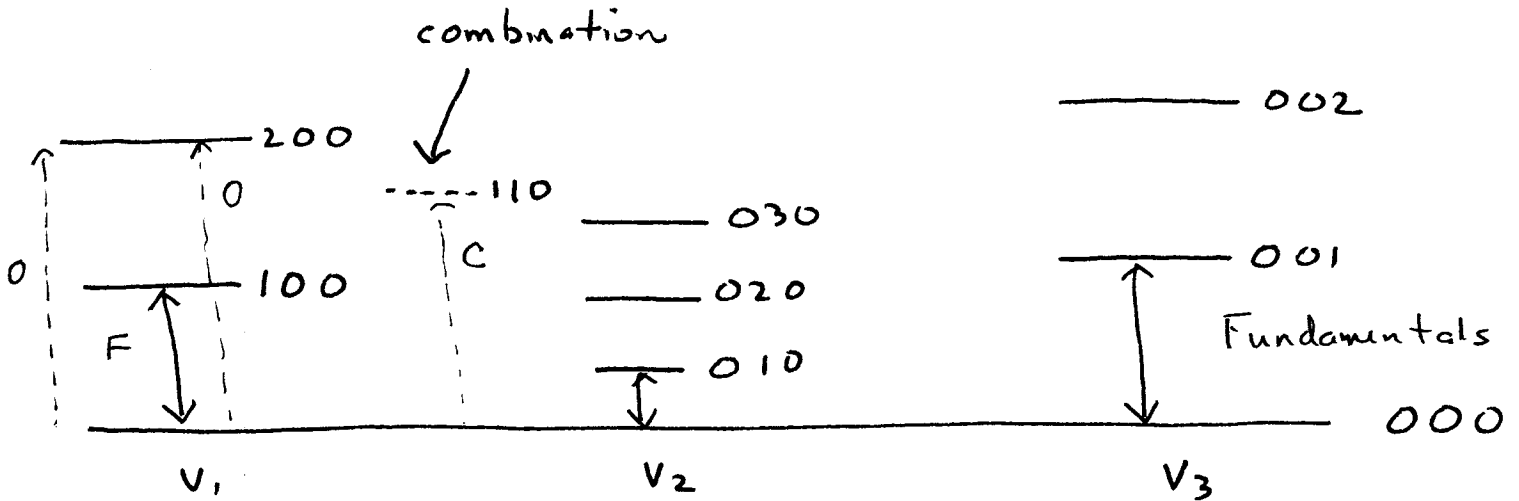
$$E_k = h\nu_k \left(\nu_k + \frac{1}{2} \right)$$

$$\nu_k = \frac{1}{2\pi} \sqrt{\lambda_k}$$

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

Levels characterise 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 $\left(\frac{\partial \mu_j}{\partial Q_i}\right)_e \neq 0$ $j = x, y, z$

$$\langle \psi_{v_i}' | \mu_j | \psi_{v_i} \rangle = \mu_{je} \langle \psi_{v_i}' | \psi_{v_i} \rangle \quad \text{pure rotation}$$

δ_{v_i', v_i}

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

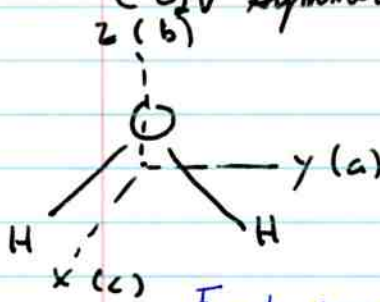
$\Delta v_i = \pm 2$

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 $\Rightarrow R \Psi_{V_k}$ eigenfunction with eigenvalue E_{V_k}]

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

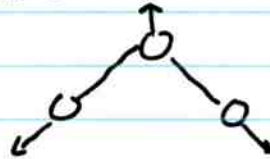


C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

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

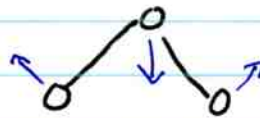
First consider symmetry of modes:

1. Symmetric Stretch



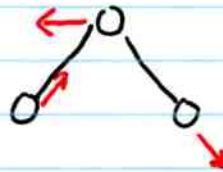
coordinates transform as A_1

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 $\Psi_{V_k}(Q_k)$ we must look only at the Hermite polynomials since the exponentials are always symmetric ($\exp[-\alpha Q_k^2]$)

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

Example: v_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 $\langle \psi_{v_i'} | \mu_{a,b,c} | \psi_{v_i} \rangle \neq 0$ iff $\chi(\psi_{v_i'} \otimes \mu_j \otimes \psi_{v_i})$ contains totally symmetric representation.

$\langle \psi_i | \mu_{a,b,c} | \psi_0 \rangle$ fundamental
 transforms as Q_i (left arrow)
 transforms as A_1 (right arrow)

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 $\mu_z(b)$ (b -type \parallel rotations) $A_1 \times A_1 \times A_1 = A_1$

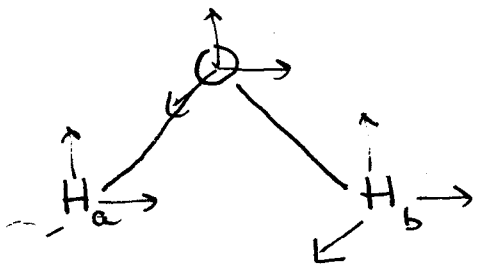
Asymmetric Stretch (B_2)

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

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

$$\begin{pmatrix} x_0 \\ y_0 \\ z_0 \\ x_{H_a} \\ y_{H_a} \\ z_{H_a} \\ x_{H_b} \\ y_{H_b} \\ z_{H_b} \end{pmatrix}$$

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

C_{2v} Elements

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

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

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

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

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

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

Via reduction theorem a trial + error:

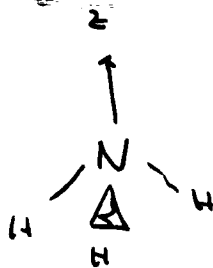
$\chi(\Gamma_g) = 3\chi(A_1) + \chi(A_2) + 2\chi(B_1) + 3\chi(B_2)$

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

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

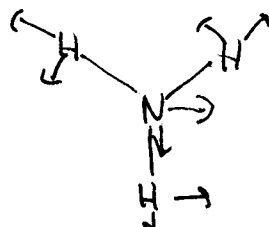
∴ Vibrons 2A₁ + B₂ Fundamentals : A₁ allowed by μ_z, B₂ by μ_y.

Example II



C_{3v}

(symmetric top)



C _{3v}	E	2C ₃	3σ _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

χ(Γ₁₂) = 12 0 2

Consider for each atom: Γ₁₂.

For Γ₁₂: χ(E) = 12

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

N: z → z One H: z → z
 x → x x → x
 y → -y y → -y

χ(σ_v) = +2

(choose simplest plane since x invariant)

C₃: H vectors all change

N: z → z

x → cos θ x + ... = cos 120° x = -1/2 x
 y → + cos γ = -1/2 y

χ(C₃) = 0

h = 6 s = 3

χ(Γ₁₂) = 3χ(A₁) + χ(A₂) + 4χ(E)

- translation: χ(A₁) χ(E)
 - rotation: χ(A₂) + χ(E)

Vibrations: 2χ(A₁) + 2χ(E)

2 doubly degenerate pairs

A₁ modes IR active due to μ_z(A₁) || bands
 <ψ₁ | μ_z | ψ₀> goes as A₁

Reduction of Reducible Representations

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

I.

$$h = s = 4$$

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

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

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

$$B_1 \quad N_{B_1} = \frac{1}{4} \{ 9 + 1 + 1 - 3 \} = 2$$

$$B_2 \quad N_{B_2} = \frac{1}{4} \{ 9 + 1 - 1 + 3 \} = 3$$

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

II. C_{3v}
 $h = 6$
 $s = 3$

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

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

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

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

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

Let's consider a degenerate pair:

$$E_1 = h\nu (v_1 + 1/2) \quad E_2 = h\nu (v_2 + 1/2)$$

$$E = h\nu (v_1 + v_2 + 1)$$

$$\Psi_{v_1 v_2} = N H_{v_1}(Q_1) H_{v_2}(Q_2) e^{-(Q_1^2 + Q_2^2)}$$

Think of Q_1 as x Q_2 as y for simplicity
($x+y$ transform as E).

$$Q_1^2 + Q_2^2 \quad ? \quad x^2 + y^2 = \text{Length}^2 \quad \text{goes as } A_1$$

$$\sigma_v: \quad x \rightarrow x \quad y \rightarrow -y \quad x^2 \rightarrow x^2 \quad y^2 \rightarrow y^2$$

$$C_3 \quad x \rightarrow -1/2 x + \sqrt{3}/2 y$$

$$y \rightarrow -\sqrt{3}/2 x + 1/2 y$$

$$x^2 + y^2 \rightarrow x^2 + y^2 \quad A_1 \text{ ignore}$$

$$\Psi_{00} = N e^{-(x^2 + y^2)} \quad A_1$$

$$\Psi_{10} = N x e^{-(x^2 + y^2)} \quad \Psi_{01} = N y e^{-(x^2 + y^2)}$$

$$\begin{pmatrix} \Psi_{10} \\ \Psi_{01} \end{pmatrix} \text{ basis for } E \text{ as are } \begin{pmatrix} x \\ y \end{pmatrix}$$

$$\langle \begin{pmatrix} \Psi_{10} \\ \Psi_{01} \end{pmatrix} | \mu_i | \Psi_{00} \rangle \neq 0$$

$$\underbrace{\quad}_E \quad x \quad \underbrace{\quad}_E \quad \underbrace{\quad}_{A_1}$$

$$\underbrace{\quad}_E + A_1 + A_2 \quad A_1 \times A_1 = A_1$$

\therefore E modes IR active \perp bands