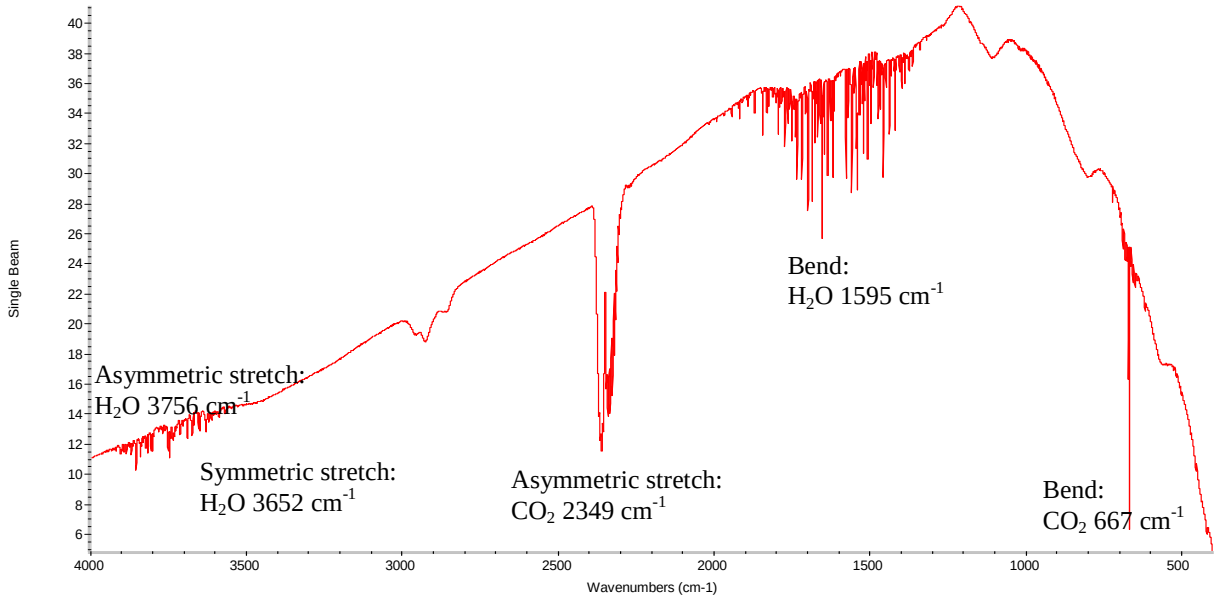
Classical Normal Mode Analysis: Harmonic Approximation

Each absorption in a vibrational spectrum corresponds to a normal mode.

Characteristics of Normal Modes

1. Each normal mode acts like a simple harmonic oscillator.
2. A normal mode is a concerted motion of many atoms.
3. The Center of mass doesn't move.
4. All atoms pass through their equilibrium positions at the same time.
5. Normal modes are independent; they don't interact.

Carbon Dioxide in Air



$$V = \frac{1}{2} k x^2 \qquad F = -\frac{dV}{dx} = -kx \qquad k = \frac{d^2 V}{dx^2} \qquad (1)$$

$$F = ma \qquad m \frac{d^2 x}{dt^2} = -kx \qquad (2)$$

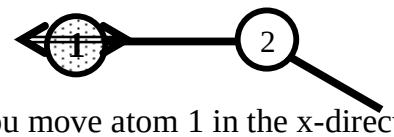
$$x = A \sin(2\pi\nu t) \qquad \frac{d^2 x}{dt^2} = -4\pi^2\nu^2 x \qquad -4\pi^2\nu^2 m x = -kx \qquad (3)$$

Coordinates:

Atom i: $X_i, Y_i, Z_i,$ Displacements: $x_i = X_i - X_{i,eq}, \quad y_i = Y_i - Y_{i,eq}$

Calculate the potential energy $V(x_1, y_1, z_1, x_2, y_2, z_2, x_3, y_3, z_3, \ldots, x_N, y_N, z_N)$

$$\frac{\partial^2 V}{\partial x_1^2} = k^{11}_{xx}$$



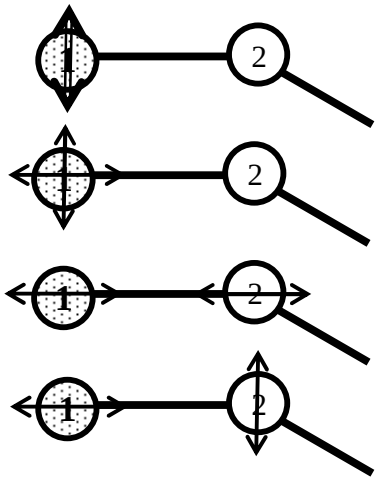
change of the force on atom 1 in the x-direction when you move atom 1 in the x-direction

$\frac{\partial^2 V}{\partial y_1^2} = k_{yy}^{11}$ same atom same direction

$\frac{\partial^2 V}{\partial x_1 \partial y_1} = k_{xy}^{11}$ same atom different directions

$\frac{\partial^2 V}{\partial x_1 \partial x_2} = k_{xx}^{12}$ different atom same direction

$\frac{\partial^2 V}{\partial x_1 \partial y_2} = k_{xy}^{12}$ different atom and direction



change of the force on atom 1 in the x-direction when you move atom 2 in the y-direction

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$$-4\pi^2\nu^2 m_1x_1 = -k_{xx}^{11}x_1 - k_{xy}^{11}y_1 - k_{xz}^{11}z_1 - k_{xx}^{12}x_2 - k_{xy}^{12}y_2 - \ldots - k_{xz}^{1N}z_N \quad (4)$$

$$-4\pi^2\nu^2 m_1y_1 = -k_{yx}^{11}x_1 - k_{yy}^{11}y_1 - k_{yz}^{11}z_1 - k_{yx}^{12}x_2 - k_{yy}^{12}y_2 - \ldots - k_{yz}^{1N}z_N$$

:

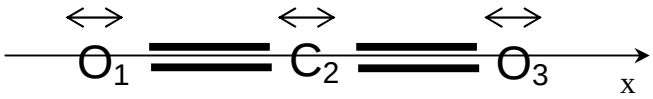
$$-4\pi^2\nu^2 m_2x_2 = -k_{xx}^{21}x_1 - k_{xy}^{21}y_1 - k_{xz}^{21}z_1 - k_{xx}^{22}x_2 - k_{xy}^{22}y_2 - \ldots - k_{xz}^{2N}z_N$$

:

$$-4\pi^2\nu^2 m_Nz_N = -k_{zx}^{N1}x_1 - k_{zy}^{N1}y_1 - k_{zx}^{N1}z_1 - k_{zx}^{N2}x_2 - k_{zy}^{N2}y_2 - \ldots - k_{zz}^{NN}z_N$$

Total of 3Nx3N terms on the right.

For example: triatomic, only allow vibration along x-axis:



$$-4\pi^2\nu^2 m_1x_1 = -k_{xx}^{11}x_1 - k_{xx}^{12}x_2 - k_{xx}^{13}x_3 \quad (5)$$

$$-4\pi^2\nu^2 m_2x_2 = -k_{xx}^{21}x_1 - k_{xx}^{22}x_2 - k_{xx}^{23}x_3 \quad (6)$$

$$-4\pi^2\nu^2 m_3x_3 = -k_{xx}^{31}x_1 - k_{xx}^{32}x_2 - k_{xx}^{33}x_3 \quad (7)$$

Use simultaneous equation solver, or…..

Convert to mass weighted coordinates and mass weighted force constants:

$$\tilde{x}_1 = \sqrt{m_1}\,x_1 \qquad \tilde{x}_2 = \sqrt{m_2}\,x_2 \qquad \tilde{k}_{xx}^{12} = \frac{k_{xx}^{12}}{\sqrt{m_1}\sqrt{m_2}} \quad (8)$$

then in the new coordinates:

$$-4\pi^2\nu^2\,\tilde{x}_1 = -\tilde{k}^{11}_{xx}\tilde{x}_1 - \tilde{k}^{12}_{xx}\tilde{x}_2 - \tilde{k}^{13}_{xx}\tilde{x}_3 \qquad (9)$$

$$-4\pi^2\nu^2\,\tilde{x}_2 = -\tilde{k}^{21}_{xx}\tilde{x}_1 - \tilde{k}^{22}_{xx}\tilde{x}_2 - \tilde{k}^{23}_{xx}\tilde{x}_3 \qquad (10)$$

$$-4\pi^2\nu^2\,\tilde{x}_3 = -\tilde{k}^{31}_{xx}\tilde{x}_1 - \tilde{k}^{32}_{xx}\tilde{x}_2 - \tilde{k}^{33}_{xx}\tilde{x}_3 \qquad (11)$$

$$-4\pi^2\nu^2\sqrt{m_1}\,x_1 = -\frac{k^{11}_{xx}}{\sqrt{m_1}\sqrt{m_1}}\sqrt{m_1}\,x_1 - \frac{k^{12}_{xx}}{\sqrt{m_1}\sqrt{m_2}}\sqrt{m_2}\,x_2 - \frac{k^{13}_{xx}}{\sqrt{m_1}\sqrt{m_3}}\sqrt{m_3}\,x_3 \qquad (12)$$

Mass weighted force constants and mass weighted displacements:

$$-\begin{pmatrix} \frac{k^{11}_{xx}}{\sqrt{m_1}\sqrt{m_1}} & \frac{k^{12}_{xx}}{\sqrt{m_1}\sqrt{m_2}} & \frac{k^{13}_{xx}}{\sqrt{m_1}\sqrt{m_3}} \\ \frac{k^{21}_{xx}}{\sqrt{m_2}\sqrt{m_1}} & \frac{k^{22}_{xx}}{\sqrt{m_2}\sqrt{m_2}} & \frac{k^{23}_{xx}}{\sqrt{m_2}\sqrt{m_3}} \\ \frac{k^{31}_{xx}}{\sqrt{m_3}\sqrt{m_1}} & \frac{k^{32}_{xx}}{\sqrt{m_3}\sqrt{m_2}} & \frac{k^{33}_{xx}}{\sqrt{m_3}\sqrt{m_3}} \end{pmatrix} \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix} = -4\pi^2\nu^2 \begin{pmatrix} \tilde{x}_1 \\ \tilde{x}_2 \\ \tilde{x}_3 \end{pmatrix} \qquad (13)$$

gives a symmetric matrix. This is an eigenvalue-eigenvector equation. The eigenvalues are the squared normal mode frequencies. The eigenvectors are the mass weighted normal coordinate displacements:

$$x_i = \frac{\tilde{x}_i}{\sqrt{m_i}}\sin(2\pi\nu t) \qquad y_i = \frac{\tilde{y}_i}{\sqrt{m_i}}\sin(2\pi\nu t) \qquad z_i = \frac{\tilde{z}_i}{\sqrt{m_i}}\sin(2\pi\nu t)$$

Units: $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$ or $4\pi^2\nu^2 = \frac{k}{m}$ with k in N m^{-1}, μ in kg molecule^{-1}

To convert to wavenumbers: $\tilde{\nu} = \frac{1}{\lambda}$ or $\nu = \frac{c}{\lambda} = c\tilde{\nu}$

with $\tilde{\nu}$ in cm^{-1}, c in cm s^{-1}, and m in g mol^{-1} :

$$\frac{4\pi^2c^2\tilde{\nu}^2}{1000\ \text{g/kg}\ N_A} = \frac{k}{m} \qquad \text{or} \qquad \tilde{\nu}^2 = \frac{k/m}{5.8921\text{x}10^{-5}}$$

Carbon Dioxide Stretches: Sym 1340 cm^{-1} Asym 2349 cm^{-1}

By symmetry : $k_{xx}^{11} = k_{xx}^{33}$ $k_{xx}^{12} = k_{xx}^{23}$

Guesses: $k_{xx}^{11} = 1600\ \text{N m}^{-1}$

$k_{xx}^{12} = -k_{xx}^{11}$ $k_{xx}^{22} = 2\,k_{xx}^{11} = 3200\ \text{N m}^{-1}$ $k_{xx}^{13} = 0$

$$\begin{array}{c} \\ O_1 \\ C_2 \\ O_3 \end{array} \begin{array}{c} \begin{array}{ccc} O_1 & C_2 & O_3 \end{array} \\ \begin{pmatrix} \frac{1600}{\sqrt{16}\sqrt{16}} & -\frac{1600}{\sqrt{16}\sqrt{12}} & 0 \\ -\frac{1600}{\sqrt{12}\sqrt{16}} & \frac{3200}{\sqrt{12}\sqrt{12}} & -\frac{1600}{\sqrt{12}\sqrt{16}} \\ 0 & -\frac{1600}{\sqrt{16}\sqrt{12}} & \frac{1600}{\sqrt{16}\sqrt{16}} \end{pmatrix} \end{array} = \begin{pmatrix} -100 & 115.47 & 0 \\ 115.47 & -266.67 & 115.47 \\ 0 & 115.47 & -100 \end{pmatrix}$$

Eigenvector 1: E=0.00175039 ≈ 0

Eigenvector 2: E= -100
-0.707107
0
0.707107

Eigenvector 3: E= -366.662
-0.369279
0.852799
-0.369279

Symmetric stretch:

$$\tilde{\nu} = \sqrt{\frac{100}{5.892\text{x}10^{-5}}} = 1303\ \text{cm}^{-1}$$

Asymmetric stretch:

$$\tilde{\nu} = \sqrt{\frac{366.66}{5.892\text{x}10^{-5}}} = 2495\ \text{cm}^{-1}$$

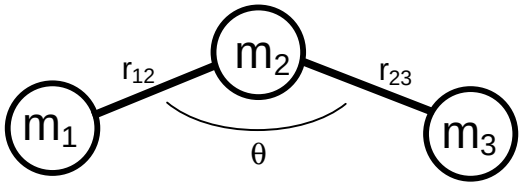
(for about 5% errors)

<u>Valence Force Field</u> For $m_1 = m_3$

$q_1 = r_{12} - r_o$

$q_2 = r_{23} - r_o$

$\delta = \theta - \theta_o$



$$V = \frac{1}{2} k_1 q_1^2 + \frac{1}{2} k_1 q_2^2 + k_\delta \delta^2$$

$$4\pi^2 \nu_{asym}^2 = \left(1 + \frac{2m_1}{m_2} \sin^2 \frac{\theta_o}{2}\right) \frac{k_1}{m_1} \quad (14)$$

$$4\pi^2 (\nu_{sym}^2 + \nu_{bnd}^2) = \left(1 + \frac{2m_1}{m_2} \cos^2 \frac{\theta_o}{2}\right) \frac{k_1}{m_1} + \frac{2}{m_1} \left(1 + \frac{2m_1}{m_2} \sin^2 \frac{\theta_o}{2}\right) \frac{k_\delta}{r_o^2} \quad (15)$$

$$16\pi^4 (\nu_{sym}^2\, \nu_{bnd}^2) = 2 \left(1 + \frac{2m_1}{m_2}\right) \frac{k_1}{m_1^2} \frac{k_\delta}{r_o^2} \quad (16)$$

G. Herzberg, “Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules,” Van Nostrand, Princeton, N. J., 1945.