4 Vibrational Spectroscopy

The field of vibrational spectroscopy is extremely important to a chemist or chemical engineer, since it is one of the primary methods used to identify molecules. Unlike rotational spectroscopy, which is applicable only to gas phase molecules, vibrational spectroscopy provides important information on condensed phase molecules as well as those in the gas phase. Although a vibrational spectrum is different in a liquid or a solid than in a gas, it still carries information that is unique to a given molecule that can be used as a “fingerprint” of that molecule. We will discuss primarily gas phase vibrational spectra, however, much of what we will do will be applicable to condensed phases as well. The difference will be that the rotational structure of a vibrational spectra cannot in general be resolved in the condensed phase except in very special circumstances.

Our discussion will begin with diatomic molecules and then progress to polyatomic molecules. In our discussion of the latter, you will find that molecular symmetry plays an important role.

4.1 Diatomic Molecules

4.1.1 Energy Levels and Selection Rules

We have already seen an expression for the energy levels of a diatomic molecule including centrifugal distortion and vibration rotation interaction:

$$F(\mathrm{v},J) = T_e + \omega_e\left(\mathrm{v}+\frac{1}{2}\right) - \omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2 + B_\mathrm{v} J(J+1) - D_\mathrm{v} J^2 (J+1)^2$$

where T_e is the electronic energy. Previously we called this $U(R_e)$. I have used D_v here instead of D to allow for the possibility that it might have vibrational dependence.

To determine what the spectrum looks like, we need to use this expression in combination with the selection rules for vibrational transitions..

In our overview of molecular spectroscopy earlier in the course, I derived an expression for the intensity of spectroscopic transitions that involved matrix elements of the dipole moment function between the initial and final state. For certain values of the quantum numbers these integrals vanish, and this gives rise to selection rules for the allowable changes in quantum number.

For radiation polarized in the *z*-direction (*i.e*. with respect to a space-fixed *z*-axis), the intensity of a spectroscopic transition is proportional to:

$$I \propto \left(\int \psi_2^* \hat{\mu}_z \psi_1 \, d\tau\right)^2$$

To obtain the vibrational/rotational selection rules, we have to separate the wave functions into electronic, vibrational and rotational parts.

$$\iiint \psi_{2el}^*(q_i;R)\psi_{2vib}^*(R)\psi_{2rot}^*(\theta,\varphi)\,\hat{\mu}_z(q_i,R)\psi_{1el}(q_i;R)\psi_{1vib}(R)\psi_{1rot}(\theta,\varphi)\,d\tau_{q_i}\,d\tau_R\,d\tau_{\theta,\varphi}$$

Recall that the *z*-component of the dipole moment refers to the *z*-component in a space fixed axis. One normally measures the dipole moment in the reference frame of the molecule. Before we called this μ_η. For the *z*-component we saw that:

$$\mu_z(q_i,R) = \mu_\eta(q_i,R)\cos\theta$$

When we separate the rotational part from the electronic and vibrational part we get:

$$\iint \psi^*_{2el}(q_i;R)\psi^*_{2vib}(R)\ \hat{\mu}_\eta(q_i,R)\psi_{1el}(q_i;R)\psi_{1vib}(R)\ d\tau_{q_i}\ d\tau_R \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\,\psi_{1rot}(\theta,\varphi)d\tau_{\theta,\varphi}$$

For vibrational/rotational transitions, we are not changing the electronic state, so that ⍰$_{⍰el}$ = ⍰$_{⍰el}$. Also (recall the Born-Oppenheimer approximation), we assume that the nuclei are essentially stationary on the timescale of the electronic motion. For treating the electronic motion, we therefore fix the nuclei and integrate over the electronic coordinates.

$$\int \psi^*_{2vib}(R)\left[\int \psi^*_{1el}(q_i;R)\,\hat{\mu}_\eta(q_i,R)\,\psi_{1el}(q_i;R)d\tau_{q_i}\right]\psi_{1vib}(R)d\tau_R \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\,\psi_{1rot}(\theta,\varphi)d\tau_{\theta,\varphi}$$

The electronic integral gives us the average value of the dipole moment integral in the given electronic state, which is a function of the nuclear coordinates. This is simply what we call the dipole moment function $\mu(R)$.

We can then write:

$$\int \psi^*_{2vib}(R)\,\hat{\mu}(R)\,\psi_{1vib}(R)d\tau_R \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\,\psi_{1rot}(\theta,\varphi)d\tau_{\theta,\varphi}$$

The integral over the angular coordinates gives the rotational selection rules for vibrational transitions. That is, when the vibrational quantum number changes, there must also be an accompanying change in the rotational quantum numbers that are consistent with this integral. Otherwise the whole expression will be zero.

You can see that this second factor is the same as for pure rotational transitions and gives rise to the selection rules of $\Delta J = \pm 1$ and $\Delta m = 0$. Recall that if we look at the *x*- or *y*-components of the dipole moment, we can also have $\Delta m = \pm 1$.

One finds the *vibrational* selection rules by evaluating the first integral. For a diatomic molecule, we can expand the dipole moment function as power series in the displacement coordinate $x = R - R_e$.

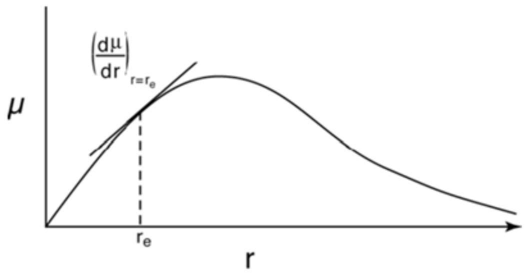
$$\mu(x) = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2\mu}{dx^2}\right|_{x=0} x^2 + \ldots$$

If we keep terms no higher than linear in *x* and substitute into the integral, we have

$$\mu_0 \int \psi^*_{2vib}(x)\psi_{1vib}(x)dx + \frac{1}{2}\left.\frac{d\mu}{dx}\right|_{x=0} \int \psi^*_{2vib}(x)\,\hat{x}\,\psi_{1vib}(x)dx + \ldots$$

The first term equals zero when the vibrational quantum number changes. Thus, the selection rules for vibrational transitions are given by the second term.

First notice that one requirement for a molecule to undergo a vibrational transition is that it produce a change in dipole moment as it vibrates. Let us look at a typical curve for a dipole moment of a heteronuclear diatomic as a function of the internuclear distance.



What matters is not the magnitude of the dipole moment, but the slope of the dipole moment function. This means that the dipole moment changes as the molecule vibrates.

In addition to a change in dipole moment, the intensity of a vibrational transition is determined by the integral

$$\int \psi_{\mathrm{v}'}^{*}(x)\hat{x}\psi_{\mathrm{v}''}(x)dx$$

where we use v′ and v″ to indicate the vibrational quantum numbers in the upper and lower state, respectively.

If we use harmonic oscillator wave functions, evaluating this integral is straightforward. We saw in the quantum chemistry course of last semester that we can write the operator $\hat{x}$ as:

$$\hat{x} = \frac{1}{\sqrt{2}}\left(\hat{a}^{\dagger} + \hat{a}\right)$$

where $\hat{a}^{\dagger}$ and $\hat{a}$ are raising and lowering operators. Substituting this into the integral gives:

$$\frac{1}{\sqrt{2}}\left[\int \psi_{\mathrm{v}'}^{*}(x)\hat{a}^{\dagger}\psi_{\mathrm{v}''}(x)dx + \int \psi_{\mathrm{v}'}^{*}(x)\hat{a}\psi_{\mathrm{v}''}(x)dx\right]$$

Using the fact that

$$\hat{a}^{\dagger}\psi_{\mathrm{v}} = \sqrt{\mathrm{v}+1}\,\psi_{\mathrm{v}+1} \qquad \text{and} \qquad \hat{a}\psi_{\mathrm{v}} = \sqrt{\mathrm{v}}\,\psi_{\mathrm{v}-1}$$

we have

$$\frac{1}{\sqrt{2}}\left[\sqrt{\mathrm{v}''+1}\int \psi_{\mathrm{v}'}^{*}(x)\psi_{\mathrm{v}''+1}(x)dx + \sqrt{\mathrm{v}''}\int \psi_{\mathrm{v}'}^{*}(x)\psi_{\mathrm{v}''-1}(x)dx\right]$$

The first integral will be zero unless v' = v'' +1 or Δv = 1
The second integral will be zero unless v' = v'' - 1 or Δv = -1

So the selection rule for vibrational transitions is: **Δv = ±1**

This selection rule is based upon two approximations:

- The vibrations are described by harmonic oscillator wave functions
- The dipole moment function is approximated by a linear function.

In the exercises you will explore the breakdown of these two assumptions and find that this results in Δv >1. In reality, the Δv = ±1 transitions are strong and Δv >1 transitions are much weaker. A rule of thumb is that the transitions get 10 times weaker for each successively larger change in Δv.

A bit of terminology:

final state	←	initial state	
v'	←	v''	
1	←	0	Fundamental band
2	←	1	*Hot* band
2	←	0	First overtone
3	←	0	Second overtone

4.1.2 Vibration-Rotation Spectra

Let us now use the energy level expression

$$F(\mathrm{v},J)=T_e+\omega_e\left(\mathrm{v}+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2+B_\mathrm{v}J\left(J+1\right)-D_\mathrm{v}J^2\left(J+1\right)^2$$

together with the Δv = ±1 and Δ*J* = ±1 selection rules to see what the spectrum will look like.

$$\nu=F(\mathrm{v}',J')-F(\mathrm{v}'',J'')$$

$$=T_e+\omega_e\left(\mathrm{v}'+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}'+\frac{1}{2}\right)^2+B_{\mathrm{v}'}J'\left(J'+1\right)-D_{\mathrm{v}'}J'^2\left(J'+1\right)^2$$

$$-T_e+\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2+B_{\mathrm{v}''}J''\left(J''+1\right)-D_{\mathrm{v}''}J''^2\left(J''+1\right)^2$$

Note that the electronic part drops out since we are not changing electronic state.

Let us now separate off the part that is purely vibrational from the part that is rotational. I will call the pure vibrational terms ν_0.

$$\nu_0=\omega_e\left(\mathrm{v}'+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}'+\frac{1}{2}\right)^2-\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)+\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2$$

I will now use the vibrational selection rule by letting v' = v'' + 1

$$\nu_0=\omega_e\left(\mathrm{v}''+1+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}''+1+\frac{1}{2}\right)^2-\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)+\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2$$

$$=\omega_e\left(\mathrm{v}''+\frac{3}{2}\right)-\omega_e x_e\left(\mathrm{v}''+\frac{3}{2}\right)^2-\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)+\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2$$

$$=\omega_e-\omega_e x_e\left[\left(\mathrm{v}''^2+3\mathrm{v}''+\frac{9}{4}\right)-\left(\mathrm{v}''^2+\mathrm{v}''+\frac{1}{4}\right)\right]$$

$$=\omega_e-\omega_e x_e\left(2\mathrm{v}''+2\right)$$

$$=\omega_e-2\omega_e x_e\left(\mathrm{v}''+1\right)$$

ν_0 is called the ***band origin*** and it is where the vibrational transition *would occur* if there were no changes in rotational quantum number as well.

Remember that the vibrational spectrum will occur in the infrared part of the spectrum. As we will see in a moment, the spectrum will have rotational structure, but all these transitions occur in the infrared.

For the present case, let us consider a transition that originates from the v'' = 0 level. In this case

$$\nu_0=\omega_e-2\omega_e x_e$$

We then have

$$\nu=\nu_0+B_{\mathrm{v}'}J'\left(J'+1\right)-B_{\mathrm{v}''}J''\left(J''+1\right)-D_{\mathrm{v}'}J'^2\left(J'+1\right)^2+D_{\mathrm{v}''}J''^2\left(J''+1\right)^2$$

where ν_0 is given above.

We must now put in the relationship between *J′* and *J″*. There are two choices corresponding to the +1 and -1 selection rule. This gives rise to two ***branches*** of the spectrum:

R **Branch**: **(Δ*J* = 1)** *J′* = *J″* + 1

$$\nu_R = \nu_0 + B_{v'}(J''+1)(J''+2) - B_{v''}J''(J''+1) - D_{v'}(J''+1)^2(J''+2)^2 + D_{v''}J''^2(J''+1)^2$$

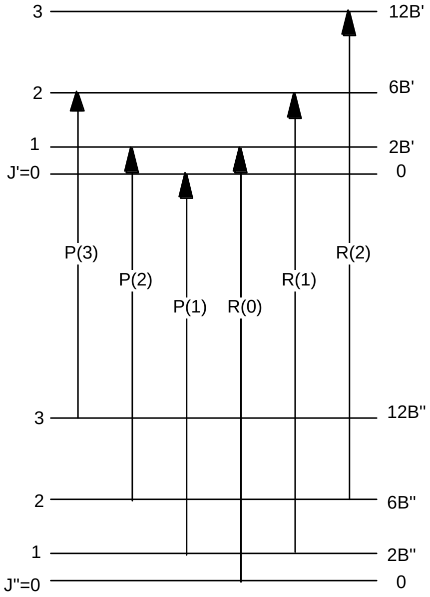
I will neglect the centrifugal distortion part for now. Rearranging, we get

$$\nu_R = R(J'') = \nu_0 + (B_{v'} + B_{v''})(J''+1) + (B_{v'} - B_{v''})(J''+1)^2 \qquad J'' = 0,1,2,3\ldots$$

P **Branch:** **(Δ*J* = -1)** *J′* = *J″* - 1

$$\nu_P = P(J'') = \nu_0 - (B_{v'} + B_{v''})J'' + (B_{v'} - B_{v''})J''^2 \qquad J'' = 1,2,3\ldots$$

Note that since *J′* = *J″* -1, the lowest value of *J″* in the *P* branch is 1. We can look at this on the following energy level schematic



Now let us think about what the spectrum will look like. There are several important things to notice.

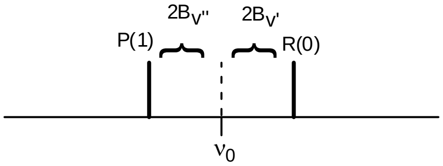
First, notice that there is no transition right at the band origin, ν_0. You can see that by letting *J″* = 0, the first transition in the *R* branch is:

$$R(0) = \nu_0 + 2B_{v'}$$

The first in the *P* branch is:

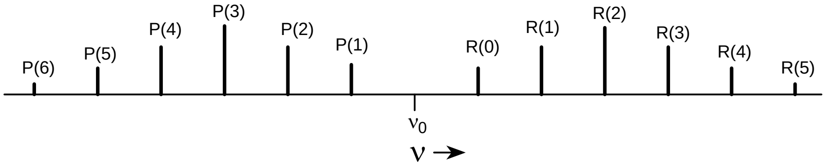
$$P(1) = \nu_0 - 2B_{v''}$$

There is no transition at ν_0. This is because the rotational selection rules must be obeyed.



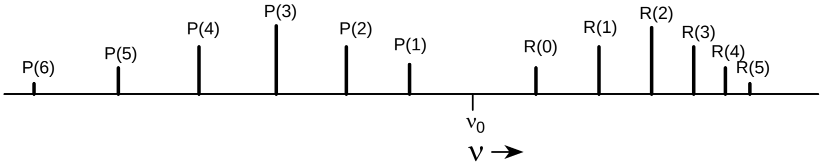
The spacing between *R*(0) and *P*(1) is 2($B_{v'}$ + $B_{v''}$). If $B_{v'}$ and $B_{v''}$ were equal, this would be a gap of 4*B*. This gap is called the ***null gap.*** The band origin, ν_0, is approximately in the center.

The second thing to note is the effect of the second term in the expressions for the *P* and *R* branches. If we were to ignore the difference between $B_{v'}$ and $B_{v''}$ for a moment (which is equivalent to saying that $\alpha = 0$), then the last term in each of these expressions would drop out. The lines would then be equally spaced by units of 2*B*.



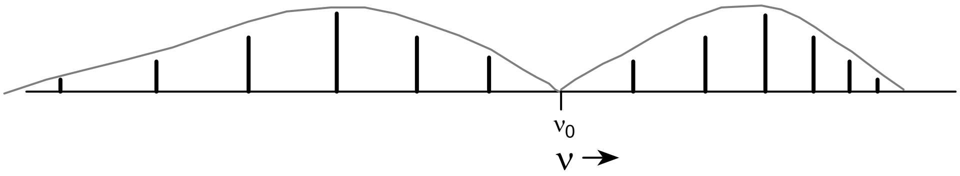
The inclusion of this second term will shift the levels in each branch by an amount that depends upon J''^2. For the infrared spectrum of a diatomic molecule, $B_{v'}$ is always less than $B_{v''}$. This is because of anharmonicity in the potential. The average bond length is always a bit longer in a vibrationally excited state and this makes α a positive term.

This means that ($B_{v'}$ - $B_{v''}$) is negative. The last term in each expression will shift the levels to lower energy. This has the effect of compressing the *R* branch and extending the *P* branch.



By measuring this effect, one measures ($B_{v'}$ - $B_{v''}$), and from this one can determine the vibration rotation interaction constant α, since $B_v = B_e - \alpha\left(v + \frac{1}{2}\right)$

The overall shape of the spectrum will always look something like:



The intensities of the transitions are determined largely by the Boltzmann distribution of initial rotational state populations.

Remember that

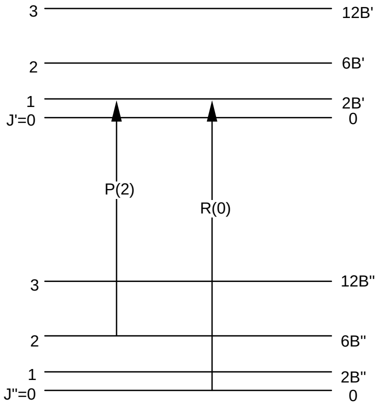
$$f_J = \frac{(2J+1)e^{-\frac{BJ(J+1)}{k_bT}}}{Q_{Rot}}$$

To calculate this, we only need to know the rotational constant in the lower vibrational state and the temperature. If we know the rotational constant of a molecule (determined by the line *positions*), then the intensities of a spectrum ***provide a direct measure of the temperature!*** *This is how one typically measures temperatures of objects in space (comets, planets, stars, etc...).* One collects light emission from these objects and looks for transitions of known molecules. The intensities provide the temperature.

There is one more comment that I need to make regarding the relative intensities of the transitions in a vibration-rotation spectrum. Remember that the intensities are proportional to the square of the transition moment integral. We used this integral to determine the selection rules, which only requires determining when the integral is identically zero. We didn't pay much attention to the proportionality constants outside the integral. If we had done things carefully we would have seen that the intensity of the *P* branch transitions are proportional to *J*/(2*J*+1) and that of the *R* branch transitions are proportional to (*J*+1)/(2*J*+1). These factors, known as the Hönl-London factors, must be taken into consideration when determining the temperature.

4.1.3 Combination Differences

Because a vibration-rotation spectrum involves transitions between two vibrational states (with different rotational constants), the frequencies of these transitions carry information on both states. We would like to separate the information about the initial and final vibrational states. We can do this using the method of ***combination differences*****.**



As an example, consider the difference in the frequencies of the *R*(0) and *P*(2) transitions. You can see that both levels terminate on *J'* =1. Their difference in energy reflects only the spacing in the lower vibrational state. You can see that

$$R(0) - P(2) = 6B_{v''} = 6B''$$

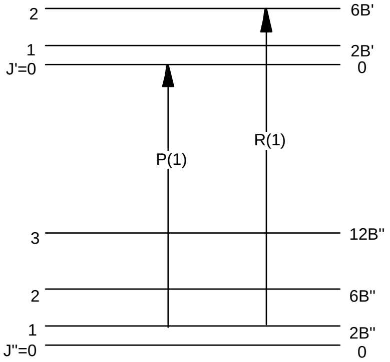
In general, one can write

$$\Delta_2 F'' = R(J-1) - P(J+1) = F_{v''}(J+1) - F_{v''}(J-1) = 4B_{v''}\left(J + \frac{1}{2}\right)$$

where *J* refers to the level that the two transitions have in common (in this case the upper state).

This gives us information only on the ground state rotational constant. It has allowed us to separate the information between the initial and final vibrational levels.

We can do the same thing to get information only about the rotational constants in the excited vibrational state. Consider the difference in energy between the *R*(1) and *P*(1) transitions:



These transitions originate on the same level but terminate on different levels. One can see that

$$R(1) - P(1) = 6B_{v'} = 6B'$$

In general

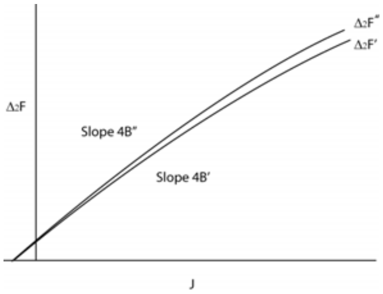
$$\Delta_2 F' = R(J) - P(J) = 4B_{v'}\left(J + \frac{1}{2}\right)$$

where *J* refers to the level in common, which in this case is the lower state.

One could take the average of $\dfrac{\Delta_2 F'}{4\left(J+\frac{1}{2}\right)}$ for different values of *J* and get $B_{v'}$.

Similarly one could take the average of $\dfrac{\Delta_2 F''}{4\left(J+\frac{1}{2}\right)}$ and get $B_{v''}$.

The other way to analyze this data is to plot $\Delta_2 F$ *vs*. *J*. This would give a slope of 4*B* and an intercept of 2*B*.



The non-linearity at high *J* comes from the centrifugal distortion term that we neglected. One can include this term and then fit these curves to a higher order function. This will give us a value for *D*.

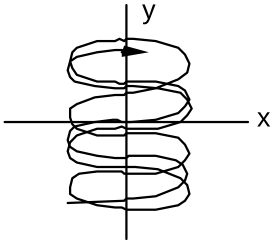
4.2 Polyatomic Vibration

4.2.1 Normal Modes of Vibration

When we consider the vibrational motion of polyatomic molecules, the situation is somewhat more complicated than diatomics as polyatomic molecules can vibrate in many different ways or *modes*.

Consider a simple classical two-dimensional harmonic oscillator that has different force constants, *k*, in each direction. If you give it initial displacement along *x* or *y*, it will undergo simple harmonic motion in that coordinate.

If you give it initial displacement off-axis (simultaneously in *x* and *y*) then the motion will be much more complex.



One can get this vibrational motion by superimposing the vibrations along the *x*-axis and the *y*-axis. These two vibrations are said to be normal vibrations or normal modes. These normal modes thus serve as the basis to describe the overall vibrational motion.

A polyatomic molecule is a multidimensional object, and its vibrational motion, analogous to the example above, can always be broken down as a linear combination of some fundamental set of vibrations. This set of vibrations forms a basis set with which all motions can be written as a linear combination. There are many ways to choose such a basis set. One choice might consist of every bond stretching vibration and a bending of every angle.

A specific type of vibrational motion of a polyatomic is called a ***normal vibration or a normal mode.*** The normal modes have special properties that are useful when solving the Schrödinger equation, or Newton's equations of motion for that matter. As we will see, at low energies where anharmonicity is not so important, these modes are the stationery states of the system.

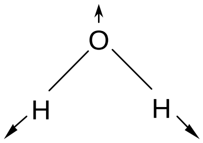
The number of normal mode for a molecule can be derived by considering the degrees of freedom. For a molecule consisting of *N* atoms the total number of degrees of freedom equals 3*N.* To describe the position of the molecule 3 degrees of freedom are required. The orientation in space of a molecule is described by 3 degrees of freedom for a non-linear and 2 for a linear molecule. We therefore find that the vibrational degree of freedom equals 3*N*-6 for a non-linear molecule and 3*N*-5 for a linear molecule.

As the number of normal modes equals the number of vibrational degrees of freedom we find for the number of normal modes:

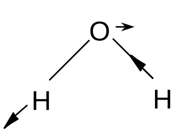
$3N$-6	for a non linear molecule
$3N$-5	for a linear molecule

Consider the case of H_2O. For water there are $3 \cdot 3 - 6 = 3$ degrees of freedom that correspond to vibrational motion of the molecule. Thus there are 3 normal modes for water.

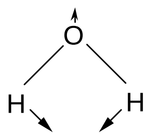
In water, as we will see later these normal vibrations are:



Symmetric Stretch

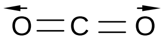


Antisymmetric Stretch

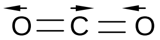


Bend

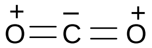
In the case of CO_2 there are $3 \cdot 3 - 5 = 4$ normal modes:



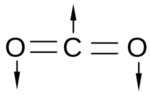
Symmetric Stretch



Antisymmetric Stretch



Bend (out of plane)



Bend (in plane)

(Note that because of symmetry the two bend vibrations are degenerate.)

As we discussed, normal modes are fundamental modes of vibration that form a basis set to describe all vibrational motions of the molecule. It is important to realize that they are not the *only* basis set. But as we will see in a moment, choosing *this particular basis* significantly siplifies solving the Schrödinger equation. We will see that within certain approximations the normal modes are the eigenfunctions of the Hamiltonian and thus the excitations of normal vibrations are what one observes in IR spectroscopy of polyatomic molecules.

As we did with diatomic molecules, the place to start in describing the vibrations is to look at the potential energy function. For a diatomic it was a one-dimensional function (remember we wrote it as a power series expansion). For a polyatomic, it is a multidimensional function.

I will start with the following set of coordinates:

Let x_1, y_1, z_1 represent the Cartesian coordinates of nucleus 1
x_2, y_2, z_2 represent the Cartesian coordinates of nucleus 2
x_3, y_3, z_3 represent the Cartesian coordinates of nucleus 3, etc. . .

I will now define a set of ***mass weighted Cartesian displacement coordinates***, q_i, where the subscript denotes the value of each coordinate at the equilibrium position.

$$q_1 = \sqrt{m_1}\left(x_1 - x_{1e}\right) \qquad q_4 = \sqrt{m_2}\left(x_2 - x_{2e}\right)$$

$$q_2 = \sqrt{m_1}\left(y_1 - y_{1e}\right) \qquad q_5 = \sqrt{m_2}\left(y_2 - y_{2e}\right)$$

$$q_3 = \sqrt{m_1}\left(z_1 - z_{1e}\right) \qquad q_6 = \sqrt{m_2}\left(z_2 - z_{2e}\right)$$

Thus

q_1, q_2, q_3 refer to nucleus 1
q_4, q_5, q_6 refer to nucleus 2
q_7, q_8, q_9 refer to nucleus 3 etc. . .

Given this coordinate system, one can write the multidimensional potential energy function as a Taylor series in the $3N$ coordinates:

$$V = V(0) + \sum_i \left(\frac{\partial V}{\partial q_i}\right)_0 q_i + \frac{1}{2!}\sum_{i,j}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j + \frac{1}{3!}\sum_{i,j,k}\left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k}\right)_0 q_i q_j q_k + \dots$$

There are 3*N* coordinates included here, which means that some of them will represent translations and rotations of the molecule.

As in the case of a diatomic molecule, we can choose the zero of energy to be the bottom of the potential well. This makes $V(0)=0$.

Also, since the power series is expanded about the equilibrium position, there must be a minimum in each coordinate. This makes all the first derivatives equal to zero.

Furthermore, we will neglect all the terms of 3rd order and higher. Neglecting the higher order terms is basically the harmonic oscillator approximation for a multidimensional system. As in the case of diatomics, this approximation is reasonably good for the lowest vibrational levels. We will examine the breakdown of this approximation later.

In this case we can write

$$V=\frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 q_i q_j=\frac{1}{2}\sum_{i,j} f_{ij} q_i q_j$$

where

$$f_{ij}=\left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0$$

The f_{ij} are generalized force constants.

In mass weighted Cartesian coordinates, we can write the kinetic energy

$$T=\frac{1}{2}\sum_{i}\left(\frac{dq_i}{dt}\right)^2$$

The total energy of the molecule, kinetic + potential, is then given by

$$E=\frac{1}{2}\sum_{i}\left(\frac{dq_i}{dt}\right)^2+\frac{1}{2}\sum_{i,j} f_{ij} q_i q_j$$

To solve the quantum mechanics of this problem, one must first find the Hamiltonian by substituting the operators for the momentum and the coordinates.

Remember that if we can write the Hamiltonian as a linear combination of terms that depend upon different sets of coordinates, then the wave function can be written as a product of wave functions that depend on each coordinate and the total energy will be a sum of energies for motion in each coordinate.

The problem here, however, is that the cross terms in the potential energy part of the Hamiltonian cause it to be non-separable. Because these terms depend upon two different coordinates, we cannot write the Hamiltonian as a sum of terms that depend on each coordinate.

Let's think about what these cross terms mean physically. The terms where $i = j$ are force constants similar to those we encountered in diatomic molecules, $V = 1/2\ k\ x^2$. It corresponds to the curvature of the potential in a particular coordinate--the proportionality constant between the energy and the displacement in that coordinate. In the case of polyatomics, there are many such force constants.

The cross terms, f_{ij}, reflect how an extension in one coordinate, *i*, effects the potential energy in another coordinate, *j*. As long as we have these cross terms, the displacement coordinates will not be an orthogonal set of coordinates with which to describe the vibrational motions of the molecule, since these terms cause motion in one coordinate to affect the motion in another.

Fortunately, it is possible to make a linear transformation from the mass weighted coordinates q_i to a new set of coordinates, Q_i, such that these cross terms no longer appear:

In other words, one must find a coordinate system in which the

$$Q_i = \sum_{j=1}^{3N} l_{ij} q_j$$

This new set of coordinates, Q_i, is called the ***normal coordinates.*** Note that there are 3*N* of these coordinates, because there were 3*N* of the mass weighted coordinates.

I will not go into the details of how to find the coefficients l_{ij} that transform the mass weighted Cartesian coordinates into the normal coordinates. It is not difficult however.

When we write down the vibrational Hamiltonian for a polyatomic molecule, the normal coordinates make the problem tractable. Using this new set of coordinates, one can write the total energy as:

$$E = \frac{1}{2}\sum_{i=1}^{3N}\left(\frac{dQ_i}{dt}\right)^2 + \frac{1}{2}\sum_{i=1}^{3N-6}\kappa_i Q_i^2$$

Note that there are 3*N* terms representing kinetic energy and 3*N*-6 potential energy terms (or 3*N*-5 for a linear molecule). This is because the coordinates that correspond to center of mass translation and overall rotation of the molecule only have kinetic energy terms and no potential energy (these coordinates do not involve bond compression or extensions).

The vibrational modes that correspond to the 3*N*-6 (or 3*N*-5) normal coordinates are the ***normal modes*** and have the properties described above.

Let us assume we have separated off the translational motion of the center of mass as well as the rotational motion of the molecule and write down the Hamiltonian for the vibrational motion. Because we are using normal coordinates, the Hamiltonian is separable into 3*N*-6 (or 3*N*-5 for a linear molecule) terms, one for each normal coordinate.
Thus,

$$\hat{H} = \sum_{i=1}^{3N-6}\hat{H}_i$$

where

$$\hat{H}_i = -\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_i^2} + \frac{1}{2}\kappa_i Q_i^2$$

Remember that whenever the Hamiltonian is separable in this way, the total wave function can be written as a product of wave functions, one for each coordinate.

$$\psi_{vib} = \psi_{\mathrm{v}1}(Q_1)\psi_{\mathrm{v}2}(Q_2)\psi_{\mathrm{v}3}(Q_3)\ldots\psi_{\mathrm{v(3N\text{-}6)}}(Q_{3N-6})$$

and the total energy is then just a sum of energies for each coordinate,

$$E = E_{\mathrm{v}1} + E_{\mathrm{v}2} + E_{\mathrm{v}3} + \ldots + E_{\mathrm{v}3N-6}$$

In addition, because solving the problem using normal coordinates eliminates the cross terms in the potential energy, the Hamiltonian for each coordinate is simply a harmonic oscillator Hamiltonian.

We already know what the wave functions and energies look like:

$$\psi_{vi}(Q_i) = N_{vi} H_{vi}\left(\sqrt{\alpha_i}\, Q_i\right) e^{-\frac{\alpha_i Q_i^2}{2}}$$

Where

$$\alpha_i = \sqrt{\frac{\kappa_i}{\hbar^2}}$$

Note that the definition of α is different than in our treatment of diatomic molecules in that it is missing a factor of $\mu^{1/2}$. This is because the Q_i are linear combinations of *mass weighted* coordinates.

The energies are given by

$$E_{vi} = h\nu_i\left(\mathrm{v}_i + \frac{1}{2}\right) \qquad \mathrm{v}_i = 0,1,2,\ldots$$

Where

$$\nu_i = \frac{1}{2\pi}\sqrt{\kappa_i}$$

Note once again, that we are missing a factor of μ. It was absorbed into the definition of κ when we used mass weighted coordinates.

There are now 3*N*-6 vibrational quantum numbers, v_i, one for each coordinate.

The total energy is just

$$E = \sum_{i=1}^{3N-6} h\nu_i\left(\mathrm{v}_i + \frac{1}{2}\right)$$

and the total wave function is a product of 3*N*-6 wave functions as given above.

Remember the approximation that we made at the beginning of this treatment -- we ignored all the terms of 3rd order and higher in the vibrational potential.

As long as this approximation is valid, the vibrational motion of a polyatomic is no more complex than that of a diatomic -- there are simply more modes.

There are several important things to notice about the solutions to this problem. One is the zero-point energy. Recall that in the v=0 level, a diatomic molecule has zero-point energy in the amount of 1/2 hν. In a polyatomic, the equivalent quantity is

$$E_0 = \sum_{i=1}^{3N-6} \frac{1}{2} h\nu_i$$

If a molecule has many vibrational modes, this can be a considerable amount of energy.

The second point is that in the lowest vibrational level, corresponding to $\mathrm{v}_i = 0$ for all *i*, the wave function is a product of one-dimensional v=0 functions which are just Gaussian functions, each of which is symmetric in its respective coordinate.

$$\psi_0 = N_{01} e^{-\frac{\alpha_1 Q_1^2}{2}} N_{02} e^{-\frac{\alpha_2 Q_2^2}{2}} N_{03} e^{-\frac{\alpha_3 Q_3^2}{2}} \ldots$$

The overall function will therefore be totally symmetric under all symmetry operations of the molecule. This point will be important when we consider selection rules.

Before I go on to the next section, let me come back to where I started and make sure it is clear what normal coordinates and normal modes really are.

Normal coordinates are linear combinations of mass weighted Cartesian coordinates chosen in such a way that the potential energy function has no quadratic cross terms (*i.e.*, no $q_i q_j$ terms). This has the effect of making the Hamiltonian separable into harmonic oscillator Hamiltonians for each coordinate. Each one commutes with the total Hamiltonian, and hence the vibrational quantum number associated with each coordinate is time independent. The vibrational motion corresponding to each coordinate is called a ***normal mode***.

When I draw the displacement vectors corresponding to normal modes, such as

$$\overset{\leftarrow}{\mathrm{O}} = \overset{\rightarrow}{\mathrm{C}} = \overset{\leftarrow}{\mathrm{O}}$$

one can see that arrows can be described by a linear combination of *x*, *y*, and *z* coordinates for each atom. This linear combination is the normal mode. The coefficients in the linear expansion depend upon the masses of the atoms, the molecular geometry, and the force constants of the bonds.

Even though we haven't gone through the diagonalization of the force constant matrix needed to find them, you should have an appreciation for what normal modes (and normal coordinates) are and why one uses them.

4.2.2 Group Vibrations

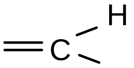
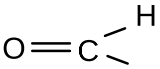
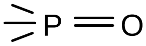
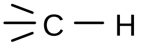
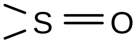
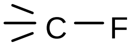
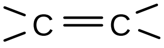
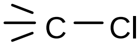
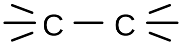
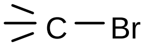
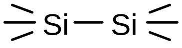
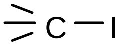
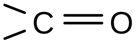
The normal modes of a molecule involve movements of essentially all the atoms (except in cases in which by symmetry a central atom must remained fixed). The normal mode is a global molecular motion in which all the atoms move in phase and at the same frequency.

However, certain types of normal modes tend to have *most* of the motion localized in just a few atoms of a molecule. This results from particular combinations of masses and force constants. For example, if at the end of a molecule you have a light atom such as hydrogen, bonded to a heavier atom, such as oxygen, there will usually be a normal mode of vibration in which most of the motion consists of OH stretch. The normal mode has all the atoms move, but the displacements are often greatest for the OH stretch. Moreover, the characteristics of this motion are relatively insensitive to the atoms in the rest of the molecule. So, for example, the OH stretch in CH_3OH occurs at a similar frequency as in CH_3CH_2OH. One can assign a characteristic frequency to the OH group, and when measuring the vibrational spectrum of an unknown molecule, one can relatively quickly assign different vibrational bands to this type of motion.

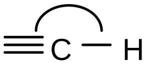
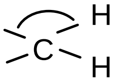
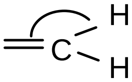
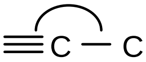
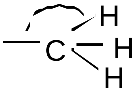
This phenomena occurs for many types of bond vibrations, and by knowing these characteristic frequencies, one can analyze many of the features of an unknown molecule. In the table below, I show a list of characteristic group wavenumbers for bond stretching and bending vibrations.

Frequencies (in cm^{-1}) of typical bond-stretching and angle bending group vibrations

Bond stretching **Bond stretching**

Group	cm^{-1}	Group	cm^{-1}
$\equiv C-H$	3300	$-O-H$	3600
	3020		3350
	2800		1295
	2960		1310
$-C\equiv C-$	2050		1100
	1650		650
	900		560
	430		500
	1700		
$-C\equiv N$	2100		

Angle bending **Angle bending**

Group	cm^{-1}	Group	cm^{-1}
	700		1450
	1100		300
	1000		

There are other types of vibrational modes that show characteristic group frequencies. I have shown you just a few as an example.

If you take an infrared spectrum of a fairly complex molecule, the appearance of certain group frequencies helps to identify which functional groups belong to the molecule.

There are certain types of vibrational modes that do not consist of primarily one type of motion but involve large components of several bond motions. While it is difficult to identify these from the spectrum, the specific pattern of coupled vibrations serves as fingerprint of a specific molecule, since these vary strongly from molecule to molecule.

Infrared spectra for the purpose of qualitative analysis (determining what something is) can be obtained from gas, liquid, or solid samples. The local environment will shift some vibrational frequencies. For example, if there is hydrogen bonding between OH groups in a liquid, the OH stretch frequency will be shifted.

4.2.3 Group Theory and Molecular Vibrations

Because the potential energy function of a molecule must be unchanged with respect to any symmetry operation associated with the point group of that molecule, each normal mode of vibration will correspond to a particular symmetry species (*i.e.*, irreducible representation) of that point group. Another way of saying this is that the displacement vectors corresponding to the normal modes form a basis for one of the irreducible representations of the molecule.

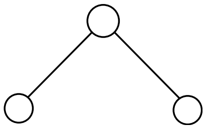
If one knows the displacement vectors corresponding to a normal mode, one can find the symmetry properties of that mode by noting the effect of the symmetry operations on these vectors. (This works well with non-degenerate vibrations but is more complex with degenerate vibrations.)

One other thing we can do is to find a *reducible* representation corresponding to all the vibrations of the molecule. The direct product decomposition of such a representation will give the symmetry species of all the vibrational modes.

The following expressions give you the character of the reducible representation for a molecule which, upon decomposition, will give you one symmetry species for every vibrational mode of the molecule. This procedure will not tell you which normal modes have which symmetry, but it tells you for the 3*N*-6 modes, how many there will be of each symmetry species.

$\chi(E) = 3N\text{-}6$ (or $3N\text{-}5$)	N is the total number of atoms
$\chi(C(\phi)) = (N_C-2)(1 + 2\cos\phi)$	N_C is the number of atoms left invariant by the C rotation
$\chi(\sigma) = N_\sigma$	N_σ is the number of atoms number left invariant by reflection
$\chi(i) = -\,3N_i$	N_i is the number of atoms left invariant by the inversion
$\chi(S(\phi)) = N_S(-1+2\cos\phi)$	N_S is the number of atoms left invariant by the S rotation

Let's look at the example of H_2O. (note: *xz*-plane is plane of molecule)



C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v'(y,z)$	
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
Γ_{vib}	3	1	3	1	

To get Γ_{vib}:

$\chi(E) = 3(3)-6 = 3$

$\chi(C_2) = (1-2)(1 - 2\cos(180)) = (-1)(-1) = 1$

$\chi(\sigma_v) = 3$

$\chi(\sigma_v') = 1$

Remember that the direct product decomposition is given by

$$\Gamma^{red} = \oplus\sum_i a_i \Gamma_i$$

where

$$a_i = \frac{1}{h}\sum_c N_c \chi^i(c)^* \chi^{red}(c)$$

$$a_1 = \frac{1}{4}\left(1\cdot 3 + 1\cdot 1 + 1\cdot 3 + 1\cdot 1\right) = 2$$

$$a_2 = \frac{1}{4}\left(1\cdot 3 + 1\cdot 1 + (-1)\cdot 3 + (-1)\cdot 1\right) = 0$$

$$a_3 = \frac{1}{4}\left(1\cdot 3 + (-1)\cdot 1 + 1\cdot 3 + (-1)\cdot 1\right) = 1$$

$$a_1 = \frac{1}{4}\left(1\cdot 3 + (-1)\cdot 1 + (-1)\cdot 3 + 1\cdot 1\right) = 0$$

Thus, $\Gamma_{vib} = 2A_1 + B_1$

This means that of the 3 normal modes of water, 2 will have A_1 symmetry and one will have B_1 symmetry. Although this procedure does not give you the displacement vectors representing the normal modes, if one knows the displacement vectors one can observe how they transform under the symmetry operations of the point group. You have already done this in one of the exercises.

4.2.4 Selection Rules

Selection rules for polyatomic molecules are determined in the same general way as for diatomics -- we must evaluate the transition moment integral. I will concentrate on the vibrational part. The rotational part will be the same as for pure rotational spectroscopy and will differ for different types of rotors. We need to evaluate

$$\int \psi^*_{2vib}\hat{\mu}_{vib}\psi_{1vib}d\tau_{vib}$$

In the case of diatomics, there was only one vibrational coordinate - the internuclear separation. In polyatomics, we have many different modes.

We can write the dipole moment function as a power series in the normal coordinates, Q_i. For example, we can write the *z*-component of the dipole moment as

$$\mu_z = \mu_{z0} + \sum_i \left(\frac{\partial \mu_z}{\partial Q_i}\right)_0 Q_i + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 \mu_z}{\partial Q_i \partial Q_j}\right)_0 Q_i Q_j + \dots$$

For the moment we will consider only the linear terms, since the higher order terms will be much smaller. However, the higher order terms do lead to a slight breakdown of the selection rules.

Remember that we can write the wave function as a product of harmonic oscillator wave functions for each mode. For the initial state 1we will write this as

$$\psi_{1vib} = \psi''_{v1}\,\psi''_{v2}\,\psi''_{v3}\cdots\psi''_{v(3N-6)}$$

where ψ''_{v1}, ψ''_{v2}, etc. represent the different normal modes for the lower state. The final state we write as:

$$\psi_{2vib} = \psi'_{v1}\,\psi'_{v2}\,\psi'_{v3}\cdots\psi'_{v(3N-6)}$$

We must take the matrix element of the dipole moment using these wave functions that are products of harmonic oscillator wave functions.

The dipole moment matrix element will be

$$\int \psi^*_{2vib}\,\hat{\mu}_z\,\psi_{1vib}\,d\tau = \int (\psi'^*_{\mathrm{v}1}\,\psi'^*_{\mathrm{v}2}\,\psi'^*_{\mathrm{v}3}\ldots\psi'^*_{\mathrm{v}(3N-6)})\,\hat{\mu}_z\,(\psi''_{\mathrm{v}1}\,\psi''_{\mathrm{v}2}\,\psi''_{\mathrm{v}3}\ldots\psi''_{\mathrm{v}(3N-6)})dQ_1\,dQ_2\,dQ_3\ldots dQ_{3N-6}$$

$$= \mu_{z0}\int (\psi'^*_{\mathrm{v}1}\,\psi'^*_{\mathrm{v}2}\,\psi'^*_{\mathrm{v}3}\ldots\psi'^*_{\mathrm{v}(3N-6)})\,(\psi''_{\mathrm{v}1}\,\psi''_{\mathrm{v}2}\,\psi''_{\mathrm{v}3}\ldots\psi''_{\mathrm{v}(3N-6)})dQ_1\,dQ_2\,dQ_3\ldots dQ_{3N-6}$$

$$+\int (\psi'^*_{\mathrm{v}1}\,\psi'^*_{\mathrm{v}2}\,\psi'^*_{\mathrm{v}3}\ldots\psi'^*_{\mathrm{v}(3N-6)})\sum_i\left(\frac{d\mu_z}{dQ_i}\right)Q_i\,(\psi''_{\mathrm{v}1}\,\psi''_{\mathrm{v}2}\,\psi''_{\mathrm{v}3}\ldots\psi''_{\mathrm{v}(3N-6)})dQ_1\,dQ_2\,dQ_3\ldots dQ_{3N-6}$$

The first term gives the selection rules for pure rotation transitions, since it will be zero if any of the vibrational quantum numbers change. The second term is really a sum of terms, one for each normal mode.

$$\left(\frac{d\mu_z}{dQ_1}\right)\int \psi'^*_{\mathrm{v}1}\,Q_1\,\psi''_{\mathrm{v}1}\,dQ_1\int(\psi'^*_{\mathrm{v}2}\,\psi'^*_{\mathrm{v}3}\ldots\psi'^*_{\mathrm{v}(3N-6)})\,(\psi''_{\mathrm{v}2}\,\psi''_{\mathrm{v}3}\ldots\psi''_{\mathrm{v}(3N-6)})dQ_2\,dQ_3\ldots dQ_{3N-6}$$

$$+\left(\frac{d\mu_z}{dQ_2}\right)\int \psi'^*_{\mathrm{v}2}\,Q_2\,\psi''_{\mathrm{v}2}\,dQ_2\int(\psi'^*_{\mathrm{v}1}\,\psi'^*_{\mathrm{v}3}\ldots\psi'^*_{\mathrm{v}(3N-6)})\,(\psi''_{\mathrm{v}1}\,\psi''_{\mathrm{v}3}\ldots\psi''_{\mathrm{v}(3N-6)})dQ_1\,dQ_3\ldots dQ_{3N-6}$$

$$+\ldots$$

In each term, the second factor is just a normalization integral for all the modes other than the one corresponding to the change in dipole moment. We therefore find that only one of the terms in this sum can be non-zero.

You can see that the transition moment integral for change in the number of quanta in any particular normal mode will be given by an integral that is identical to that for a one-dimensional harmonic oscillator. Thus for each mode *i*, we have

$$\left(\frac{d\mu_z}{dQ_i}\right)\int \psi'^*_{\mathrm{v}i}\,Q_i\,\psi''_{\mathrm{v}i}\,dQ_i$$

This will give rise to a Δv = ± 1 selection rule for each normal mode *i*. (One could use the same procedure with raising and lowering operators to evaluate this integral for each coordinate.) It also has the requirement that the dipole moment has a non-zero change along that particular normal mode. That is, when the molecule vibrates in that mode, the dipole moment must change.

We must not forget that any one of the components of μ (*x*, *y*, or *z*) can give rise to a transition, so there are similar integrals for the *x* and *y* components.

Thus, to get a transition to occur in a particular mode, the molecule must change its dipole moment when vibrating in that mode (example of CO_2). Moreover, if the integral is not identically zero by symmetry, it will give rise to the selection rule $\Delta \mathrm{v}_i = \pm 1$ for each normal mode *i*.

We can use group theoretical methods to evaluate whether or not the transition moment integral is identically zero on the basis of symmetry. In the one-dimensional case integrals over function that are odd, *i.e.* non even, yield zero. Analogous arguments hold for multi-dimensional integrals of the type:

$$\int \psi^*_{2vib}\hat{\mu}_z\psi_{1vib}d\tau_{vib}$$

To determine whether this integral is zero one has to turn to group theory. One can show that for the integral to be non-zero, the direct sum of the function in the integral must contain the totally symmetric representation:

$$\Gamma_{integrand} = \Gamma(\psi_2) \otimes \Gamma(\mu_z) \otimes \Gamma(\psi_1) = \oplus \sum_i a_i \Gamma_i$$

Thus the coefficient a_i for the totally symmetric representation should be non-zero

Recall that the ground state is totally symmetric. If ψ_1 is the ground state, then the direct product

$$\Gamma(\psi_2) \otimes \Gamma(\mu_z)$$

must contain the totally symmetric species for this to happen

$$\Gamma(\psi_2) = \Gamma(\mu_z)$$

and similarly for the *y*- and *x*-components.

Remember that the species of the dipole moment components are the same as translation in that coordinate.

The procedure for finding the selection rules for transitions from the ground state is as follows:

(1) Assign the molecule to a point group.
(2) Look up the translation species in the character table.
(3) The allowed transitions from the ground state will be to those states that have the symmetry of the translations in the *x*-, *y*-, and *z*-direction. Simply find where these occur in the relevant character table.

Consider, for example, for H_2O which is C_{2v}.

C_{2v}	E	C_2	$\sigma_v(x,z)$	$\sigma_v'(y,z)$	
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

Transitions from the ground state (which is A_1) are allowed to vibrations of the species A_1 (polarized along the *z* axis), B_1 (polarized along the *x*-axis), and B_2 (polarized along the *y*-axis). The expression "polarized along the *x*, *y*, or *z* axes means that this is the direction of the change in dipole moment.

If one is not starting from the ground state, then the selection rules are given more generally by the symmetry species of the integrand

$$\Gamma_{integrand} = \Gamma(\psi_2) \otimes \Gamma(\mu_z) \otimes \Gamma(\psi_1) = \oplus \sum_i a_i \Gamma_i$$

and similarly for the other components of μ.

Note that overtone transitions are not forbidden on the basis of symmetry. When symmetry says something will be non-zero, it doesn't say how large it will be -- in fact it can be infinitesimally small. Overtone transitions can be allowed by symmetry but forbidden on the basis of selection rules. (Recall from the exercises that there are certain ways the selection rules can break down.)

The symmetry species of a non-degenerate normal mode with *n* quanta is given by the direct product of the species with itself taken *n* times. So, for 2 quanta in a B_1 mode of water

$$\Gamma(\psi_{v=2}) = (B_1)^2 = B_1 \otimes B_1 = A_1$$

This is not so simple in the case of an overtone of a ***degenerate*** normal mode such as one with *E* species,

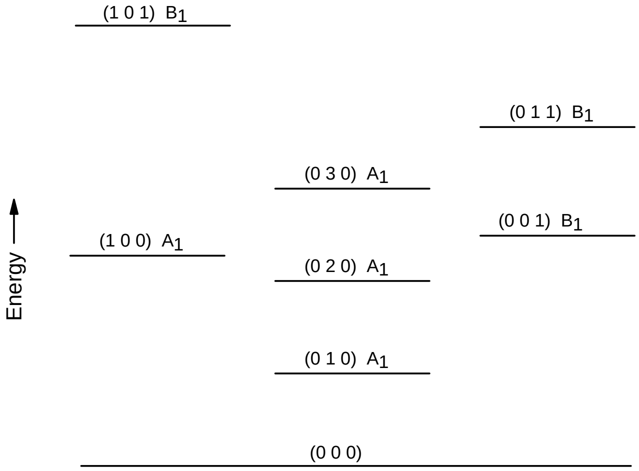
$$\Gamma\left(\psi_{v=2}\right)=\left(E\right)^2 \neq E\otimes E$$

If you decompose $E\otimes E$ it may include extra symmetry species, depending upon the point group. There are ways to figure out which species are extra, but it is easier to look up the result of the decomposition in tables.

To determine whether a transition from the ground state to an overtone level is allowed by symmetry, one simply finds the species of the transition moment integrand.
A state with one or more quanta in more than one normal mode is called a ***combination level*** and transitions to a combination level are called ***combination bands.***

For H_2O we have the following situation:

(010)	A_1	bend	1585 cm^{-1}
(020)	A_1	bend overtone	3151 cm^{-1}
(100)	A_1	symmetric stretch	3651.7 cm^{-1}
(011)	B_1	stretch bend combination	5332 cm^{-1}
(001)	B_1	asymmetric stretch	3751.7 cm^{-1}



To determine whether transitions to combination levels are allowed by symmetry, one must find the symmetry species of a combination level. This is simply done since the symmetry species of a level with one quanta in each of two normal modes is simply the direct product of the symmetry species of the separate modes with one quantum. Combination levels of different degenerate vibrations do not pose the same problems as overtones of degenerate vibrations.

The direct product of combination levels can then be used in finding the symmetry species of the integrand in the transition moment integral.

4.3 Rovibrational Spectra of Polyatomic Molecules

The rovibrational spectra of polyatomics, that is, the spectrum taking into account both the vibrational and rotational selection rules, is somewhat particular for each type of rotor. Given what we have already done on diatomic rotation-vibration spectra, you should be able to determine what such a spectrum would look like if you know the expression for the energy levels and the relevant rotational selection rules. I will just do one example – the case of a symmetric top.

4.3.1 Symmetric tops

Recall the energy level expression for the rotational levels of a symmetric top:

$$F(J,K) = BJ\left(J+1\right) + \left(A-B\right)K^2$$

There are two rotational quantum numbers, *J* and *K*, where *J* represents end over end rotation and *K* is the projection of *J* onto the symmetry axis of the molecule.

In pure rotational spectroscopy, the selection rules only allowed $\Delta K=0$ transitions (*i.e.*, transitions within a single *K* stack). The rotational selection rules for rovibrational spectra can be different from the pure rotation spectrum insofar as the direction of the change of dipole moment can be different from the direction of the permanent dipole moment (note that this was not possible in the case for diatomics). This allows rotational transitions that are not allowed in pure rotational spectra.

In the case of a symmetric top the selection rules for a rotation-vibration transition are:

- If the change in dipole moment is parallel to the top axis (parallel band):

  $\Delta K = 0$, $\Delta J = \pm 1$ if $K = 0$
  $\Delta K = 0$, $\Delta J = 0, \pm 1$ if $K \neq 0$

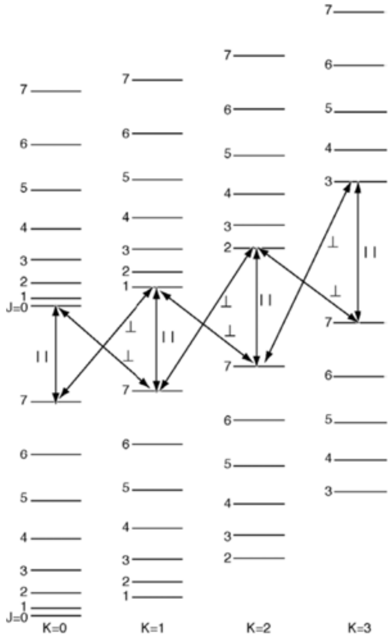
- If the change in dipole moment is perpendicular to the top axis (perpendicular band):

  $\Delta K = \pm 1$, $\Delta J = 0, \pm 1$

The different possibilities are shown in the schematic below.

Each *K* stack will have its own *J* structure, and this is called a sub-band.

To determine whether a transition is parallel or perpendicular one can use group theory. In case the transition moment corresponds to a translation in the *z*-direction (which is usually taken as the direction of the symmetry axis) a parallel transition results. In case the transition moment corresponds to a translation in the *x* or *y*-direction a perpendicular transition will result.



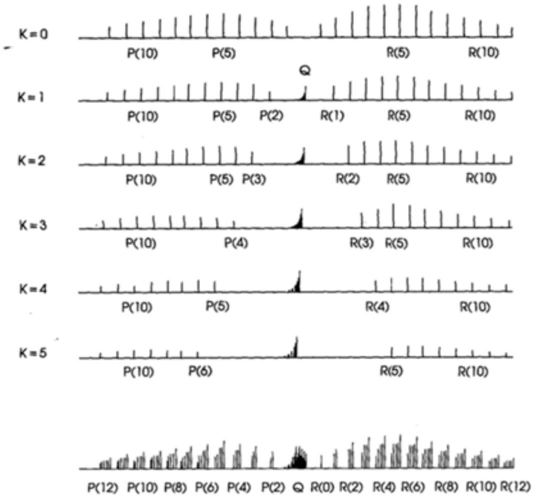
(Note that the arrows indicate only the change in *K*, not the change in *J*)

Parallel bands

In a parallel band, because $\Delta K = 0$, all the different K sub-bands stack on top of one another, just like a pure rotational spectrum. The difference, however, is now one has a Q branch (ΔJ=0) in addition to a P and R branch. The sub-band origin for a parallel band is given by:

$$\nu_0^{sub} = \nu_0 + \left[\left(A' - A''\right) - \left(B' - B''\right)\right]K^2$$

The figure above shows each sub-band separately and then the superposition of the two sub-bands.

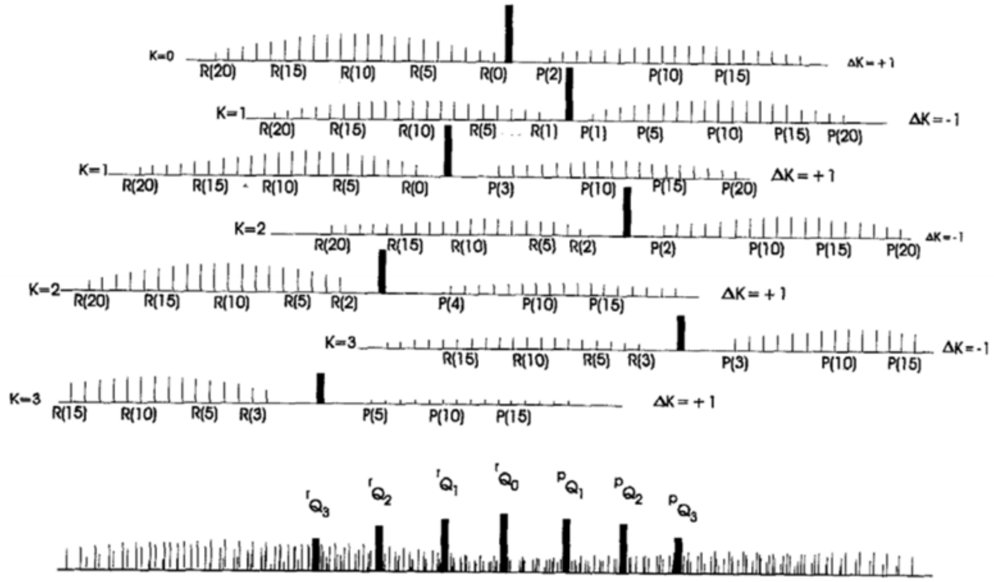


Perpendicular bands

The sub-band origins for a perpendicular band are given by

$$\nu_0^{sub} = \nu_0 + \left(A' - B'\right) \pm 2\left(A' - B'\right)K + \left[\left(A' - A''\right) - \left(B' - B''\right)\right]K^2$$

Because of the $2\left(A' - B'\right)K$ term, each sub-band is widely shifted from the previous one. This is shown in the schematic spectrum shown below.



As you can see the spectra for parallel and a perpendicular transition are markedly different. A brief inspection of the spectrum therefore will immediately tell you if you are dealing with a parallel or perpendicular transition.

Notation for symmetric top rovibrational transitions

Because there is the possibility of changing both the *J* and *K* quantum numbers during a rovibrational transition of a symmetric top, one must have a notation that carries the information on what those changes are. Recall that for a diatomic molecule we labeled them *R*(*J*) or *P*(*J*) to indicate Δ*J*=± 1 and the initial *J* state. For symmetric tops, the notation is as follows:

$$^{\Delta K}\Delta J_{K''}\left(J''\right)$$

where the value of Δ*K* or Δ*J* is indicated by the *P Q R* notation.

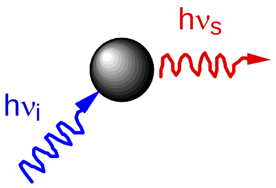
Thus, if one writes ${}^{Q}P_2(3)$ this means a transition that starts with *K*=2 and *J*=3 in the lower vibrational state and goes to *K*=2 and *J*=2 in the upper vibrational state.

4.4 Raman Spectroscopy

4.4.1 Introduction

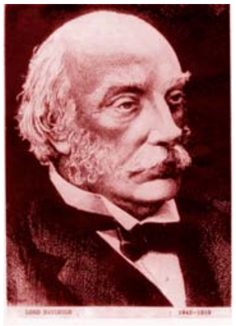
Now I would like to address the subject of Raman Spectroscopy. Although one cannot truly do justice to this subject in the time we have, I will try to give you an appreciation for its important features.

The Raman effect is a light scattering phenomenon.



In the simplest sense, one can consider the Raman effect as a collision between a photon and a molecule. Light of incident frequency ν_i impinges on a molecule and is scattered. The frequency of scattered light can either be at the same frequency as the incident light (elastic scattering), or it can be at some shifted frequency (inelastic scattering).

The elastic scattering case, in which the molecule is returned to is original state is called ***Rayleigh Scattering***. The inelastic case, in which the final state of the molecule changes is called ***Raman Scattering***, after the Indian physicist Chandrasekhara Raman who first observed this effect in 1928 (and won the Nobel Prize in 1930).

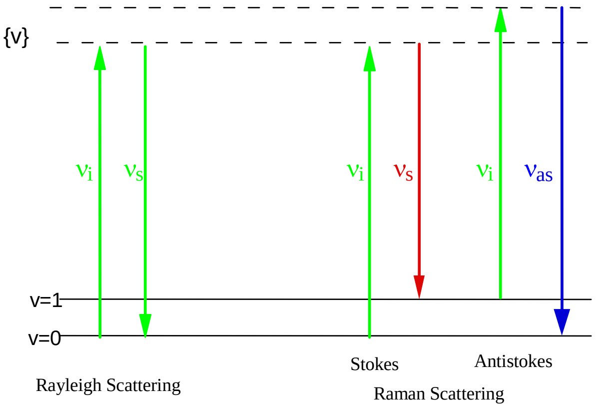


Lord Rayleigh

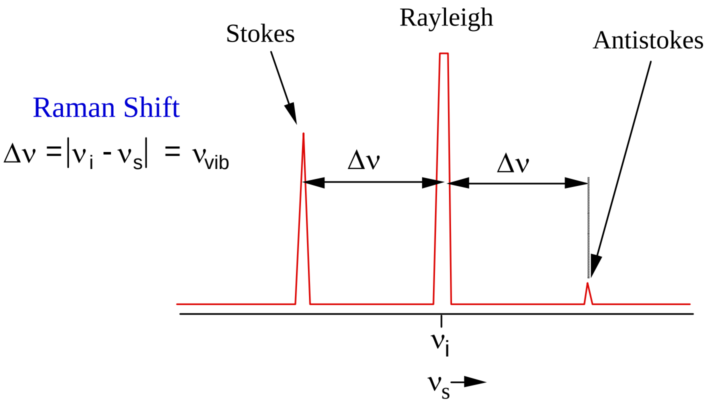
Chandrasekhara Raman

Raman scattering occurs through the interaction of the incident photon with a molecule's charge distribution and results in the transfer of energy from the radiation field to the internal (vibrational and rotational) motions of the molecule or vice versa.

Raman Scattering is a two-photon process. Conceptually, one can view this process as a transition from some initial state to some intermediate or “virtual state” followed by a transition back to one of the real states of the molecule.



The inelastic scattering event in which energy is transferred *from the radiation field to the molecule* resulting in a lower energy photon is called **stokes scattering** while the case in which energy is given up *from the molecule to the field* is called **antistokes scattering**.

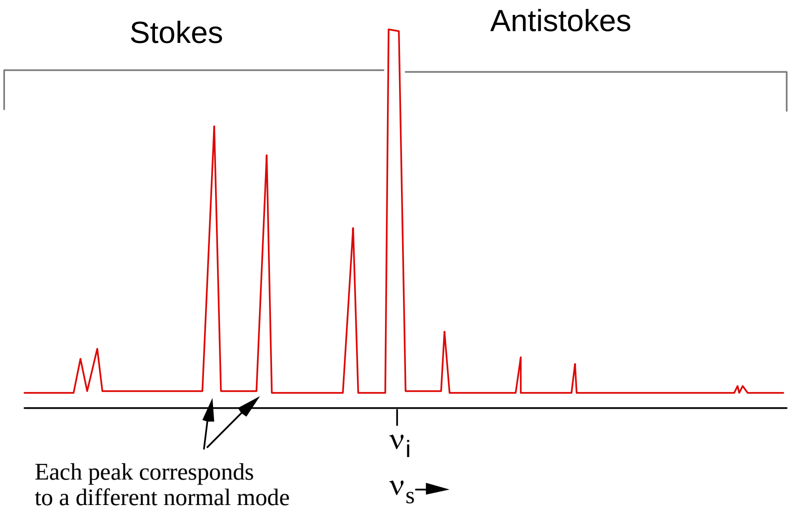


In Raman Scattering, information is contained in the difference in frequency between the incident and scattered photons, for this corresponds to vibrational and rotational energy level spacings of the molecule. This difference, $\Delta\nu$, is called the **Raman Shift.**

The intense peak at the excitation frequency (*i.e.*, Rayleigh scattering) emphasizes that Raman scattering is a relatively inefficient process, and this means that it requires high intensity excitation sources.

The greater intensity of the stokes lines compared to the antistokes lines reflect, in part, the different initial population of these states. You can see that antistokes scattering requires molecules in the vibrationally excited level which are typically much less populated at room temperature (see our earlier discussion of state populations).

The picture above shows Raman scattering for a system with only one vibrational mode (*i.e.*, a diatomic). In a polyatomic molecule, one can induce transitions to different normal modes, and so the Raman spectrum may have a number of peaks.



The principal advantages of Raman Scattering are twofold:

- One can get information about vibrational state of a molecule without working in the infrared region of the spectrum because the energy level information is contained in the difference in frequency between the incident and scattered photon. Since the virtual level {v} need not correspond to an actual molecular eigenstate, one can use incident photons of whatever frequency is easily available.
- The second advantage is that it does not require a tunable excitation source, but rather the ability to analyze the frequency of the scattered radiation which is easily done with a monochromator. The intensity of light scattering is proportional to the 4th power of the frequency, so using higher frequency sources results in a more intense spectrum. It is this strong dependence on the frequency that gives the sky its blue color. Particles and molecules in the atmosphere preferentially scatter blue light.

4.4.2 Quantum Mechanical Considerations

The basic physics of the Raman effect arise from the interaction of electromagnetic radiation with a molecular charge distribution. When one applies an electric field to a distribution of charges such as a molecule, the field will polarize the charges, giving rise to an induced dipole moment. If the applied field is not too strong, the induced dipole moment will be proportional to the applied field:

$$\boldsymbol{\mu}_{ind} = \boldsymbol{\alpha}\mathbf{E}$$

α is simply the proportionality constant between the electric field and the induced moment and is called the ***polarizability***.

For highly symmetrical molecules, the induced dipole moment is in the same direction as the applied field. However, for less symmetrical molecules, $\boldsymbol{\mu}_{ind}$ and $\mathbf{E}$ can point in different directions. So we must write:

$$\mu_x = \alpha_{xx}E_x + \alpha_{xy}E_y + \alpha_{xz}E_z$$

$$\mu_y = \alpha_{yx}E_x + \alpha_{yy}E_y + \alpha_{yz}E_z$$

$$\mu_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z$$

The polarizability can be represented by a 3 x 3 symmetric matrix called the **polarizability tensor**:

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

In the quantum mechanical treatment of vibrational Raman scattering, the intensity (and selection rules) depend upon the square of integrals of the type

$$\int \psi^*_{2vib}\, \hat{\alpha}_{ij}\, \psi_{1vib}\, dQ \qquad\qquad i,j = x, y, z$$

This is analogous to the dependence of infrared transitions upon the square of the dipole moment matrix element.

I only show the vibrational part here, but similar to the case for infrared transitions, there is a rotational part that arises when one goes from the spaced fixed coordinates to molecule fixed coordinates. As we will see later, for a simple diatomic molecule without electronic angular momentum, the rotational selection rules are $\Delta J = 0, \pm 2$.

For this integral to be non-zero, the integrand must contain the totally symmetric representation.

That is,

$$\Gamma\left(\psi_2^*\right) \otimes \Gamma\left(\alpha_{ij}\right) \otimes \Gamma\left(\psi_1\right)$$

must contain the totally symmetric representation.

The six elements of the polarizability tensor, $\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}, \alpha_{xz}, \alpha_{yz}$, have the same symmetry behavior as the binary products of coordinates x^2, y^2, z^2, xy, xz, yz,. The symmetry of these products (or properly symmetrized combinations of them) are listed on the right side of the character tables.

If we consider transitions in which the initial state is the ground vibrational state, then ψ_1 has A_1 symmetry. For the integrand to contain the A_1 representation, then

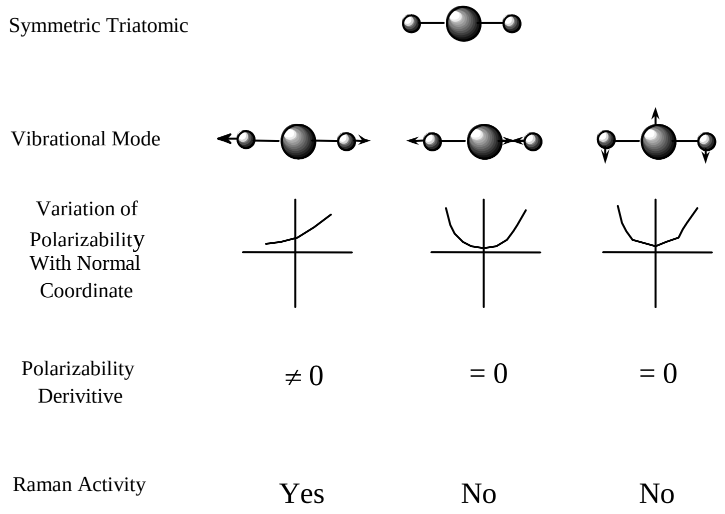
$$\Gamma\left(\psi_2^*\right) = \Gamma\left(\alpha_{ij}\right)$$

One simply looks in the character table for the different components of ����The allowed Raman transitions will be to vibrational states which have the same symmetry of these components of the polarizability tensor. There is an example of this in the exercises.

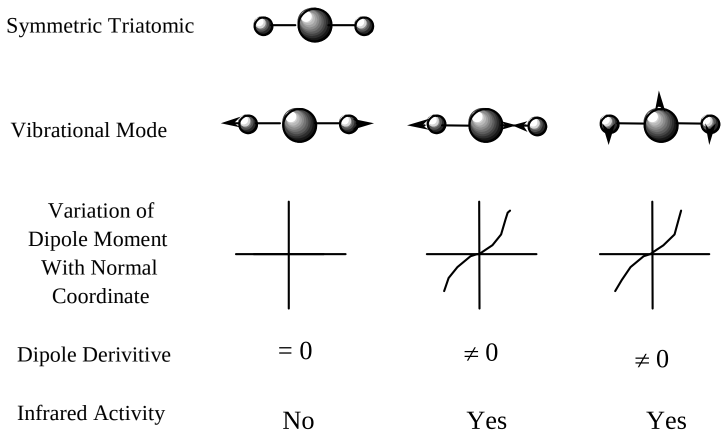
There is one important to thing to notice. If you look at character tables for a group in which there is a center of inversion, you will find that the symmetry species that contain the translations in the *x*, *y*, and *z* directions will be mutually exclusive from those that have the components of the polarizability tensor. Thus, for a molecule with a center of symmetry, no fundamental mode will be both infrared and Raman active.

The physical basis of Raman scattering relies upon a change in the molecular polarizability (and hence the induced dipole moment) as the molecule vibrates. This is analogous to normal infrared spectroscopy which relies on a change in the permanent dipole moment as the molecule vibrates.

By comparing the expected polarizability at each turning point of the vibration, you can get a good idea of whether the derivative will be zero at the equilibrium position.



It is instructive to make the corresponding figures for the change in dipole moments which are required for infrared transitions and compare them to the requirements for Raman transitions:



You can see that there is a complementarity here. The transitions that are Raman active are infrared inactive and vice versa. As we will see in a moment, this is true for all molecules that have a center of inversion.

There is one extremely important feature of Raman scattering that I haven't yet mentioned. Because it depends upon the change of polarizability and not on change in dipole moment, homonuclear diatomic molecules have a Raman spectrum. Some of the most accurate information on homonuclear diatomics comes from Raman spectra. Let us think about how □ might change in a symmetric linear triatomic.

4.4.3 Vibrational Selection Rules

The considerations above give us the symmetry restrictions but not the selection rules. The selection rules come from actually evaluating the matrix elements of the components of the polarizability tensor

$$\int \psi^*_{2vib}\,\hat{\alpha}_{ij}\,\psi_{1vib}\,dQ$$

rather than simply noting when it is zero on the basis of symmetry.

To evaluate this integral, we can expand one component of the polarizability as a power series in the normal coordinates Q_k.

$$\alpha_{xx} = (\alpha_{xx})_0 + \sum_k \left(\frac{\partial \alpha_{xx}}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\sum_{k,l}\left(\frac{\partial^2 \alpha_{xx}}{\partial Q_k \partial Q_l}\right)_0 Q_k Q_l + \ldots$$

If we neglect all the terms higher than the linear term we have

$$\alpha_{xx} = (\alpha_{xx})_0 + \sum_k \left(\frac{\partial \alpha_{xx}}{\partial Q_k}\right)_0 Q_k$$

If we want the selection rule for only the change in the mode corresponding to Q_k we only need to consider one term of the sum.

The matrix element of this component of the polarizability will then be

$$\int \psi^*_{2vib}\, \hat{\alpha}_{xx}\, \psi_{1vib}\, dQ_k = (\alpha_{xx})_0 \int \psi^*_{2vib}\, \psi_{1vib}\, dQ_k + \left(\frac{\partial \alpha_{xx}}{\partial Q_k}\right)_0 \int \psi^*_{2vib}\, Q_k\, \psi_{1vib}\, dQ_k$$

The first term on the right is only non-zero in the case that the vibrational state doesn't change. This term gives the requirements for Rayleigh scattering (non-zero polarizability).

The second term gives rise to Raman selection rules. The integral is the same as for infrared transitions and will lead to the same selection rule: $\Delta v = \pm 1$.

The breakdown of this selection rule occurs in a similar fashion to that for infrared transitions, since the relevant integral is the same. Anharmonicity in the potential will cause the wave functions to deviate from harmonic oscillator functions, and this will allow greater changes in the vibrational quantum number. Also non-linear terms in the polarizability will cause the selection rules to break down.

The other requirement for having a Raman spectrum, as we have stated before, is that the polarizability derivative (the change as the molecule vibrates in a particular mode), must be non-zero.

4.4.4 Vibration-rotation Raman Spectra of Diatomics

One of the most important features of Raman spectroscopy is its ability to provide information on homonuclear diatomic molecules, since these have no infrared spectrum due to the lack of change in dipole moment and no microwave spectrum due to the lack of permanent dipole moment. Thus, the rotational structure of the Raman spectrum provides information not available by other methods.

The details of a Raman spectrum for a diatomic molecule is simply determined by the vibrational and rotational selection rules.

Recall that the vibrational selection rule, in the harmonic oscillator approximation, is the same as for infrared spectroscopy: $\Delta v = \pm 1$.

The rotational selection rules are different however. Because Raman scattering is a two-photon process, conservation of total angular momentum dictates that the selection rule must be $\Delta J = 0, \pm 2$.

Thus the spectrum will have a *O*, *Q*, and *S* branch corresponding to $\Delta J = -2, 0, +2$ respectively.

Knowing the energy level spacings for the rovibrational levels of a diatomic molecule, you should be able to determine what the spectrum will look like, both in the case in which vibration-rotation interaction is neglected (*i.e.*, $B' = B''$) and in the case in which the change in *B* is explicitly taken into account.