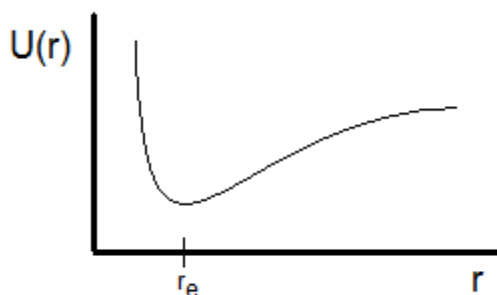


## Chapter 4: The Harmonic Oscillator and Vibrational Spectroscopy

One of the four important problems in quantum mechanics that can be solved analytically is that of the Harmonic Oscillator. This problem is very important to chemists as it provides the model for vibrating molecules and explains what we see in infrared and Raman spectra of molecules. In this chapter we will develop the problem, discuss the limitations of the simple problem and how we deal with them, and the applications of the conclusions to molecular spectroscopy and the measurement of molecular properties.

### The Potential Energy Surface for a Diatomic Molecule

Consider the **potential energy surface** for a diatomic molecule. The functional form can be seen in the following graph.



In the surface, it is easy to see the “hard wall” on the left side, where the repulsive force between atoms is strong (which is why the curve is so steep) and the “soft wall” on the right side of the well, where the restorative force of the chemical bond exists. The bond length at the potential minimum is indicated by  $r_e$ , the equilibrium bond length.

The function can be expressed as a **Taylor series** expansion. For convenience, we can define  $x = (r-r_e)$ . We will also define the zero of energy to be the bottom of the potential well. Given these definitions and the Taylor expansion about  $x = 0$  which can be expressed by

$$U(x) = U(0) + \left. \frac{d}{dx} U(x) \right|_{x=0} (x) + \frac{1}{2} \left. \frac{d^2}{dx^2} U(x) \right|_{x=0} (x^2) + \frac{1}{6} \left. \frac{d^3}{dx^3} U(x) \right|_{x=0} (x^3) + \dots$$

We can evaluate these terms qualitatively based on the above diagram and the definitions provided above. The first two terms of the expansion are zero, by the choice of the zero of

energy and because the derivative is zero at the potential minimum. The third and fourth terms are simplified by making the following substitutions

$$\left. \frac{d^2}{dx^2} U(x) \right|_{x=0} \equiv k \quad \text{and} \quad \left. \frac{d^3}{dx^3} U(x) \right|_{x=0} \equiv \gamma$$

The new function can be rewritten as

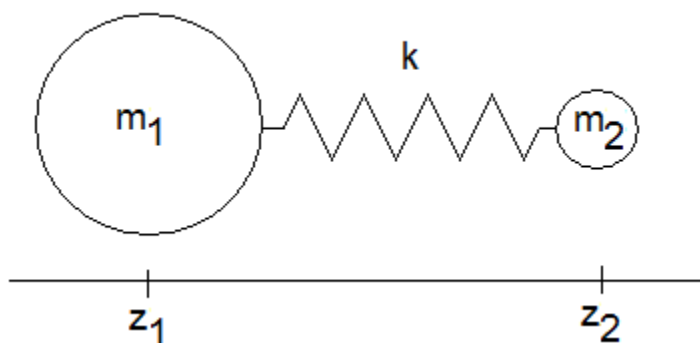
$$U(x) = \frac{1}{2} k x^2 + \frac{1}{6} \gamma x^3 + \dots$$

And if the series is truncated at the  $x^2$  term, it yields the familiar Harmonic Oscillator potential energy function that corresponds to a Hook's Law oscillator.

$$U(x) = \frac{1}{2} k x^2$$

### Transforming to Center of Mass Coordinates

Consider a diatomic molecule that can be modeled as two masses ( $m_1$  and  $m_2$ ) attached by a spring that has a force constant  $k$ . The location of atom 1 is  $z_1$  and that of atom 2 is  $z_2$ . The equilibrium length of the spring is  $r_e$ .



The force acting on either atom can be expressed in two ways.

$$F = ma \quad \text{and} \quad F = -kx$$

where  $m$  is either  $m_1$  or  $m_2$  and  $x$  is the displacement from the equilibrium distance, given by

$$x = (z_2 - z_1 - r_e)$$

The force acting on atom 1 is in the opposite direction of that acting on atom 2. This suggests two equations that will govern the motion of atom 1 and atom 2 respectively.

$$m_1 \frac{d^2}{dt^2} z_1 = k(z_2 - z_1 - r_e) \quad \text{and} \quad -m_2 \frac{d^2}{dt^2} z_2 = k(z_2 - z_1 - r_e)$$

Dividing both equations by the masses yields the following pair of equations.

$$\frac{d^2}{dt^2} z_1 = \frac{k}{m_1} (z_2 - z_1 - r_e) \quad \text{and} \quad -\frac{d^2}{dt^2} z_2 = \frac{k}{m_2} (z_2 - z_1 - r_e)$$

Add these two equations yields

$$\frac{d^2}{dt^2} z_1 - \frac{d^2}{dt^2} z_2 = \left( \frac{1}{m_1} + \frac{1}{m_2} \right) k (z_2 - z_1 - r_e)$$

The term  $\left( \frac{1}{m_1} + \frac{1}{m_2} \right)$  has important significance, as it is the reciprocal of the reduced mass.

$$\begin{aligned} \left( \frac{1}{m_1} + \frac{1}{m_2} \right) &= \frac{m_1 + m_2}{m_1 m_2} = \frac{1}{\mu} \\ \mu &= \frac{m_1 m_2}{m_1 + m_2} \end{aligned}$$

The reduced mass is introduced as a consequence of moving to center of mass coordinates. It is the mass of a single object that would move with the same frequency of oscillation were it attached to a fixed point by a spring of the same force constant. It is important to note that  $\mu$  has units of mass. Also, in the limit that  $m_1$  and  $m_2$  have the same value (let's call it  $m_1$ )

$$\begin{aligned} \mu &= \frac{m_1 m_1}{m_1 + m_1} \\ &= \frac{m_1^2}{2m_1} \\ &= \frac{m_1}{2} \end{aligned}$$

This result makes a great deal of sense because for equal masses, the motion of the molecule will involve equal and opposite motions of the two atoms relative to the center of mass (which will be the middle of the bond.) Thus, a single mass oscillating with the same frequency is moving

relative to a distance that is in the middle of the spring. Hence, the mass will have to be half of the mass of one of the atoms, or the frequency would be different.

The other important limit is when one mass is significantly larger than the other. Consider what happens when  $m_1 \gg m_2$

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} \\ &\approx \frac{m_1 m_2}{m_1} \\ &= m_2\end{aligned}$$

This result makes a great deal of sense because if one mass is significantly larger than the other, it will be the light atom that undergoes the larger motion. In the limit that  $m_1 = \infty$ , the center of mass is located at  $z_1$  and the heavy atom becomes a fixed point in the motion.

The next task is to simplify things further by introducing a mass-weighted coordinate,  $Z$ .

$$Z \equiv \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

This expression gives the location of the center of mass of the molecule. The utility of this substitution is found in taking the difference of the two equations

$$m_1 \frac{d^2}{dt^2} z_1 = k(z_2 - z_1 - r_e) \quad \text{and} \quad -m_2 \frac{d^2}{dt^2} z_2 = k(z_2 - z_1 - r_e)$$

which yields

$$\begin{aligned}m_1 \frac{d^2}{dt^2} z_1 + m_2 \frac{d^2}{dt^2} z_2 &= 0 \\ \frac{d^2}{dt^2} (m_1 z_1 + m_2 z_2) &= 0\end{aligned}$$

Dividing both sides by  $(m_1 + m_2)$  yields

$$\begin{aligned}\left( \frac{1}{m_1 + m_2} \right) \frac{d^2}{dt^2} (m_1 z_1 + m_2 z_2) &= 0 \\ \frac{d^2}{dt^2} \left( \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2} \right) &= 0\end{aligned}$$

Finally, making the substitution for the center of mass

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$$\frac{d^2}{dt^2} Z = 0$$

which tells us that the center of mass of the system does not move in time.

## Solving the Schrödinger Equation

It is convenient to make the substitution that

$$x = (z_2 - z_1 - r_e)$$

This allows us to write the Hamiltonian for the system then as

$$\hat{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

where  $\mu$  is the reduced mass given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$k$  is the force constant of the bond and  $x$  is defined by

$$x = (r - r_e)$$

as previously state. The Schrödinger equation is then given by

$$\left( -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right) \psi(x) = E \psi(x)$$

## Energy Levels

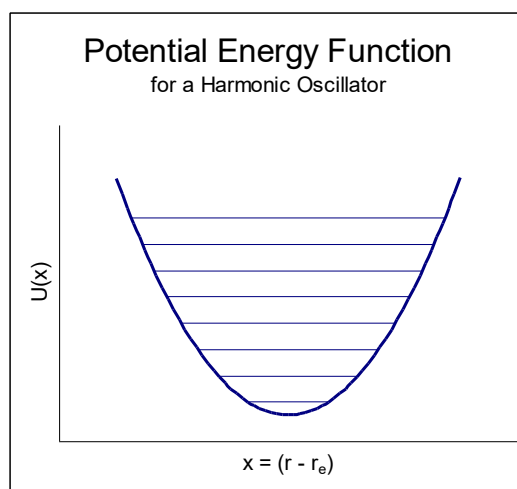
The boundary conditions require that the square of the wavefunction must have a finite area below it in order to ensure that the wavefunction is normalizable. The only way this happens is if the following conditions are met

$$\lim_{x \rightarrow \pm\infty} \psi(x) = 0$$

The resulting energy levels are the set of eigenvalues that correspond to the functions that satisfy the above stated boundary condition. These energies have values given by

$$E_v = \hbar \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) \quad v = 0, 1, 2, 3, \dots$$

Notice how the use of the boundary conditions is what leads to the instruction of quantized energies.



The resulting energy levels are evenly spaced with increasing energy. The actual spacing is determined by the physical characteristics of a given molecule, namely the reduced mass and the force constant.

### *Spectroscopic Constants and Force Constants*

Vibrational spectroscopy is often done using units of  $\text{cm}^{-1}$ . Energies expressed in terms of this unit are called **term values**. The term value is given as the energy divided by Planck's constant and the speed of light ( $E/hc$ ). Standard notation uses the symbol  $G_v$  to indicate the term value for vibrational energy.  $G_v$  is given by

$$G_v = \frac{E_v}{hc} = \omega_e \left( v + \frac{1}{2} \right)$$

where

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

The vibrational constant  $\omega_e$  can be determined experimentally for specific molecules. Consider the following values for various molecules.

Molecule	$\omega_e$ (cm <sup>-1</sup> )	k (N/m)	$\mu$ (kg)
<sup>1</sup> H <sup>35</sup> Cl	2989.74	516	1.627 x 10 <sup>-27</sup>
<sup>1</sup> H <sup>79</sup> Br	2649.67	412	1.652 x 10 <sup>-27</sup>
<sup>1</sup> H <sup>127</sup> I	2309.5	314	1.660 x 10 <sup>-27</sup>
<sup>19</sup> F <sup>19</sup> F	916.64	347	1.577 x 10 <sup>-26</sup>
<sup>16</sup> O <sup>16</sup> O	1580.93	1177	1.328 x 10 <sup>-26</sup>
<sup>14</sup> N <sup>14</sup> N	2359.61	3116	1.163 x 10 <sup>-26</sup>

Two important points can be made from this data. First, a typical force constant for a single bond is on the order of a couple hundred N/m. Secondly, multiple bonds lead to significantly larger force constants. This is not too surprising since the force constant gives a measure of the stiffness of the bond.

## The Wavefunctions

The wavefunctions for the harmonic oscillator are determined by solving the Schrödinger equation. As stated before, the only wavefunctions that obey the boundary conditions have eigenvalues given by

$$E_v = \hbar \sqrt{\frac{k}{\mu}} (v + \frac{1}{2})$$

where  $v = 0, 1, 2, 3, \dots$ . The wavefunctions themselves can be determined by solving the differential equation using a power-series solution. In the end, we find that the resulting function involve a set of **orthogonal polynomials** known as the **Hermite Polynomials**. We will discuss some properties of this important set of functions before discussing the wave functions themselves.

## Hermite Polynomials

The **Hermite polynomials** are a set of orthogonal polynomials. Like all sets of orthogonal polynomials, they have 1) a generator formula, 2) an orthogonality relationship and 3) a (or several) recursion relations that relate one function in the series to others.

The Hermite polynomials can be generated using the following function

$$H_v(y) = (-1)^v e^{y^2} \frac{d^v}{dy^v} e^{-y^2}$$

Using this function, the first few Hermite polynomials can be generated.

v	H <sub>v</sub> (y)
0	1
1	2y
2	4y <sup>2</sup> -2

Further members of the set of functions can be generated using one of the important recursion relations.

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

Using this function, we can generate a longer list of Hermite polynomials without having to take so many derivatives.

v	H <sub>v</sub> (y)
0	1
1	2y
2	4y <sup>2</sup> -2
3	8y <sup>3</sup> -12y
4	16y <sup>4</sup> -48y <sup>2</sup> +12
5	32y <sup>5</sup> -160y <sup>3</sup> +120y
	<i>Etc.</i>

Another important relationship between these functions is that

$$\frac{d}{dy} H_v(y) = 2vH_{v-1}(y)$$

In addition to these relationships, the Hermite polynomials have an important orthogonality relationship.

$$\int_{-\infty}^{\infty} H_v(y)H_{v'}(y)e^{-y^2} dy = v! 2^v \sqrt{\pi} \delta_{vv'}$$

The Hermite polynomials also have important symmetry properties. Each function in the set is an eigenfunction of the **inversion operator**. The inversion operator is a symmetry operator that is defined by the operation (in one dimension)



$$\hat{i}f(x) = f(-x)$$

Functions that are eigenfunctions of this operator can be classified as being either **even function** or **odd functions**.

Even	$f(-x)=f(x)$
Odd	$f(-x) = -f(x)$

Even functions are **symmetric** eigenfunctions of the inversion operator and odd functions are **antisymmetric** eigenfunctions as their eigenvalues are +1 and -1 respectively. Even and odd functions also have important properties when integrated over symmetric intervals.

Even	$\int_{-a}^a f(x)dx = 2 \int_0^a f(x)dx$
Odd	$\int_{-a}^a f(x)dx = 0$

These properties can greatly simplify integration involving these types of functions!

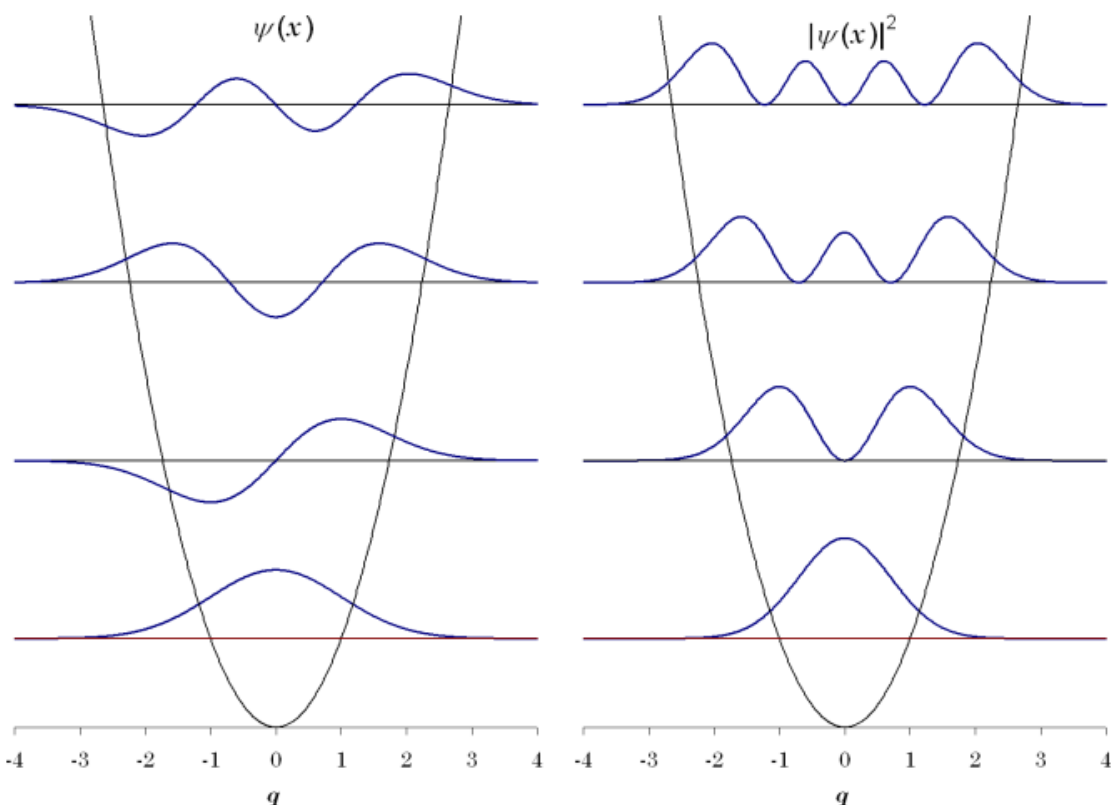
### *The Harmonic Oscillator Wavefunctions*

The wavefunctions for the Harmonic Oscillator have three important parts: 1) a normalization constant, 2) a Hermite polynomial and 3) an exponential function that insures the orthogonality of the wavefunctions.

$$\psi_v(x) = N_v H_v \left( \alpha^{1/2} x \right) e^{-\alpha x^2 / 2}$$

where

$$\alpha = \sqrt{k \cdot \mu} \quad \text{and} \quad N_v = \sqrt{\frac{\sqrt{\alpha/\pi}}{2^v \cdot v!}}$$



## Expectation Values

The simplicity of the wavefunctions makes the calculation of expectation values very simple for the harmonic oscillator problem.

### Position

The expectation value of position can be determined solely based on symmetry arguments. Recall that harmonic oscillator wavefunctions are either even or odd functions. The symmetry of the products of even or odd functions can be summarized as follows.

	even	odd
even	even	odd
odd	odd	even

It is easy to recognize this multiplication table as arising from taking the products of the eigenvalues of the functions with respect to the inversion operator.

	1	-1
1	1	-1

$$-1 \quad | \quad -1 \quad 1$$

These results will be used to demonstrate that the expectation value of position is the same for all of the stationary wavefunction. Consider the integral required to calculate this value.

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi_v \cdot x \cdot \psi_v dx$$

The wavefunction  $\psi_v$  is either an even or odd function depending only on whether  $v$  is even or odd. Since the  $\hat{x}$  operator is itself an odd function (always), there are only two possibilities for the total symmetry of the integrand.

$\psi_v$	$x$	$\psi_v$	Integrand Symmetry
even	odd	even	odd
odd	odd	odd	odd

The pattern emerges due to the fact that the product of even and odd function produces a resulting function according to the following symmetry multiplication table.

Regardless of whether the wavefunction is an even or odd function, the product

$$\psi_v \cdot x \cdot \psi_v$$

is always an odd function. And as we have seen before, the integral of an odd function over any symmetric interval is zero by symmetry.

Therefore, the expectation value of  $x$ ,  $\langle x \rangle$ , is always 0 for any eigenstate of the harmonic oscillator. This means that  $\langle r \rangle = r_e$ , the equilibrium bond length.

## Momentum

The evaluation of the expectation value of momentum can be made following the same symmetry arguments. In order to do this, one must consider the effect of taking a derivative of a function.

Consider the following even function

$$f(x) = 4x^2 - 2$$

The first derivative of this function is given by

$$\frac{d}{dx} f(x) = 8x$$

which is an odd function. The derivative of this function

$$\frac{d}{dx} 8x = 8$$

yields an even function. The following set of properties will hold for the symmetries of functions and their derivatives.

$f(x)$	$\frac{d}{dx} f(x)$
even	odd
odd	even

As such, the symmetry of the integrand for the calculation of the expectation value of momentum

$$\int_{-\infty}^{\infty} \psi_v \hat{p} \psi_v dx$$

must always be an odd function, since the  $\hat{p}$  takes the first derivative of the wavefunction.

$\psi_v$	$\hat{p}\psi_v$	Integrand Symmetry
even	odd	odd
odd	even	odd

The result is that the expectation value of momentum,  $\langle p \rangle$ , must also be 0 for any eigenstate of the harmonic oscillator problem. Again, this can be reasoned by noting that half of the time the momentum measured will be in the direction of the bond stretching, and the other half of the time in the direction of the bond being compressed. On average, these two circumstances will cancel, yielding an average value of  $\langle p \rangle = 0$ .

### Energy

As with any eigenstate, the expectation value of energy  $\langle E \rangle$  is easy to calculate. Recall that the wavefunctions were determined to be eigenfunctions of the Hamiltonian.

$$\hat{H}\psi_v = E_v\psi_v$$

As such, The expectation value of energy is trivially easy to find for a system in an eigenstate.

$$\begin{aligned}
\langle E \rangle &= \int_{-\infty}^{\infty} \psi_v \hat{H} \psi_v dx \\
&= \int_{-\infty}^{\infty} \psi_v E_v \psi_v dx \\
&= E_v \int_{-\infty}^{\infty} \psi_v \psi_v dx \\
&= E_v
\end{aligned}$$

since the wavefunctions are normalized. The expectation value of energy is always an eigenvalue of the Hamiltonian for a system that is in an eigenstate of the Hamiltonian.

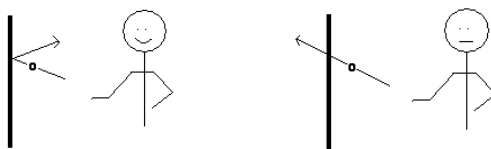
## Tunneling

One of the curious consequences of quantum mechanics can be seen in the form of **tunneling**. This odd behavior becomes possible whenever the square of the wavefunction extends beyond a classical barrier to the motion of the particle or molecule. In the case of the harmonic oscillator, this is seen as possible since the squared wavefunction extends beyond the classical turning points of the oscillation.

The classical turning point is defined as the point in the motion where all energy has been converted from kinetic energy to potential energy. At this point, the motion switches direction as potential energy is converted back into kinetic energy. Since there is a non-zero value of the squared wavefunction beyond this point for all eigenstates, there is a non-zero probability of measuring the position of the system to lie beyond these classical turning points. And then if there is a new potential well accessible if the system tunnels through the classical barrier, there is a non-zero probability of finding the system in that well, meaning that the system may have changed states completely!

This result is another example of the bizarreness of quantum mechanics. If one were to consider a classical ball that is thrown against the wall at the front of the classroom, one expects that the ball will return to the thrower after bouncing off the wall every time. But for a quantum mechanical ball, there is a non-zero possibility of finding the ball on the other side of the wall! If this were to be the case, the ball would have been said to have tunneled through the wall.

The probability for this happening is proportional to that fraction of the area under the squared wavefunction curve that lies beyond the classical barrier. This probability will be decreased for heavier objects as the fraction of wavefunction beyond the classical barrier will be smaller.



## Strengths and Weaknesses

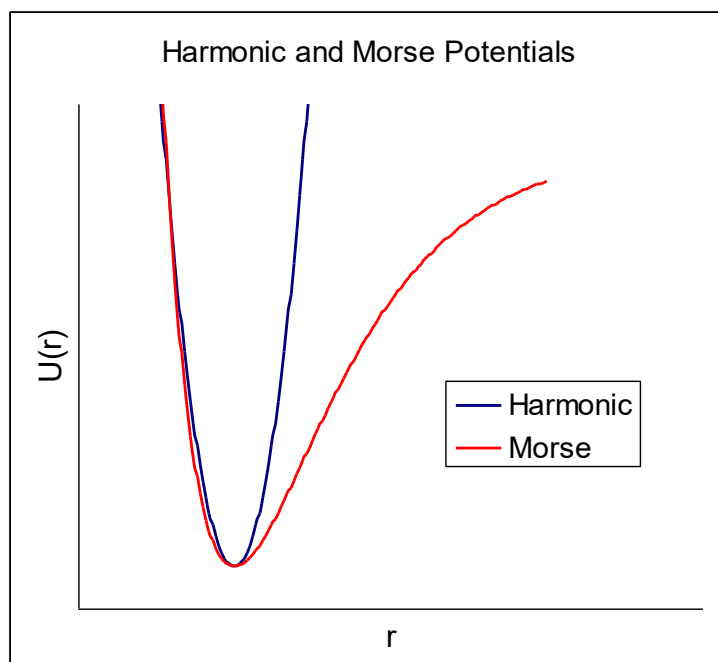
Keeping in mind that the harmonic oscillator model is an approximate model, it should not come as a surprise that there are a number of shortcomings to it.

The harmonic oscillator does not place any constraints on bond length. At the short bond length side of the potential, there is nothing in the model to prevent the bond length from becoming zero or even negative (implying that it is possible for one atom to pass through the other in a molecule). Additionally, the harmonic oscillator does not allow for molecular dissociation as the potential energy just keeps increasing with increasing bond length. None the less, the harmonic oscillator model works quite well for small displacements from the equilibrium bond length.

## The Morse Potential

One improved form of a potential energy function was provided by Phillip Morse (Morse, 1929). The Morse potential is given by the following function

$$U(r) = D_e \left(1 - e^{-\beta(r-r_e)}\right)^2$$



where  $D_e$  is the dissociation energy of the molecule. While this function still allows for negative bond lengths, it does allow for molecular dissociation at long bond lengths.

The force constant for the Morse potential is determined by evaluating the second derivative of the potential energy function at the potential minimum.

$$k = \left. \frac{d^2}{dr^2} U(r) \right|_{r=r_e}$$

Based on the expression given above for the Morse potential, the following result is obtained.

$$k = 2D_e\beta^2$$

### Anharmonicity

A solution to the Schrödinger equation using the Morse potential produces an additional constant in the energy expression for vibrational energy.

$$G_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2$$

The new constant,  $\omega_e x_e$ , is called an **anharmonicity constant**, as it accounts for deviation from the harmonic potential. For a more general potential energy function, the expression for the vibrational term value can be expressed as a longer power series in  $(v + \frac{1}{2})$ .

$$G_v = \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 + \dots$$

For well-behaved molecules, the magnitude of the anharmonicity constants decreases with increasing order in  $(v + \frac{1}{2})$ . Thus, the series can be truncated at some point and will provide an adequate model for the purposes of fitting experimental data.

## Vibrational Spectroscopy Techniques

Infrared and Raman spectroscopy are two experimental methods that are commonly used by chemists to measure vibrational frequencies ( $\omega_e$ ). Infrared spectroscopy generally involves direct absorption whereas Raman spectroscopy involves scattering of light.

### Infrared Spectra

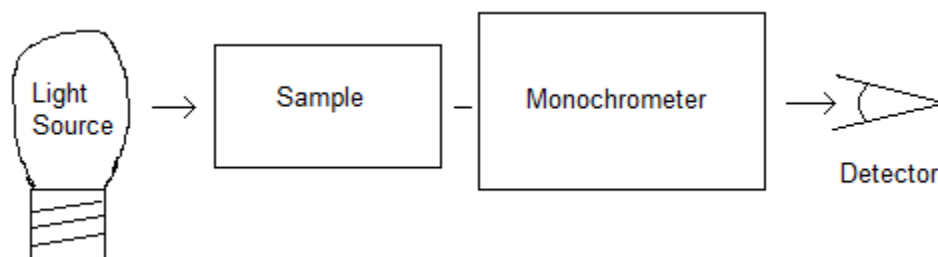
Infrared spectroscopy is a commonly used technique in the identification of molecular compounds. It is also a very convenient technique to use in determining molecular force constants, since the spectrum records vibrational frequencies.

Based on the results of the harmonic oscillator problem, the selection rules for an infrared spectrum are determined to be

$$\Delta v = \pm 1$$

That means that as a molecule absorbs or emits a single infrared photon (meaning the electronic state of the molecule does not change) the vibrational quantum number can go up or down (depending on absorption or emission) by one quantum. For a typical experiment, the theory predicts a single band in the spectrum of a molecule, and that band will be centered at a frequency equal to  $\omega_e$  for the molecule.

A schematic diagram of a typical infrared absorption spectroscopy experiment is shown below. The light is produced at the source (typically an incandescent light bulb or a glowbar), passes through the sample where some of the light can be absorbed, and then the monochromator (which is typically either a grating or an interferometer) which is used to distinguish between the various frequencies of light, and finally the light is detected by a detector. Plotting detected intensity as a function of frequency produces the spectrum.



### *Determining a Force Constant*

Consider the experimentally determined value for carbon monoxide (CO.) The spectrum shows a strong absorption at  $2143\text{ cm}^{-1}$  due to CO. Using this value for  $\omega_e$  (it is actually a little off due to anharmonicity), the force constant can be determined for the molecule.

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Using a value of  $1.14 \times 10^{-26}\text{ kg}$  for the reduced mass of the molecule, the force constant is found to be  $1856\text{ N/m}$ . The literature value for this force constant is  $1860\text{ cm}^{-1}$ . Given that this calculation did not treat anharmonicity, the agreement is pretty good!

### *Progressions in Electronic Spectra*

Electronic transition in diatomic molecules which can be observed in the visible and ultraviolet regions of the spectrum can have a great deal of vibrational structure as the molecule is free to vibrate in both the upper and lower states. The following figure shows vibrational progressions in the emission spectrum of AlBr near  $2800\text{ Å}$  (Fleming & Mathews, 1996).



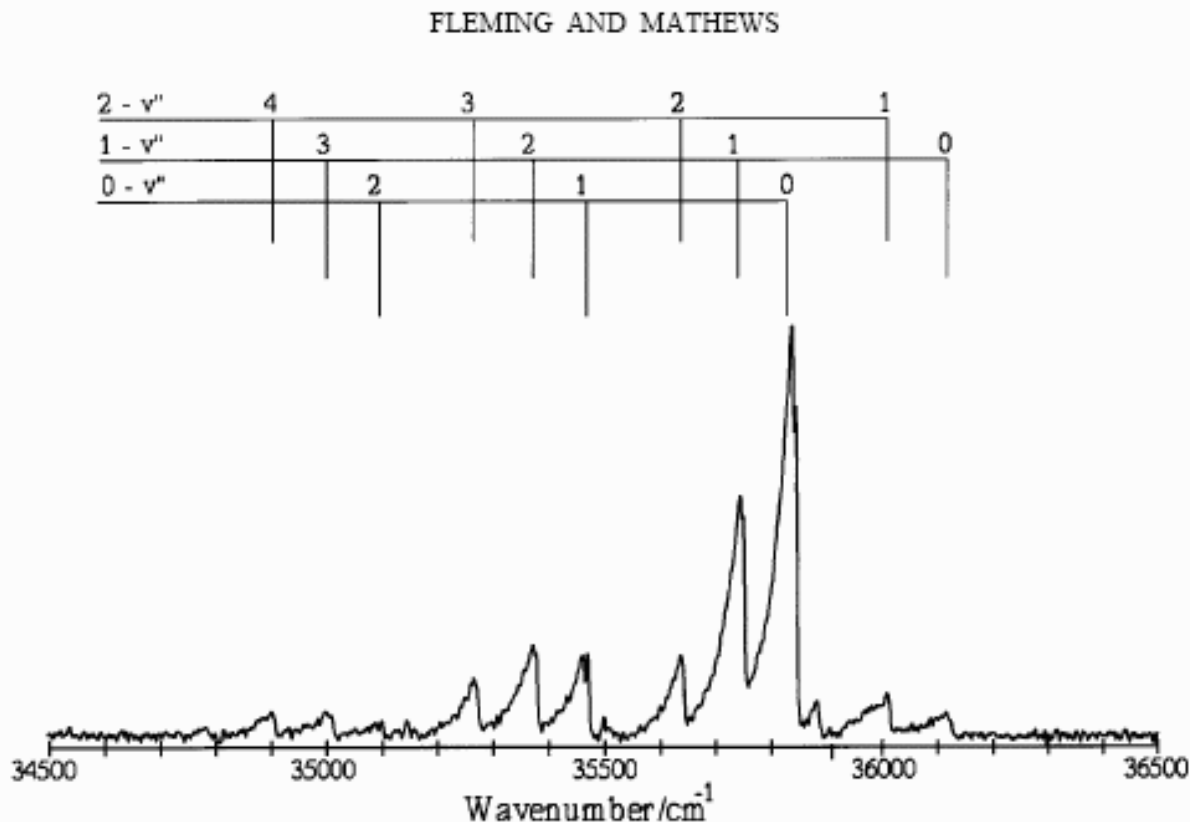


FIG. 1.  $A-X$  transition of  $\text{AlBr}$  near  $2800 \text{ \AA}$ .

These progressions can be analyzed to provide dissociation energies for the electronic states involved in the transition.

If the vibrational energy function is truncated at the  $v_{\text{ex}}$  level (as predicted by the Morse potential) the vibrational term value will reach a maximum value at some value of  $v$ . Any further vibrational excitation is predicted to lower the molecular energy. This is actually the dissociation limit. Therefore, the maximum value of  $v$  for a bound state ( $v_{\text{max}}$ ) is the largest value of  $v$  for which the vibrational energy spacing is positive. The dissociation energy of the molecule is then given by the sum of vibrational energy spacings from  $v=0$  to  $v=v_{\text{max}}$ .

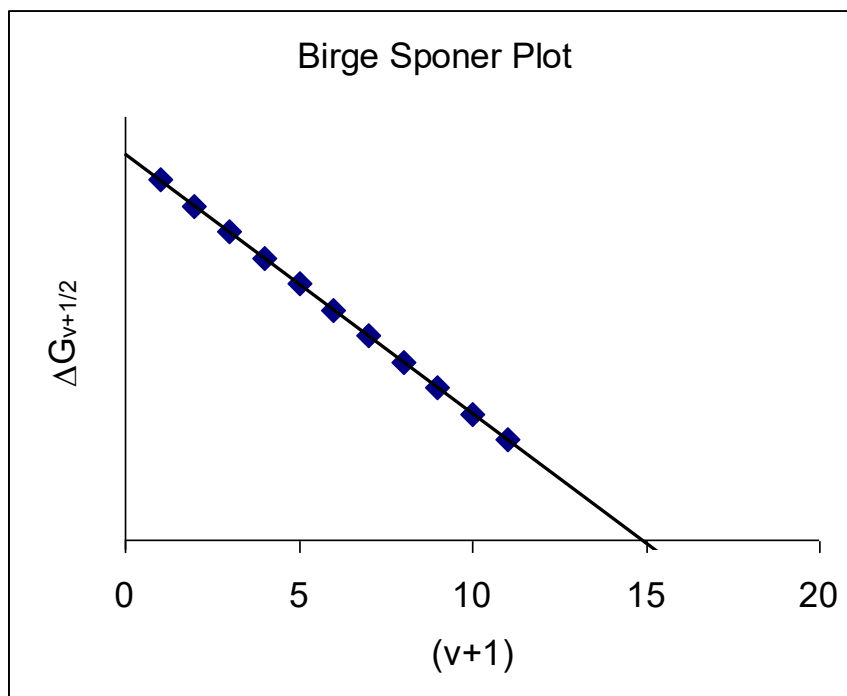
### *Determining a Dissociation Energy*

To find the value of the dissociation energy, it is convenient to define the difference between successive vibrational terms as

$$\Delta G_{v+1/2} \equiv G_{v+1} - G_v$$

Using the expression for  $G_v$  as predicted by the Morse potential,

$$\begin{aligned}
 \Delta G_{v+1/2} &= \omega_e \left(v + \frac{3}{2}\right) - \omega_e x_e \left(v + \frac{3}{2}\right)^2 - \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2 \\
 &= \omega_e \left(v + \frac{3}{2} - v - \frac{1}{2}\right) - \omega_e x_e \left(v^2 + 3v + \frac{9}{4} - v^2 - v - \frac{1}{4}\right) \\
 &= \omega_e - \omega_e x_e (2v + 2) \\
 &= \omega_e - 2\omega_e x_e (v + 1)
 \end{aligned}$$

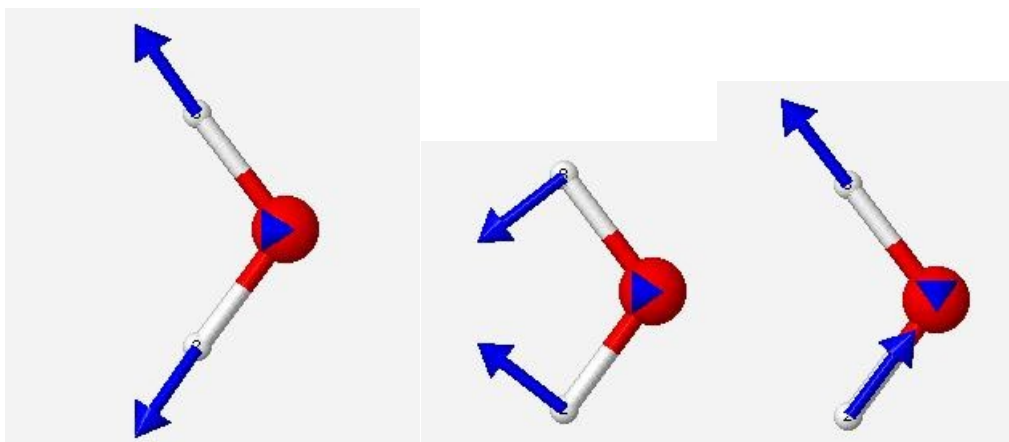


This suggests that a set of values of  $\Delta G_{v+1/2}$  vs.  $(v+1/2)$  should yield a straight line with a slope equal to  $-2\omega_e x_e$  and an intercept equal to  $\omega_e$ . And  $v_{\max}$  is determined by setting  $\Delta G_{v+1/2}$  to zero and solving for  $v$ .

The Birge-Sponer method (Gaydon, 1946) can be used to determine the sum of vibrational spacings, and thus the dissociation of a molecule. The method involves plotting  $\Delta G_{v+1/2}$  vs.  $(v+1)$ . The dissociation energy is taken as the area under the curve.

## Vibrations of Polyatomic Molecules

Nonlinear molecules have  $3N-6$  vibrational degrees of freedom, where  $N$  is the number of atoms in the molecule. Thus, a triatomic molecule such as water has three vibrational degrees of freedom. These account for the three vibrational modes of water (symmetric stretch, bend and antisymmetric stretch.)



Each mode will have a characteristic frequency. If each mode is treated as a harmonic oscillator, the total vibrational energy is given by

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + \frac{1}{2})$$

where  $\omega_i$  is the frequency of the  $i^{\text{th}}$  vibrational mode, and  $v_i$  is the quantum number indicating the number of quanta of the  $i^{\text{th}}$  mode excited. If anharmonicity is to be included, the expression becomes

$$G = \sum_{i=1}^{3N-6} \omega_i (v_i + \frac{1}{2}) - \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} x_{ij} (v_i + \frac{1}{2})(v_j + \frac{1}{2})$$

where  $x_{ij}$  is the anharmonicity term that couples the vibrational modes.

## Group Theory Considerations

Group theory provides a powerful set of tools for predicting and interpreting vibrational spectra. In this section, we will consider how Group Theory helps us to understand these important phenomena.

### Transformation of Axes and Rotations

It is possible to determine the symmetry species or irreducible representation by which each of the three Cartesian coordinate axes transform. This is useful, particularly in determining selection rules in spectroscopy, as the components of a molecule's dipole moment will transform as these axes. The rotations are also useful in understanding the rotational selection rules.

Recall the character table for the  $C_{2v}$  point group.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
<b>A<sub>1</sub></b>	1	1	1	1
<b>A<sub>2</sub></b>	1	1	-1	-1
<b>B<sub>1</sub></b>	1	-1	1	-1
<b>B<sub>2</sub></b>	1	-1	-1	1

It is useful to determine how each axis (x, y and z) is transformed under each symmetry operation. Once this is done, it will be easy to determine the representation that transforms the axis in this way. A table might be useful. Recalling our designation of the  $\sigma_v$  operation as reflection through the xz plane, it can be shown easily that the axes transform as follows:

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
<b>x</b>	x	-x	x	-x
<b>y</b>	y	-y	-y	y
<b>z</b>	z	z	z	z

The z-axis is unchanged by any of the symmetry operations. Another way of saying this is that the z-axis is symmetric with respect to all of the operations. (In this point group, all of the symmetry elements happen to intersect on the z-axis, which is why it is unchanged by any of the symmetry operations.) The conclusion is that the z-axis transforms with the A<sub>1</sub> representation.

The other axes can be described the same way. Note that the x-axis is symmetric with respect to the  $\sigma_v$  operation and the E operation. (Everything is symmetric with respect to the E operation, oddly enough.) The x-axis is antisymmetric, however, with respect to the  $\sigma_v'$  and  $C_2$  operations. The results for all axes can be summarized in the character table.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$	
<b>A<sub>1</sub></b>	1	1	1	1	z
<b>A<sub>2</sub></b>	1	1	-1	-1	
<b>B<sub>1</sub></b>	1	-1	1	-1	x
<b>B<sub>2</sub></b>	1	-1	-1	1	y

Rotations about the x, y and z axes can be characterized in a similar fashion. Consider the angular momentum vector for each rotation and how it transforms. Such a vector can be constructed using the right-hand rule. If the fingers on your right hand point in the direction of the rotation, your thumb points in the direction of the angular momentum vector.

Rotation about the z-axis ( $R_z$ ) is symmetric with respect to the operations E and  $C_2$ , but antisymmetric with respect to operations  $\sigma_v$  and  $\sigma_v'$ . Rotation about the x-axis is symmetric with respect to E and  $C_2$ . Clearly, this operation transforms as the irreducible representation A<sub>2</sub>. Rotation about the x-axis and y-axis can also be characterized as following the properties of the B<sub>2</sub> and B<sub>1</sub> representations respectively. As such, the character table for  $C_{2v}$  can be augmented to include this information.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$		
$A_1$	1	1	1	1	z	
$A_2$	1	1	-1	-1		$R_z$
$B_1$	1	-1	1	-1	x	$R_y$
$B_2$	1	-1	-1	1	y	$R_x$

Another interpretation of the transformation of the x, y and z-axes is that the representations that indicate the symmetries of these axes in the point group also indicate how the  $p_x$ ,  $p_y$  and  $p_z$  orbitals transform. The set of d orbital wavefunctions can also be used. These transformations are generally given in another column in the character table. (This information is also useful for calculating polarizabilities, and hence selection rules for Raman transitions!)

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$			
$A_1$	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

## Characterizing Vibrational Modes

Vibrational wave functions describing the normal modes of vibrations will be eigenfunctions of the symmetry properties of the group. As such, group theory can be quite useful in determining the vibrational selection rules needed to predict infrared spectra.

The number of vibrational degrees of freedom for a molecule is given by  $(3N-6)$  if the molecule is non-linear and  $(3N-5)$  if it is linear. In these expressions, N is the number of atoms in the molecule. One way to think of these numbers is that it takes  $3N$  Cartesian coordinates (an x, y and z variable) for each atom in the molecule to fully specify the structure of a molecule. As such,  $3N$  is the total number of degrees of freedom.

Since the molecule can translate through space in the x, y or z directions, three (3) degrees of freedom belong to translation. One can also think of these three degrees of freedom being the three Cartesian coordinates needed to specify the location of the center of mass of the molecule – or for the translation of the center of mass of the molecule.

For non-linear molecules, rotation can occur about each of the three Cartesian axes as well. So three (3) degrees of freedom belong to rotation for non-linear molecules. Linear molecules only have rotational degrees of freedom about the two axes that are perpendicular to the molecular axis (which remember is the  $C_\infty$  axis – and thus the z-axis.) So linear molecules only have two (2) rotational degrees of freedom.

The sum of the irreducible representations by which the vibrational modes transform can be found fairly easily using group theory. The first step is to determine how the three Cartesian axes transform under the symmetry operations of the point group. As an example, let's use water

(H<sub>2</sub>O), which belongs to the C<sub>2v</sub> point group since it is familiar. Later, we will work through a more complex example.

Consider the character table for the C<sub>2v</sub> point group.

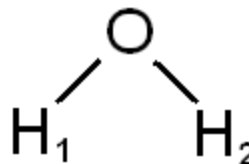
C <sub>2v</sub>	E	C <sub>2</sub>	σ <sub>v</sub>	σ <sub>v</sub> '			
A <sub>1</sub>	1	1	1	1	z		x <sup>2</sup> -y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	-1		R <sub>z</sub>	xy
B <sub>1</sub>	1	-1	1	-1	x	R <sub>y</sub>	xz
B <sub>2</sub>	1	-1	-1	1	y	R <sub>x</sub>	yz

The sum of the representations by which the axes transform will be given by B<sub>1</sub> + B<sub>2</sub> + A<sub>1</sub>.

C <sub>2v</sub>		E	C <sub>2</sub>	σ <sub>v</sub>	σ <sub>v</sub> '	
Γ <sub>1</sub>	A <sub>1</sub>	1	1	1	1	z
Γ <sub>2</sub>	B <sub>1</sub>	1	-1	1	-1	x
Γ <sub>3</sub>	B <sub>2</sub>	1	-1	-1	1	y
Γ <sub>xyz</sub>	A <sub>1</sub> + B <sub>1</sub> + B <sub>2</sub>	3	-1	1	1	

The reducible representation (Γ<sub>xyz</sub>) is then multiplied by the representation generated by counting the number of atoms in the molecule that remain unmoved by each symmetry element. This representation for water is generated as follows:

C <sub>2v</sub>	E	C <sub>2</sub>	σ <sub>v</sub>	σ <sub>v</sub> '
O	↖	↖	↖	↖
H <sub>1</sub>	↖	-	-	↖
H <sub>2</sub>	↖	-	-	↖
Γ <sub>unmoved</sub>	3	1	1	3



The reducible representation that describes the transformation of the Cartesian coordinates of each of the atoms in the molecule are given by the product of Γ<sub>xyz</sub> · Γ<sub>unmoved</sub> as shown in the following table.

C <sub>2v</sub>	E	C <sub>2</sub>	σ <sub>v</sub>	σ <sub>v</sub> '
Γ <sub>xyz</sub>	3	-1	1	1
Γ <sub>unmoved</sub>	3	1	1	3
Γ <sub>total</sub> = Γ <sub>xyz</sub> · Γ <sub>unmoved</sub>	9	-1	1	3

Note that the order of Γ<sub>total</sub> is given by 3N. This is the sum of representations needed to describe the transformation of each of the Cartesian coordinates for each atom. If the representation for the Cartesian coordinates (Γ<sub>xyz</sub>) is subtracted from Γ<sub>total</sub>, the remainder

describes the sum of representations by which the rotations and vibrations transform, and this result should be of order (3N-3). Let's see . . .

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$\Gamma_{\text{total}}$	9	-1	1	3
$\Gamma_{\text{xyz}}$	3	-1	1	1
$\Gamma_{\text{vib+rot}}$	6	0	0	2

So far, so good. Now let's subtract the sum of the representations by which the rotations transform. The remainder of this operation should be of order (3N-6) and give the sum of irreducible representations by which the vibrations transform.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$\Gamma_{\text{vib+rot}}$	6	0	0	2
$\Gamma_{\text{rot}}$	3	-1	-1	-1
$\Gamma_{\text{vib}}$	3	1	1	3

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$A_1$	1	1	1	1
$A_1$	1	1	1	1
$B_2$	1	-1	-1	1
$\Gamma_{\text{vib}}$	3	1	1	3

A quick calculation shows that this result is generated by the sum of  $A_1 + A_1 + B_2$ . To see this, we can use the Great Orthogonality Theorem. (I told you it was *great*!) In this case, the number of vibrational modes that transform as the *i*th irreducible representation is given by the relationship

$$N_i = \frac{1}{h} \sum_R \chi_i(R) \chi_{\text{vib}}(R)$$

For the  $A_1$  representation, this sum looks as follows.

$$\begin{aligned} N_{A_1} &= \frac{1}{h} (\chi_{A_1}(E) \cdot \chi_{\text{vib}}(E) + \chi_{A_1}(C_2) \cdot \chi_{\text{vib}}(C_2) + \chi_{A_1}(\sigma_v) \cdot \chi_{\text{vib}}(\sigma_v) + \chi_{A_1}(\sigma_v') \cdot \chi_{\text{vib}}(\sigma_v')) \\ &= \frac{1}{4} ((1) \cdot (3) + (1) \cdot (1) + (1) \cdot (1) + (1) \cdot (3)) \\ &= \frac{1}{4} (8) \\ &= 2 \end{aligned}$$

The result for the  $A_2$  representation should come to zero since no vibrational modes transform as  $A_2$ . For the  $A_2$  representation, this sum looks as follows.

$$N_{A_2} = \frac{1}{4}((1) \cdot (3) + (1) \cdot (1) + (-1) \cdot (1) + (-1) \cdot (3))$$

$$= \frac{1}{4}(0) = 0$$

For  $B_1$  and  $B_2$  the sum looks as follows:

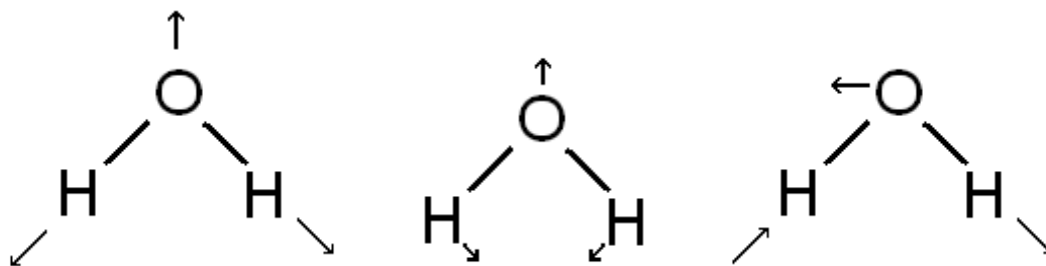
$$N_{B_1} = \frac{1}{4}((1) \cdot (3) + (-1) \cdot (1) + (1) \cdot (1) + (-1) \cdot (3))$$

$$= \frac{1}{4}(0) = 0$$

$$N_{B_2} = \frac{1}{4}((1) \cdot (3) + (-1) \cdot (1) + (-1) \cdot (1) + (1) \cdot (3))$$

$$= \frac{1}{4}(4) = 1$$

Let's see if that makes sense! Consider the three normal-mode vibrations in water. These (the symmetric stretch, the bend and the antisymmetric stretch) can be depicted as follows:



It is fairly simple to show that the symmetric stretch and the bending mode both transform as the  $A_1$  representation. Similarly, the antisymmetric stretching mode transforms as the  $B_2$  representation. (Note that we have chosen the  $xz$  plane (or the  $\sigma_v$  plane) to lie perpendicular to the molecule!)

**Example:** Find the symmetries of the normal vibrational modes of ammonia.

**Solution:** Recall the character table for the  $C_{3v}$  point group:

$C_{3v}$	E	$2 C_3$	$3 \sigma_v$		
$A_1$	1	1	1	$z$	
$A_2$	1	1	-1		$R_z$
E	2	-1	0	$x, y$	$R_x, R_y$

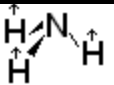
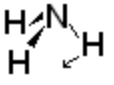
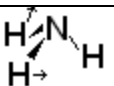
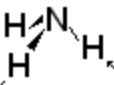
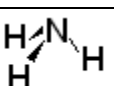
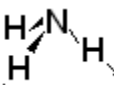


The representation for  $\Gamma_{\text{total}}$  can be found in the same way as before. Once we have  $\Gamma_{\text{total}}$ ,  $\Gamma_{\text{vib}}$  is determined as before.

$C_{3v}$	E	2 $C_3$	3 $\sigma_v$
$\Gamma_{xyz}$	3	1	1
$\Gamma_{\text{unmoved}}$	4	1	2
$\Gamma_{\text{total}}$	12	1	2

$C_{3v}$	E	2 $C_3$	3 $\sigma_v$
$\Gamma_{\text{total}}$	12	1	2
$\Gamma_{xyz}$	3	1	1
$\Gamma_{\text{rot}}$	3	0	-1
$\Gamma_{\text{vib}}$	6	0	2

The GOT can be used to find how many modes of each symmetry are present.

Mode		Freq. ( $\text{cm}^{-1}$ )	Sym.
Umbrella		1139	$A_1$
Bend		1765	E
			
Antisym. Str.		3464	E
			
Sym. Str.		3534	$A_1$

$$N_{A_1} = \frac{1}{6}[(1) \cdot (6) + 2(1) \cdot (0) + 3(1) \cdot (2)]$$

$$= \frac{1}{6}(12) = 2$$

$$N_{A_2} = \frac{1}{6}[(1) \cdot (6) + 2(1) \cdot (0) + 3(-1) \cdot (2)]$$

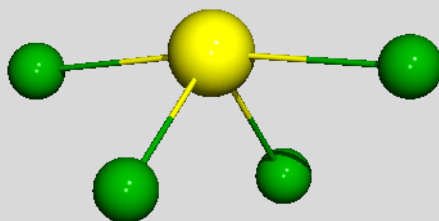
$$= \frac{1}{6}(0) = 0$$

$$N_E = \frac{1}{6}[(2) \cdot (6) + 2(-1) \cdot (0) + 3(0) \cdot (2)]$$

$$= \frac{1}{6}(12) = 2$$

So there are two (2)  $A_1$  modes and two (2) doubly degenerate E modes of vibration. These can be summarized in the table to the right.

**Another Example:** The vibrational modes of  $\text{SF}_4$



$\text{SF}_4$  is an example of a molecule with a “see saw” geometry. It belongs to the point group  $C_{2v}$  like water. Let’s find the symmetries of the normal modes of vibration using group theory. First, we must generate  $\Gamma_{\text{total}}$ .

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{\text{unmoved}}$	5	1	3	3
$\Gamma_{\text{total}}$	15	-1	3	3

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$\Gamma_{\text{total}}$	15	-1	3	3
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{\text{rot}}$	3	-1	-1	-1
$\Gamma_{\text{vib}}$	9	1	3	3

Now, subtract  $\Gamma_{xyz}$  and  $\Gamma_{\text{rot}}$  to generate  $\Gamma_{\text{vib}}$  as shown above.

So this implies that there are nine degrees of freedom due to vibration. This is the result we expect since for the 5-atom non-linear molecule,  $(3N-6) = 9$ . To generate the number of vibrational modes that transform as the  $A_1$  irreducible representation, the follow expression must be evaluated.

$$\begin{aligned}
 N_{A_1} &= \frac{1}{h} (\chi_{A_1}(E) \cdot \chi_{vib}(E) + \chi_{A_1}(C_2) \cdot \chi_{vib}(C_2) + \chi_{A_1}(\sigma_v) \cdot \chi_{vib}(\sigma_v) + \chi_{A_1}(\sigma'_v) \cdot \chi_{vib}(\sigma'_v)) \\
 &= \frac{1}{4} ((1) \cdot (9) + (1) \cdot (1) + (1) \cdot (3) + (1) \cdot (3)) \\
 &= \frac{1}{4} (16) \\
 &= 4
 \end{aligned}$$

Similarly,

$$\begin{aligned}
 N_{A_2} &= \frac{1}{4} ((1) \cdot (9) + (1) \cdot (1) + (-1) \cdot (3) + (-1) \cdot (3)) \\
 &= \frac{1}{4} (4) = 1
 \end{aligned}$$

$$\begin{aligned}
 N_{B_1} &= \frac{1}{4} ((1) \cdot (9) + (-1) \cdot (1) + (1) \cdot (3) + (-1) \cdot (3)) \\
 &= \frac{1}{4} (8) = 2
 \end{aligned}$$

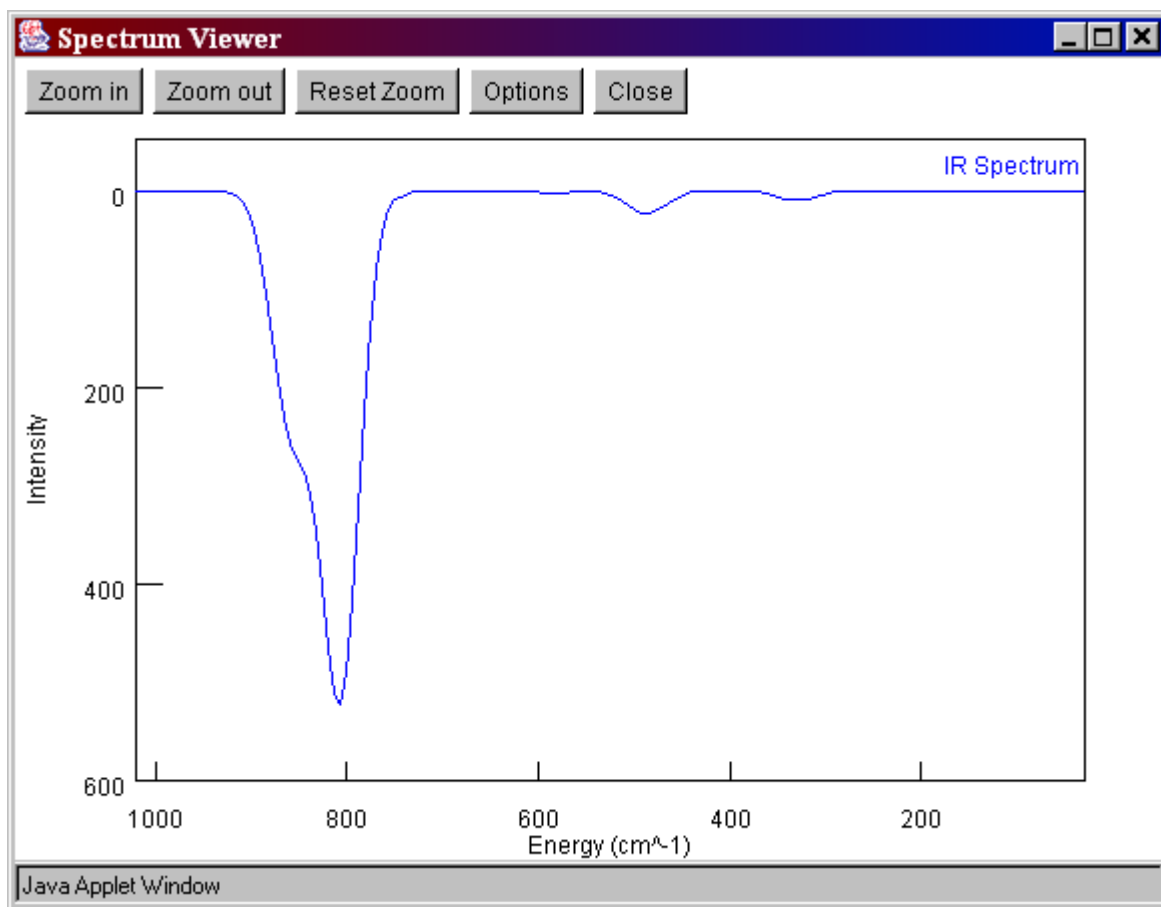
$$\begin{aligned}
 N_{B_2} &= \frac{1}{4} ((1) \cdot (9) + (-1) \cdot (1) + (-1) \cdot (3) + (1) \cdot (3)) \\
 &= \frac{1}{4} (8) = 2
 \end{aligned}$$

So there should be 4 vibrational modes of  $A_1$  symmetry, 1 of  $A_2$  symmetry and two each of  $B_1$  and  $B_2$  symmetry. A calculation of the structure and vibrational frequencies in  $\text{SF}_4$  at the B3LYP/6-31G(d) level of theory<sup>1</sup> yields the following.

Mode	Freq. (cm <sup>-1</sup> )	Symmetry	Mode	Freq. (cm <sup>-1</sup> )	Symmetry
1	189	$A_1$	6	584	$A_1$
2	330	$B_1$	7	807	$B_2$
3	436	$A_2$	8	852	$B_1$
4	487	$A_1$	9	867	$A_1$
5	496	$B_2$			

The calculation also allows for the simulation of the infrared spectrum of  $\text{SF}_4$ .

<sup>1</sup> Calculation performed using Gaussian 98 (<http://www.gaussian.com/>) using the WebMO (<http://www.webmo.net/>) web-based interface.



What would be exceptionally useful is if group theory could help to identify which vibrational modes are active – or if any are inactive. Fortunately, it can! (And *now* how much would you pay?) The tools for determining selection rules depend on direct products.

## Intensity

Group theory provides tools to calculate when a spectral transition will have zero intensity, and this will not be seen. In this section, we will see how group theory can help to determine the **selection rules** that govern which transitions can and cannot be seen.

$$\text{Intensity} \propto \left| \int (\psi')^* \vec{\mu}(\psi'') d\tau \right|^2$$

The intensity of a transition in the spectrum of a molecule is proportional to the magnitude squared of the transition moment matrix element.

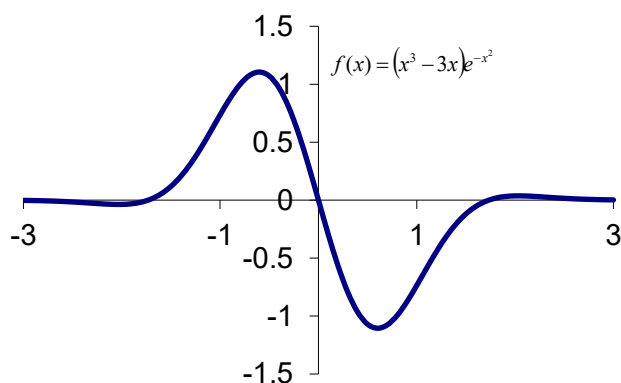
By knowing the symmetry of each part of the integrand, the symmetry of the product can be determined as the **direct product** of the symmetries of each part  $(\psi')^*$ ,  $(\psi'')$  and  $\vec{\mu}$ . This is

helpful, since the integrand must not be antisymmetric with respect to any symmetry elements or the integral will vanish by symmetry. Before exploring that concept, let's look at the concept of direct products.

This is a concept many people have seen, in that the integral of an odd function over a symmetric interval, is zero. Recall what it means to be an “odd function” or an “even function.”

Symmetry	definition	Intensity
Even	$f(-x) = f(x)$	$\int_{-a}^a f(x)dx = 2\int_0^a f(x)dx$
Odd	$f(-x) = -f(x)$	$\int_{-a}^a f(x)dx = 0$

Consider the function  $f(x) = (x^3 - 3x)e^{-x^2}$ . A graph of this function looks as follows:



One notes that the area under the curve on the side of the function for which  $x > 0$  has exactly the same magnitude but opposite sign of the area under the other side of the graph. Mathematically,

$$\begin{aligned}
 \int_{-a}^a f(x)dx &= \int_{-a}^0 f(x)dx + \int_0^a f(x)dx \\
 &= -\int_0^a f(x)dx + \int_0^a f(x)dx \\
 &= 0
 \end{aligned}$$

It is also interesting to note that the function  $f(x)$  can be expressed as the product of two functions, one of which is an odd function ( $x^3 - 3x$ ) and the other which is an even function ( $e^{-x^2}$ ). The result is an odd function. By determining the symmetry of the function as a product of the eigenvalues of the functions with respect to the inversion operator, as discussed below, one can derive a similar result.

The even/odd symmetry is an example of inversion symmetry. Recall that the inversion operator (in one dimension) affects a change of sign on  $x$ .

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$$\hat{i}f(x) = f(-x)$$

“Even” and “odd” functions are eigenfunctions of this operator, and have eigenvalues of either +1 or -1. For the function used in the previous example,

$$f(x) = g(x)h(x)$$

where

$$g(x) = x^3 - 3x \quad \text{and} \quad h(x) = e^{-x^2}$$

Here,  $g(x)$  is an odd function and  $h(x)$  is an even function. The product is an odd function. This property is summarized for any  $f(x) = g(x)h(x)$ , in the following table.

<b>g(x)</b>	<b>h(x)</b>	<b>f(x)</b>	<b><i>ig</i>(x)=__g(x)</b>	<b><i>ih</i>(x)=__h(x)</b>	<b><i>if</i>(x)=__f(x)</b>
even	even	even	1	1	1
even	odd	odd	1	-1	-1
odd	odd	even	-1	-1	1

Note that the eigenvalue (+1 or  $-1$ ) is simply the character of the inversion operation for the irreducible representation by which the function transforms! In a similar manner, any function that can be expressed as a product of functions (like the integrand in the transition moment matrix element) can be determined as the direct product of the irreducible representations by which each part of the product transforms.

Consider the point group  $C_{2v}$  as an example. Recall the character table for this point group.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$			
<b>A<sub>1</sub></b>	1	1	1	1	z		$x^2-y^2, z^2$
<b>A<sub>2</sub></b>	1	1	-1	-1		$R_z$	xy
<b>B<sub>1</sub></b>	1	-1	1	-1	x	$R_y$	xz
<b>B<sub>2</sub></b>	1	-1	-1	1	y	$R_x$	yz

The direct product of irreducible representations can by the definition

$$\chi_{prod}(R) = \chi_i(R) \cdot \chi_j(R)$$

So for the direct product of  $B_1$  and  $B_2$ , the following table can be used.

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$
$B_1$	1	-1	1	-1

<b>B<sub>2</sub></b>	1	-1	-1	1
<b>B<sub>1</sub>⊗B<sub>2</sub></b>	1	1	-1	-1

The product is actually the irreducible representation given by A<sub>2</sub>! As it turns out, the direct product will always yield a set of characters that is either an irreducible representation of the group, or can be expressed as a sum of irreducible representations. This suggests that a multiplication table can be constructed. An example (for the C<sub>2v</sub> point group) is given below.

<b>C<sub>2v</sub></b>	<b>A<sub>1</sub></b>	<b>A<sub>2</sub></b>	<b>B<sub>1</sub></b>	<b>B<sub>2</sub></b>
<b>A<sub>1</sub></b>	A <sub>1</sub>	A <sub>2</sub>	B <sub>1</sub>	B <sub>2</sub>
<b>A<sub>2</sub></b>	A <sub>2</sub>	A <sub>1</sub>	B <sub>2</sub>	B <sub>1</sub>
<b>B<sub>1</sub></b>	B <sub>1</sub>	B <sub>2</sub>	A <sub>1</sub>	A <sub>2</sub>
<b>B<sub>2</sub></b>	B <sub>2</sub>	B <sub>1</sub>	A <sub>2</sub>	A <sub>1</sub>

Studying this table reveals some useful generalizations. Two things in particular jump from the page. These are summarized in the following tables.

	A	B
A	A	B
B	B	A

	1	2
1	1	2
2	2	1

This pattern might seem obvious to some. It stems from the idea that

$$\begin{aligned}
 \text{symmetric} * \text{symmetric} &= \text{symmetric} \\
 \text{symmetric} * \text{antisymmetric} &= \text{antisymmetric} \\
 \text{antisymmetric} * \text{antisymmetric} &= \text{symmetric}
 \end{aligned}$$

Noting that A indicates an irreducible representation is *symmetric* with respect to the C<sub>2</sub> operation and B indicates that the irreducible representation is *antisymmetric* . . and that the subscript 1 indicates that an irreducible representation is *symmetric* with respect to the  $\sigma_v$  operation, and that a subscript 2 indicates that the irreducible representation is *antisymmetric* . . the rest seems to follow! Some point groups have irreducible representations use subscripts g/u or primes and double primes. The g/u subscript indicates symmetry with respect to the inversion (*i*) operator, and the prime/double prime indicates symmetry with respect to a  $\sigma$  plane (generally the plane of the molecule for planar molecules).

This method works well for singly degenerate representations. But what does one do for products involving doubly degenerate representations? As an example, consider the C<sub>3v</sub> point group.

<b>C<sub>3v</sub></b>	<b>E</b>	<b>2 C<sub>3</sub></b>	<b>3 <math>\sigma_v</math></b>		
<b>A<sub>1</sub></b>	1	1	1	z	
<b>A<sub>2</sub></b>	1	1	-1		R <sub>z</sub>
<b>E</b>	2	-1	0	(x, y)	(R <sub>x</sub> , R <sub>y</sub> )

<b>C<sub>3v</sub></b>	<b>E</b>	<b>2 C<sub>3</sub></b>	<b>3 <math>\sigma_v</math></b>
<b>A<sub>2</sub></b>	1	1	-1
<b>E</b>	2	-1	0
<b>A<sub>2</sub>⊗E</b>	2	-1	0

Consider the direct product of  $A_2$  and E.

This product is clearly just the E representation. Now one other example – Consider the product  $E \otimes E$ .

$C_{3v}$	E	$2 C_3$	$3 \sigma_v$
E	2	-1	0
E	2	-1	0
$E \otimes E$	4	1	0

To find the irreducible representations that comprise this reducible representation, we proceed in the same manner as determining the number of vibrational modes belonging to each symmetry.

$$N_{A_1} = \frac{1}{6} [(1)(4) + 2(1)(1) + 3(1)(0)] = 1$$

$$N_{A_2} = \frac{1}{6} [(1)(4) + 2(1)(1) + 3(-1)(0)] = 1$$

$$N_E = \frac{1}{6} [(2)(4) + 2(-1)(1) + 3(0)(0)] = 1$$

This allows us to build a table of direct products. Notice that the direct product always has the total dimensionality that is given by the product of the dimensions.

$C_{3v}$	$A_1$	$A_2$	E
$A_1$	$A_1$	$A_2$	E
$A_2$	$A_2$	$A_1$	E
E	E	E	$A_1 + A_2 + E$

Now that we have a handle on direct products, we can move on to selection rules.

## Selection Rules

According to quantum mechanics, transitions will only be allowed (have non-zero intensity) if the squared magnitude of the transition moment ( $|\int \psi'^* \bar{\mu} \psi'' d\tau|^2$ ) is not zero. If the integral vanishes by symmetry, obviously the transition moment will have zero magnitude and the transition is **forbidden** and will not be seen. In order to determine if the integral vanishes by symmetry, it is necessary to determine the symmetry by which the dipole moment operator transforms.



This ( $\vec{\mu}$ ) is a vector operator and can be decomposed into x, y and z components. As such, the transition moment is also a vector property that can have x-, y- and/or z-axis components. Clearly, it will be important to determine how the three axes transform. Fortunately, this information is contained in character tables! Consider the following two point groups,  $C_{3v}$  and  $C_{2v}$ .

$C_{3v}$	E	2 $C_3$	3 $\sigma_v$		
$A_1$	1	1	1	z	
$A_2$	1	1	-1		$R_z$
E	2	-1	0	(x, y)	( $R_x, R_y$ )

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$		
$A_1$	1	1	1	1	z	
$A_2$	1	1	-1	-1		$R_z$
$B_1$	1	-1	1	-1	x	$R_y$
$B_2$	1	-1	-1	1	y	$R_x$

In the case of  $C_{2v}$ , it is clear that the x-, y- and z-axes transform as the  $B_1$ ,  $B_2$  and  $A_1$  irreducible representations respectively. In the case of  $C_{3v}$ , the z-axis transforms as  $A_1$ , but the x- and y-axes come as a pair and transform as the E irreducible representation. It will always require two axes to complete the basis for a doubly degenerate representation.

Under the  $C_{2v}$  point group, any vector quantity will transform as the sum of  $A_1+B_1+B_2$  as we saw for  $\Gamma_{xyz}$  before. Further, one can say that the x-axis component transforms as  $B_1$ , the y-axis component as  $B_2$  and the z-axis component as  $A_1$ . By a similar token, under the  $C_{3v}$  point group, a vector quantity transforms as the sum of  $A_1+E$ . The z-axis component transforms as  $A_1$  and the x- and y-axis components come as a pair that transform by the E representation. All that is needed to complete the picture is to determine the symmetries of the upper and lower state wave functions.

### Infrared Active Transitions

In order for a spectral transition to be allowed by electric dipole selection rules, the transition moment integral must not vanish.

$$\int \psi'^* \vec{\mu} \psi'' d\tau$$

This can be determined by using the irreducible representations by which the two wavefunctions transform and the three components of the transition moment operator, which will be x, y and z.

$$\int \Gamma_{\psi'} \Gamma_{\vec{\mu}} \Gamma_{\psi''} d\tau$$

If the direct product of the integrand does not contain at least a component of the totally symmetric irreducible representation, the integral will vanish by symmetry.

**Example:** The three vibrational modes of  $H_2O$  transform by  $A_1$  (symmetric stretch),  $A_1$  (bend) and  $B_2$  (antisymmetric stretch.) Will the symmetric stretch mode be infrared active?

**Solution:** For the symmetric stretch, which transforms as  $A_1$ , the transition moment integrand will have symmetry properties determined by the product

$$\psi' \begin{pmatrix} x \\ y \\ z \end{pmatrix} \psi'' \quad A_1 \begin{pmatrix} B_1 \\ B_2 \\ A_1 \end{pmatrix} A_1$$

where one of the irreducible representations from the set in the middle of the product may be used. (They are the irreducible representations by which the x, y and z axes transform.) In this case, the z-axis must be used.

$$A_1 \cdot A_1 \cdot A_1 = A_1$$

This is the only component that will not vanish.

When the z-axis component must be used to make the transition moment operator not vanish, the transition is said to be a parallel transition. Transition moments that lie along axis perpendicular to the z-axis are said to be perpendicular transitions. Parallel and Perpendicular Transitions often have very different selection rules and thus very different band contours.

### Another Method

Another method that can be used to see if a mode is infrared active is to take the direct product of the irreducible representations of the wavefunction, and use  $\Gamma_{xyz}$  for the transition moment. If the resulting product has a component that is totally symmetric, the mode will be infrared active.

**Example:** Is the antisymmetric stretch mode of water predicted to be infrared active?

**Solution:** This mode transforms as the  $B_2$  irreducible representation.  $\Gamma_{xyz}$  is given by

$$\Gamma_{xyz} = B_1 + B_2 + A_1$$

So:

$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$
$B_2$	1	-1	-1	1
$\Gamma_{xyz}$	3	-1	1	1
$\Gamma_{prod}$	3	1	-1	1

The resulting reducible representation will have a component of the totally symmetric irreducible representation.

$$A_1 \cdot \Gamma_{\text{prod}} = (1)(3) + (1)(1) + (1)(-1) + (1)(1) = 4$$

So the  $A_1$  irreducible representation appears once in the product reducible representation. In fact, the component that does not vanish is due to the presence of  $B_2$  in  $\Gamma_{\text{xyz}}$ . Hence, the transition is predicted to be a perpendicular  $\perp$  transition, since the transition moment lies along the y-axis.

**Example:** Will the E modes in  $\text{NH}_3$  be infrared active?

**Solution:**

In the  $C_{3v}$  point group,  $\Gamma_{\text{xyz}}$  is given by  $A_1 + E$

$C_{3v}$	E	2 $C_3$	3 $\sigma_v$
E	2	-1	0
$\Gamma_{\text{xyz}}$	3	0	1
$\Gamma_{\text{prod}}$	6	0	0

$\Gamma_{\text{prod}}$  clearly has the totally symmetric irreducible representation as a component.

$$A_1 \cdot \Gamma_{\text{prod}} = (1)(6) + 2(1)(0) + 3(1)(0) = 6$$

In fact, it is the E component of  $\Gamma_{\text{xyz}}$  that makes this transition allowed (and so it is a perpendicular ( $\perp$ ) transition.

$C_{3v}$	E	2 $C_3$	3 $\sigma_v$
E	2	-1	0
E	2	-1	0
$\Gamma_{\text{prod}}$	4	1	0

$$A_1 \cdot \Gamma_{\text{prod}} = (1)(4) + 2(1)(1) + 3(1)(0) = 6$$

## Vibrational Raman Spectra

Vibrational Raman spectroscopy is often used as a complementary method to infrared spectroscopy. The selection rules for Raman spectroscopy can be determined in much the same way, except that a polarizability integral must be used. The polarizability operator can be expressed as a 3x3 tensor of the form

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$$\alpha = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix}$$

This tensor is symmetric along the diagonal, and the elements transform in the same ways as the functions  $x^2$ ,  $y^2$ ,  $z^2$ ,  $xy$ ,  $xz$  and  $yz$ .

**Example:** What are the vibrational mode symmetries for the molecule  $\text{H}_2\text{CCH}_2$  which transforms as the  $D_{2h}$  point group? Which modes will be infrared active? Which will be Raman active?

**Solution:**

Set up the vibrational analysis table in the usual manner.

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$	
$A_g$	1	1	1	1	1	1	1	1	$x^2, y^2, z^2$
$B_{1g}$	1	1	-1	-1	1	1	-1	-1	$R_z$ xy
$B_{2g}$	1	-1	1	-1	1	-1	1	-1	$R_y$ xz
$B_{3g}$	1	-1	-1	1	1	-1	-1	1	$R_x$ yz
$A_u$	1	1	1	1	-1	-1	-1	-1	
$B_{1u}$	1	1	-1	-1	-1	-1	1	1	z
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	y
$B_{3u}$	1	-1	-1	1	-1	1	1	-1	x
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1	
$\Gamma_{rot}$	3	-1	-1	-1	3	-1	-1	-1	

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1
$\Gamma_{unm}$	6	0	0	2	0	6	2	0
$\Gamma_{tot}$	18	0	0	-2	0	6	2	0
$\Gamma_{xyz}$	3	-1	-1	-1	-3	1	1	1
	15	1	1	-1	3	5	1	-1
$\Gamma_{rot}$	3	-1	-1	-1	3	-1	-1	-1
$\Gamma_{vib}$	12	2	2	0	0	6	2	0

Decomposing to the individual components:

$D_{2h}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma_{xy}$	$\sigma_{xz}$	$\sigma_{yz}$	sum	#(h)
$A_g \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(1)(0)	(1)(6)	(1)(2)	(1)(0)	24	3
$B_{1g} \cdot \Gamma_{vib}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(1)(0)	(1)(6)	(-1)(2)	(-1)(0)	16	2
$B_{2g} \cdot \Gamma_{vib}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(1)(0)	(-1)(6)	(1)(2)	(-1)(0)	8	1

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$B_{3g} \cdot \Gamma_{\text{vib}}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(1)(0)	(-1)(6)	(-1)(2)	(1)(0)	0	0
$A_u \cdot \Gamma_{\text{vib}}$	(1)(12)	(1)(2)	(1)(2)	(1)(0)	(-1)(0)	(-1)(6)	(-1)(2)	(-1)(0)	8	1
$B_{1u} \cdot \Gamma_{\text{vib}}$	(1)(12)	(1)(2)	(-1)(2)	(-1)(0)	(-1)(0)	(-1)(6)	(1)(2)	(1)(0)	8	1
$B_{2u} \cdot \Gamma_{\text{vib}}$	(1)(12)	(-1)(2)	(1)(2)	(-1)(0)	(-1)(0)	(1)(6)	(-1)(2)	(1)(0)	16	2
$B_{3u} \cdot \Gamma_{\text{vib}}$	(1)(12)	(-1)(2)	(-1)(2)	(1)(0)	(-1)(0)	(1)(6)	(1)(2)	(-1)(0)	16	2

So

$$\Gamma_{\text{vib}} = 3 A_g + 2 B_{1g} + B_{2g} + A_u + B_{1u} + 2 B_{2u} + 2 B_{3u}$$

Of these, the 6 gerade modes will be Raman active, and the five  $B_{nu}$  modes ( $n = 1, 2, 3$ ) will be infrared active. The  $A_u$  mode will be dark.

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## Vocabulary and Concepts

anharmonicity constant .....	98	potential energy surface .....	85
direct product .....	111	Taylor series .....	85
even function .....	92	term values .....	90
Hermite polynomials .....	91	tunneling .....	96
odd function .....	92		

## Problems

- For each molecule, calculate the reduced mass (in kg) and the force constant for the bond (in N/m).

Molecule	$\omega_e$ (cm <sup>-1</sup> )	$\mu$ (kg)	k (N/m)
<sup>1</sup> H <sup>79</sup> Br	2648.975		
<sup>35</sup> Cl <sub>2</sub>	559.72		

$^{12}\text{C}^{16}\text{O}$	2169.81358		
$^{69}\text{Ga}^{35}\text{Cl}$	365.3		

- The typical carbonyl stretching frequency is on the order of  $1600\text{--}1900\text{ cm}^{-1}$ . Why is this value smaller than the value of  $\omega_e$  for CO given in the table above?
- The first few Hermite polynomials are given below.

$v$	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$

$$H_{v+1}(y) = 2yH_v(y) - 2vH_{v-1}(y)$$

- Use the recursion relation to generate the functions  $H_3(y)$  and  $H_4(y)$ .
  - Demonstrate that the first three Hermite polynomials ( $H_0(y)$ ,  $H_1(y)$  and  $H_2(y)$ ) form an orthogonal set.
- The Morse Potential function is given by

$$U(x) = D_e(1 - e^{-\beta x})$$

where  $x = (r - r_e)$ .

- Find an expression for the force constant of a Morse Oscillator bond by evaluating
  - For  $^1\text{H}^{35}\text{Cl}$ ,  $D_e = 7.31 \times 10^{-19}\text{ J}$  and  $\beta = 1.8 \times 10^{10}\text{ m}^{-1}$ . Use your above expression to evaluate  $k$  for the bond in HCl.
  - On what shortcoming of the Harmonic Oscillator model does the Morse Potential improve? What shortcoming does the Morse model share with that of a Harmonic Oscillator?
- The following data are observed in the vibrational overtone spectrum in  $^1\text{H}^{35}\text{Cl}$  (Meyer & Levin, 1929).

$v' \leftarrow v''$	$\tilde{\nu}_{obs} (\text{cm}^{-1})$
$1 \leftarrow 0$	2885.9
$2 \leftarrow 0$	5666.8
$3 \leftarrow 0$	8347.0
$4 \leftarrow 0$	10923.1
$5 \leftarrow 0$	13396.5

From these data, calculate a set of  $\Delta G_{v+1/2}$  values. Fit these results to the form

$$\Delta G_{v+\frac{1}{2}} = \omega_e - 2 \omega_e x_e (v + 1)$$

to determine values for  $\omega_e$  and  $\omega_e x_e$  for HCl.

6. The following wavenumber frequencies are reported for the band origins for the  $1 - v''$  bands in an electronic transition of a diatomic molecule. Using the Birge-Sponer method, determine the dissociation energy of the molecule in its ground electronic state.

$v''$	Wavenumber ( $\text{cm}^{-1}$ )	$\Delta G_{v+1/2}$ ( $\text{cm}^{-1}$ )
	19586.9	
	19522.3	
	19504.8	
	19465.9	
	19418.3	
	19375.1	
	19323.2	
	19275.7	
	19223.8	
	19167.6	
	19111.4	
	19050.9	
	18990.4	
	18925.6	
	18860.7	
	18795.9	
	18722.4	
	18653.3	
	18579.8	
	18506.3	
27	18428.5	
	18342.1	
	18259.9	
	18177.8	
	18091.5	
	17996.3	
	17909.8	
	17814.8	
	17719.7	
	17624.6	