CHM 504 - Vibrations of Polyatomic Molecules

Prof. Marissa Weichman

Spring 2022

We've talked extensively now about the vibrational quantum structure of diatomic molecules, and it's time now to extend this treatment to polyatomic molecules.

## 1   A classical treatment of polyatomic vibrations

For a molecule with N atoms, there are a total of $3N$ degrees of freedom in free space, since we can think about each atom moving along the three Cartesian coordinate axes. Three of the collective modes will involve translation of the entire molecule along the three Cartesian directions. 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, there are $3N - 6$ collective vibrational degrees of freedom for symmetric and asymmetric tops, and only $3N - 5$ for linear molecules.

Let's consider displacements within the molecule-fixed (e.g. body-fixed) frame:

$$(a,\, b,\, c)_\alpha \qquad \text{molecule-fixed coordinate for atom } \alpha \qquad (1)$$

$$(a,\, b,\, c)_{\alpha,e} \qquad \text{molecule-fixed equilibrium positions} \qquad (2)$$

$$(x, y, z)_\alpha = (a_\alpha - a_{\alpha,e},\, b_\alpha - b_{\alpha,e},\, c_\alpha - c_{\alpha,e}) \qquad \text{displacement coordinates} \qquad (3)$$
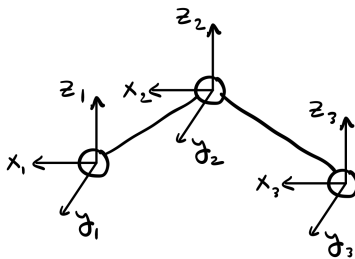
To examine the energetics of this system, let's start by writing down an expression for kinetic energy. The kinetic energy of vibration is given by:

$$KE = \frac{1}{2} \sum_{\alpha=1}^{N} m_\alpha \left[\left(\frac{dx_\alpha}{dt}\right)^2 + \left(\frac{dy_\alpha}{dt}\right)^2 + \left(\frac{dz_\alpha}{dt}\right)^2 \right] \qquad (4)$$

Let's simplify this a bit by introducing mass weighted coordinates:

$$q_1 = m_1^{1/2} x_1, \quad q_2 = m_1^{1/2} y_1, \quad \ldots \quad q_{3N} = m_N^{1/2} z_N \qquad (5)$$

so we can write

$$KE = \frac{1}{2}\sum_{\alpha=1}^{3N}\left(\frac{dq_i}{dt}\right)^2 = \frac{1}{2}\sum_{\alpha=1}^{3N}\dot{q}_i^2 \equiv \frac{1}{2}\dot{\mathbf{q}}^\mathsf{T}\cdot\dot{\mathbf{q}} \tag{6}$$

where in matrix form

$$\dot{\mathbf{q}} = \begin{bmatrix} \dot{q}_1 \\ \dot{q}_2 \\ \vdots \\ \dot{q}_{3N} \end{bmatrix} \tag{7}$$

Next, we can consider the (classical) potential energy, which for now we'll label $U(q_1, \ldots, q_{3N})$. As we have often done in this course, it is helpful to expand the potential energy in a Taylor series about the equilibrium molecule-fixed positions where $U_e = U(q_1 = 0, \ldots, q_{3N} = 0)$:

$$U(q_1, \ldots, q_{3N}) = U_e + \sum_{i=1}^{3N}\left(\frac{\partial U}{\partial q_i}\right)_e q_i + \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N}\left(\frac{\partial^2 U}{\partial q_i \partial q_k}\right)_e q_i q_k \tag{8}$$
$$+ \frac{1}{6}\sum_{i=1}^{3N}\sum_{j=1}^{3N}\sum_{k=1}^{3N}\left(\frac{\partial^3 U}{\partial q_i \partial q_j \partial q_k}\right)_e q_i q_j q_k + \cdots$$

Now we can always define our energy scale such that $U_e = 0$. Further, if we are at or close to the equilibrium positions of the atoms, then U is always near a potential minimum, and

$$\left(\frac{\partial U}{\partial q_i}\right)_e \simeq 0 \tag{9}$$

If we make the further assumption that vibrations may be treated harmonically (e.g. that Hooke's law is valid), then all terms with third-order derivatives and higher vanish in our Taylor expansion. We can therefore write:

$$U \simeq \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N}\left(\frac{\partial^2 U}{\partial q_i \partial q_j}\right)_e q_i q_j \tag{10}$$

$$= \frac{1}{2}\begin{bmatrix} q_1 & \cdots & q_{3N} \end{bmatrix} \begin{bmatrix} \left(\dfrac{\partial^2 U}{\partial q_1 \partial q_1}\right)_e & \cdots & \left(\dfrac{\partial^2 U}{\partial q_1 \partial q_{3N}}\right)_e \\ \vdots & \ddots & \vdots \\ \left(\dfrac{\partial^2 U}{\partial q_{3N} \partial q_1}\right)_e & \cdots & \left(\dfrac{\partial^2 U}{\partial q_{3N} \partial q_{3N}}\right)_e \end{bmatrix} \begin{bmatrix} q_1 \\ \cdots \\ q_{3N} \end{bmatrix} \tag{11}$$

$$\equiv \frac{1}{2}\mathbf{q}^\mathsf{T}\cdot\mathbf{U}\cdot\mathbf{q} \tag{12}$$

For our later manipulations, it will be useful to define the matrix elements of $\mathbf{U}$ as:

$$U_{ik} = \left(\frac{\partial^2 U}{\partial q_i \partial q_k}\right)_e \tag{13}$$

2

Now that we have expressions for the kinetic and potential energy of the system, we can approach a solution for the classical equations of motion of the system using Newtonian mechanics ($F = ma$).

First let's consider the force and acceleration of atom α along the x_α coordinate. First, force is given by the derivative of the potential with respect to displacement (e.g. work over distance):

$$F_{x,\alpha} = -\frac{\partial U}{\partial x_\alpha} = -\frac{\partial U}{\partial q_j}\frac{\partial q_j}{\partial x_\alpha} = -m_\alpha^{1/2}\frac{\partial U}{\partial q_j} \tag{14}$$

where we had defined $q_j = m_\alpha^{1/2}x_\alpha$ and therefore $\partial q_j/\partial x_\alpha = m_\alpha^{1/2}$.

Next, let's write down an expression for mass $\times$ acceleration of this atom, which we can then equate with Eqn. 14 using Newton's second law.

$$m_\alpha \cdot a_{x,\alpha} \equiv m_\alpha \frac{d^2 x_\alpha}{dt^2} = m_\alpha \frac{d^2}{dt^2}\left(\frac{q_j}{m_\alpha^{1/2}}\right) = m_\alpha^{1/2}\frac{d^2 q_j}{dt^2} \tag{15}$$

Setting Eqns. 14 and 15 equal, we find;

$$-m_\alpha^{1/2}\frac{\partial U}{\partial q_j} = m_\alpha^{1/2}\frac{d^2 q_j}{dt^2} \tag{16}$$

$$\rightarrow \boxed{\frac{d^2 q_j}{dt^2} + \frac{\partial U}{\partial q_j} = 0} \tag{17}$$

This is true for each degree of freedom of each atom with $j = 0, \ldots, 3N$. This gives us a system of $3N$ coupled equations. To evaluate this, we can recall our definition for U as a function of the coordinates q_i. Recall:

$$U \simeq \frac{1}{2}\sum_{i=1}^{3N}\sum_{k=1}^{3N}U_{ik}q_i q_k \tag{18}$$

$$= \frac{1}{2}\left[U_{11}q_1^2 + U_{12}q_1 q_2 + \cdots + U_{1k}q_1 q_k + U_{k1}q_k q_1 + \cdots + U_{kk}q_k^2 + \ldots\right] \tag{19}$$

$$\rightarrow \frac{\partial U}{\partial q_j} = \frac{1}{2}\left[U_{jj}\cdot 2\cdot q_j\right] + \frac{1}{2}\sum_{\substack{k=1\\k\neq j}}^{3N}\left[U_{jk} + U_{kj}\right]q_k \tag{20}$$

$$= U_{jj}\cdot q_j + \sum_{\substack{k=1\\k\neq j}}^{3N}U_{jk}\cdot q_k \quad = \quad \sum_{k=1}^{3N}U_{jk}\cdot q_k \tag{21}$$

And therefore, Eqn. 17 can be re-expressed as:

$$\frac{d^2 q_j}{dt^2} + \sum_{k=1}^{3N}U_{jk}\cdot q_k = 0 \tag{22}$$

It now becomes clear that this set of $3N$ equations of motion will take some effort to solve because each equation involves all $3N$ of the q_i coordinates. We can posit a solution to this problem by

defining *normal coordinates*, Q_i, which are linear combinations of the atomic displacements:

$$Q_i = \sum_{k=1}^{3N} c_{ik} q_k \tag{23}$$

where the c_{ik} coefficients are to be determined. Note that we can also define the vector form of these coordinates:

$$\mathbf{Q} = \begin{bmatrix} Q_1 \\ Q_2 \\ \vdots \\ Q_{3N} \end{bmatrix} \tag{24}$$

We want to define $\mathbf{Q}$ such that each $Q_i(t)$ can be found by solving a differential equation that is independent of the dynamics of all other $Q_{k \neq i}$. So, how do we find these new coordinates? In brief, we need to find a coordinate transformation $\{q_i\} \to \{Q_i\}$ that diagonalizes $\mathbf{U}$, since it is the off-diagonal terms U_{jk} that make Eqn. 22 difficult to solve.

We'll therefore carry out the following procedure:

1. Find the $3N$ eigenvalues λ_m of $\mathbf{U}$ given by $\det(\mathbf{U} - \lambda_m \mathbb{I}) = 0$.

2. Find the $3N$ eigenvectors $\mathbf{L}_m$ of $\mathbf{U}$ such that $\mathbf{U}\mathbf{L}_m = \lambda_m \mathbf{L}_m$. Normalize each $\mathbf{L}_m$ such that $\mathbf{L}_m^\mathsf{T} \mathbf{L}_m = 1$.

3. Construct the matrix $\mathbf{L}$ whose columns are the $\mathbf{L}_m$ eigenvectors:

$$\mathbf{L} = [\mathbf{L}_1; \mathbf{L}_2; \ldots; \mathbf{L}_{3N}] \tag{25}$$

   Because each $\mathbf{L}_m$ is normalized, $\mathbf{L}$ will be unitary, e.g. $\mathbf{L}^\mathsf{T} \mathbf{L} = \mathbb{I}$.

4. It turns out that through the magic of linear algebra, our $\mathbf{L}$ matrix provides a coordinate transformation between q_i and the Q_i coordinates which will diagonalize $\mathbf{U}$. In particular:

$$\mathbf{Q} = \mathbf{L}^\mathsf{T} \mathbf{q} \qquad \mathbf{q} = \mathbf{L}\mathbf{Q} \tag{26}$$

5. $\mathbf{L}$ also allows us to perform the following transformation of $\mathbf{U}$:

$$\mathbf{L}^\mathsf{T} \mathbf{U} \mathbf{L} = \mathbf{\Lambda} \qquad \text{with } \Lambda_{ij} = \delta_{ij} \cdot \lambda_i \tag{27}$$

   $\mathbf{\Lambda}$ is a diagonal matrix with the same eigenvalues as $\mathbf{U}$. We can say that $\mathbf{L}$ diagonalizes $\mathbf{U}$ through a unitary transformation.

Now, let's recall our expression for the potential energy from Eqn. 12:

$$U(q_1, \ldots q_{3N}) = \frac{1}{2} \mathbf{q}^\mathsf{T} \mathbf{U} \mathbf{q} \tag{28}$$

$$= \frac{1}{2} (\mathbf{L}\mathbf{Q})^\mathsf{T} \mathbf{U} (\mathbf{L}\mathbf{Q}) \tag{29}$$

$$= \frac{1}{2} \mathbf{Q}^\mathsf{T} \mathbf{L}^\mathsf{T} \mathbf{U} \mathbf{L} \mathbf{Q} \tag{30}$$

$$= \frac{1}{2} \mathbf{Q}^\mathsf{T} \mathbf{\Lambda} \mathbf{Q} = U(Q_1, \ldots Q_{3N}) \tag{31}$$

Since $\boldsymbol{\Lambda}$ is a diagonal matrix, we arrive at the following beautiful result:

$$U(Q_1, \ldots Q_{3N}) = \frac{1}{2} \sum_{k=1}^{3N} \lambda_k Q_k^2 \tag{32}$$

Finally, we note that (for a nonlinear molecule), three of our Q_k normal modes will represent translations of the entire system and three will represent rotations, neither of which distort the bond lengths between atoms. In free space, these translational and rotational degrees of freedom will not alter the potential energy of the system, and their λ_k will be zero. We can therefore write:

$$U(Q_1, \ldots Q_{3N}) = \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \tag{33}$$

for a nonlinear molecule. This represents a dramatic simplification in that U is now a single sum, rather than a double sum obtained in the original mass-weighted Q_i coordinates.

For good measure, let's also find the kinetic energy in our new normal coordinates. We can start from Eqn. 6 and find:

$$KE = \frac{1}{2} \dot{\mathbf{q}}^\mathsf{T} \cdot \dot{\mathbf{q}} = \frac{1}{2} (\mathbf{L}\dot{\mathbf{Q}})^\mathsf{T} \mathbf{L}\dot{\mathbf{Q}} \tag{34}$$

$$= \frac{1}{2} \dot{\mathbf{Q}}^\mathsf{T} \mathbf{L}^\mathsf{T} \mathbf{L}\dot{\mathbf{Q}} = \frac{1}{2} \dot{\mathbf{Q}}^\mathsf{T} \dot{\mathbf{Q}} \tag{35}$$

Evaluating Newton's second law for force and acceleration along the Q_k coordinates, just as we did in Eqn. 17 with q_k, we find:

$$\frac{\partial^2 Q_k}{\partial t^2} + \frac{\partial U}{\partial Q_k} = 0 \tag{36}$$

$$= \frac{\partial^2 Q_k}{\partial t^2} + \frac{\partial}{\partial Q_k} \left[\frac{1}{2} \sum_i \lambda_k Q_i^2 \right] \tag{37}$$

$$\rightarrow \boxed{\frac{\partial^2 Q_k}{\partial t^2} + \lambda_k Q_k = 0} \tag{38}$$

We've finally arrived at the major result here. Just as the principal axes diagonalized the moment of inertia tensor for polyatomic molecules, normal coordinates "diagonalize" the kinetic energy and potential energy expressions and yield a set of $3N - 6$ *independent* differential equations. The definition of these normal coordinates depend sensitively on both the symmetry of the molecule and the potential. It's also worth remembering that normal mode theory depends on the harmonic approximation!

Eqn. 38 is very simple to solve and allows us to extract the resonant frequencies of the system. The classical solutions are:

$$Q_k(t) = A_k \sin(\lambda_k^{1/2} t + \phi_k) \tag{39}$$

$$\omega_k = \lambda_k^{1/2} \tag{40}$$

2   A quantum mechanical treatment of polyatomic vibrations

Our classical normal mode solutions derived above provide a very straightforward quantum mechanical generalization of the one-dimensional harmonic oscillator. In normal coordinates, the vibrational Schrödinger equation becomes:

$$\left[-\frac{\hbar^2}{2} \sum_{k=1}^{3N-6} \frac{\partial^2}{\partial Q_k^2} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \right] |\Psi\rangle = E |\Psi\rangle \tag{41}$$

Since the Hamiltonian is now a linear sum over $3N - 6$ independent harmonic oscillator equations, the overall vibrational wavefunction $|\Psi\rangle$ can be written as a neatly-factored product of the wavefunctions for each vibrational degree of freedom:

$$\Psi(Q_1, Q_2, \cdots Q_{3N-6}) = \prod_{k=1}^{3N-6} \psi_{n_k}(Q_k) \tag{42}$$

where n_k is the vibrational quantum number of the kth normal mode. The individual ψ_{n_K} are simply those of a one-dimensional harmonic oscillator in the individual normal mode coordinates.

The energy of each normal mode is therefore

$$E_{n_k} = \hbar \omega_k \left(n_k + \frac{1}{2} \right) \tag{43}$$

where $\omega_k = \lambda_k^{1/2}$. The total vibrational energy of the system is

$$E = \sum_{k=1}^{3N-6} \hbar \omega_k \left(n_k + \frac{1}{2} \right) \tag{44}$$

Where of course for linear molecules, the expressions above run to $3N - 5$ instead of $3N - 6$.

States with one normal mode quantum number $n_k = 1$, and all others $n_{i \neq k} = 0$ are called *fundamental* vibrations. States in which $n_k \geq 2, n_{i \neq k} = 0$ are called overtones. States in which two or more normal mode quantum numbers are non-zero are called combination modes.

The intensities of transitions between, e.g., the vibrational ground state and the various fundamental, overtone, and combination bands is governed, as always, by the electric dipole selection rules. If we expand the Cartesian components of the dipole moment in a power series in the normal mode coordinates, we have:

$$\mu_{x,y,z} = \mu_{x,y,z}^0 + \sum_{k=1}^{3N-6} \left(\frac{\partial \mu_{x,y,z}}{\partial Q_k} \right)_0 Q_k + \cdots \tag{45}$$

through first order. For the kth normal mode, the harmonic oscillator selection rules can be generalized to:

$$\Delta n_1 = 0, \Delta n_2 = 0, \cdots, \Delta n_k = \pm 1, \cdots, \Delta n_{3N-6} = 0 \tag{46}$$

with an absolute intensity that is proportional to the square of the dipole derivative with respect to Q_k evaluated at the equilibrium geometry: $|\partial \mu_{x,y,z} / \partial Q_k|_0^2$.

Again, we see that the normal modes are uncoupled, and that to first order overtone and combination transitions are not allowed. The addition of anharmonicity does allow $\Delta n_k = \pm 2, \pm 3, \cdots$ *overtone* transitions. Combination transitions $\Delta n_i, \Delta n_k = \pm 1, \cdots$ will not appear unless there is a coupling of the dipole moment surface between two or more normal modes. Symmetry and group theory offers the easiest route to deciding whether a transition is permitted or forbidden. That is the topic to which we turn next.

3 Normal modes and molecular symmetry

Let's dip our toe briefly into group theory now, which we can use to drastically simplify finding and working with vibrational normal modes. Molecules are assigned to point groups which characterize their various symmetry elements. We'll use the C_{2v} point group to treat water here as a representative example.

Molecules that belong to the C_{2v} point group have one C_2 rotational axis, which we define to fall along the z molecular-frame axis, and two σ_v mirror planes that lie parallel to the C_2 axis. The character table for the C_{2v} point group is reproduced below, and features four irreducible representations that govern how symmetric objects like molecular orbitals and vibrational normal modes transform with respect to these symmetry elements. Irreducible representations labeled with $A(B)$ are (anti)symmetric with respect to rotation about the C_2 axis, while labeled with $1(2)$ are (anti)symmetric with respect to reflection through the xz mirror plane.

Table 1: C_{2v} character table

| C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear	quadratic
A_1	$+1$	$+1$	$+1$	$+1$	z	x^2, y^2, z^2
A_2	$+1$	$+1$	-1	-1	R_z	xy
B_1	$+1$	-1	$+1$	-1	x, R_y	xz
B_2	$+1$	-1	-1	$+1$	y, R_x	yz
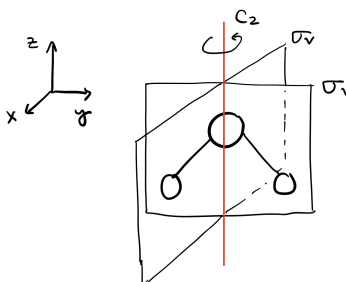
Why are these symmetry operations useful? Consider for a moment the (e.g. electronic or vibrational) wavefunction of a molecule, which obeys $\hat{H}\psi_n = E_n\psi_n$. If $\hat{O}_R$ is an operator corresponding to one of the symmetry operations in the point group of the molecule, then it can be shown that $\hat{O}_R$ commutes with the Hamiltonian:

$$[\hat{O}_R, \hat{H}] = 0 \tag{47}$$

This makes sense! The symmetry operations of a molecule reorganize its framework into a new state that is indistinguishable from the original, and so we do not expect the energy of the system

to be changed. Thus, we are free to choose wavefunctions such that they are eigenfunctions not only of the Hamiltonian, but also of the symmetry operations within our point group. We'll therefore demand that our vibrational normal modes transform as an irreducible representation of the relevant molecular point group.

So let's return to considering the vibrational normal modes of water. Recall that we have $3N = 9$ degrees of freedom for this system. $3N - 6 = 3$ of these will be vibrations, 3 will be rotations, and 3 will be translations. How do we find the symmetries of the vibrational normal modes?
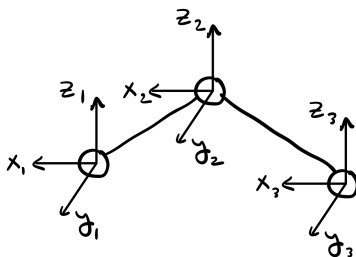
To examine the symmetries of the system, we must look at the effects of the four symmetry operations, $\hat{E}$, $\hat{C}_2$, $\hat{\sigma}_v(xz)$, and $\hat{\sigma}_v(yz)$ on the $3N$ atomic coordinates. To do this properly for water, one would create 9×9 matrix representations of the symmetry operators which would then act on the $[x_1, y_1, z_1, \ldots, x_{3N}, y_{3N}, z_{3N}]$ vector of coordinates. $\hat{E}$ for instance would be given by the identity matrix. All we will actually need are the traces of these matrices, which are given below:

Table 2: Reducible representation of the $3N$ atomic coordinates of H_2O

Operation	$\hat{E}$	$\hat{C}_2(z)$	$\hat{\sigma}_v(xz)$	$\hat{\sigma}_v(yz)$
$\Gamma_{3N}(H_2O)$	9	-1	$+1$	3

Another way to think about this "reducible" representation of our $3N$ coordinates is that it gives us a count of how many atomic coordinates are either "preserved" or "flipped" by each symmetry operation. $\hat{E}$ preserves all 9 coordinates. $\hat{C}_2$ rotates the molecule by 180 degrees about the z axis, so only z_2 is preserved while x_2 and y_2 are flipped to $-x_2, -y_2$. The coordinates on atoms 1 and 3 are swapped to entirely new locations in space, so they are discarded from this count. The final count is one "preserved" coordinate minus two "flipped" coordinates, to yield a sum of -1 in the $\hat{C}_2$ column.

The full $\Gamma_{3N}(H_2O)$ reducible representation can then be broken into a linear combination of $3N$ irreducible parts which transform according to the rows in the character table given earlier. In the case of water, we can show that Γ_{3N} can be decomposed as:

$$\Gamma_{3N}(H_2O) = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2 \tag{48}$$

Our last task is to break down this sum of irreducible representations into rotation, translation, and vibration. The simplest way to do this is to consult the last columns of the character table. Translation has the same symmetry properties as x, y, z, while rotation goes like R_x, R_y, R_z. From the C_{2v} table we can see that $x \to B_1$, $y \to B_2$, $z \to A_1$, and $R_x \to B_2$, $R_y \to B_1$, $R_z \to A_2$.

Therefore, for H_2O:

$$\Gamma_{trans} = 1A_1 \oplus 1B_1 \oplus 1B_2 \tag{49}$$

$$\Gamma_{rot} = 1A_2 \oplus 1B_1 \oplus 1B_2 \tag{50}$$

$$\Gamma_{vib} = 2A_1 \oplus 1B_2 \tag{51}$$

Thus, there are two normal modes of A_1 symmetry, which is totally symmetry with respect to all symmetry operations, and one of B_1 symmetry, which is symmetric only with respect to $\hat{E}$ and one of the $\hat{\sigma}_v$ operations. The modes of A_1 symmetry must maintain the C_{2v} nature of the molecular framework throughout the vibration and are clearly the symmetric stretch and the bend. The remaining B_2 mode is the asymmetric stretch. These three fundamental modes are by convention labeled ν_1, ν_2, ν_3 in the order given below:
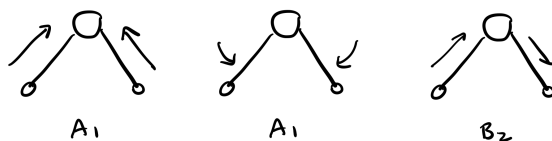
Although the group theory treatment tells us what the symmetries of the vibrational modes are, we must carry out the full normal mode analysis in order to predict their frequencies. This requires a detailed knowledge of the potential energy surface, and falls into the domain of problems best solved with your favorite quantum chemistry package.

We will examine, however, the role of symmetry in examining polyatomic vibrational selection rules. Group theory will immediately allow us to state whether a certain transition is electric dipole allowed or not.

Recall Fermi's golden rule, which states that a transition between two pairs of states i and f is allowed if:

$$\langle \psi_i | \vec{\mu} \cdot \hat{\epsilon} | \psi_f \rangle = \int \psi_i^* \cdot \vec{\mu} \cdot \hat{\epsilon} \cdot \psi_f \, dx \, dy \, dz \neq 0 \tag{52}$$

Using direct products of the relevant irreducible representations gives us an extremely convenient shorthand for performing these integrals. In order for the transition to be allowed, the integrand $\psi_i^* \cdot \vec{\mu} \cdot \hat{\epsilon} \cdot \psi_f$ must be a totally symmetric function, because otherwise the integration over the whole coordinate space will give zero. In group theoretical language, the product of the symmetry types of the wavefunctions and that of the dipole operator must contain the totally symmetric A_1 representation:

$$\Gamma(\psi_i) \otimes \Gamma(\vec{\mu} \cdot \hat{\epsilon}) \otimes \Gamma(\psi_f) \supset A_1 \tag{53}$$

The dipole operator always transforms like x, y, z, while for magnetic dipole, electric quadrupole, or Raman transitions, we must examine matrix element symmetries involving higher-order operators like x^2, y^2, xy, etc. which is why these various terms are included in the listings of character tables in most spectroscopy textbooks. The most succinct rule of thumb is the following: **Normal modes that transform as (x, y, z) in a given point group will be infrared active, while normal modes that transform as $(xy, xz, yz, x^2, y^2, z^2)$ will be Raman active.**

Table 3: C_{2v} product table

C_{2v}	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1

To wrap up this discussion, let's consider again the C_{2v} water molecule, where (x, y, z) corresponds to (B_1, B_2, A_1), and the (ν_1, ν_2, ν_3) transitions have (A_1, A_1, B_2) character. The product table for the C_{2v} point group is given above.

For the $(000) \to (001)$ transition we therefore have:

$$\langle 000|(x, y, z)|001\rangle = A_1 \otimes [B_1, B_2, A_1] \otimes B_2 = [A_2, A_1, B_2] \supset A_1 \quad \checkmark \tag{54}$$

and so this transition is allowed. Similarly, we find that the other two fundamental transitions, which involve A_1 upper states, are allowed by the z component of the electric dipole.

Group theory will only tell you if a transition is allowed or not by symmetry. The quantitative values of the dipole derivatives and anharmonicities determine the absolute strength.