5.80 Small-Molecule Spectroscopy and Dynamics

Fall 2008

Lecture #22: Rotation of Polyatomic Molecules I

A diatomic molecule is very limited in how it can rotate and vibrate.

* $\vec{R}$ is $\perp$ to internuclear axis
* only one kind of vibration

A polyatomic molecule can have $\vec{\vec{R}}$ oriented along any body fixed direction — symmetric and asymmetric tops†
A polyatomic molecule can stretch any bond or bend any bond pair — Normal modes of vibration
A lot of very complicated classical mechanics.

TODAY: Derive $\hat{\mathbf{H}}^{ROT} = \frac{\vec{R}_x^2}{2I_x} + \frac{\vec{R}_y^2}{2I_y} + \frac{\vec{R}_z^2}{2I_z}$ and evaluate matrix elements in $|KJM\rangle$ basis set, where I_x, I_y, and I_z are called principal components (i.e. eigenvalues) of the 3×3 moment of inertia tensor, **I**, and are analogous to μR_{AB}^2 in an AB diatomic.

1. Center of mass.
2. rigid body rotation
   $\hat{T}^{ROT}$ in terms of $\vec{\omega}$ (angular velocity), m_i, (x_i, y_i, z_i)
   (positions of atom i in center of mass body frame)
   $1/2\ \boldsymbol{\omega}^\dagger\ \mathbf{I}\boldsymbol{\omega}$

$$\mathbf{T}^\dagger\mathbf{I}\mathbf{T} \rightarrow \text{principal axes} \begin{pmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{pmatrix}$$

3. $\hat{\mathbf{H}}^{ROT}$ and matrix elements in $|KJM\rangle$ basis.
4. Symmetric tops - prolate and oblate energy level formulas.

Consider a rigid N-body system. Each atom has mass m_i and body-fixed coordinate $\vec{q}$ (defined relative to an arbitrary body-fixed origin).

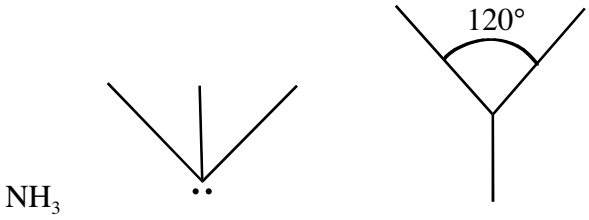
Our first task is to locate the center of mass, because we expect to separate the 3N degrees of freedom into 3 center of mass translations, 3 rotations about the center of mass, and 3N – 6 vibrations.

Center of Mass: 3 **Cartesian** component equations.

$$0 = \sum_{\substack{i=1 \\ \text{atoms}}}^{3N} m_i \left(\vec{q}_i - \vec{q}_{CM} \right)$$

† In fact, the definition of body fixed axis system is not even obvious for vibrating molecule.

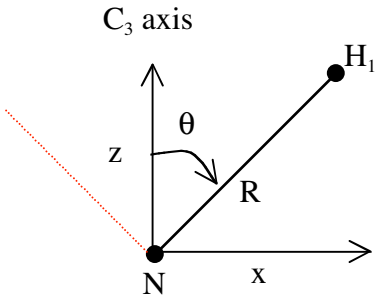
Example:



NH_3 (projected onto xy plane)

Take advantage of symmetry whenever possible!

pick C_3 (3-fold rotation axis) axis as z axis
locate origin at N atom (a convenient way to start)
locate H_1 at $\phi = 0$ (i.e. in xz plane)



bond length

$$\vec{q}_{H_1} = \underbrace{(r,\theta,\phi) = (R,\theta,0)}_{\text{spherical polar}} \Rightarrow \overbrace{(x_1,y_1,z_1) = (R\sin\theta, 0, R\cos\theta)}^{\text{Cartesian}}$$

$$\vec{q}_{H_2} = \left(R,\theta,\frac{2\pi}{3}\right) \Rightarrow (x_2,y_2,z_2) = \left(-\frac{1}{2}R\sin\theta, \frac{\sqrt{3}}{2}R\sin\theta, R\cos\theta\right)$$

$$\vec{q}_{H_3} = \left(R,\theta,\frac{4\pi}{3}\right) \Rightarrow (x_3,y_3,z_3) = \left(-\frac{1}{2}R\sin\theta, -\frac{\sqrt{3}}{2}R\sin\theta, R\cos\theta\right)$$

$$\vec{q}_N = (0,0,0)$$

Now solve for center of mass.

$x_{CM} = y_{CM} = 0$ are trivial

z equation

$$0 = \sum_i m_i (z_i - z_{CM}) = 3m_H (R\cos\theta - z_{CM}) + m_N (0 - z_{CM})$$

$$z_{CM} = \underbrace{\frac{3m_H}{3m_H + m_N}}_{=M} R\cos\theta$$

So we have coordinates of all atoms relative to new origin now at center of mass, expressed in terms of 2 unknown bond coordinates, R and θ.

$$R\cos\theta - \frac{3m_H}{M}R\cos\theta = R\cos\theta\left[\frac{M - 3m_H}{M}\right] = R\cos\theta\frac{m_N}{M}$$

$$q_{H_1} = \left(R\sin\theta, 0, R\cos\theta\frac{m_N}{M}\right)$$

$$q_{H_2} = \left(-\frac{1}{2}R\sin\theta, \frac{\sqrt{3}}{2}R\sin\theta, R\cos\theta\frac{m_N}{M}\right)$$

$$q_{H_3} = \left(-\frac{1}{2}R\sin\theta, -\frac{\sqrt{3}}{2}R\sin\theta, R\cos\theta\frac{m_N}{M}\right)$$

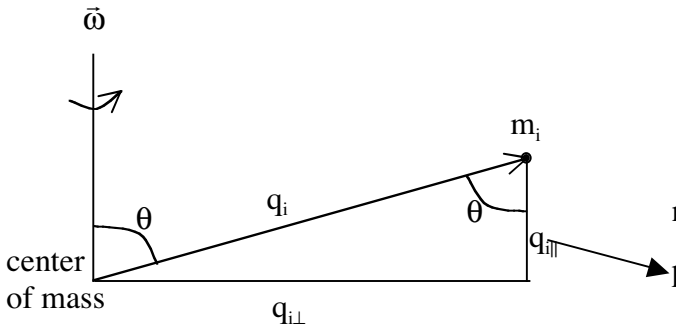
$$q_N = \left(0, 0, -\frac{3m_N}{M}R\cos\theta\right)$$

Next we need to write out $\mathbf{H}^{ROT}$ and put it into a convenient form.

$$\underbrace{\hat{\mathbf{H}}^{ROT} = \hat{\mathbf{T}}^{ROT} + V^{ROT}}_{\text{free rotor, thus } V^{ROT}=0}$$

$$\hat{\mathbf{T}}^{ROT} = \frac{1}{2}\sum_i m_i v_i^2$$

Want to re-express all v_i's in terms of $\vec{q}_i$ and $\vec{\omega}$ where $\vec{\omega}$ specifies the direction and magnitude of the angular velocity of the rigid body rotations. (All atoms experience the same $\vec{\omega}$.)



$$q_{i\parallel} = \frac{\vec{q}_i\cdot\vec{\omega}}{|\omega|} = \frac{|q_i||\omega|\cos\theta}{|\omega|}$$

need velocities for T^{ROT}

parallel to $\frac{\vec{\omega}}{|\omega|}$ unit vector

$\vec{v}_i = -\vec{q}_i \times \vec{\omega}$ (right hand rule requires minus sign)

$|v_i| = |q_i|\,|\omega| \sin\theta_i$ q_i, ω known. Must solve for $\sin\theta_i$.

$$\sin\theta_i = \frac{q_{i\perp}}{q_i} = \frac{\left[q_i^2 - \left(\frac{q_i\cdot\omega}{|\omega|}\right)^2\right]^{1/2}}{q_i}$$

($q_{i\parallel}$)

so $v_i^2 = q_i^2\omega^2\sin^2\theta_i = \left[q_i^2\omega^2 - (q_i\cdot\omega)^2\right]$ $(\sin^2\theta_i = 1 - \cos^2\theta_i)$

$$\hat{\mathbf{H}}^{ROT} = \frac{1}{2}\sum_i m_i\left[q_i^2\omega^2 - (q_i\cdot\omega)^2\right]$$

Go to Cartesian coordinates (always safe for setting up quantum mechanical Hamiltonian operator).

$$\hat{\mathbf{H}}^{ROT} = \frac{1}{2}\sum_i m_i\left[\left(x_i^2+y_i^2+z_i^2\right)\left(\omega_x^2+\omega_y^2+\omega_z^2\right)-\left(x_i\omega_x+y_i\omega_y+z_i\omega_z\right)^2\right]$$

awful mess!

a bit of algebra

$$= \frac{1}{2}\sum_i m_i\left[\left(x_i^2+y_i^2\right)\omega_z^2+\left(x_i^2+z_i^2\right)\omega_y^2+\left(y_i^2+z_i^2\right)\omega_x^2-2x_iy_i\omega_x\omega_y-2x_iz_i\omega_x\omega_z-2y_iz_i\omega_y\omega_z\right]$$

Reformulate as matrix diagonalization problem!

Define

$$I_{xx} \equiv \sum_i m_i\left(y_i^2+z_i^2\right) \qquad \text{etc.} \qquad \text{perpendicular distance squared from x axis}$$

$$I_{xy} = -\sum_i m_i\left(x_iy_i\right) = I_{yx} \qquad \text{etc.}$$

$\hat{\mathbf{H}}^{ROT} = \frac{1}{2}\boldsymbol{\omega}^\dagger\mathbf{I}\boldsymbol{\omega}$ This is a compact form for messy equation above!

$$\boldsymbol{\omega} \equiv \begin{pmatrix}\omega_x\\ \omega_y\\ \omega_z\end{pmatrix} \qquad \mathbf{I} \equiv \begin{vmatrix} I_{xx} & I_{xy} & I_{xz}\\ I_{yx} & I_{yy} & I_{yz}\\ I_{zx} & I_{zy} & I_{zz}\end{vmatrix} \qquad \omega^\dagger = \begin{pmatrix}\omega_x & \omega_y & \omega_z\end{pmatrix}$$

"moment of inertia tensor"

I is a real, symmetric matrix.

It can be diagonalized (by a coordinate transformation, a rotation about center of mass) to give

$$\mathbf{T}^\dagger\mathbf{I}\mathbf{T} = \begin{vmatrix} I_a & 0 & 0\\ 0 & I_b & 0\\ 0 & 0 & I_c\end{vmatrix}$$

$I_a \le I_b \le I_c$ by definition and are called the "principal moments of inertia".

$\mathbf{T}^\dagger\mathbf{T} = \mathbb{1}$ $\hat{\mathbf{H}}^{ROT} = \frac{1}{2}\boldsymbol{\omega}^\dagger\mathbf{I}\boldsymbol{\omega} = \frac{1}{2}(\boldsymbol{\omega}^\dagger\mathbf{T})(\mathbf{T}^\dagger\mathbf{I}\mathbf{T})(\mathbf{T}^\dagger\boldsymbol{\omega})$

$$\mathbf{T}^{\dagger}\begin{pmatrix}\omega_x\\ \omega_y\\ \omega_z\end{pmatrix}=\begin{pmatrix}\omega_a\\ \omega_b\\ \omega_c\end{pmatrix}$$

$$\mathbf{T}^{\dagger}\begin{pmatrix}x\\ y\\ z\end{pmatrix}=\begin{pmatrix}a\\ b\\ c\end{pmatrix}$$

We find a special body fixed coordinate system with origin at the center of mass which causes **I** to be diagonal.

Usually possible to find principal axes by inspection.

1. One axis is axis of highest order rotational symmetry, called z by convention.
2. Another axis is $\perp$ to C_n and $\perp$ to a σ_v plane. E.g. if $\sigma(xz)$ exists, then

   $\sum_i m_i x_i y_i = \sum_i m_i y_i z_i = 0$ because there is always an identical nucleus at (x, +y, z) and at (x, –y, z). (What happens when there is no σ_v plane? e.g. S_1 acetylene.)
3. 3rd is $\perp$ to first 2 axes.

So when **I** is diagonal

$$\hat{\mathbf{H}}^{ROT}=\frac{1}{2}\left(I_a\omega_a^2+I_b\omega_b^2+I_c\omega_c^2\right)$$

the nuclear rotational angular momentum is defined as

$$\mathbf{J}=\mathbf{I}\,\boldsymbol{\omega}$$

should actually use notation of **R** or **N**

$$\hat{\mathbf{H}}^{ROT}=\frac{1}{2}\mathbf{J}^{\dagger}\mathbf{I}^{-1}\mathbf{J}=\frac{J_a^2}{2I_a}+\frac{J_b^2}{2I_b}+\frac{J_c^2}{2I_c}$$

like $\frac{p^2}{2m}\rightarrow\frac{J^2}{2I}$

(The reciprocal or inverse of a diagonal matrix is trivial.)

We can now define <u>three</u> rotational constants

$$A = \frac{h}{c}\frac{1}{8\pi^2 I_a} \quad \text{cm}^{-1}\,(\text{E/hc})$$

$$B = \frac{h}{c}\frac{1}{8\pi^2 I_b} \quad \text{cm}^{-1}$$

$$C = \frac{h}{c}\frac{1}{8\pi^2 I_c} \quad \text{cm}^{-1}$$

$A \geq B \geq C$ (again, by definition)

Note that we will sample "rotational constants" with $\mathbf{I}^{-1}$ averaged over specific vibrational state, not at the equilibrium geometry. Want equilibrium geometry, get strange average. Note that we are eventually going to want to compute derivatives of $\mathbf{I}^{-1} \equiv \boldsymbol{\mu}$ with respect to each of the 3N – 6 normal coordinate displacements.

One obtains A, B, C by picking bond lengths and angles, specifying atomic masses, and diagonalizing **I**. For each change in masses (isotopic substitution) or iterative change in geometry, **I** must be rediagonalized.

Example: Principal Moments for NH_3 (refer to table on page 2)

C_3 axis must be one principal axis

$$\text{so } I_z = R^2 \sin^2\theta \left[m_{H_1} + \left(\overbrace{\frac{1}{4}}^{x^2} + \overbrace{\frac{3}{4}}^{y^2} \right) m_{H_2} + \left(\frac{1}{4} + \frac{3}{4} \right) m_{H_3} \right]$$

$$= 3 m_H R^2 \sin^2\theta$$

(the $\perp$ distance^2 of each atom from axis specified)

existence of reflection plane

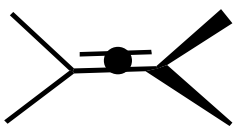
$$\sigma_v(xz) \xrightarrow[\text{implies}]{} I_y = R^2 \cos^2\theta \left(\frac{3 m_N m_H}{M} \right) + \overbrace{R^2 \sin^2\theta}^{x^2} \left(\frac{3 m_H}{2} \right)$$

principal component $\perp$ to the xz plane. You show that $I_x = I_y$ (for any symmetric top).

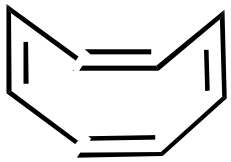
[General rule, every molecule with $n \geq 3$ C_n rotation axis has two equal moments of inertia!]

Special case of $D_{2d} \rightarrow S_4$ axis: cycloctatetrene and allene

allene



C_3H_4



cyclo-octa-tetra-ene
C_8H_8

$\hat{\mathbf{H}}^{ROT}$ for symmetric top.

By convention, $I_x = I_y$, I_z is unique (for all sym. tops).

$$\hat{\mathbf{H}}^{ROT} = \frac{\hat{J}_x^2}{2I_x} + \frac{\hat{J}_y^2}{2I_y} + \frac{\hat{J}_z^2}{2I_z}$$ manipulate this into a form convenient for $|JKM\rangle$ basis set.

$I_x = I_y$ $\qquad \hat{J}^2 - \hat{J}_z^2 = \hat{J}_x^2 + \hat{J}_y^2$ key step!

$$\hat{\mathbf{H}}^{ROT} = \frac{1}{2I_x}\left[\hat{J}_x^2 + \hat{J}_y^2\right] + \frac{\hat{J}_z^2}{2I_z} = \frac{1}{2I_x}\left(\hat{J}^2 - \hat{J}_z^2\right) + \frac{\hat{J}_z^2}{2I_z}$$

$$\hat{\mathbf{H}}^{ROT} = \frac{1}{2I_x}\hat{J}^2 + \left[\frac{1}{2I_z} - \frac{1}{2I_x}\right]\hat{J}_z^2$$ **remember this!!**

Use $|JKM\rangle$ symmetric top basis functions which are just like $|J\Omega M\rangle$ functions for a diatomic molecule.

So

$$E^{ROT} = \underbrace{\frac{\hbar^2}{2I_x} J(J+1)}_{\text{like a diatomic molecule}} + \left[\frac{\hbar^2}{2I_z} - \frac{\hbar^2}{2I_x}\right] K^2$$

projection of $\hat{J}$ onto unique (i.e. symmetry) axis of body (like Ω)

2 types of symmetric top:

1. $I_z \equiv I_a$ is unique, $I_b = I_c > I_a$, prolate top, like a cigar. Coefficient of K^2 is > 0 because $A > B$ by definition.

$$\frac{E^{ROT}_{prolate}}{hc} = BJ(J+1) + (A-B)K^2$$

2. $I_z \equiv I_c$ is unique. $I_a = I_b < I_c$, oblate top, like a frisbee. Coefficient of K^2 is < 0.

$$\frac{E^{ROT}_{oblate}}{hc} = BJ(J+1) - (B-C)K^2$$

$J = 0, 1, 2, \ldots$ $K = 0, \underline{\pm 1, \ldots \pm J}$ denote as (J,K) or J_K

possible levels