5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #27: Polyatomic Vibrations III: s-Vectors and H_2O

Last time:

F-matrix: too many F_{ij}'s even at quadratic-only level

Internal coordinates: types
3N–6 independent ones
constraints * translation
* rotation

$\underset{\sim}{s}$-vectors $\underset{\sim}{\nabla}_\alpha S_t \equiv \underset{\sim}{s}_{t\alpha}$ * direction of fastest increase
* magnitude resulting from unit displacement in optimum direction

$$S_t\left(\{\vec{\rho}_\alpha\}\right) = \sum_{\alpha=1}^{N} \underset{\sim}{s}_{t\alpha} \bullet \vec{\rho}_\alpha$$

rigid translation $\vec{\rho}_\alpha = \vec{\varepsilon}$ for all α

constraint $\sum_\alpha \underset{\sim}{s}_{t\alpha} = 0$ no center of mass translation

rigid rotation by $d\vec{\Omega}$ $\vec{\rho}_\alpha(d\vec{\Omega}) = \vec{R}_\alpha \times d\vec{\Omega}$

$$S_t(d\vec{\Omega}) = d\vec{\Omega} \bullet \sum_\alpha \underset{\sim}{s}_{t\alpha} \times \vec{R}_\alpha$$

constraint $\sum_\alpha s_{t\alpha} \times \vec{R}^{\,e}_\alpha = 0$ ECKART
(minimizes vibrational angular momentum)

If the normal displacements are built from $\underset{\sim}{s}_{t\alpha}$ vectors that satisfy these constraints, then, for infinitesimal displacements from equilibrium, there is no rotation. For large displacements, or for small displacements away from a non-equilibrium configuration, there is a small vibrational angular momentum. This definition of vibrations embeds a specific partitioning between rotation and vibration.

TODAY:

G from $\underset{\sim}{s}_{t\alpha}$'s

Examples of $\underset{\sim}{s}_{t\alpha}$'s
1. valence bond stretch Δr
2. valence angle bend $\Delta\phi$

G matrix using diagrams and tables from WDC pages 304 and 305
H_2O **FG** handout
$\mathbf{G} \equiv \mathbf{D}\mathbf{D}^\dagger$

recall $|S\rangle = \mathbf{B}|\xi\rangle = \mathbf{D}|q\rangle = \mathbf{D}\mathbf{M}^{1/2}|\xi\rangle$

$$\mathbf{B} = \mathbf{D}\mathbf{M}^{1/2}$$

$$\mathbf{B}\mathbf{M}^{-1/2} = \mathbf{D}$$

$$\mathbf{G} = \mathbf{D}\mathbf{D}^\dagger = \mathbf{B}\mathbf{M}^{-1/2}\left(\mathbf{M}^{-1/2}\right)^\dagger \mathbf{B}^\dagger = \mathbf{B}\mathbf{M}^{-1}\mathbf{B}^\dagger$$

$$G_{tt'} = \sum_{i=1}^{3N} \frac{1}{m_i} B_{ti} B^*_{t'i}$$

definition of $|S\rangle = \mathbf{B}|\xi\rangle \rightarrow$ $\boxed{\left(\frac{\partial S_t}{\partial \xi_i}\right)_0}$ $\boxed{\left(\frac{\partial S_{t'}}{\partial \xi_i}\right)_0}$

$$= \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \left(\nabla_\alpha S_t\right)_0 \cdot \left(\nabla_\alpha S_{t'}\right)_0$$

$$G_{tt'} = \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \underset{\sim}{s}_{t\alpha} \cdot \underset{\sim}{s}_{t'\alpha}$$

This way to derive **G** is convenient

* locally defined $\underset{\sim}{s}_{t\alpha}$. Easy to compute $\underset{\sim}{s}_{t\alpha} \cdot \underset{\sim}{s}_{t'\alpha}$.
* Each S_t involves small number of $s_{t\alpha}$'s (only the involved atoms).
* Small number of topological cases for internal displacements. All analyzed in WDC, pages 303-306.

$\underset{\sim}{s}$-Vector Method. WDC pages 54-63.

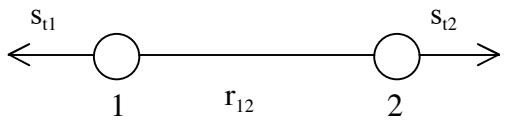
* start with all atoms at equilibrium positions;
* direction of $\underset{\sim}{s}_{t\alpha}$ is direction of α'th atom must move to yield maximum increase in S_t;
* magnitude of $\underset{\sim}{s}_{t\alpha}$ is increase in S_t that results from unit displacement of atom α in optimal direction;
* must verify or impose the 6 constraints (3 Cartesian components for the two vector constraint equations).

$$\sum_\alpha \underset{\sim}{s}_{t\alpha} = 0 \qquad \sum_\alpha \vec{R}^e_\alpha \times \underset{\sim}{s}_{t\alpha} = 0$$

Several possible types of internal displacements.

1. Bond Stretch
2. Valence angle bend
3. angle between a bond and a plane (non-planar $\tilde{A}\,^1A_2$ state of H_2CO) defined by 2 bonds
4. torsion → *trans*-bent excited $\tilde{A}\,^1A_u$ state of HCCH

1. <u>Bond Stretch</u> $S_t \equiv \Delta r$



only 2 nonzero $\underset{\sim}{s}$ vectors (even in a long linear chain)!

Atom 1	unit displacement	$\lvert s_{t1}\rvert = 1$	$\vec{s}_{t1} = \vec{e}_{21} = -\vec{e}_{12}$
Atom 2		$\lvert s_{t2}\rvert = 1$	$\vec{s}_{t2} = -\vec{e}_{21} = \vec{e}_{12}$

$$S_t\left(\{\vec{\xi}_\alpha\}\right) = \hat{e}_{21}\left(\vec{\rho}_1 - \vec{\rho}_2\right)$$

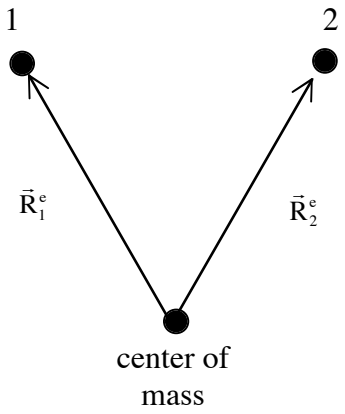
(displacements of all other atoms have no effect on Δr_{12})
These are the vector representations of $S_{\Delta r}$.

Are the constraints satisfied?

$$\sum_\alpha \underset{\sim}{s}_{t\alpha} = \underset{\sim}{s}_{t1} + \underset{\sim}{s}_{t2} = -\hat{e}_{12} + \hat{e}_{12} = 0!$$

$$\sum_\alpha \vec{R}^e_\alpha \times \underset{\sim}{s}_{t\alpha} = \vec{R}^e_1 \times \left(-\hat{e}_{12}\right) + \vec{R}^e_2 \times \left(\hat{e}_{12}\right)$$

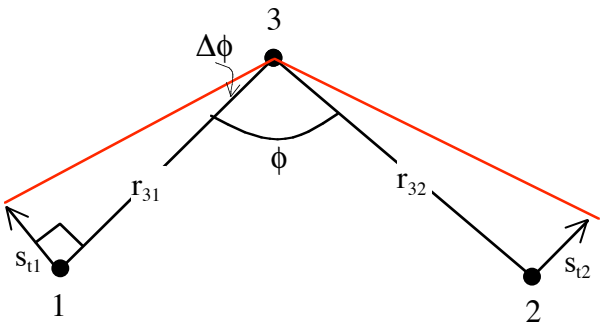
$$= \left(\vec{R}^e_2 - \vec{R}^e_1\right) \times \hat{e}_{12}$$



$$\vec{R}^e_2 - \vec{R}^e_1 = \vec{R}^e_{12} \quad \| \vec{e}_{12}$$

$$\therefore \vec{R}^e_{12} \times \vec{e}_{12} = 0!$$

2. Valence Angle Bend $S_t \equiv \Delta\phi$



Exactly 3 atoms are involved. 3 nonzero $\underset{\sim}{s}_{t\alpha}$'s.

How to move each atom to increase ϕ by maximum amount?

$$\tan\Delta\phi \approx \Delta\phi = \frac{|s_{t1}|}{r_{31}}$$

How to define a UNIT VECTOR pointing in correct direction?

$$\hat{e}_{\underset{\sim}{s}_{t1}} = \hat{e}_{31} \times \frac{\hat{e}_{31} \times \hat{e}_{32}}{\sin\phi} \qquad \text{Recall } |\hat{e}_{31} \times \hat{e}_{32}| = \sin\phi$$

right hand rule

$\perp$ to plane, up out of board

Rules for vector triple product

$$\hat{e}_{\underset{\sim}{s}_{t1}} = \frac{(\hat{e}_{31}\cdot\hat{e}_{32})\hat{e}_{31} - (\hat{e}_{31}\cdot\hat{e}_{31})\hat{e}_{32}}{\sin\phi}$$

($\hat{e}_{31}\cdot\hat{e}_{32} = \cos\phi$; $\hat{e}_{31}\cdot\hat{e}_{31} = 1$)

$$\boxed{\hat{e}_{\underset{\sim}{s}_{t1}} = \frac{\cos\phi\hat{e}_{31} - \hat{e}_{32}}{\sin\phi}}$$

Now, how much does unit displacement of atom 1 in $\hat{e}_{\underset{\sim}{s}_{t1}}$ direction increase S_t?

$$\tan|\Delta S_t| \approx |\Delta S_t| = \frac{\text{unity}}{r_{31}} = \frac{1}{r_{31}} = |s_{t1}|$$

$$\therefore \boxed{\underset{\sim}{s}_{t1} = |\underset{\sim}{s}_{t1}|\hat{e}_{\underset{\sim}{s}_{t1}} = \frac{\cos\phi\hat{e}_{31} - \hat{e}_{31}}{r_{31}\sin\phi}}$$

this is a vector of specified length and direction

similarly for atom 2

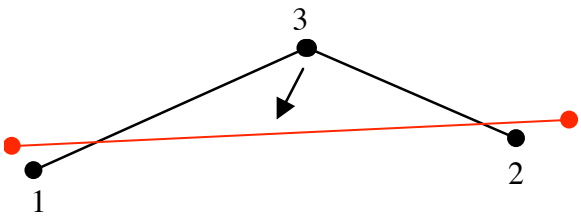
$$\boxed{\underset{\sim}{s}_{t2} = \frac{\cos\phi\hat{e}_{32} - \hat{e}_{31}}{r_{32}\sin\phi}}$$

now for the hard one: atom 3!

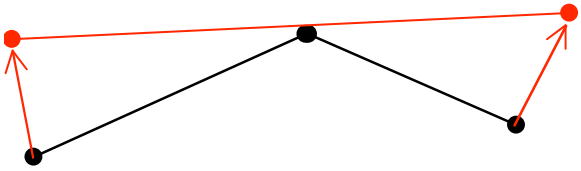
Easy way: impose constraint $\sum_{\alpha} \underset{\sim}{s}_{t\alpha} = 0$

$$\therefore \underset{\sim}{s}_{t3} = -(\underset{\sim}{s}_{t1} + \underset{\sim}{s}_{t2}) = \frac{(r_{31} - r_{32}\cos\phi)\hat{e}_{31} + (r_{32} - r_{31}\cos\phi)\hat{e}_{32}}{r_{31}r_{32}\sin\phi}$$

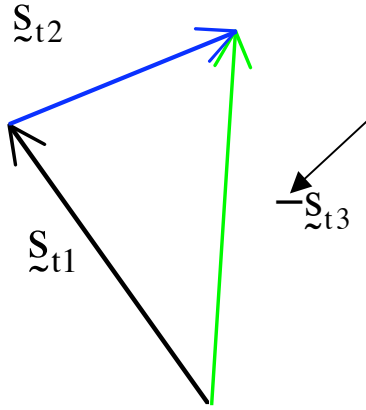
Hard way: move atom 3 1 unit in optimal direction, then translate deformed molecule rigidly to put atom 3 back at its original position. This evidently leaves atoms 1 and 2 displaced by $\underset{\sim}{s}_{t1}$ and $\underset{\sim}{s}_{t2}$ respectively.



move atom 3



translate distorted structure back to put atom 3 in original location



$\underset{\sim}{s}_{t3} = -(\underset{\sim}{s}_{t1} + \underset{\sim}{s}_{t2})$

This obviously satisfies $\sum_{\alpha} \underset{\sim}{s}_{t\alpha} = 0$

It is harder to show that it also satisfies $0 = \sum \vec{R}^{e}_{\alpha} \times \underset{\sim}{s}_{t\alpha}$.
Grind out the algebra! (see Non-Lecture on next page)

Alternative definition of $S_{\Delta\theta}$ as a linear displacement rather than an angular displacement is possible.

e.g. $r_{31}\Delta\phi$, $r_{32}\Delta\phi$, or $(r_{31}r_{32})^{1/2}\Delta\phi$.

Then $S_{\Delta\phi}$ would have dimension of length and all bending force constants would have same units as stretching ones. The derivation of $S_{\Delta\phi}$ would follow same path, but each $\underset{\sim}{s}_{t\alpha}$ gets multiplied by the relevant length factor, r_{31} or r_{32} or $(r_{31}r_{32})^{1/2}$.

NON-LECTURE

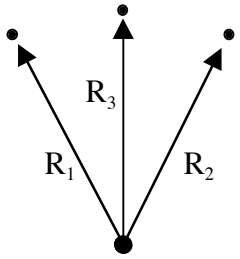
Proof that $\underset{\sim}{s}_{t\alpha}$'s satisfy Eckart Condition

$$\underset{\sim}{s}_{t1} = \frac{\cos\phi\hat{e}_{31} - \hat{e}_{32}}{r_{31}\sin\phi}$$

$$\underset{\sim}{s}_{t2} = \frac{\cos\phi\hat{e}_{32} - \hat{e}_{31}}{r_{32}\sin\phi}$$

$$\underset{\sim}{s}_{t3} = \frac{(r_{31} - r_{32}\cos\phi)\hat{e}_{31} + (r_{32} - r_{31}\cos\phi)\hat{e}_{32}}{r_{31}r_{32}\sin\phi}$$

$$0 \stackrel{?}{=} R_1^e \times \underset{\sim}{s}_{t1} + R_2^e \times \underset{\sim}{s}_{t2} + R_3^e \times \underset{\sim}{s}_{t3}$$



$$\vec{R}_3 = \vec{R}_2 + \vec{R}_{23}$$
$$\vec{R}_3 = \vec{R}_1 + \vec{R}_{13}$$

$$0 \stackrel{?}{=} (\vec{R}_3 - \vec{R}_{13}) \times \underset{\sim}{s}_{t1} + (\vec{R}_3 - \vec{R}_{23}) \times \underset{\sim}{s}_{t2} + \vec{R}_3 \times \underset{\sim}{s}_{t3}$$

$$0 \stackrel{?}{=} \vec{R}_3 \times \underbrace{(\underset{\sim}{s}_{t1} + \underset{\sim}{s}_{t2} + \underset{\sim}{s}_{t3})}_{=0} - (\vec{R}_{13} \times \underset{\sim}{s}_{t1} + \vec{R}_{23} \times \underset{\sim}{s}_{t2})$$

$$\vec{R}_{13} \times \hat{e}_{31} = 0 \quad \vec{R}_{23} \times \hat{s}_{32} = 0$$

$$0 \stackrel{?}{=} \vec{R}_{13} \times \left(\frac{-\hat{e}_{32}}{r_{31}\sin\phi}\right) - \vec{R}_{23} \times \left(\frac{-\hat{e}_{31}}{r_{32}\sin\phi}\right)$$

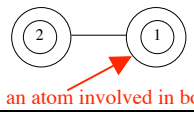
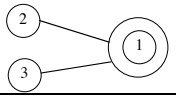
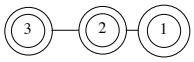
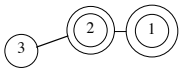
$$\vec{R}_{13} \times \hat{e}_{32} = r_{31}\hat{e}_{13} \times \hat{e}_{32} = -r_{31}\hat{e}_{31} \times \hat{e}_{32}$$

$$\vec{R}_{23} \times \hat{e}_{31} = r_{32}\hat{e}_{23} \times \hat{e}_{31} \qquad \text{QED}$$

G-Matrix

$$G_{tt'} = \sum_{\alpha=1}^{N} \frac{1}{m_\alpha} \underset{\sim}{s}_{t\alpha} \times \underset{\sim}{s}_{t'\alpha}$$

Could compute directly from $\underset{\sim}{s}_{t\alpha}$'s, but easier to use diagrams from WDC page 304 and table on WDC, page 305.

DIAGRAMS		
	diagonal stretch-stretch	# of atoms common to both t and t′ → G^2_{rr} ← stretch
	off-diagonal stretch-adjacent stretch	G'_{rr}
	diagonal bend-bend	$G^3_{\phi\phi}$ ← bend
	off-diagonal bend-internal stretch	$G^2_{r\phi}$

etc.

TABLE

$$G^2_{rr} = \mu_1 + \mu_2 \qquad \mu_\alpha \equiv \frac{1}{m_\alpha}$$

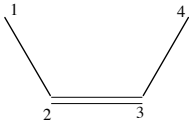
$$G^1_{rr} = \mu_1 c\phi \qquad c\phi \equiv \cos\phi$$

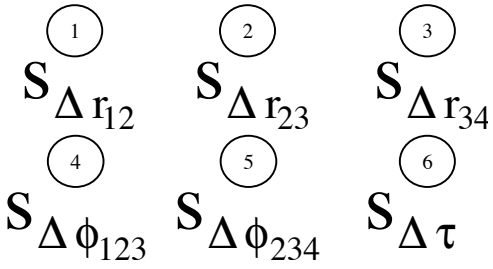
$$G^3_{\phi\phi} = \rho^2_{12}\mu_1 + \rho^2_{23}\mu_3 + \left(\rho^2_{12} + \rho^2_{23} - 2\rho_{12}\rho_{23}c\phi\right)\mu_2$$

$$\rho_{ij} \equiv \left(r^e_{ij}\right)^{-1}$$

$$G^2_{r\phi} = -\rho_{23}\mu_2 s\phi \qquad s\phi = \sin\phi$$

cis bent acetylene





G matrix has $\frac{6 \times 7}{2} = 21$ independent elements

$$\mathbf{G}: \begin{array}{c} \textcircled{1} \\ \textcircled{2} \\ \textcircled{3} \\ \textcircled{4} \\ \textcircled{5} \\ \textcircled{6} \end{array} \begin{pmatrix} G^{2}_{rr} & G^{1}_{rr} & 0 & G^{2}_{r\phi} & G^{1}_{r\phi}\begin{pmatrix}1\\2\end{pmatrix} & G^{2}_{r\tau} \\ & G^{2}_{rr} & G^{1}_{rr} & & & \\ & & G^{2}_{rr} & & & \\ & & & G^{3}_{\phi\phi} & & \\ & & & & G^{3}_{\phi\phi} & \\ & & & & & G^{4}_{\tau\tau} \end{pmatrix}$$

See J. C. Decius *Journal of Chemical Physics* **16** 1025 (1948)! for torsion and out of plane bend distortions!