

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:

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

$$\therefore 2T = \sum_i \dot{\eta}_i^2 \quad 2V = \sum_{i,j} b_{ij} \eta_i \eta_j \quad b_{ij} = b'_{ij}$$

$\mathcal{L} = T - V$; 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:

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

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 nm. 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.

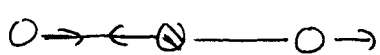
For $\lambda = \lambda_m$, label the η_i^0 as $\eta_{1m}^0, \eta_{2m}^0, \dots, \eta_{3N,m}^0$

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:



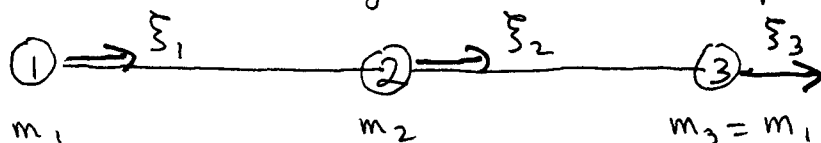
We refer to the collective modes as "normal modes".

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 = $\frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \propto N \begin{pmatrix} 1 \\ \sqrt{m_1/m_2} \\ 1 \end{pmatrix}$
 (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 , $\xi_2^0 = 0$ $\xi_3^0 = -\xi_1^0$ $\frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix}$ $\leftarrow \begin{array}{c} \text{O} - \text{O} - \text{O} \\ \rightarrow \quad \leftarrow \end{array} \right.$
 "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) $\Rightarrow \eta_2^0 = -\frac{2k}{m_2} \frac{\sqrt{m_1 m_2}}{k} \eta_1^0 = -2 \sqrt{\frac{m_1}{m_2}} \eta_1^0$

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

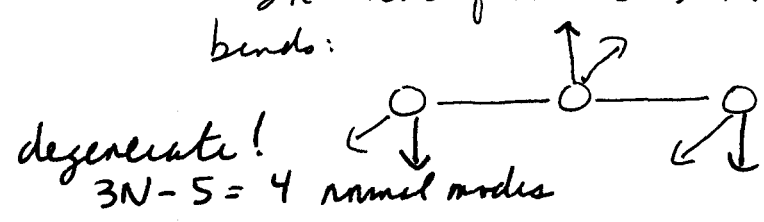
Note that $m_1 \xi_1^0 + m_2 \xi_2^0 + m_1 \xi_3^0 = 2m_1 \xi_1^0 + m_2 \left(-\frac{2m_1}{m_2} \right) \xi_1^0$

$= 0$
 \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:

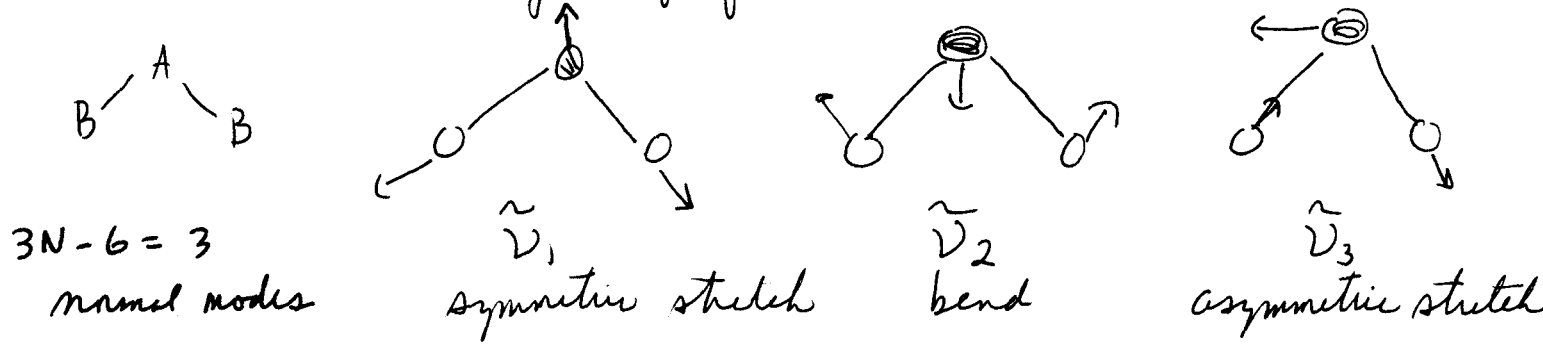


which preserve the center of mass.

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:



$3N - 6 = 3$
normal modes

$\tilde{\nu}_1$
symmetric stretch

$\tilde{\nu}_2$
bend

$\tilde{\nu}_3$
asymmetric stretch

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.

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

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

unitary

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

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

It can be shown that $Q_k = \sum_{\ell} \eta_{\ell} \rho_{\ell k}$
 where η_{ℓ} are nuclear coordinates and $\rho_{\ell k}$ 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:

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

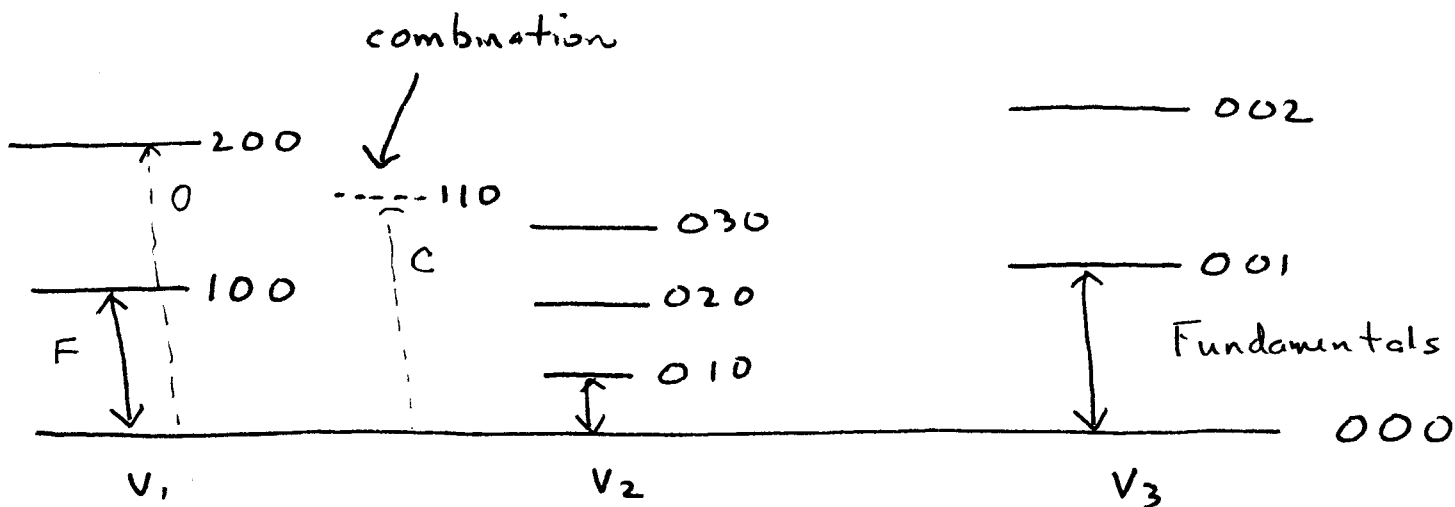
$$\Psi = \prod_k \psi_k(Q_k) \quad E = \sum_k E_k$$

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

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

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

$\Delta v_i = \pm 2$

