5.80 Small-Molecule Spectroscopy and Dynamics
Fall 2008

Lecture #28: Polyatomic Vibrations IV: Symmetry

What is a normal mode?

all atoms undergoing oscillation at the same frequency and phase and with amplitudes determined by the eigenvectors of the **GF** matrix.

$$|Q\rangle = \mathbf{L}^{-1}|S\rangle \qquad \underset{\sim}{s}_{t\alpha} = \left|s_{t\alpha}(t)\right| \hat{e}_{\underset{\sim}{s}_{t\alpha}}$$

we built in specific relative lengths of displacements

$$\left|s_{t\alpha}(t)\right| \downarrow \left|s_{t\alpha}(t)\right|\cos(\lambda t + \delta)$$

$$\text{e.g.} \qquad Q_j = \sum_i \mathbf{L}^{-1}_{ji} S_i$$

eigenvectors are rows of $\mathbf{L}^{-1}$

If we represent S_i by a set of $\underset{\sim}{s}_{i\alpha}$ vectors of prescribed lengths and directions, then $\mathbf{L}^{-1}$ tells us how to weight and add the vectors at each atom associated with the various internal displacements

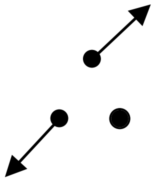
e.g. H_2O (page 4 of H_2O example in 4/24/96 notes)

$Q_1 = 0.685\,(S_2 - S_1)$

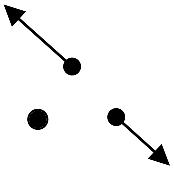
$Q_2 = 0.695\,(S_1 + S_2) + 0.037S_3$

$Q_3 = 0.655S_3$

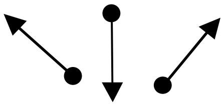
$S_1 =$



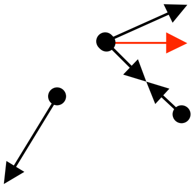
$S_2 =$



$S_3 =$



Q_1 =



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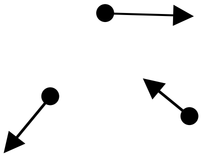
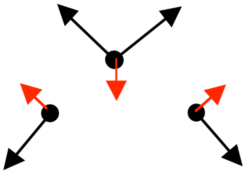


Q_2 =



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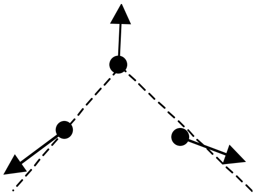
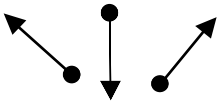


Q_3 =



names of normal modes

from pictures or from equations?

Note that each of the **pictures** involves some change of bond angle. So which mode is the "bend"?

Q_1 involves dominantly a compression of one bond and an expansion of the other equivalent one;

Q_2 involves dominantly two equivalent bonds expanding and contracting in phase;

Q_3 pure internal bend.

equations: $S_1 \pm S_2$ "symmetric" "antisymmetric"

mixed character — no S_3 in Q_1

some S_3 character in Q_2

Why no $(S_1 + S_2)$ character in Q_3? Actually, there is some, but very small.

NON-LECTURE

$$\mathbf{L}^{-1}\mathbf{L} \overset{?}{=} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \left(\begin{array}{ccc} -0.685 & +0.685 & 0 \\ 0.695 & 0.695 & 0.037 \\ \multicolumn{2}{c}{\underbrace{0 \qquad\qquad\qquad 0}_{\boxed{\text{actually small, not 0 by symmetry}}}} & 0.655 \end{array}\right) \begin{pmatrix} -0.732 & 0.720 & -0.041 \\ 0.732 & 0.720 & -0.041 \\ 0.000 & -0.001 & 1.529 \end{pmatrix}$$

$$= \begin{pmatrix} 1.003 & 0 & 0 \\ 0 & 1.001 & 0.004 \\ 0 & 0.001 & 1.001 \end{pmatrix}$$

Why are there mixtures of internal coordinates in the normal coordinates?

This perturbation theory kind of argument is OK for symmetric matrix.

Some are due solely to symmetry.
Others are due to the structure of the **F** and **G** matrices. The detailed character of the modes depends on ratios of off diagonal matrix elements of **GF** to differences between diagonal values, just as for **H** (even though **GF** is not symmetric).

Best to see the cause of mixed character normal modes by going to symmetrized internal coordinates.

Let $|\tilde{S}\rangle = \mathbf{U}|S\rangle$

$$\mathbf{U} = \begin{pmatrix} 2^{-1/2} & 2^{-1/2} & 0 \\ 2^{-1/2} & -2^{-1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\langle S|\mathbf{F}|S\rangle = \langle S|\overbrace{\mathbf{U}^{\dagger}\mathbf{U}}^{1}\mathbf{F}\overbrace{\mathbf{U}^{\dagger}\mathbf{U}}^{1}|S\rangle = \langle\tilde{S}|\tilde{\mathbf{F}}|\tilde{S}\rangle$$

similarly $\tilde{\mathbf{F}} = \mathbf{UFU}^\dagger$
$\tilde{\mathbf{G}} = \mathbf{UGU}^\dagger$

$$\mathbf{F} = \begin{pmatrix} 8.454 \text{ md/Å} & -0.100 \text{ md/Å} & 0.224 \text{ md} \\ -0.100 \text{ md/Å} & 8.454 \text{ md/Å} & 0.244 \text{ md} \\ 0.224 \text{ md} & 0.224 \text{ md} & 0.697 \text{ md·Å} \end{pmatrix}$$

(md = millidyne, dyne is the cgs unit of force, now illegal.)

Note that each term in expansion of determinant |**F**| has same units: md^3/Å even though individual terms in **F** do not.

An easy way for humans, not computers, to compute new $\tilde{\mathbf{F}}$ matrix is term by term rather than multiplying out.

$$\tilde{\mathbf{F}}_{\mathbf{11}} = 2^{-1/2}\left\langle (S_1 + S_2) |\mathbf{F}| (S_1 + S_2) \right\rangle 2^{-1/2}$$

$$= \frac{1}{2}\left[F_{11} + F_{22} + 2F_{12}\right] = 8.454 \text{md/Å} - 0.200 \text{md/Å}$$

$$= 8.254 \text{md/Å}$$

$$\tilde{\mathbf{F}}_{\mathbf{12}} = \frac{1}{2}\left\langle (S_1 - S_2) |\mathbf{F}| (S_1 + S_2) \right\rangle = \frac{1}{2}\left[F_{11} - F_{22} + F_{12} - F_{21}\right] = 0$$

etc.

$$\tilde{\mathbf{F}} = \begin{pmatrix} 8.254 \text{md/Å} & 0 & 0.317 \text{md} \\ 0 & 8.654 \text{md/Å} & 0 \\ 0.317 \text{md} & 0 & 0.697 \text{md·Å} \end{pmatrix}$$

rearrange

$$\tilde{\mathbf{F}} = \begin{array}{cc} \begin{pmatrix} 8.254\,\text{md}/\text{Å} & 0.317\,\text{md} & 0 \\ \text{sym} & 0.697\,\text{md}\cdot\text{Å} & 0 \\ 0 & 0 & 8.654\,\text{md}/\text{Å} \end{pmatrix} & \begin{matrix} 1 \\ 3 \\ 2 \end{matrix} \end{array}$$

Similarly for

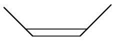
$$\mathbf{G} = \begin{pmatrix} 1.054\ \text{amu}^{-1} & -0.015\ \text{amu}^{-1} & -0.063\ \text{amu}^{-1}\text{Å}^{-1} \\ -0.015\ \text{amu}^{-1} & 1.054\ \text{amu}^{-1} & -0.063\ \text{amu}^{-1}\text{Å}^{-1} \\ -0.063\ \text{amu}^{-1} & -0.063\ \text{amu}^{-1}\text{Å}^{-1} & 2.336\ \text{amu}^{-1}\text{Å}^{-2} \end{pmatrix}$$

and, in re-arranged form

$$\tilde{\mathbf{G}} = \begin{array}{cc} \begin{pmatrix} 1.039\ \text{amu}^{-1} & -0.089\ \text{amu}^{-1}\text{Å}^{-1} & 0 \\ \text{sym} & 2.336\ \text{amu}^{-1}\text{Å}^{-2} & 0 \\ 0 & 0 & 1.069\ \text{amu}^{-1} \end{pmatrix} & \begin{matrix} 1 \\ 3 \\ 2 \end{matrix} \end{array}$$

Notice that both $\tilde{\mathbf{F}}$ and $\tilde{\mathbf{G}}$ are block diagonalized.

This is a symmetry effect → Group Theory.

(torsions in  would have been a separate block in symmetry coordinates)

What would cause the coupling between $\tilde{S}_1$ and $\tilde{S}_3$ to get larger or smaller? $\boxed{\text{IVR}}$

Look at $\tilde{G}_{13}$ and $\tilde{F}_{13}$.

$$\underset{\text{mass \& geometry effects}}{\tilde{\mathbf{G}}_{13}} = -2^{-1/2}\left(r^{e}_{32}\right)^{-1}\underbrace{\sin\theta^{e}}_{\boxed{\begin{array}{l}\to \text{0 at linear}\\ \to \text{max at } 90^\circ\\ \to \text{small for very heavy center atom}\end{array}}}\frac{1}{\underset{\text{center atom}}{m_3}} \quad \text{with respect to} \left|\underbrace{\tilde{\mathbf{G}}_{11}-\tilde{\mathbf{G}}_{33}}_{\text{small for heavy end atoms}}\right|$$

$$\tilde{\mathbf{F}}_{13} \qquad \text{with respect to } \left|\tilde{\mathbf{F}}_{11}-\tilde{\mathbf{F}}_{33}\right|$$

bend and stretch have very different F_{ii} but
two stretches or two bends have
more similar ones

Physical basis for “bend” vs. “stretch” as dominant
character in a normal mode, even though there is no
symmetry reason that stretches and bends should
not mix strongly.

Alternate approach to vibrational analysis.

See Bernath pages 220-225.

Work in mass weighted Cartesian displacement representation rather than internal coordinates. Convenient for electronic structure calculations. No insight. No transferability.

3N × 3N **f** matrix

- **f** is symmetric
- $\boldsymbol{\ell}\mathbf{f}\boldsymbol{\ell}^{+} = \boldsymbol{\Lambda}$ eigenvalues of <u>**f** matrix</u> (6 are zero)
- $\boldsymbol{\ell}^{+} = \boldsymbol{\ell}^{-1}$ unitary → $|Q\rangle = \boldsymbol{\ell}|q\rangle$

Once we obtain $\{\lambda_i\}$ and $\boldsymbol{\ell}$ can get to $|S\rangle$ and **F** representations if desired.

Now for quantum mechanics and treatment beyond harmonic level.

We know what individual atom motions are involved in each Q. Set up matrix representation of **H**(P,Q).

$$\mathbf{H} = \sum_{n=1}^{3N-6} h_n^0 \left(Q_n, P_n\right) + V'\left(Q_1, \ldots Q_{3N-6}\right)$$

$$h_n^0 = h\omega_n \begin{pmatrix} 1/2 & & & & \\ & 3/2 & & \mathbf{0} & \\ & & \ddots & & \\ & \mathbf{0} & & v_n + 1/2 & \\ & & & & \ddots \end{pmatrix}$$

find out about this!

$\hat{P} = \frac{\hbar}{i}\frac{\partial}{\partial Q}$

$\hat{T} = \hat{P}^2 / 2$ because ?

$$V = \sum_{ijk} F_{ijk} Q_i Q_j Q_k + \sum_{ijkl} F_{ijkl} Q_i Q_j Q_k Q_l$$

matrix elements

$$\mathbf{H}_{v_1 \ldots v_{3N-6}; v'_1 \ldots v'_{3N-6}}$$

infinite matrix
how to truncate?
how to organize?
- * in order of increasing energy
- * polyads

What is a polyad?
2 mode frequencies are near integer multiples of each other, e.g. 2 : 1.

2 : 1 polyad
$\omega_1 \approx 2\omega_2$
etc.

hexad	(0,10)	(1,8)	(2,6)	(3,4)	(4,2)	(5,0)
…						
triad	(0,4)		(1,2)		(2,0)	
	(0,3)		(1,1)			
dyad	(0,2)		(1,0)			
	(0,1)					
	$(v_1,v_2) = (0,0)$					

# of levels in polyad increase monotonically, but all matrix elements are related to 1st example.

$$\mathbf{H}_{0,2;1,0} \propto F_{122}(2\cdot 1)^{1/2}(1) = 2^{1/2}F_{122}$$

$$\mathbf{H}_{nm;n+1\ m-2} \propto F_{122}(m\cdot m-1)^{1/2}(n+1)^{1/2}$$

$$= \mathbf{H}_{02;10}\left[\frac{m(m-1)(n+1)}{2}\right]^{1/2}$$

"superpolyad" — two interlocking polyads, as in acetylene $\omega_1 : \omega_2 : \omega_3 : \omega_4 : \omega_5 = 5 : 3 : 5 : 1 : 1$

Darling-Dennison $Q_1^2Q_3^2$

2345 $Q_2Q_3Q_4Q_5$

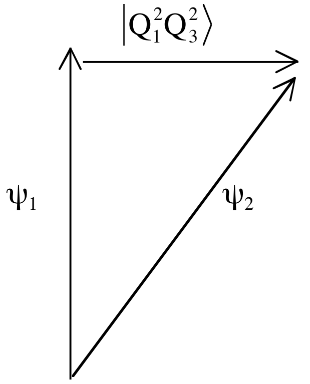
Resonance Vectors

Basis Vectors $(v_1, v_2, v_3, v_4, \ell_4, v_5, \ell_5)$ 7 dimensional vector

each harmonic oscillator product state represented by a 7 dimensional vector

each coupling term represented by a vector that describes its selection rules.

$Q_1^2Q_3^2$ (2 0 –2 0 0 0 0)



Find conserved quantum numbers by listing all relevant resonance vectors, then find directions ⊥ to all of those.

In HCCH n_{res} n_s ℓ are the conserved quantities: "polyad quantum numbers". Tells you which block of **H** to diagonalize.