Chemistry 21b – Spectroscopy

Lecture # 9 – The Classical Treatment of Molecular Vibrations

For a gas phase molecule with N atoms, there will be a total of $3N$ degrees of freedom in free space. Three of these will be involved in translation, which may be factored out as demonstrated previously for diatomic systems. Symmetric and asymmetric tops have an additional three degrees of freedom involved in rotation, while diatomic and linear molecules only have two rotational degrees of freedom (because there is no moment of inertia about the internuclear axis). Thus, the vibrational degrees of freedom are $3N - 6$ for symmetric or asymmetric tops, and $3N - 5$ for linear molecules. We now define the displacement coordinates $x_\alpha = a_\alpha - a_{\alpha,e}$, $y_\alpha = b_\alpha - b_{\alpha,e}$, $z_\alpha = c_\alpha - c_{\alpha,e}$:

$$(x, y, z)_\alpha \quad = \quad \text{displacement coordinates of atom } \alpha$$

$$(a, b, c)_\alpha \quad = \quad \textbf{molecule}- \text{ (or body}-\text{) fixed coordinates}$$
$$(a, b, c)_{\alpha,e} \quad = \quad \text{molecule fixed equilibrium positions} \quad . \tag{9.1}$$

Classically, the kinetic energy of vibration is thus

$$T \quad = \quad \frac{1}{2}\sum_{\alpha=1}^{N} m_\alpha \left[\left(\frac{dx_\alpha}{dt}\right)^2 + \left(\frac{dy_\alpha}{dt}\right)^2 + \left(\frac{dz_\alpha}{dt}\right)^2\right] \tag{9.2}$$

The first step in simplifying this expression is to use *mass weighted coordinates*, that is $q_1 = m_1^{1/2} x_1$; $q_2 = m_2^{1/2} y_1$; ... , $q_{3N} = m_N^{1/2} z_N$, which results in

$$T \quad = \quad \frac{1}{2}\sum_{\alpha=1}^{3N}\left(\frac{dq_i}{dt}\right)^2 \qquad \text{or}$$

$$T \quad = \quad \frac{1}{2}\sum_{\alpha=1}^{3N} \dot{q}_i^2 \quad \equiv \quad \frac{1}{2}\dot{\mathbf{q}}^2 \quad = \quad \frac{1}{2}\dot{\mathbf{q}} \cdot \dot{\mathbf{q}} \quad , \tag{9.3}$$

using matrix notation, where the dots over the characters denote time derivatives, and the last expression is the dot product of the row and column vector containing the $\dot{q}_i$.

Next we examine the potential energy of vibration, which we'll label $U(q_1, ..., q_{3N})$. As we have often done in this class, to make progress it is helpful to expand the potential energy in a Taylor series about the equilibrium body-fixed positions $(a, b, c)_{\alpha,e}$, or

$$U \quad = \quad U_e + \sum_{i=1}^{3N}\left(\frac{\partial U}{\partial q_i}\right)_e q_i + \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N}\left(\frac{\partial^2 U}{\partial q_i \partial_k}\right)_e q_i q_k$$
$$+ \frac{1}{6}\sum_{i=1}^{3N}\sum_{j=1}^{3N}\sum_{k=1}^{3N}\left(\frac{\partial^3 U}{\partial q_i \partial q_j \partial q_k}\right)_e q_i q_j q_k + ... \tag{9.4}$$

Now, we can always pick our reference energy such that $U_e = 0$. Further, if we are at or close to the equilibrium positions of the atoms $(\partial U/\partial q_i)_e \approx 0$ since at equilibrium we are at a potential minimum. If we make the further assumption that vibrations may be treated harmonically (i.e. that Hooke's law is valid), then the $(\partial^3 U/\partial q_i \partial q_j \partial q_k)_e$ and higher terms vanish in the Taylor series expansion of U. In matrix form we can then write

$$U \approx \frac{1}{2}\mathbf{q}'\mathbf{U}\mathbf{q} \tag{9.5}$$

where $\mathbf{q}'$ is the transpose of $\mathbf{q}$ and $\mathbf{U}$ is the matrix of all

$$U_{ik} = \frac{\partial^2 U}{\partial q_i \partial_k} = (m_i m_k)^{-1/2}(k_i k_k)^{1/2} \tag{9.6}$$

if the harmonic approximation is valid.

The equations of motion can be solved classically using Newtonian mechanics, that is $F = ma$:

$$F_{x,\alpha} = -\frac{\partial U}{\partial x_\alpha} = -\frac{\partial U}{\partial q_j}\frac{\partial q_j}{\partial x_\alpha} = -m_\alpha^{1/2}\frac{\partial U}{\partial q_j} \tag{9.7}$$

since $q_j = m_\alpha^{1/2} x_\alpha$ and $(\partial q_j/\partial x_\alpha) = m_\alpha^{1/2}$. Thus,

$$a = \frac{d^2 x_\alpha}{dt^2} = \frac{d^2}{dt^2}\left(\frac{q_i}{m_\alpha^{1/2}}\right) = m_\alpha^{-1/2}\frac{d^2 q_j}{dt^2} \tag{9.8}$$

From Eqs. (9.7) and (9.8) it is clear that

$$\frac{d^2 q_j}{dt^2} + \frac{\partial U}{\partial q_j} = 0$$

for $j = 1, ..., 3N$. This $3N$ system of equations can be simplified because

$$U \approx \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N} U_{ik} q_i q_k \quad ,$$

and only one of the sums survives the partial derivative (say k), which leads to

$$\frac{d^2 q_j}{dt^2} + \frac{1}{2}\sum_{k=1}^{3N} U_{jk} q_k = 0 \qquad j = 1, ..., 3N. \tag{9.9}$$

This set of $3N$ equations are not trivial to solve since each equation involves *all* $3N$ coordinates! Looking more carefully at U will make life a little easier. Some properties of U include:

a) $\mathbf{U}$ is a *real, symmetric* matrix (i.e. $U_{ij} = U_{ji} = U_{ij}^*$). From matrix theory we therefore know that there is another matrix $\mathbf{L}$ such that:

b) $\mathbf{L}\mathbf{L}' = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix and $\mathbf{L}'$ is the transpose of $\mathbf{L}$. This statement says that $\mathbf{L}$ is *unitary*. From this we can then state:
c) $\mathbf{U}\mathbf{L} = \mathbf{L}\boldsymbol{\Lambda}$, or $\mathbf{L}'\mathbf{U}\mathbf{L} = \boldsymbol{\Lambda}$, where $\Lambda_{ij} = \delta_{ij}\lambda_i$. This statement says that L diagonalizes U. Thus,
d) $|\mathbf{U} - \mathbf{I}\lambda_m| = 0$
e) $(\mathbf{U} - \lambda_m\mathbf{I})\mathbf{L}^m = 0$, where $\mathbf{L}^m$ is the mth column of $\mathbf{L}$.

To make a long story short, it turns out that such a matrix $\mathbf{L}$ is composed of the normalized eigenvectors of $\mathbf{U}$ (remember the eigenvalues are obtained via the determinant outlined in d); while the eigenvectors for the system of equations in (9.9) are obtained from the matrix equations outlined in e)).

Using these mathematical tools we are now in a position to define the *normal modes* of the molecule. The normal modes, which we will label $\mathbf{Q}$, are given in terms of the mass-weighted coordinates $\mathbf{q}$ in terms of

$$Q_i = \sum_{k=1}^{3N} l_{ki} q_k \qquad \text{or} \qquad q_i = \sum_{k=1}^{3N} l_{ik} Q_k \tag{9.10}$$

In matrix terms, we have

$$\mathbf{Q} = \mathbf{L}'\mathbf{q} \qquad \text{or} \qquad \mathbf{q} = \mathbf{L}\mathbf{Q}$$

with the matrix $\mathbf{L}$ as defined above. Now, since $U \approx \frac{1}{2}\mathbf{q}'\mathbf{U}\mathbf{q}$, we can substitute Eq. (9.10) and the relations above to find

$$U = \frac{1}{2}(\mathbf{L}\mathbf{Q})'\mathbf{U}(\mathbf{L}\mathbf{Q}) = \frac{1}{2}\mathbf{Q}'\mathbf{L}'\mathbf{U}\mathbf{L}\mathbf{Q} = \frac{1}{2}\mathbf{Q}'\boldsymbol{\Lambda}\mathbf{Q} \ . \tag{9.11}$$

Since $\boldsymbol{\Lambda}$ is a diagonal matrix, this means that

$$U = \frac{1}{2}\sum_{k=1}^{3N} \lambda_k Q_k^2 = \frac{1}{2}\sum_{k=1}^{3N-6} \lambda_k Q_k^2 \tag{9.12}$$

Eq. (9.12) represents a dramatic simplification in that it is now a single sum, rather than the double sum previously obtained in the mass-weighted coordinates. The sum in the second part is reduced to $3N-6$ (or $3N-5$ for linear molecules) since the translational and rotational roots are zero since they don't change $(a,b,c)_{\alpha,e}$ in the harmonic aproximation. By convention, these roots run from $3N-6$ to $3N$ and can be ignored in what follows.

For the kinetic energy we have

$$T = \frac{1}{2}\dot{\mathbf{q}}'\dot{\mathbf{q}} = \frac{1}{2}(\mathbf{L}\dot{\mathbf{Q}})'\mathbf{L}\dot{\mathbf{Q}} = \frac{1}{2}\dot{\mathbf{Q}}'\mathbf{L}'\mathbf{L}\dot{\mathbf{Q}} = \frac{1}{2}\dot{\mathbf{Q}}'\dot{\mathbf{Q}} \ . \tag{9.13}$$

Thus, the classical equations of motion become:

$$\frac{\partial^2 Q_k}{\partial t^2} + \frac{\partial U}{\partial Q_k} = 0 \qquad k = 1, ..., 3N \ . \tag{9.14}$$

Since U is single sum over the Q_k (Eq. 9.12), we may write

$$\frac{\partial^2 Q_k}{\partial t^2} + \lambda_k Q_k = 0 \qquad\qquad k = 1, ..., 3N \ , \tag{9.15}$$

or $3N$ "easy to solve" differential equations (again, 5 or 6 of the λ_k roots will be zero due to translation and rotation)!

Eq. (9.15) is the important one, for it shows that just as the principle axes diagonalized the moment of inertia tensor, normal coordinates "diagonalize" the kinetic energy and potential energy expressions to yield a set of $3N - 6$ (or $3N - 5$) *independent* differential equations. The principal axes were fairly straightforward to set up in the general case, but normal coordinates are highly variable and depend sensitively on both the symmetry of the molecule and the potential. It is also worth remembering that normal mode theory depends on the harmonic approximation. We'll go through some basic group theory and example cases next time, for now we'll outline some general results and a very simple example...

The classical solutions to the above equations are:

$$Q_k = B_k \sin(\lambda_k^{1/2} t + b_k) \qquad\qquad k = 1, ..., 3N$$

$$q_i = \sum_{k=1}^{3N} l_{ik} B_k \sin(\lambda_k^{1/2} t + b_k) \tag{9.16}$$

Note that if all $B_k = 0$ except B_j, then

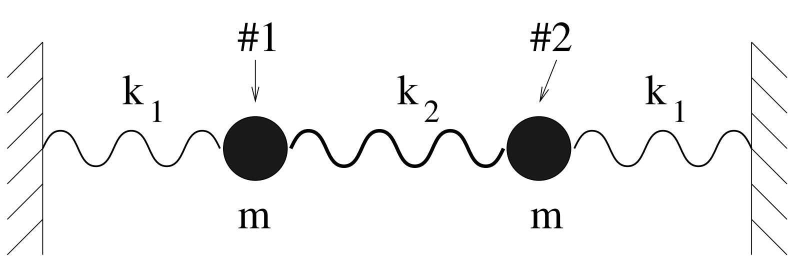
$$q_i = l_{ij} B_j \sin(\lambda_j^{1/2} t + b_j) \ ,$$

that is, *all* atoms move with the same frequency and phase, the frequency being

$$\nu_j = \lambda_j^{1/2} / 2\pi \tag{9.17}.$$

A Simple Example

Consider the one-dimensional model of two identical masses m show below in which each mass is tied to an infinite wall with a spring of force constant k_1 and to each other by a spring of force constant k_2. In this case, the potential in cartesian coordinates is given by



$$U = \frac{1}{2}k_1(x_1 - x_{1,e})^2 + \frac{1}{2}k_1(x_2 - x_{2,e})^2 + \frac{1}{2}k_2[(x_2 - x_1) - (x_{2,e} - x_{1,e})]^2 \ , \quad (9.18)$$

while the mass-weighted coordinates are simply $q_1 = (x_1 - x_{1,e})m^{1/2}$ and $q_2 = (x_2 - x_{2,e})m^{1/2}$. Thus, in mass-weighted coordinates the potential becomes

$$U = \frac{1}{2}k_1 q_1^2/m + \frac{1}{2}k_1 q_2^2/m + \frac{1}{2}k_2(q_2 - q_1)^2/m \ , \quad (9.19)$$

and the potential derivatives are given by

$$\frac{\partial U}{\partial q_1} = \frac{k_1 q_1}{m} - \frac{k_2(q_2 - q_1)}{m} \qquad \frac{\partial U}{\partial q_2} = \frac{k_1 q_2}{m} + \frac{k_2(q_2 - q_1)}{m}$$

$$\frac{\partial^2 U}{\partial q_1^2} = \frac{k_1}{m} + \frac{k_2}{m} \qquad \frac{\partial^2 U}{\partial q_2^2} = \frac{k_1}{m} + \frac{k_2}{m}$$

$$\frac{\partial^2 U}{\partial q_1 q_2} = -\frac{k_2}{m} \quad (9.20)$$

We want to calculate $|\mathbf{U} - \mathbf{I}\lambda_m| = 0$, which means

$$\begin{vmatrix} \frac{1}{m}(k_1 + k_2) - \lambda & -\frac{k_2}{m} \\ -\frac{k_2}{m} & \frac{1}{m}(k_1 + k_2) - \lambda \end{vmatrix} = 0 \ . \quad (9.21)$$

Thus,

$$\lambda^2 + \frac{(k_1 + k_2)^2}{m^2} - \frac{2\lambda(k_1 + k_2)}{m} - \frac{k^2}{m^2} = 0$$

or

$$\lambda^2 - \frac{2\lambda}{m}(k_1 + k_2) + \frac{1}{m^2}[k_1^2 + 2k_1k_2 + k^2 - k^2] = 0.$$

The quadratic roots of this equation are

$$\lambda = \frac{1}{m}(k_1 + k_2) \pm \frac{1}{2}\sqrt{\frac{4}{m^2}[(k_1 + k_2)^2 - (k_1^2 + 2k_1k_2)]}$$

which is easily solved to yield the two values

$$\lambda_1 = k_1/m \qquad \lambda_2 = (k_1 + 2k_2)/m \quad (9.22)$$

for the two vibrational roots.

Now, to get the eigenvectors we need to solve $(\mathbf{U} - \lambda_m \mathbf{I})\mathbf{L}^m = 0$ by inserting the two eigenvalues, or

$$\begin{pmatrix} \frac{k_1+k_2}{m} - \lambda_j & -\frac{k_2}{m} \\ -\frac{k_2}{m} & \frac{k_1+k_2}{m} - \lambda_j \end{pmatrix} \begin{pmatrix} L_{j1} \\ L_{j2} \end{pmatrix} = 0 \ .$$

For $\lambda_1 = (k_1)/m$, $L_{11} = L_{12}$; while for $\lambda_2 = (k_1 + 2k_2)/m$, $L_{21} = -L_{22}$. From $\mathbf{L}\mathbf{L}' = \mathbf{I}$, $L_{11} = L_{22} = \sqrt{\frac{1}{2}}$, and the unitary coordinate transform matrix $\mathbf{L}$ is just

$$\mathbf{L} \quad = \quad \begin{pmatrix} \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \\ -\sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \end{pmatrix}$$

and

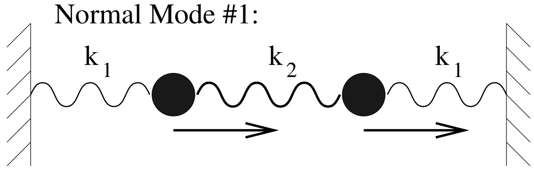
$$\mathbf{Q} \quad = \quad \mathbf{L}'\mathbf{q} \quad = \quad \begin{pmatrix} \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{2}} & \sqrt{\frac{1}{2}} \end{pmatrix} \begin{pmatrix} q_1 \\ q_2 \end{pmatrix} \quad = \quad \sqrt{\frac{1}{2}} \begin{pmatrix} q_1 - q_2 \\ q_1 + q_2 \end{pmatrix}$$

for the normal coordinates. The two normal mode frequencies are given by

$$\nu_1 \quad = \quad \frac{1}{2\pi}\sqrt{\frac{k_1}{m}} \qquad\qquad \nu_2 \quad = \quad \frac{1}{2\pi}\sqrt{\frac{k_1 + 2k_2}{m}} \qquad .$$

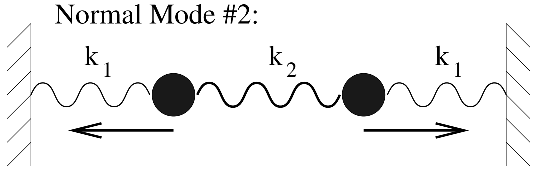
Pictorially:

Normal Mode #1:



Stretch or compress k 1 only

Normal Mode #2:



Stretch/compress both k 1 and k 2

which we could have guessed by symmetry!