Chemistry 21b – Spectroscopy
Lecture # 10 – The Quantum & Group Theoretical Treatment of Molecular Vibrations

The classical normal mode solution derived in Lecture #9 provides a very straightforward quantum mechanical generalization of the one-dimensional harmonic oscillator. In normal coordinates, the vibrational Schrödinger equation becomes:

\[
\left( -\frac{\hbar^2}{2} \sum_{i=1}^{3N} \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_{i=1}^{3N} \lambda_i Q_i^2 \right) \Psi = E \Psi .
\]

Since the Hamiltonian is now a linear sum over $3N$ (or really $3N - 6/3N - 5$ since the translational and rotational $\lambda_i$ are zero) harmonic oscillator equations, this means that the overall vibrational wavefunction $\Psi$ may be written as a product of one-dimensional wavefunctions, or

\[
\Psi = \psi_{n_1}(Q_1)\psi_{n_2}(Q_2) \cdots \psi_{n_{3N-6}}(Q_{3N-6}) ,
\]

where $n_i$ is the vibrational quantum number of the $i$th normal mode. The energy of each normal mode is simply

\[
E_{n_k} = (n_k + \frac{1}{2})\hbar \nu_k ,
\]

and the total energy is

\[
E_{n_k} = \sum_{k=1}^{3N-6} (n_k + \frac{1}{2})\hbar \nu_k .
\]

For linear molecules, the sums above run over $3N - 5$, of course. The total zero-point energy for the molecule is now

\[
E_0 = \sum_{k=1}^{3N-6} \frac{1}{2} \hbar \nu_k ,
\]

The individual $\psi_{n_i}$ are simply those of a one-dimensional harmonic oscillator in the individual normal mode coordinates. That is, they are the product of a Hermite polynomial times a $e^{-\alpha_k Q_k^2/2}$ exponential. In explicit terms, the normalized quantum mechanical normal mode eigenfunctions are given by

\[
\psi_{n_k}(Q_k) = \frac{1}{(2^{n_k} n_k! \pi)^{1/2}} \left( \frac{\alpha_k}{\pi} \right)^{1/4} e^{-\alpha_k Q_k^2/2} H_{n_k} \left( \alpha_k^{1/2} Q_k \right) ,
\]

where $H_{n_k}$ is the Hermite polynomial of order $n_k$ and $\alpha_k = 2\pi \nu_k/\hbar$. Thus, in the harmonic limit the normal modes are uncoupled. States with one normal mode quantum number equal to one and all others equal to zero are called fundamental vibrations, or modes. States in which one normal mode quantum is equal to two or more, and all others zero,
are called overtones. Finally, states in which two or more normal mode quantum numbers are equal to or greater than one are called combination modes.

The intensities of various fundamental, overtone, and combination bands are governed, as always, by the electric dipole selection rules. If we again expand the dipole moment function in a power series, as before, in the normal mode coordinates, we have

$$\mu_g = \mu_g^0 + \sum_{i=1}^{3N-6} \left( \frac{\partial \mu_g}{\partial Q_i} \right)_{0=e} Q_i + \ldots$$

g = x, y, z

through first order. For the $k$th normal mode, the harmonic oscillator selections rules as thus generalized to

$$n_1 = n'_1, n_2 = n'_2, \ldots, n_k = n'_k \pm 1, \ldots, n_{3N-6} = n'_{3N-6},$$

with an absolute intensity that is proportional to $|\left( \frac{\partial \mu_g}{\partial Q_k} \right)_{0=e}|^2$, the square of the dipole derivative evaluated at the equilibrium geometry. Again we see that the normal modes are uncoupled, and that, to first order, the overtones and combination bands are not allowed. The addition of anharmonicity does allow $\Delta n_k = \pm 1, \pm 2, \ldots$ overtones, but not combinations unless there is coupling of the dipole moment surface between two or more normal modes. Symmetry and group theory again offers the easiest route to deciding simply whether a transition is permitted or forbidden, a topic to which we turn next.

**Symmetry and Normal Modes**

Just as was true for the overall Hamiltonian, the vibrational Hamiltonian in normal mode coordinates commutes with the various symmetry operators of the molecular point group. Thus, the vibrational wavefunctions can be constructed such that they can be classified according to one of the irreducible representations, and we can use the machinery developed in Lecture #8 to examine selections rules, etc. As an example case, let's consider the $C_{2v}$ group again, in particular water. The total number of degrees of freedom is nine, and since water is non-linear they are spread equally among rotation, translation, and vibration. How do we find out what symmetries of the normal modes are?

![Figure 10.1 An outline of the $\Gamma_{3N}$ coordinates for water, which will be used to examine the normal mode symmetries.](image)

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The figure above illustrates the $\Gamma_{3N} = \Gamma_9$ coordinates for water. To examine the symmetries of the system, we must look at the effects of the four symmetry operations, $\hat{I}$, $\hat{C}_2$, $\hat{\sigma}_{xz}$ and $\hat{\sigma}_{yz}$ on the coordinates. To do this, we’d need to set up $9 \times 9$ matrices for each. $\hat{I}$ is easy since $\hat{I} \xi_1 \rightarrow \xi_1$, $\hat{I} \xi_2 \rightarrow \xi_2$, ..., $\hat{I} \xi_9 \rightarrow \xi_9$. In matrix notation, the identity operator is just the $9 \times 9$ unit matrix, with 1’s on the diagonal and zeroes elsewhere. Remember, all we’ll need to generate the character table are the traces of the matrices, and so in $\Gamma_{3N}$ for water the trace, or $\chi\Gamma(\hat{I})$, is 9, and $\Gamma_{3N} = 9$.

For the other symmetry operations the matrices are a bit more complex, but from their traces we can construct the following character table for $\Gamma_{3N}(\text{H}_2\text{O})$:

<table>
<thead>
<tr>
<th>Operation</th>
<th>$\hat{I}$</th>
<th>$\hat{C}_2$</th>
<th>$\hat{\sigma}_{xz}$</th>
<th>$\hat{\sigma}_{yz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{3N}(\text{H}_2\text{O})$</td>
<td>9</td>
<td>-1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

We must next decompose the $\Gamma_{3N}(\text{H}_2\text{O})$ reducible character table into the direct sum of its irreducible parts. The order of the group is four, and so to do this we take the character table products of $\Gamma_{3N}(\text{H}_2\text{O})$ with the individual irreducible representations in $C_{2v}$, normalized by the order of the group:

$$a_1 = a(A_1) = \frac{1}{4}(9 \times 1 - 1 \times 1 + 1 \times 1 + 3 \times 1) = 3$$

$$a_2 = a(A_2) = \frac{1}{4}(9 \times 1 - 1 \times 1 + 1 \times (-1) + 3 \times (-1)) = 1$$

$$b_1 = a(B_1) = \frac{1}{4}(9 \times 1 - 1 \times (-1) + 1 \times 1 + 3 \times (-1) = 2$$

$$b_2 = a(B_2) = \frac{1}{4}(9 \times 1 - 1 \times (-1) + 1 \times (-1) + 3 \times 1) = 3$$

Thus, the full $\Gamma_{3N}(\text{H}_2\text{O})$ irreducible representation, which includes translation, rotation, and vibration, is composed of

$$\Gamma_{3N}(\text{H}_2\text{O}) = 3A_1 \oplus A_2 \oplus 2B_1 \oplus 3B_2$$

Just how is this sum of irreducible representations broken down into rotation, translation, and vibration? We could write down the matrices corresponding to each of the relevant operators, but here it is much simpler to consult the last columns of the character tables listed in Atkins. Translation has the same symmetry properties as $x$, $y$, and $z$; while rotation goes like $R_x$, $R_y$, and $R_z$. From the $C_{2v}$ table we see that: $x \rightarrow B_1$, $y \rightarrow B_2$, $z \rightarrow A_1$; and $R_x \rightarrow B_2$, $R_y \rightarrow B_1$, $R_z \rightarrow A_2$. Thus,

$$\Gamma_{3N}(\text{H}_2\text{O}) = 3A_1 \oplus 1A_2 \oplus 2B_1 \oplus 3B_2$$

$$\Gamma_{Trans} = 1A_1 \oplus 0A_2 \oplus 1B_1 \oplus 1B_2$$

$$\Gamma_{Rot} = 0A_1 \oplus 1A_2 \oplus 1B_1 \oplus 1B_2$$

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Thus, there are two normal modes of $A_1$ symmetry, that is, which are totally symmetric, and one of $B_1$ symmetry, that is, which is symmetric only with respect to $I$ and one of the $\sigma_v$ operations. The modes of $A_1$ symmetry must maintain the $C_{2v}$ nature of the molecular framework, and are clearly the symmetric stretch and the bend. Thus, the only mode left, the asymmetric stretch, must be $B_2$.

As another quick example, consider the $XY_3$ pyramidal molecule. The group is $C_{3v}$, and following the above procedure yields:

$$\Gamma_{3N}(XY_3) = 3A_1 \oplus 1A_2 \oplus 4E$$
$$\Gamma_{Trans} = 1A_1 \oplus 0A_2 \oplus 1E$$
$$\Gamma_{Rot} = 0A_1 \oplus 1A_2 \oplus 1E$$

and so

$$\Gamma_{Vib} = 2A_1 \oplus 0A_2 \oplus 2E$$

Thus, of the 6 vibrational modes, two will be non-degenerate $A_1$ (the symmetric stretch and bend) vibrations, while the other four will consist of two doubly degenerate pairs.

**Wavefunction Symmetry and Selection Rules**

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 we’ll not consider the quantitative, algebraic analysis of normal modes here (which uses what are called $F$ and $G$ matrices for the potential and kinetic energy, respectively) since a number of computer routines are now available which do the job numerically.

We will examine, however, the role of symmetry in examining polyatomic vibrational selection rules. Since the overall wavefunction is the product of one-dimensional harmonic oscillator wavefunctions in which the exponentials are all even, the symmetry of the individual 1D wavefunctions follows that of the appropriate Hermite polynomial – and therefore will be even or odd depending on the value of the vibrational quantum number.

Let’s consider the case of water, again. There are three fundamental modes, and the state of the molecule is labeled $(\nu_1, \nu_2, \nu_3)$, where $\nu_1$ = the symmetric stretch, $\nu_2$ = the bend, and $\nu_3$ = the asymmetric stretch. For other triatomic molecules, the bend is always labeled $\nu_2$ by convention. An outline of the fundamental modes and their symmetries for water are shown below, from which we see that the fundamental vibration wavefunction symmetries follow those of the normal modes. What about overtones and combination bands? If there are no degeneracies, then overtones alternate with odd overtones having the same symmetry as the fundamental and even ones being totally symmetric. We can use direct products to verify this and to examine the combinations modes. For $C_{2v}$, we find

$$\psi(111) = A_1 \otimes A_1 \otimes B_2 = B_2$$
$$\psi(120) = A_1 \otimes A_1 \otimes A_1 = A_1$$
Having classified the vibrational states of $XY_2$ (say water) as having “symmetry types” within the $C_{2v}$ group, we can then say immediately using group theory whether a certain transition will be, e.g., electric dipole allowed or not. The physical reasoning is the same as described earlier, namely that the integrand in the matrix element(s) 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 the of the dipole (or higher order) operator must be $A_1$.

(1) For vibrational spectra, it is the symmetry of the normal modes that must be considered.

(2) For electronic spectra, we’ll find it is the molecular orbital symmetry that must be considered.

In either case, for electric dipole transitions we must examine the matrix element symmetries involving $x, y, z$, while for magnetic dipole, electric quadrupole, or Raman transitions (more on this next time) we must examine matrix element symmetries involving operators like $x^2, y^2, xy, \ldots$, which is why these various terms are including in the listings of character tables in most spectroscopy textbooks.

To wrap this up, let’s consider the $C_{2v}$ example again, where $(x, y, z)$ correspond to $(B_1, B_2, A_1)$; while the vibrations have $(A_1, A_1, B_2)$ character for $(\nu_1, \nu_2, \nu_3)$. For the $(000) \rightarrow (001)$ transition, we have:

$$<000|x|001> = A_1 \otimes B_1 \otimes B_2 = A_2 \neq A_1$$

$$<000|y|001> = A_1 \otimes B_1 \otimes B_2 = A_1 = A_1$$

$$<000|z|001> = A_1 \otimes A_1 \otimes B_2 = B_2 \neq A_1$$

Figure 10.2 Symmetries of the fundamental vibrations for water.

$$\psi(003) = A_1 \otimes A_1 \otimes B_2 = B_2$$

and so forth. For this sort of work it is most convenient to use the product table of the group rather than the character tables. For $C_{2v}$, the product table looks like:

$$\begin{array}{c|cccc}
C_{2v} & A_1 & A_2 & B_1 & B_2 \\
\hline
A_1 & A_1 & A_2 & B_1 & B_2 \\
A_2 & A_2 & A_1 & B_2 & B_1 \\
B_1 & B_1 & B_2 & A_1 & A_2 \\
B_2 & B_2 & B_1 & A_2 & A_1 \\
\end{array}$$
and so this transition is allowed. Similarly, we find that the other two transitions, which involve $A_1$ upper and lower states, are allowed by the $z$ electric dipole term. Similarly, for the bent XY$_2$ molecule, all of the (000) $\rightarrow$ even overtones (which are also $A_1$) are electric dipole allowed, as are essentially all other bands. A summary of the mode structure and allowed transitions for the bent XY$_2$ molecule are summarized in the figure above.

Group theory will only tell you if a suite of transitions is allowed or not by symmetry, the quantitative values of the dipole derivatives and anharmonicities determine the absolute strength! For linear YXY or XYY molecules the appropriate groups are $D_{\infty h}$ or $C_{\infty v}$. Since degeneracy is involved, things are a bit more difficult. In particular, we need to utilize what are called symmetrical products $[\Gamma \otimes \Gamma]^+$ rather than the direct products we have used above. We’ll look at this more next time when we examine the Raman spectroscopy and rotational band structure of linear molecules.

Figure 10.3 An outline of the fundamental, overtone, and combination modes for a bent XY$_2$ molecule, along with their symmetries in the $C_{2v}$ point group.