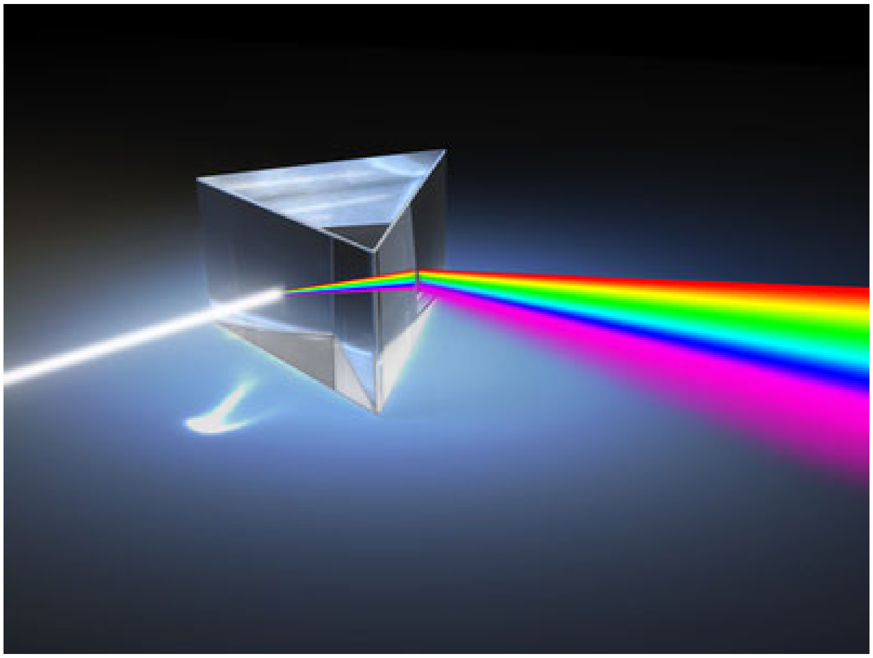
Spectroscopy

Dr. Marcel Drabbels



EPFL

Spring 2024

Table of Contents

1 Introduction

1.1 General comments

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Documentation – Lecture notes, exercises, and solutions can be downloaded via Moodle.

Exercises - **Solving problems is an essential part of the course**. I encourage you not only to come to the exercise sessions, but also to work on the problems before you come.

Reference Books

Primary References:

- J. M. Hollas, *Modern Spectroscopy*
- C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*
- D. A. McQuarrie, *Quantum Chemistry*

Secondary References:

- G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*
- G. Herzberg, *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*
- G. Herzberg, *Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules*

This course will give you an introduction spectroscopy. In the time we have here we can only cover the basics, but once you understand these basics you will be able to go on and learn about more advanced topics on your own. It is therefore not important exactly how much material we cover in class. What I am most concerned about is that you understand the material that we do cover. If we don't get through everything that is no problem, as long as you understand what we discussed during class. My goal is that everyone understands the material. This puts also a certain burden on you, *i.e*. you should ask questions if a subject or point made is not clear to you. When you leave the classroom you should feel that you understand everything that I covered.

1.2 Usefulness of Spectroscopy

Spectroscopy can be broadly defined as the interaction of light with matter by which molecules make a transition from one quantum state to another. It is at work everywhere around us determining everything from the color of your clothes to the color of the sky. It is responsible for the lasers that scan the bar-codes at Migros, the ones that connect computers over the internet and the ones that determine the distance to the moon. Spectroscopy forms the basis for understanding problems like global warming and the ozone hole.

Spectroscopy provides innumerable ways to learn about chemistry in the research laboratory. One can use it to monitor how fast a reaction happens, to determine how chemistry proceeds on surfaces, to learn how energy flows within and between molecules, to assist in the synthesis of new molecules. It also provides the basis for remote diagnostics of chemical systems in the real world, such as combustion processes in automobile engines, chemistry in the atmosphere and cancer photo-therapy. It is essential in organic and inorganic chemistry for the identification for new compounds. It will also form the basis for understanding some of the TP experiments in the 6th semester.

2 Overview of Molecular Spectroscopy

When discussing molecular spectroscopy, we will use the results that we have obtained from quantum chemistry quite frequently. I will start by giving you an overview of the field of molecular spectroscopy, dealing with issues that are common to all types of spectra. For this I will mostly use diatomic molecules as an example. We will then become more specific and consider particular types of spectroscopy (*i.e.*, transitions between different types of energy levels). Occasionally I will need to introduce new concepts related to quantum chemistry.

Because molecular spectroscopy involves making light-induced transitions between quantum states of a molecule, you can see how the basis of molecular spectroscopy would be quantum chemistry. One needs to know both the energy levels of molecules and their wave functions to be able to predict their spectra. However, the spectra themselves provide the most powerful means to investigate the energy levels and wave functions of molecules.

The approach of spectroscopy is to cause molecules to absorb and emit light and then measure the frequencies at which those transitions occur. The energy or frequency of each transition corresponds to a difference in energy levels. Recall that the separations of energy levels depend upon the potential energy term in the Hamiltonian for the system. We saw this in the simple one-dimensional problems such as the particle in a box and harmonic oscillator. For polyatomic molecules, this function is multidimensional. One of the primary goals of spectroscopy is to determine the multidimensional potential energy function, also called a potential energy surface, for a molecule from measuring these levels. Recall that the bottom of the potential well in a simple one-dimensional potential (*i.e.*, for a diatomic molecule) gives us the bond length. In a polyatomic case, the global minimum of the potential energy surface gives the geometry of the molecule.

After measuring the energy levels of a molecule, we can compare them to those predicted from calculated potential energy surfaces. This allows us to go back and refine the techniques used to calculate the surface. The goal would be to calculate these potential functions accurately enough to determine accurate molecular geometries and predict exactly where all the levels would be. This would allow us to predict at which frequencies molecules would absorb and emit light.

2.1 Starting Point: The Born-Oppenheimer Approximation

At the end of the Quantum Chemistry course we were discussing ways of solving the Schrödinger Equation for simple molecules. Although I didn't make it so clear at the time, this is only one part of the Schrödinger Equation, *i.e.*, the electronic part. As you will soon see, the Born-Oppenheimer approximation divides the Schrödinger equation into two parts.

Solving the electronic part of the Schrödinger Equation determines the potential energy curves (or surfaces) for the nuclei, *i.e.*, the potential function in which the nuclei move. Hence, we get the electronic (potential) energy as a function of the nuclear coordinates, the electronic wave functions, and, by analysis of the potential energy function, the geometry. This, however, does not solve for the total energy of the molecule, since we have neglected the nuclear kinetic energy. We need to take the result of our solution of the electronic part (the potential energy as a function of the position of the nuclei) and insert it into the nuclear part of the Schrödinger Equation (together with the nuclear kinetic energy) and solve this equation. <u>The solutions of the nuclear Schrödinger Equation will give us the eigenvalues for the total energy</u>. It is these eigenvalues that we measure in a spectroscopic experiment.

Thus, the Born-Oppenheimer approximation divides quantum chemistry (the electronic Schrödinger Equation) from molecular spectroscopy (the nuclear Schrödinger Equation) and hence lies at the foundation of the latter.

Because of its importance, I would like to go back and look at the Born-Oppenheimer approximation in a slightly more general way. After doing this, we will come back and focus once again on the case of a simple diatomic molecule, using it to display many of the general principles about spectroscopy.

Let's write down (using atomic units) the Hamiltonian for a molecule neglecting relativistic interactions.

$$\hat{H} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} - \frac{1}{2}\sum_{i}\nabla_{i}^{2} + \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}} - \sum_{\alpha}\sum_{i}\frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}}$$

α, β denote nuclei; *i,j* denote electrons.
$r_{\alpha\beta}$ is the distance between nucleus α and nucleus β
$r_{i\alpha}$ is the distance between electron *i* and nucleus α
r_{ij} is the distance between electron *i* and electron *j*

For understanding spectroscopy, we need to find both the wave functions and energies of a molecule.

These are found from the Schrödinger Equation

$$\hat{H}\psi(q_i, q_{\alpha}) = E\psi(q_i, q_{\alpha})$$

where q_i represents the electron coordinates and q_{α} the nuclei coordinates

You can see how things are getting pretty complicated for atoms with more than two electrons. Solving the Schrödinger Equation for a molecule with more than *two atoms* might appear hopeless. However, the Born-Oppenheimer approximation greatly simplifies the problem and is quite accurate. It essentially allows us to separate both the Hamiltonian and its eigenfunctions into electronic and nuclear parts.

Recall that the physical basis of the Born-Oppenheimer approximation lies in the fact that the masses of the nuclei are much greater than that of the electrons. The ratio of the rest mass of the proton to that of electron is

$$\frac{m_p}{m_e} \approx 1835$$

The ratio of the mass of a nucleus containing several protons and neutrons to that of an electron is even higher. As a result of this difference in mass, for the same coulombic forces between the nuclei and the electrons, the ***electrons move much faster than the nuclei.*** To a very good approximation, the nuclei can be considered to be fixed while the electrons carry out their motions. Making this approximation amounts to neglecting the nuclear kinetic energy term from the Hamiltonian for electronic motion.

We can then write the Schrödinger Equation for the electronic motion:

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = U\psi_{el}$$

where

$$\hat{H}_{el} = -\frac{1}{2}\sum_{i}\nabla_{i}^{2} - \sum_{\alpha}\sum_{i}\frac{Z_{\alpha}}{r_{i\alpha}} + \sum_{j}\sum_{i>j}\frac{1}{r_{ij}}$$

and

$$V_{nucl} = \sum_{\alpha}\sum_{\beta>\alpha}\frac{Z_{\alpha}Z_{\beta}}{r_{\alpha\beta}}$$

The energy *U* is the electronic energy including nuclear repulsion. Remember that we only neglected nuclear kinetic energy, not the repulsion of the nuclei.

Note that since we make the approximation that the nuclei don't move, then $r_{\alpha\beta}$ aren't really variables but parameters. That is, we fix them and solve the electronic problem for fixed values of $r_{\alpha\beta}$. We choose values for the $r_{\alpha\beta}$ (designated more generally by q_{α}), evaluate V_{nuc}, and then solve our electronic Schrödinger Equation. *We must repeat this process for many values of the nuclear coordinates,* q_{α}.

Since the Hamiltonian depends on q_α , the energy we get will also depend parametrically on q_α.

$$U = U(q_\alpha)$$

So for each set of q_α we get a different Schrödinger equation, different energies U, and different electronic wavefunctions.

$$\psi_{el} = \psi_{el,n}(q_i; q_\alpha)$$

where n is the electronic quantum number, q_i are the electron positions and the ; signifies that the q_α are parameters.

Now, once we pick our q_α, the nuclear potential term V_{nuc} is constant.

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = U\psi_{el}$$

We can write this like:

$$\left(\hat{H}_{el} + V_{nucl}\right)\psi_{el} = \left(E_{el} + V_{nucl}\right)\psi_{el}$$

where E_{el} is simply the eigenvalue of $\hat{H}_{el}$:

$$\hat{H}_{el}\psi_{el} = E_{el}\,\psi_{el}$$

We often call this equation the electronic Schrödinger equation.

The total electronic energy, U, (including nuclear repulsion terms) is then given by

$$U = E_{el} + V_{nucl}$$

So we can leave out V_{nuc} from our Schrödinger equation and simply add it to E_{el} after solving the electronic Schrödinger equation.

Note that $\hat{H}_{el}$ still contains inter-electronic repulsion and attraction to the nucleus.

Let's say for the moment we know how to solve the electronic Schrödinger Equation using some of the techniques we discussed in our treatment of quantum chemistry.

$$\hat{H}_{el}\psi_{el} = E_{el}\,\psi_{el}$$

In practice, this is not trivial, but assume we can find a way to do this, for example using the Hartree-Fock method. Let us think about the procedure one would take in solving the full problem.

Consider the case of a diatomic molecule.

E_{el} and ψ_{el} depend on $r_{\alpha\beta}$

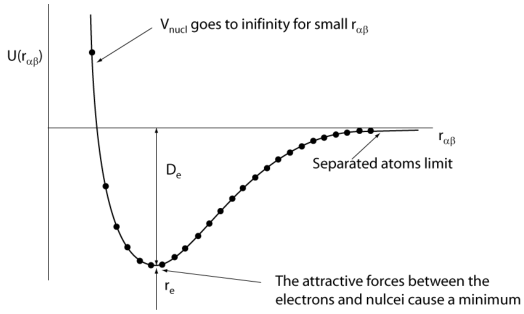
First fix $r_{\alpha\beta}$ at some value and solve this equation for E_{el}. We will get a whole set of solutions $\psi_{el,n}$, $E_{el,n}$. Let's now look only at the lowest energy state.

U, the total electronic energy (including nuclear repulsion) is

$$U = E_{el} + V_{nucl} = E_{el} + \frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

We then go through this procedure for a series of different $r_{\alpha\beta}$, each time finding a different value of E_{el} and hence another value for U. It is important to realize that every time we change the nuclear coordinates, we must resolve the electronic Schrödinger Equation.

If we plot U vs. $r_{\alpha\beta}$ we get something like this:



Once calls this plot a potential energy curve, since it represents the potential energy of interaction between the two nuclei. At each point along the curve (that is, each value of r) we have solved the electronic Schrödinger equation and then added the nuclear repulsion to get the total electronic energy U.

The fact that the electronic energy U has a minimum *vs*. r indicates that there is some equilibrium internuclear separation that corresponds to a state in which the two nuclei are bound and stable.

One usually denotes the $r_{\alpha\beta}$ at the minimum as r_e, and the difference between U at r_e and U at ∞ as D_e.

$$D_e = U(\infty) - U(r_e)$$

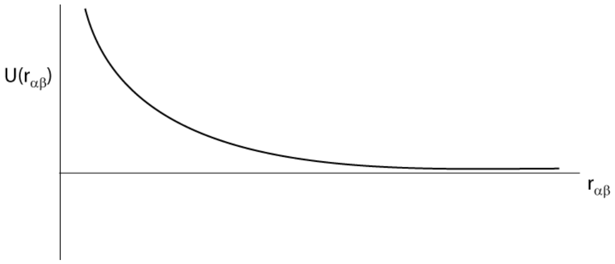
D_e is the energy needed to separate the two atoms of the diatomic, or in other words the binding energy or bond energy.

Notice that our nuclear term is purely repulsive:

$$V_{nucl} = +\frac{Z_\alpha Z_\beta}{r_{\alpha\beta}}$$

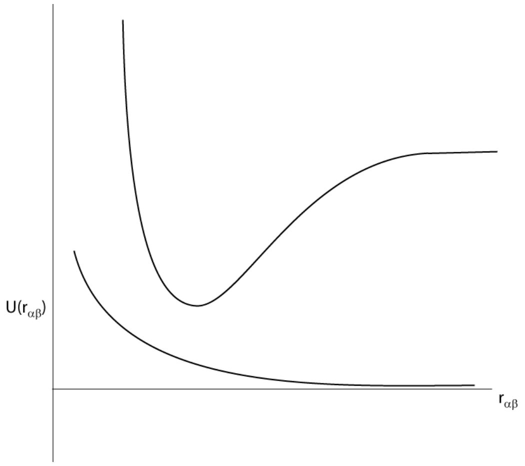
Thus it is electronic energy, E_{el}, which gives you the minimum in the potential.

There doesn't have to be a minimum in the potential. One can have an electronic state in which the potential energy curve looks like the following:



This is a purely dissociative electronic state since it has no stable minimum (no value of $r_e < \infty$ where the nuclei are at their lowest energy). This is the case for He_2 for example.

Molecules will in general have both bound and dissociative states. For stable molecules, obviously the ground state is bound. However, in the He dimer, He_2, the first two potential curves look something like that shown below (we already saw this when we discussed molecular last semester):



For this molecule, the lowest state is dissociative and first excited state is bound. A molecule that is bound in the excited state but dissociative in the ground state is called an ***excimer*** (or ***exciplex*** in the case where the two atoms are different).

Each one of these curves represents an electronic state, in the same way that each energy of the particle in box represents a quantum mechanical state. There is therefore an entire ladder of electronic states. However, we have added an additional coordinate that the electronic energy depends upon, *i.e.*, the internuclear separation. If we take a cut along the axis representing the internuclear separation, we get a series of energy levels corresponding to increasing values of the quantum numbers for electronic degrees of freedom. When I refer to an electronic state of a diatomic, I am speaking of the entire potential energy curve representing the electronic energy as a function of the internuclear coordinates. Most of the time I will only consider the lowest or the lowest few potential curves (*i.e.*, electronic states).

Solving the electronic part of the Schrödinger equation represents a field one would call ***chemical bonding***, since it is the electronic part of the Schrödinger equation that results in stable minima between the atoms and hence a chemical bond. I will say more about this in a moment.

The electronic part of the Schrödinger equation is only half the problem, however. We haven't yet considered nuclear motion.

Since electrons move much faster than the nuclei, they are able to immediately readjust as the nuclei move. In the diatomic case, if the nuclei move from $r_{\alpha\beta}$ to $r_{\alpha\beta'}$, the electronic wave function changes from $\psi_{el}(q_i;r_{\alpha\beta})$ to $\psi_{el}(q_i;r_{\alpha\beta'})$. The electronic energy changes smoothly from $U(r_{\alpha\beta})$ to $U(r_{\alpha\beta'})$ as one moves along the potential curve. In effect, $U(r_{\alpha\beta})$ (or in the general case $U(q_\alpha)$) becomes the potential in which the nuclei move. One solves the electronic Schrödinger equation for different q_α and then fits the results to some functional form (one dimensional if diatomic; higher dimensional if more than two nuclei).

The Schrödinger equation for nuclear motion can be written.

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

where

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} + U(q_{\alpha})$$

E_{Tot} is the total energy, electronic + nuclear, since we are including electronic terms in the Hamiltonian though the potential, $U(q_{\alpha})$.

For a diatomic, the potential, $U(q_{\alpha})$, is a one-dimensional curve and can be treated like our simple model quantum mechanical systems.

So you can see that we have incorporated the solution to the electronic problem (*i.e.*, the electronic energy) into the nuclear problem through this quantity *U*. The solution to the nuclear Schrödinger equation, which has the nuclear kinetic energy added back in, will give us the total energy eigenvalues for the molecule. If the potential has a global minimum, these eigenvalues will be quantized.

Remember that quantization of energy occurs upon application of the boundary conditions to the Schrödinger equations. For energies below the asymptote, the energy will therefore be quantized. For higher energies (above the asymptote), there are no bound states (*i.e.*, no quantized energies). The same holds for purely dissociative electronic states, here also there are no bound levels.

Potential curves like this (or in many dimensions, potential energy surfaces) are called ***Born Oppenheimer potential surfaces***, since in deriving them the Born-Oppenheimer approximation is assumed. They allow us to solve each problem separately, using the eigenvalues from solving the electronic problem as the potential for the nuclear problem.

So, there are basically two sides of the Born-Oppenheimer approximation.

Electronic Part:

$$\hat{H}_{el}\psi_{el} = E_{el}\,\psi_{el}$$

$$U(q_{\alpha}) = E_{el} + V_{nuc}$$

Chemical Bonding
Electronic Structure Calculations

Nuclear Part:

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_{\alpha}}\nabla_{\alpha}^{2} + U(q_{\alpha})$$

Molecular Spectroscopy

The connection between the two sides is the function *U*.

The electronic part is what one would call *chemical bonding*, and people who do research in methods for solving this part of the Schrödinger equation are called *Electronic Structure Theoreticians* or *Quantum Chemists*. The people who work on electronic structure calculations try to determine accurate potential energy surfaces, *U*, using *ab initio* methods, like for example Hartree-Fock calculations.

The field of research that investigates the nuclear part of the Schrödinger equation is what we would call *Molecular Spectroscopy* and people who work in this field are called *molecular spectroscopists*. Molecular spectroscopists measure energy levels (among other things) and from their experimental data can provide potential energy functions to test the theoretical calculations. (Many spectroscopists also do electronic structure calculations, but there is a real art to these calculations, and those who do it at the highest level, usually specialize in the field.)

Thus, you can see that the Born-Oppenheimer approximation serves as a dividing point in quantum chemistry between electronic structure calculations (chemical bonding) and molecular spectroscopy. It is clear that the two branches must closely interact as they are connected to each other by $U(q_{\alpha})$.

I will spend most of this semester discussing the nuclear side of the Born-Oppenheimer approximation. Towards the end of the course I will go back and say more about the electronic part of the Schrödinger equation when we need to treat electronic spectroscopy of polyatomic molecules.

2.2 Nuclear Side of the Born-Oppenheimer Approximation

2.2.1 General Treatment

We had reduced our nuclear problem to:

$$\hat{H}_{nuc}\psi_{nuc} = E_{Tot}\,\psi_{nuc}$$

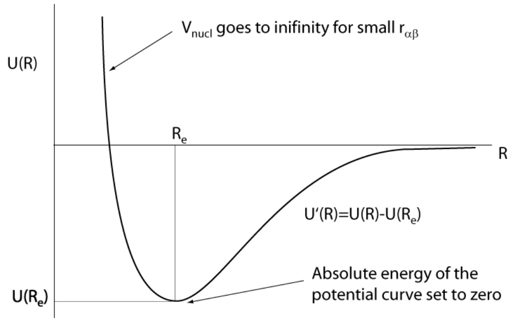
and

$$\hat{H}_{nuc} = -\frac{1}{2}\sum_{\alpha}\frac{1}{m_\alpha}\nabla_\alpha^2 + U(q_\alpha)$$

Let us confine our discussion to diatomics for the moment, realizing that we could generalize the result to larger molecules. For a diatomic, $U(q_\alpha)$ simply becomes $U(R)$.

Up to now we haven't considered the center of mass motion explicitly. If we are going to use relative (internal coordinates), we must separate the center of mass part of the Hamiltonian. We know, however, that we can always do this, we simply get an additional (kinetic energy) term added to the internal energy. Let us assume that we have separated off the center of mass motion. In this case the translational energy will not be included in our expression for the total energy. To signify that we use relative coordinates we will denote the corresponding wavefunction as ψ_{Int}

The function $U(R)$ will consist of a constant part and a part which varies with R. Call the constant part $U(R_e)$ and the variable part $U'(R)$



Thus we write: $U(R) = U'(R) + U(R_e)$

We can easily evaluate $U(R_e)$ by our definition of U

$$U = E_{el} + \frac{Z_\alpha Z_\beta}{R}$$

$U(R_e)$ is simply $U(R)$ evaluated at the minimum.

Solving $\hat{H}_{nuc}\psi_{Int} = E_{Tot}\,\psi_{Int}$

with

$$\hat{H}_{nuc} = \hat{H}_{KE} + U(R)$$

$$= \hat{H}_{KE} + U'(R) + U(R_e)$$

gives $$\left(\hat{H}_{KE} + U'(R) + U(R_e)\right)\psi_{Int} = E_{Tot}\psi_{Int}$$

and

$$\left(\hat{H}_{KE} + U'(R)\right)\psi_{Int} = \left(E_{Tot} - U(R_e)\right)\psi_{Int}$$

$$= E_{Int}\psi_{Int}$$

where $$E_{Int} = E_{Tot} - U(R_e)$$

One can then see that the total energy E_{Tot} can be written

$$E_{Tot} = E_{Int} + U(R_e)$$

E_{Int} is therefore found from the Hamiltonian

$$\hat{H}_{KE} + U'(R)$$

So the net result is that we separated the wave function into

$$\psi = \psi_{el}\psi_{Int}$$

and the eigenvalues are

$$E_{Tot} = E_{Int} + U(R_e)$$

where $U(R_e)$ is the constant part of the electronic energy (the absolute offset of the curve).

Note that we have included some of the electronic energy in E_{Int} in the sense that we used the part that varied with R as the potential for nuclear motion. One typically talks about the electronic energy as being that at the bottom of the potential well (*i.e.*, the constant part $U(R_e)$). The part that varies with R is considered the nuclear potential energy. This essentially says that the electronic and internal energies are separable. This allows us to draw potential curves and draw in energy levels which are solutions to the internal or nuclear motion problem, adding the electronic energy as a constant offset for all the vibrational levels.

The nuclear Schrödinger equation for a diatomic in internal or relative coordinates (assuming we have separated the center of mass motion) is given by:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

where μ is the reduced mass.

We want to be able to solve this equation to get the values of E_{Int}, and after doing so, we can add $U(R_e)$ to get the total energies.

2.2.2 Separation of Rotational Motion

Starting with the Schrödinger equation for the nuclear motion as shown above we find:

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

Recall that in Cartesian coordinates, the operator ∇^2 is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Converting this operator to spherical polar coordinates gives

$$\nabla^2 = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{R^2\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)$$

If we now substitute for ∇^2 in spherical polar coordinates into the Schrödinger equation for nuclear motion we get

$$\left[-\frac{\hbar^2}{2\mu R^2}\left(\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right) + U'(R)\right]\psi_{Int}(R,\theta,\varphi) = E_{Int}\psi_{Int}(R,\theta,\varphi)$$

Notice that all the angular dependence is contained in the second and third terms. If you look back in your lecture notes of Quantum Chemistry, you will see that the $\hat{L}^2$ operator in spherical polar coordinates equals:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\left(\frac{\partial^2}{\partial\varphi^2}\right)\right]$$

Using this, one can write the Schrödinger equation as

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{int}(R,\theta,\varphi)}{\partial R}\right) + \frac{\hat{L}^2}{2\mu R^2}\psi_{int}(R,\theta,\varphi) + U'(R)\psi_{int}(R,\theta,\varphi) = E_{int}\psi_{int}(R,\theta,\varphi)$$

Note that the potential is only a function of *R*, and thus falls into the category of a *spherically symmetric potential*. Recall that whenever the potential is of this type (such as the rigid rotor or the hydrogen atom problem), the solution to the angular part will always be the spherical harmonic functions.

We can see this more clearly if we rearrange the above equation.

$$-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{Int}(R,\theta,\varphi)}{\partial R}\right) + \frac{\hat{L}^2}{2\mu R^2}\psi_{Int}(R,\theta,\varphi) + \left(U'(R) - E_{Int}\right)\psi_{Int}(R,\theta,\varphi) = 0$$

If we multiply through by $2\mu R^2$ and rearrange, we get

$$-\hbar^2\frac{\partial}{\partial R}\left(R^2\frac{\partial\psi_{Int}(R,\theta,\varphi)}{\partial R}\right) + \hat{L}^2\psi_{Int}(R,\theta,\varphi) + 2\mu R^2\left(U'(R) - E_{int}\right)\psi_{Int}(R,\theta,\varphi) = 0$$

You can see the only part of the operator that has angular dependence is the $\hat{L}^2$ term. We can therefore use the separation of variables and assume wave functions $\psi_{Int}(R,\theta,\varphi)$ of the form

$$\psi_{Int}(R,\theta,\varphi) = \psi_{vib}(R)Y_J^m(\theta,\varphi)$$

where the $Y_J^m(\theta,\varphi)$ are the spherical harmonics. We chose the spherical harmonics because they are eigenfunctions of the $\hat{L}^2$ operator. Please note that in spectroscopy often the quantum number *J* is used to describe angular momentum.

$$\hat{L}^2 Y_J^m(\theta,\varphi) = \hbar^2 J\left(J+1\right) Y_J^m(\theta,\varphi)$$

The part of the Hamiltonian that has derivatives with respect to *R* will do nothing to the angular part of the wave function.

Substituting for ψ_{int} and rearranging yields:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+\frac{\hbar^2 J\left(J+1\right)}{2\mu R^2}\psi_{vib}(R)+U'(R)\psi_{vib}(R)=E_{int}\psi_{vib}(R)$$

↑	↑	↑
This term is the radial KE	This term is simply the rotational KE	Potential Energy

Note that we have made no other approximations other than the Born-Oppenheimer to get to this point, and that one is very accurate.

Since the rotational kinetic energy term depends on $1/R^2$, we cannot completely separate vibrational motion and rotational motion. To separate the vibrational and rotational motion, we have to make another approximation. This one isn't particularly accurate, but it can give a pretty good physical picture of diatomic energy levels. We will use it as a first order approximation.

If we recognize that the vibrational amplitudes of most diatomic molecules are very small, one can replace the *R* in the denominator of the rotational kinetic energy by R_e, the equilibrium internuclear distance. We can see that the rotational kinetic energy term now becomes

$$E_{rot}=\frac{\hbar^2 J\left(J+1\right)}{2\mu R_e^2}$$

where this term is now <u>independent of *R*</u>.

We can rewrite our equation:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=\left(E_{Int}-E_{rot}\right)\psi_{vib}(R)$$

or

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

where

$$E_{Int}=E_{vib}+E_{rot}$$

This leaves us with

$$E_{Tot}=U(R_e)+E_{Int}=U(R_e)+E_{vib}+E_{rot}$$ (neglecting translation, as usual)

and

$$\psi_{Tot}=\psi_{el}\psi_{Int}=\psi_{el}\psi_{vib}\psi_{rot}$$

So to a first level of approximation, we can consider the electronic, vibrational and rotational motions of a molecule separately and write the total wave function as a product and the total energy as a sum. We can then solve each problem separately.

Note that from this treatment, we found the rotational energy to be

$$E_{rot} = \frac{\hbar^2 J\left(J+1\right)}{2\mu R_e^2}$$

and the rotational part of the wave functions to be the spherical harmonics:

$$\psi_{rot} = Y_J^m(\theta,\varphi)$$

Our only approximation was to assume that the bond length R was constant. This is *the Rigid Rotor approximation* that we have already seen. We have already have solved the quantum mechanics of the Rigid Rotor model.

Before we go on to the vibrational part of the nuclear Schrödinger Equation, I would like to review the quantum mechanics of the Rigid Rotor.

2.2.2.1 REVIEW OF THE RIGID ROTOR MODEL

We first wrote down the classical expression for the rotational kinetic energy

$$KE_{classical} = \frac{1}{2} I\omega^2 = \frac{L^2}{2I}$$

and then found the Hamiltonian by substituting the $\hat{L}^2$ operator.

The Schrödinger equation for rotational motion is then

$$\begin{aligned} \hat{H}\psi_{rot}(\theta,\varphi) &= E_{rot}\psi_{rot}(\theta,\varphi) \\ \frac{\hat{L}^2}{2\mu R^2}\psi_{rot}(\theta,\varphi) &= E_{rot}\psi_{rot}(\theta,\varphi) \end{aligned}$$

where there is no R dependence of the wave function since R is fixed. The solutions to this are the eigenfunctions of $\hat{L}^2$, which are the spherical harmonics, $Y_J^m(\theta,\varphi)$.

Because the eigenvalues of $\hat{L}^2$ are $\hbar^2 J\left(J+1\right)$, we can write

$$\frac{\hat{L}^2}{2\mu R^2}\psi_{rot}(\theta,\varphi) = \frac{\hbar^2 J\left(J+1\right)}{2\mu R^2}\psi_{rot}(\theta,\varphi)$$

and thus

$$E_{rot} = \frac{\hbar^2 J\left(J+1\right)}{2\mu R^2} = \frac{\hbar^2 J\left(J+1\right)}{2I}$$

Where $I = 2\mu R^2$

This is the same expression we obtained for our more general treatment when we assumed the bond length of a diatomic molecule to be fixed at R=R_e.

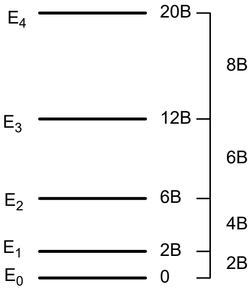
If we define the *rotational constant* as,

$$B = \frac{h}{8\pi^2 cI} \qquad \text{(note the conversion to units of cm}^{-1}\text{)}$$

We can write for the rotational energy expressed in cm^{-1}:

$$E_{rot} = BJ(J+1) \qquad J = 0,1,2,\ldots$$

Let's now evaluate the implications of the energy expression. The first level (J=0) occurs at an energy of 0. The second level occurs at 2B. The next at 6B. This is shown in the figure below.



Energy Levels

Because the energy levels are spaced by $BJ(J+1)$, the spacings between adjacent levels starts at 2B and increase by 2B for each successively higher level. We will use this result extensively when we begin to discuss rotational spectra.

The corresponding eigenfunctions are the spherical harmonics:

$$Y_J^m(\theta,\varphi) = \left[\frac{(2J+1)}{4\pi}\frac{(J-|m|)!}{(J+|m|)!}\right]^{\frac{1}{2}} P_J^{|m|}(\cos\theta)e^{im\varphi}$$

where the $P_J^{|m|}$ are the Associated Legendre functions.

The first few spherical harmonics are:

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$
$$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$$
$$Y_1^1 = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{i\varphi}$$
$$Y_1^{-1} = \sqrt{\frac{3}{8\pi}}\sin\theta\, e^{-i\varphi}$$

Note that these eigenfunctions for the rigid rotor are the same as found for the angular part of the hydrogen atom and thus have the same angular dependence.
To understand the transitions between these states (*i.e.*, upon the absorption of light), we must consider how light interacts with molecules and in particular we must discuss the subject of selection rules. I will do this shortly.

2.2.3 The Vibrational Problem

Once we separated off rotational motion by making the rigid rotor approximation, we were left with the following equation for the vibrational part of the wave function:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

To simplify this, let us expand the derivatives in the first term

$$\frac{1}{R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)=\frac{1}{R^2}\left(2R\frac{d\psi_{vib}(R)}{dR}+R^2\frac{d^2\psi_{vib}(R)}{dR^2}\right)$$

$$=\frac{2}{R}\frac{d\psi_{vib}(R)}{dR}+\frac{d^2\psi_{vib}(R)}{dR^2}$$

So we can write for the Schrödinger Equation

$$-\frac{\hbar^2}{2\mu}\left(\frac{2}{R}\frac{d\psi_{vib}(R)}{dR}+\frac{d^2\psi_{vib}(R)}{dR^2}\right)+U'(R)\psi_{vib}(R)=E_{vib}\psi_{vib}(R)$$

To simplify this a bit further, let us define a new function $\chi(R)=R\,\psi_{vib}(R)$. If we can find the function $\chi(R)$ then we can go back and get the original function $\psi_{vib}(R)$ by dividing by *R*.

We can put this equation in terms of $\chi(R)$ by substituting for the derivatives of $\psi_{vib}(R)$ in terms of $\chi(R)$.

Since $\chi(R)=R\,\psi_{vib}(R)$

and thus $\psi_{vib}(R)=\frac{\chi(R)}{R}$

we find for the first derivative:

$$\frac{d\psi_{vib}(R)}{dR}=\frac{1}{R}\frac{d\chi(R)}{dR}-\frac{1}{R^2}\chi(R)$$

For the second derivative:

$$\frac{d^2\psi_{vib}(R)}{dR^2}=-\frac{1}{R^2}\frac{d\chi(R)}{dR}+\frac{1}{R}\frac{d^2\chi(R)}{dR^2}+\frac{2}{R^3}\chi(R)-\frac{1}{R^2}\frac{d\chi(R)}{dR}$$

$$=\frac{1}{R}\frac{d^2\chi(R)}{dR^2}-\frac{2}{R^2}\frac{d\chi(R)}{dR}+\frac{2}{R^3}\chi(R)$$

Substituting these back into the Schrödinger equation one gets:

$$-\frac{\hbar^2}{2\mu}\left(\frac{2}{R}\left[\frac{1}{R}\frac{d\chi(R)}{dR}-\frac{1}{R^2}\chi(R)\right]+\left[\frac{1}{R}\frac{d^2\chi(R)}{dR^2}-\frac{2}{R^2}\frac{d\chi(R)}{dR}+\frac{2}{R^3}\chi(R)\right]\right)+U'(R)\frac{\chi(R)}{R}=E_{vib}\frac{\chi(R)}{R}$$

After canceling a few terms, one gets

$$-\frac{\hbar^2}{2\mu}\frac{1}{R}\frac{d^2\chi(R)}{dR^2}+U'(R)\frac{\chi(R)}{R}=E_{vib}\frac{\chi(R)}{R}$$

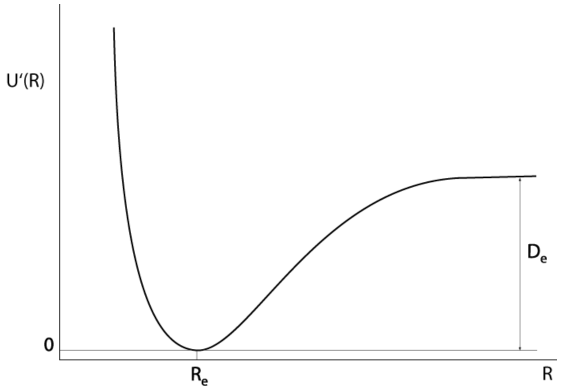
Finally, multiplying both sides by *R* gives

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(R)}{dR^2}+U'(R)\,\chi(R)=E_{vib}\chi(R)$$

This looks like a simple one-dimensional problem where the first term represents the kinetic energy, and the second term is the potential energy. Both the internal kinetic energy (*i.e.*, with the center of mass separated) and the potential energy depend only upon the separation of the nuclei, *R*.

Remember where the potential *U*'(*R*) comes from. It is the potential that results from solving the electronic part of the Schrödinger equation at a series of points (*i.e.*, a number of values for the internuclear separation *R*). I distinguish *U*(*R*) from *U*'(*R*) in that the latter has the electronic energy at the minimum of the curve, $U(R_e)$, subtracted off.

Because *U*'(*R*) is a parametric function of *R*, no simple analytical form exists. Instead, one typically uses empirical forms for *U*'(*R*).



Let us use a Taylor series expansion for the potential *U'*(*R*) about the position $R=R_e$, and then we can keep only as many terms as we like.

$$U'(R)=U'(R_e)+\left.\frac{dU'(R)}{dR}\right|_{R=R_e}(R-R_e)+\frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}(R-R_e)^2+\frac{1}{3!}\left.\frac{d^3U'(R)}{dR^3}\right|_{R=R_e}(R-R_e)^3+\frac{1}{4!}\left.\frac{d^4U'(R)}{dR^4}\right|_{R=R_e}(R-R_e)^4+\ldots$$

Remember how we defined *U*'(*R*). We introduced the prime when we subtracted off the electronic energy at the minimum in the potential, $U'(R_e)$. By definition therefore, $U'(R_e) = 0$.

Also, because we expanded the potential about the minimum, the first derivative

$$\left.\frac{dU'(R)}{dR}\right|_{R=R_e}=0$$

We are then left with

$$U'(R)=\frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}(R-R_e)^2+\frac{1}{3!}\left.\frac{d^3U'(R)}{dR^3}\right|_{R=R_e}(R-R_e)^3+\frac{1}{4!}\left.\frac{d^4U'(R)}{dR^4}\right|_{R=R_e}(R-R_e)^4+\ldots$$

We haven't introduced any additional approximations to this point. If the amplitude of the vibrational motion is sufficiently small, the $(R\text{-}R_e)^2$ term will be larger than the terms involving higher powers of $(R\text{-}R_e)$ (*i.e.*, cubic, quartic, etc.). As a first approximation, we can neglect these higher terms. We are then left with

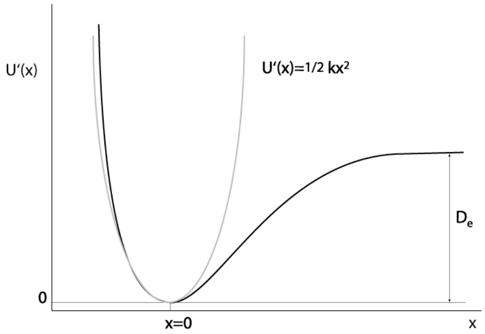
$$U'(R) = \frac{1}{2!}\left.\frac{d^2U'(R)}{dR^2}\right|_{R=R_e}\left(R-R_e\right)^2$$

If we define $x = R - R_e$ and $k = \left.\dfrac{d^2U'(R)}{dR^2}\right|_{R=R_e}$

We can then write:

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

This is the equation for a parabola. What we are doing in neglecting higher order terms is to say that near the bottom of the well, the potential is well approximated by a parabola.



This expression for the potential energy is the potential for a simple harmonic oscillator. To a first approximation, the *quantum mechanical* harmonic oscillator is a reasonable model for molecular vibrational motion.

2.2.3.1 REVIEW OF THE HARMONIC OSCILLATOR MODEL

I will briefly review the solutions (*i.e.*, the eigenvalues and wave functions) to the Schrödinger equation for the harmonic oscillator:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2}+\frac{1}{2}k\,x^2\right]\chi(x) = E_{vib}\chi(x)$$

Eigenvalues of the Quantum Mechanical Harmonic Oscillator

The eigenvalues are given by:

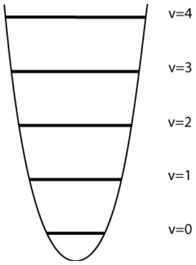
$$E_{\mathrm{v}} = h\nu\left(\mathrm{v}+\frac{1}{2}\right) \qquad \mathrm{v} = 0,1,2,3,\ldots$$

where

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

Note that ν is the same as the frequency of the classical harmonic oscillator.

If we superimpose these levels on the potential curve, they look as follows:



There are several important things to note about the Harmonic Oscillator energy levels:

1) The energy levels are equally spaced in integral units of the classical frequency.

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

Remember that *k* is related to the width of the potential (which is a parabola):

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

2) The second point to notice is that even when the quantum number v=0, there is still energy in the amount of $h\nu/2$. This is called **zero point energy.**

Eigenfunctions of the Quantum Mechanical Harmonic Oscillator

Recall that wave functions corresponding to the eigenvalues E_v are non-degenerate and are given by

$$\chi_n(x) = N_n H_n(\alpha^{\frac{1}{2}}x)e^{-\frac{1}{2}\alpha x^2}$$

where

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}}$$

The normalization constant N_n is

$$N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}$$

and the $H_n(\alpha^{\frac{1}{2}}x)$ are polynomials called Hermite polynomials

The first few Hermite polynomials are:

$$H_0(\xi) = 1$$

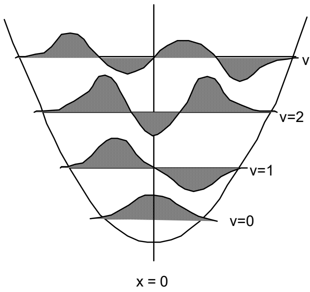
$$H_1(\xi) = 2\xi$$

Note: $\xi = \alpha^{\frac{1}{2}}x$

$$H_2(\xi) = 4\xi^2 - 2$$

$$H_3(\xi) = 8\xi^3 - 12\xi$$

The full harmonic oscillator wave functions look something like this:



2.2.4 Vibration-Rotation Interaction

If one makes spectroscopic measurements with any reasonable degree of accuracy, one finds that these simple models for vibration and rotation are not very good.

Thus, one must solve the coupled vibration-rotation problem to account for the experimental observations. I will not do this in class, but I will outline how it is done and give you the result.

If you go back to the Schrödinger equation:

$$-\frac{\hbar^2}{2\mu R^2}\frac{d}{dR}\left(R^2\frac{d\psi_{vib}(R)}{dR}\right)+\left[U'(R)+\frac{\hbar^2 J(J+1)}{2\mu R^2}\right]\psi_{vib}(R)=E_{Int}\psi_{vib}(R)$$

As before, we can make the substitution

$$\psi_{vib}(R)=\frac{\chi(R)}{R}$$

to simplify the kinetic energy term and find a new equation for $\chi(R)$.

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(R)}{dR^2}+\left[U'(R)+\frac{\hbar^2 J(J+1)}{2\mu R^2}\right]\chi(R)=E_{int}\chi(R)$$

Then, rather than assuming that the potential is harmonic, we can expand $U'(R)$ in a Taylor series in the displacement from R_e, $x=R-R_e$.

$$U'(x)=U'(0)+\left.\frac{dU'(x)}{dx}\right|_{x=0}x+\frac{1}{2!}\left.\frac{d^2U'(x)}{dx^2}\right|_{x=0}x^2+\frac{1}{3!}\left.\frac{d^3U'(x)}{dx^3}\right|_{x=0}x^3+\frac{1}{4!}\left.\frac{d^4U'(x)}{dx^4}\right|_{x=0}x^4+\ldots$$

The first term is zero by definition, and the second is zero because we are expanding about the bottom of the well.

We are then left with

$$U'(x)=\frac{1}{2}kx^2+\frac{1}{6}ax^3+\frac{1}{24}bx^4+\ldots$$

where we have simplified the coefficients of x

One can also expand the $1/R^2$ term in a Taylor series in x.

$$\frac{\hbar^2 J(J+1)}{2\mu R^2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2\left(1+\frac{x}{R_e}\right)^2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left(1+\frac{x}{R_e}\right)^{-2}$$

Note that

$$(1+y)^s = 1 + sy + \frac{s(s-1)}{2!}y^2 + \frac{s(s-1)(s-2)}{3!}y^3 + \ldots$$

We can therefore write

$$\frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left(1+\frac{x}{R_e}\right)^{-2} = \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\left[1 - 2\left(\frac{x}{R_e}\right) + \frac{(-2)(-3)}{2!}\left(\frac{x}{R_e}\right)^2 + \frac{(-2)(-3)(-4)}{3!}\left(\frac{x}{R_e}\right)^3 + \ldots\right]$$

$$= \frac{\hbar^2 J(J+1)}{2\mu R_e^2} - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{3\hbar^2 J(J+1)}{2\mu R_e^4}x^2 + \ldots$$

Putting it all together, we get something that looks like:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[\frac{1}{2}kx^2 + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots \frac{\hbar^2 J(J+1)}{2\mu R_e^2} - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{3\hbar^2 J(J+1)}{2\mu R_e^4}x^2 + \ldots\right]\chi(x) = E_{Int}\chi(x)$$

where the constants k, a, b come from the expansion of U, and the $1/R_e$ terms come from the expansion of the $1/R^2$ term.

After rearranging we get:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[-\frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{1}{2}\left(k + \frac{3\hbar^2 J(J+1)}{\mu R_e^4}\right)x^2 + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots\right]\chi(x) = \left(E_{Int} - \frac{\hbar^2 J(J+1)}{2\mu R_e^2}\right)\chi(x)$$

We can simplify this expression by including the Rigid Rotor term (first term in expansion of the $1/R^2$ term) into the energy by defining

$$E'_{Int} = E_{Int} - E_{RigidRotor}$$

and defining an effective force constant

$$k' = k + \frac{3\hbar^2 J(J+1)}{\mu R_e^4}$$

This yields then

$$-\frac{\hbar^2}{2\mu}\frac{d^2\chi(x)}{dx^2} + \left[\frac{1}{2}k'x^2 - \frac{\hbar^2 J(J+1)}{\mu R_e^3}x + \frac{1}{6}ax^3 + \frac{1}{24}bx^4 + \ldots\right]\chi(x) = E'_{int}\chi(x)$$

You can see that this looks like a perturbed Harmonic Oscillator (a harmonic oscillator with a few extra small terms added into the potential). We can use perturbation theory to solve this problem. I will not go through the details of the perturbation theory solution to this problem, but using the tools that we already have developed (particularly the raising and lowering operators), it is not difficult.

The result for the energy E_{Int} (now also called $E_{\mathrm{v}J}$) is as follows:

$$F(\mathrm{v},J)=\frac{E_{\mathrm{v}J}}{hc}=\underset{\substack{\uparrow\\ \text{HO}}}{\omega_e\left(\mathrm{v}+\frac{1}{2}\right)}+\underset{\substack{\uparrow\\ \text{rigid}\\ \text{rotor}}}{B_eJ\left(J+1\right)}-\underset{\substack{\uparrow\\ \text{anharmonicity}}}{\omega_e x_e\left(\mathrm{v}+\frac{1}{2}\right)^2}-\underset{\substack{\uparrow\\ \text{vib-rot}\\ \text{interaction}}}{\alpha\left(\mathrm{v}+\frac{1}{2}\right)J\left(J+1\right)}-\underset{\substack{\uparrow\\ \text{centrifugal}\\ \text{distortion}}}{DJ^2\left(J+1\right)^2}+\ldots$$

where the constants are given in units of cm^{-1}.

The constants ω_e, B_e, $\omega_e x_e$, α, and D can be simply related to the coefficients in our Taylor series expansion of the potential and centrifugal term, a, b, k, R_e. (*i.e.* related to the potential)

This expression results from taking a certain number of terms in $\hat{H}'$ in the perturbation theory treatment. If we were to take more terms, our energy expression would also contain more terms. You can see that the energy expression looks like a power series in the quantum numbers v and $J(J+1)$, and one can take it to higher order.

The terms that I have included here give a reasonably accurate expression for the energy levels of a diatomic molecule. How accurate you need to be depends upon how precisely you measure. However, the higher order terms begin to lose their physical significance.

I would like you to have a good feel what these constants in the $E_{\mathrm{v}J}$ formula mean physically.

1) $\omega_e\left(\mathrm{v}+\frac{1}{2}\right)$

This term represents the vibrational energy. We know that

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

is the frequency of the classical harmonic oscillator (expressed in units of cm^{-1}). Remember that k is the width of the parabola, the force constant of vibration. Small k means that it is a wide parabola and a "loose" vibration. The wider the parabola the more closely spaced the levels. A thin parabola (large k) results in wide spacing and a "stiff" vibration.

2) $B_eJ\left(J+1\right)$

This term gives the rotational energy. Remember that

$$B_e=\frac{h}{8\pi^2 cI} \qquad \text{(in units of cm}^{-1}\text{)}$$

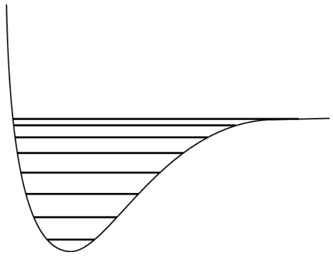
where I is the moment of inertia $I=\mu R_e^2$. Remember the rigid rotor energy levels are given by:

$$E_{rot}=BJ\left(J+1\right).$$

Consequently larger B_e means more widely spaced levels. This corresponds to smaller R_e or smaller μ. Light atoms → large B_e. H_2 has the largest B_e.

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

This term is due to the anharmonicity of the potential. It accounts for lowering of the energy levels due to the widening of the parabola:



As the bond weakens as *R* increases, the potential gets looser and the level spacing decreases. The negative sign in front of the term accounts for this decrease of the level spacings.

4) $-DJ^2\left(J+1\right)^2$

This term is named the centrifugal distortion term. Remember that

$$B=\frac{h}{8\pi^2 cI} \qquad \text{(in units of cm}^{-1}\text{)}$$

As *R* increases due to rotation, *B* will decrease. So *B* will be smaller than B_e , and the level spacings will be smaller than rigid rotor spacings. The minus sign in front of this term is responsible for reducing the level spacings with increasing rotation.

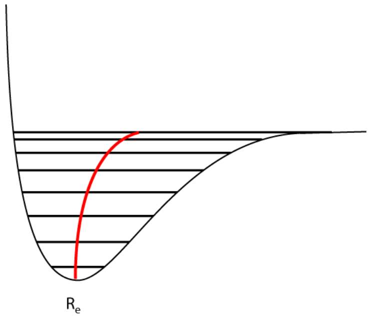
One could show that

$$D=\frac{h^3}{32\pi^4 I^2 ckR_0^2}=\frac{4B_e^3}{\omega_e^2}$$

5) $-\alpha\left(\text{v}+\frac{1}{2}\right)J\left(J+1\right)$

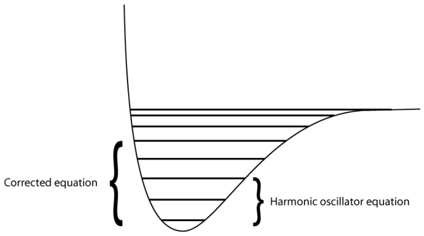
This term describes the vibration-rotation interaction. The rotational spacing depends on *B* which in turn depends on *R*. Up to now we considered a rigid molecule with *R* fixed.

But the <u>vibrational state</u> affects the average value of *R*.



> $\langle R \rangle$ changes with vibrational state. This results from the anharmonicity of the vibration. (If the potential were a parabola, $\langle R \rangle$ wouldn't change.) You can see that the anharmonicity and the vibration-rotation interaction are related. They both are related to the "*a*" constant in the power series expansion of *U*'(*R*).

The best evidence for the fact that we solved the problem correctly is that it works. Using this expression for the energy levels, one can account reasonably well for the measured energy spacings.



One can measure these spacings very well using modern spectroscopic techniques.

2.3 What is a Spectrum?

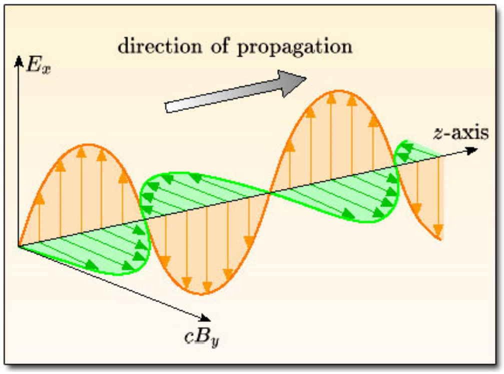
Up to this point I have reviewed much of the important quantum mechanical background. All I have talked about, however, is spacings of energy levels. I have said little about spectroscopic transitions. The field of molecular spectroscopy involves causing molecules to make transitions from one state to another, and we must consider the details of how this occurs.

Before I go any further, however, I want to define some of the ***terminology*** that we will be using. Much of the difficulty in understanding a subject is often simply understanding what the different terms mean. I will start by addressing the questions:

What is a spectral line or spectral transition? and What is a spectrum?
I will then go on to define what we mean by **spectral intensity** or **transition strength** and the **linewidth** of a transition.

Before I answer these questions, I need to remind you of a few things about the nature of electromagnetic radiation or light. Light usually refers to only visible wavelengths, but I will often use it in the more general sense meaning all electromagnetic radiation.

In a wave picture, electromagnetic radiation contains, as its name implies, oscillating electric and magnetic fields. These fields are oriented perpendicular to each other and perpendicular to the direction of propagation. This is best shown in the figure below, by considering linearly polarized light.



The magnitude of the electric and magnetic field vectors can be given by:

$$E(z,t) = E_{x0}\sin(2\pi\nu t + kz + \phi) \qquad B(z,t) = B_{y0}\sin(2\pi\nu t + kz + \phi)$$

with

E_{x0}, B_{y0} the electric and magnetic field amplitudes, respectively ($B_{y0} = E_{x0}/c$)

$\nu = \dfrac{c}{\lambda}$ is the frequency of the light, given by the speed of light, c, divided by the wavelength of the light, λ.

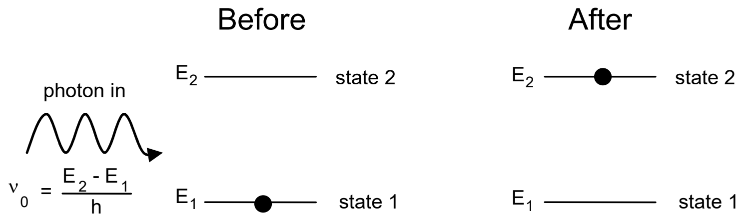
$k = \dfrac{2\pi}{\lambda}$ is called the wave vector

ϕ is the relative phase

Recall that light can be treated either as a wave or as a particle. In the particle picture, light consists of photons with energy:

$$E = h\nu$$

When light shines on a molecule in a particular quantum state, it is *possible* for that molecule to absorb a photon. If the energy of the photon, defined by the expression $E = h\nu$, corresponds precisely to the difference in energy between the quantum state that the molecule is in and some other quantum state, then it is possible for the molecule to absorb a photon and make a transition from the initial quantum state to the final quantum state.



The frequency or energy of the photon must be such that

$$E_{photon} = h\nu_0 = \Delta E = E_{final} - E_{initial}$$

or

$$\nu_0 = \frac{E_{final} - E_{initial}}{h}$$

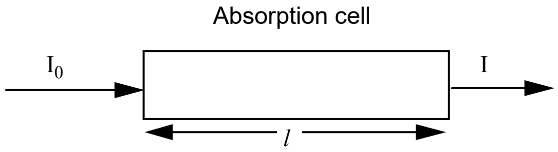
This expression is called the *Bohr frequency condition*

Note that I said it was *possible* for the molecule to absorb the radiation. Whether it does or not depends upon several factors that we will consider shortly.

A ***spectral line*** is what one calls a plot of the absorption of light by a molecule or atom as a function of the frequency of that light. This is also referred to simply as a ***transition***, although this latter term is used more generally to refer to the act of going from one state to the other.

The ***intensity*** or ***strength*** of a transition is related to the probability that the molecule or atom will undergo the transition when illuminated by light at the proper frequency.

To be more specific, assume we have an absorption cell of length l containing a sample of the material which we are studying at concentration c in moles per liter. Let I_0 be the intensity of light going into the cell (*i.e*. the number of photons per unit time per unit area) and I be the intensity of the light coming out.

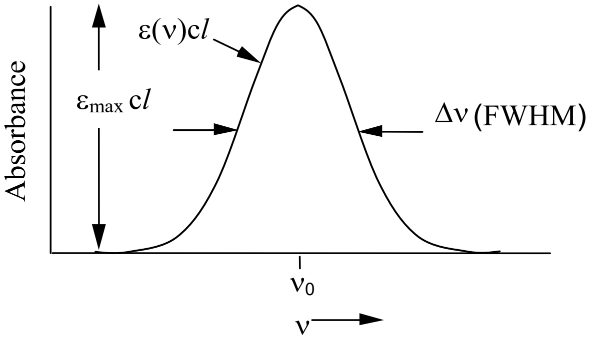


According to the Beer-Lambert Law, the absorbance A is given by

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon(\nu)cl$$

$\varepsilon(\nu)$ is a function of the frequency ν and is called the *molar absorption coefficient, c* is the concentration and l the length of the cell.

Often what we are plotting when we show a spectral line is the absorbance as a function of the frequency or sometimes the molar absorption coefficient as a function of frequency.



One usually plots the absorption coefficient as a function of the frequency, since it is proportional to the absorbance and independent of c and l. It is a property of the molecule alone.

This is what we would call a ***spectral line***. The term comes from early experiments observing the emission from excited atoms. If I showed this spectral feature on a wide enough frequency scale, it would appear as a spike or a line.

Strictly speaking, the **intensity** of a transition or the **transition strength** is proportional to the integral of the function $\varepsilon(\nu)$ across the entire profile

$$\text{Transition strength} \propto \int_{\nu_1}^{\nu_2} \varepsilon(\nu)\,d\nu$$

I will not be so concerned with the units that we use for the intensity of a transition.

As we will as the course progresses, the intensity of the transitions is related to the wavefunctions corresponding to the energy levels involved in the transition.

The **linewidth**, $\Delta\nu$, of a transition is usually defined as the width at half the height of the maximum of the curve (Full Width Half Maximum or FWHM). We will see later that the linewidth can provides us information on the dynamics or kinetics of the molecules.

The **frequency of the line center**, ν_0, provides information on the energy levels of the atom or molecule, and as we have seen to some degree already and will see more later, this can tell us things like the geometry of a molecule, the vibrational force constants, etc.

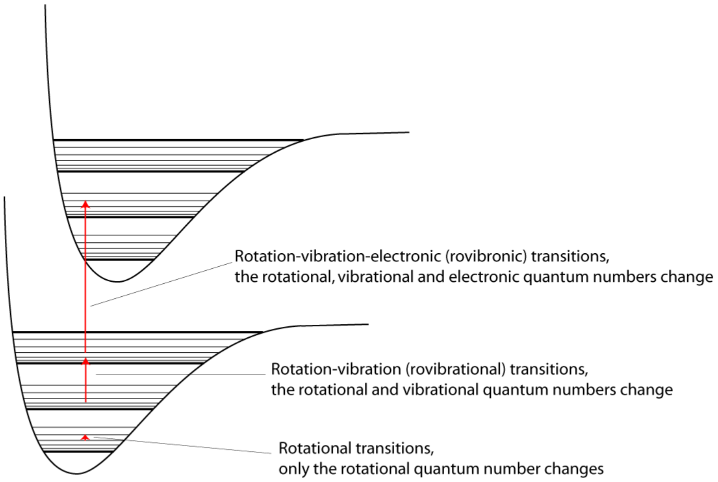
I still haven't defined the term **spectrum**.

A ***spectrum*** is a collection of many spectral lines that results when one measures the absorption of a molecule as a function of frequency. As you will see, spectral lines tend to be clumped together in certain frequency regions and a spectrum is usually a measurement of an entire clump. However, one *could* call even a single spectral line a spectrum.

We will consider 3 types of spectroscopic transitions (indicated on the figure below):

1. pure rotational → microwave
2. rotational-vibrational → infrared
3. rotational-vibrational-electronic → Visible-UV

Spectroscopic transitions occur at frequencies (energies) corresponding to the difference between two energy levels. For the most part, energy level spacing for different types of motion are sufficiently different that it is straightforward to tell what type of transition one is observing given the frequency.



It is important to have a good physical feel for the relative magnitudes of the transition frequencies (energies).

Molecular process	**Wavelength (m)**	**Wave number (cm^{-1})**	**Region**
polyatomic rotation	0.3 - 0.003	0.033 - 3.3	Microwave
rotation of small molecules	$3x10^{-3}$ - $3x10^{-5}$	3.3 - 330	Far infrared
vibrational motion	$3x10^{-5}$ - $3x10^{-6}$	330 - 3300	Infrared
electronic transitions	$3x10^{-6}$ - $3x10^{-8}$	3300 - 3.3 $x10^{5}$	Visible and Ultraviolet

You should be able to look at a spectrum and immediately tell if it is a pure rotational, rovibrational, or rovibronic (rotational-vibrational-electronic) spectrum.

We will spend much time later in the semester discussing the expected frequencies for different types of transitions. This is simply a question of where the different energy levels occur. It will be specific to each type of motion and will have different patterns for different classes of molecules.

In the present chapter, which is meant as an overview of molecular spectroscopy, I will discuss the subject of spectroscopic intensities and linewidths. There are a number of different factors that determine the intensity and linewidth of a spectral line. I will discuss them in a general sense now, and then we will apply these general concepts later to different types of spectroscopic transitions.

2.4 Spectroscopic Intensities

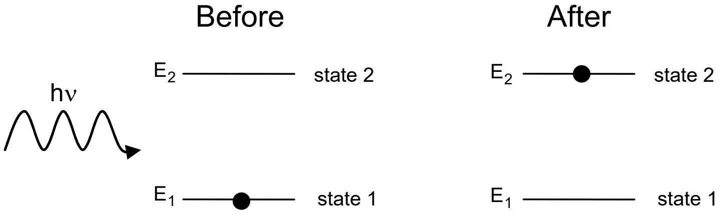
2.4.1 Kinetics of Optical Absorption

Not all transitions occur with equal intensity. In fact, many transitions are completely forbidden. If this weren't the case, it would be much more difficult to interpret molecular spectra.

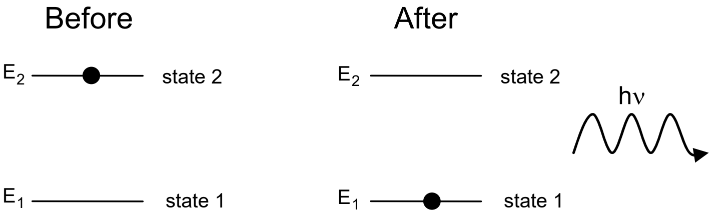
To fully understand the intensities of transitions between discrete states in an atom or molecule, one must have some understanding of the interaction of radiation with matter. In particular, we must consider the rates of transitions from one state to another induced by electromagnetic radiation.

In 1916, Einstein published a treatment of a quantum mechanical system (*i.e.*, a system with discrete energy levels) in a classical radiation field. The following discussion follows his treatment.

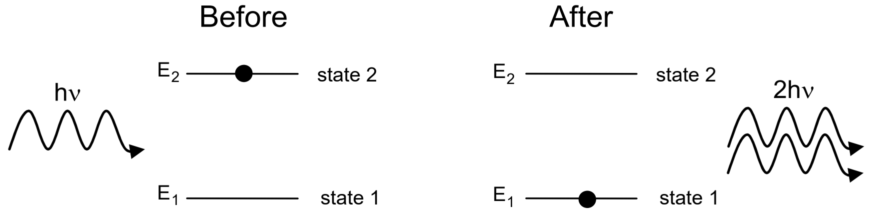
Let us start by considering a few of the processes that could occur when light interacts with an atom or molecule (or any two level quantum mechanical system). I have already introduced to you the process that we call ***absorption***. In this process, a photon with energy $E = h\nu$, which is equal to the difference in energy between state 1 and state 2, causes the system to make a transition from state 1 to state 2. During this process, the photon is absorbed.



Now consider the case in which the molecule is *initially in the upper state* rather than starting in the lower state.One process that can occur in this situation is that the molecule can spontaneously make a transition from the upper state to the lower state, giving off a photon of energy $E=h\nu$ where this energy is equal to the difference in energy between the two levels. This process is called ***spontaneous emission.*** The term spontaneous comes from the fact that it happens without any external influence (*i.e.*, not initiated by a photon).



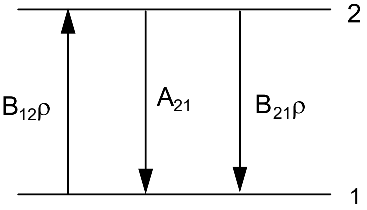
In a third type of process, the molecule initially in the excited state encounters a photon with energy equal to the separation between states 1 and 2. In this case, the photon can induce or stimulate a downward transition from state 2 to state 1.



In this case, the original photon remains and is accompanied by the emission of a second photon of the same frequency. This process is called ***stimulated emission*** because the emission of the second photon is *stimulated* by the presence of the first. Stimulated emission is essentially the inverse process of absorption. Both are induced by the radiation field (*i.e.*, the photon). In one case a photon is destroyed, in the other a photon is created. You can see from the conservation of energy that stimulated emission must be accompanied by the creation of a photon.

With these three processes in mind, consider the following:

Let's say we have a collection of *N* two level systems with lower level 1 and upper level 2. The energies of these states are given by W_1 and W_2 respectively (I use *W* rather than *E* because we will use *E* for electric field). Assume that these systems are all at the temperature *T* and are put in a bath of ambient radiation of density $\rho(\nu)$ (the energy of radiation between frequencies ν and $\nu + d\nu$ in unit volume being $\rho(\nu)d\nu$). The system is at equilibrium (*i.e.*, no net change in the populations of levels 1 and 2). We will denote the populations of levels 1 and 2 by N_1 and N_2. Consider the rates of transitions between these states due to absorption, spontaneous emission, and stimulated emission.



Absorption:

The rate at which the systems are promoted from level 1 to level 2 due to absorption of radiation of the proper frequency must be proportional to

1. the radiation density, $\rho(\nu_{12})$
2. the number of molecules in state 1 (clearly, if there were no molecules in state 1 there would be no transitions from 1 to 2.).

Thus we can write the rate of change of the population of state 2 due to absorption as

$$\frac{dN_2}{dt} = B_{12}\rho(\nu_{12})N_1$$

where B_{12} is simply the rate constant or proportionality constant. This constant is called the Einstein *B* coefficient.

Spontaneous Emission:

Spontaneous emission takes the systems initially in state 2 and brings them down to state 1.

1. This process is independent of the radiation density, since it is spontaneous.
2. It will be proportional to the number of systems in state 2 (clearly, if there were no systems in state 2, there would be no spontaneous transitions from 2 to 1).

We can therefore write:

$$\frac{dN_2}{dt} = -A_{21}N_2$$

where A_{21} is the proportionality constant or **rate constant for spontaneous emission**. This is called the Einstein A coefficient. The negative sign arises from the fact that state 2 is being *depopulated* by this process.

Note that since the rate of spontaneous emission is proportional to the Einstein *A* coefficient and not the radiation density, the *lifetime* of a molecule in a particular state in the absence of radiation is given by

$$\tau = \frac{1}{A_{21}}$$

Thus, the *A* coefficient is the inverse of the lifetime.

Stimulated Emission:

Finally, stimulated emission will induce transitions from state 2 to state 1.

1. As in the case of absorption, it will be proportional to the radiation density.
2. It will also be proportional to the number of systems in state 2.

We can write:

$$\frac{dN_2}{dt} = -B_{21}\rho(\nu_{12})N_2$$

where B_{21} is the Einstein coefficient for stimulated emission.

If the system is at equilibrium, the populations in systems 1 and 2 must not be changing. This means that the rate of transitions from 1 to 2 must be equal to the rate of transitions from 2 to 1. Another way to say this is that the net rate $\frac{dN_2}{dt}$ (or $\frac{dN_1}{dt}$) must equal zero. Thus we can sum all the contributions to $\frac{dN_2}{dt}$ and set them equal to zero.

We then have:

$$B_{12}\rho(\nu_{12})N_1 - A_{21}N_2 - B_{21}\rho(\nu_{12})N_2 = 0$$

Rearranging, one gets:

$$B_{12}\rho(\nu_{12})N_1 = A_{21}N_2 + B_{21}\rho(\nu_{12})N_2$$

$$= \left[A_{21} + B_{21}\rho(\nu_{12})\right]N_2$$

or

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\nu_{12})}{A_{21} + B_{21}\rho(\nu_{12})}$$

We know from statistical thermodynamics that the equilibrium populations of states 1 and 2 are related by the Boltzmann distribution law:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1}e^{-\frac{(W_2 - W_1)}{k_bT}} = \frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}$$

where k_b is the Boltzmann constant and g_1 and g_2 are the degeneracies of states 1 and 2.

Thus, we can write

$$\frac{B_{12}\rho(\nu_{12})}{A_{21}+B_{21}\rho(\nu_{12})}=\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}$$

or solving for ρ

$$\rho(\nu_{12})=\frac{A_{21}\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}}{B_{12}-B_{21}\frac{g_2}{g_1}e^{-\frac{h\nu_{12}}{k_bT}}}$$

$$=\frac{A_{21}}{B_{12}\frac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}}-B_{21}}$$

There is one more thing that we know. I originally stated that the system was bathed in radiation density $\rho(\nu)$. We know from *Planck's law of black body radiation* that:

$$\rho(\nu_{12})=\frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{k_bT}}-1}$$

Setting the two expressions for ρ equal gives:

$$\frac{8\pi h\nu_{12}^3}{c^3}\frac{1}{e^{\frac{h\nu_{12}}{k_bT}}-1}=\frac{A_{21}}{B_{12}\frac{g_1}{g_2}e^{\frac{h\nu_{12}}{k_bT}}-B_{21}}$$

You can see that there are two conditions that must be met for this equality to hold:

1. $B_{12}\frac{g_1}{g_2}=B_{21}$ (note that if $g_1 = g_2$ then $B_{21} = B_{12}$)
   this will always be true for non-degenerate states since $g_1 = g_2 = 1$

2. $A_{21}=\frac{8\pi h\nu_{12}^3B_{21}}{c^3}$

The first tells us that for non-degenerate states, the strength of the upward transition is equal to the strength of the downward transition.

The second gives us a relationship between the strength of a transitions and the lifetime of the state, since $A = 1/\tau$. Also, note the ν^3 factor in the numerator. This says that as the frequency increases, the rate of spontaneous emission increases rapidly compared to stimulated emission.

One could show that the Einstein *B* coefficient for absorption, B_{12} is directly related to the integrated band intensity:

$$B_{12}=\frac{\ln 10}{1000N_Ah\nu_{12}}\int\varepsilon(\nu)d\nu$$

where ε is defined by

$$\frac{I}{I_0} = 10^{-\varepsilon(\nu)cl}$$

c is the concentration in moles per liter. N_A is Avogadro's number.

I will demonstrate shortly how the Einstein coefficient is directly related to properties of the molecular wave function.

2.4.2 Time Dependent Perturbation Theory

We now need to understand *which* levels can be connected by a spectroscopic transition. Up to now we have only considered the interaction between radiation and matter in a general way. We have not at all considered the nature of the quantum mechanical levels (*i.e.*, the wave functions). We now need to connect the expression for the band strength to properties of the wave functions. This will allow us to determine *selection rules* for spectroscopic transitions (*i.e.,* the rules that tell us which transitions can occur).

In order to do this, we need to use *time dependent perturbation theory*.

The very nature of a spectroscopic transition implies a time-dependent phenomenon, and so we must consider the time-dependent Schrödinger equation.

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

If the Hamiltonian does not explicitly depend upon time, we know that

$$\Psi_n(\mathbf{r},t) = \psi_n(\mathbf{r})e^{-\frac{iW_nt}{\hbar}}$$

where $\psi_n(\mathbf{r})$ is the solution to the Time Independent Schrödinger Equation (*i.e.*, is an eigenfunction of the Hamiltonian) and is called a stationery state (since $\Psi_n^*(\mathbf{r},t)\Psi_n(\mathbf{r},t) = \psi_n^*(\mathbf{r})\psi_n(\mathbf{r})$)

When we consider the interaction of matter with radiation, we must take into account the fact that electromagnetic field depends upon time:

$$\mathbf{E} = \mathbf{E}_0\cos(2\pi\nu t)$$

In all the types of spectroscopy that we will consider, the electric field interacts with the molecule through its electric dipole moment. There are other types of interactions between a radiation field and a molecule, but these are much weaker in general. We will only consider electric dipole induced transitions. The electric dipole moment is defined as:

$$\boldsymbol{\mu} = \sum_j q_j\mathbf{r}_j$$

where q_j is the charge of particle *j* and $\mathbf{r}_j$ its position.

Knowing the charge of the electrons and of the nuclei this can also be written as:

$$\boldsymbol{\mu} = \sum_i -e\mathbf{r}_i + \sum_\alpha Z_\alpha e\mathbf{r}_\alpha$$

where $\mathbf{r}_j$ is the position of electron *i* and Z⍰ and $\mathbf{r}_\alpha$ are the charge and position, respectively, of nucleus α.

If $\boldsymbol{\mu}$ is the dipole moment of the molecule, the interaction energy between the field and the molecule is

$$\hat{H}' = -\boldsymbol{\mu}\cdot\mathbf{E} = -\boldsymbol{\mu}\cdot\mathbf{E}_0\cos(2\pi\nu t)$$

We therefore need to solve

$$\hat{H}\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

Where:

$$\hat{H} = \hat{H}_0 - \boldsymbol{\mu}\cdot\mathbf{E}_0\cos(2\pi\nu t) = \hat{H}_0 + \hat{H}'$$

This looks like a problem for perturbation theory if the second term on the right is sufficiently small.

Recall that in Time Independent Perturbation Theory, we expressed the first order correction to the wave function as a linear combination of the zeroth-order wave functions (since they form a complete orthonormal set).

$$\psi_n^{(1)} = \sum_{m\neq n}\frac{H'_{mn}}{\left(W_n^{(0)} - W_m^{(0)}\right)}\psi_m^{(0)} = \sum_{m\neq n}a_m\psi_m^{(0)}$$

We can do the same thing here, but because the perturbation depends upon time, *the expansion coefficients will also depend upon time* in a manner more complex than the simple exponential time dependence we have discussed earlier. You can see how this might lead to transitions between zeroth-order states.

To simplify matters, let us consider a system in which the unperturbed problem has only two states. (The development for a real molecule which has an infinite number of states is analogous to this simple case).

For such a system:

$$\hat{H}_0\Psi(\mathbf{r},t) = i\hbar\frac{\partial\Psi(\mathbf{r},t)}{\partial t}$$

The stationery state solutions are

$$\Psi_1(\mathbf{r},t) = \psi_1(\mathbf{r})e^{-\frac{iW_1t}{\hbar}} \qquad \text{and} \qquad \Psi_2(\mathbf{r},t) = \psi_2(\mathbf{r})e^{-\frac{iW_2t}{\hbar}}$$

We will assume that the wave function at any time *t* can be written as a linear combination of the zeroth-order wave functions:

$$\Psi(\mathbf{r},t) = a_1(t)\Psi_1(\mathbf{r},t) + a_2(t)\Psi_2(\mathbf{r},t)$$

where the expansion coefficient are time dependent. This is essentially saying that although the wave function is changing in time, at any instant it can be written as a linear combination of the zeroth-order eigenfunctions.

Assume that the system starts at *t*=0 in state 1 (*i.e*. in the ground state).

This means that:

$$a_1(t=0) = 1 \qquad \text{and} \qquad a_2(t=0) = 0$$

To determine the time dependence of the expansion coefficients, we need to substitute $\Psi(\mathbf{r},t)$ into the Time dependent Schrödinger equation:

$$a_1(t)\hat{H}_0\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}_0\Psi_2(\mathbf{r},t)+a_1(t)\hat{H}'\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}'\Psi_2(\mathbf{r},t)=$$

$$i\hbar\Psi_1(\mathbf{r},t)\frac{\partial a_1(t)}{\partial t}+i\hbar\Psi_2(\mathbf{r},t)\frac{\partial a_2(t)}{\partial t}+i\hbar a_1(t)\frac{\partial\Psi_1(\mathbf{r},t)}{\partial t}+i\hbar a_2(t)\frac{\partial\Psi_2(\mathbf{r},t)}{\partial t}$$

Note that the first and second terms on the left hand side cancel with the third and fourth terms on the right hand side.
This leaves:

$$a_1(t)\hat{H}'\Psi_1(\mathbf{r},t)+a_2(t)\hat{H}'\Psi_2(\mathbf{r},t)=i\hbar\Psi_1(\mathbf{r},t)\frac{\partial a_1(t)}{\partial t}+i\hbar\Psi_2(\mathbf{r},t)\frac{\partial a_2(t)}{\partial t}$$

If we now multiply by ψ_2^* and integrate over spatial coordinates and use the fact that ψ_1 and ψ_2 are orthogonal we get (after some rearranging):

$$i\hbar\frac{\partial a_2(t)}{\partial t}=a_1(t)e^{-\frac{i(W_1-W_2)t}{\hbar}}\int\psi_2^*(\mathbf{r})\hat{H}'\psi_1(\mathbf{r})d\mathbf{r}+a_2(t)\int\psi_2^*(\mathbf{r})\hat{H}'\psi_2(\mathbf{r})d\mathbf{r}$$

Note that I have separated the wave functions ψ_1 and ψ_2 into the spatial parts and the exponential time dependent part.

Since $\hat{H}'$ is a small perturbation, there are not enough transitions out of state 1 that a_1 and a_2 differ significantly from their initial values. This approximation is called the "weak field limit".

Thus we can assume $a_1 \approx 1$ and $a_2 \approx 0$ at all times. This gives

$$i\hbar\frac{\partial a_2(t)}{\partial t}=e^{-\frac{i(W_1-W_2)t}{\hbar}}\int\psi_2^*(\mathbf{r})\hat{H}'\psi_1(\mathbf{r})d\mathbf{r}$$

Now, let us take the electric field to be in the *z*-direction. (We need not do this, but it is easy to generalize to isotropic radiation).

We then have

$$\hat{H}'=-\hat{\mu}_z E_{0z}\cos(2\pi\nu t)$$

$$=-\frac{1}{2}\hat{\mu}_z E_{0z}\left(e^{i2\pi\nu t}+e^{-i2\pi\nu t}\right)$$

If we substitute this into the above equation we get the instantaneous transition rate:

$$\frac{\partial a_2(t)}{\partial t}=\frac{i}{2\hbar}\left(\mu_z\right)_{21}E_{0z}\left[e^{\frac{i(W_2-W_1+h\nu)t}{\hbar}}+e^{\frac{i(W_2-W_1-h\nu)t}{\hbar}}\right]$$

where

$$\left(\mu_z\right)_{21}=\int\psi_2^*(\mathbf{r})\hat{\mu}_z\psi_1(\mathbf{r})d\mathbf{r}$$

This quantity, $\left(\mu_z\right)_{21}$, is the *z*-component of the ***dipole moment matrix element*** (otherwise known as the ***transition moment***) between states 1 and 2. The rate of transitions out of state 1 into state 2 is proportional to $\left(\mu_z\right)_{21}$. If this term is zero, transitions will not occur.

It is this term that gives rise to the selection rules for transitions induced by electromagnetic radiation. We will show this more explicitly in a moment. However, first I will integrate the preceding equation for the duration of the perturbation (*i.e.* the finite time the molecule interacts with the field). This gives

$$a_2(t) = -\frac{1}{2}\left(\mu_z\right)_{21} E_{0z}\left[\frac{1-e^{\frac{i(W_2-W_1+h\nu)t}{\hbar}}}{W_2-W_1+h\nu} + \frac{1-e^{\frac{i(W_2-W_1-h\nu)t}{\hbar}}}{W_2-W_1-h\nu}\right]$$

Note that in each term within the brackets, the complex exponential can only vary between 1 and -1 (since a complex exponential is simply sines and cosines). Thus, the numerator of each of these terms can only vary between 0 and 2. For either one of these two terms to get large, the denominator must become very small.

Because $W_2 > W_1$, the second term gets much larger than the first when $W_2 - W_1 = h\nu$. This occurs when the radiation is on resonance with an upward transition (*i.e.,* leading to absorption). In this case one could neglect the first term.

Note that the second term goes to infinity when the radiation is on resonance. This arises because we treated the field classically. Treating the electric field quantum mechanically will still give a resonance, but it won't go to infinity.

The magnitude of the coefficient a_2 depends strongly upon the frequency of the radiation, as $\left|a_2(t)\right|^2$ gives the probability that the system which started in state 1 will have made a transition to state 2 by time *t*. Thus, when the radiation is tuned to a resonance (*i.e.*, $W_2 - W_1 = h\nu$), the probability of making a transition is at a maximum.

If we neglect the first term and only consider the absorption process, we can obtain (after some rearrangement):

$$\left|a_2(t)\right|^2 = a_2^*(t)a_2(t) = \left(\mu_z\right)_{21}^2 E_{0z}^2 \frac{\sin^2\left(\frac{W_2-W_1-h\nu}{2\hbar}t\right)}{\left(W_2-W_1-h\nu\right)^2}$$

This expression has been derived assuming an oscillating electric field at only a single frequency. In practice we always deal with a range of frequencies, and we must integrate this expression over the range of frequencies near the resonance condition. Because the integrand will only be significant over the region of ν near ν_{12}, we can take E_{0z}^2 outside of the integral and evaluate it only at ν_{12}.

We then have:

$$\left|a_2(t)\right|^2 = \left(\mu_z\right)_{21}^2 E_{0z}^2\left(\nu_{12}\right)\int \frac{\sin^2\left(\frac{W_2-W_1-h\nu}{2\hbar}t\right)}{\left(W_2-W_1-h\nu\right)^2}d\nu$$

We can integrate this from -∞ to +∞ because the integrand will only be significant near resonance. We can then make use of the fact that

$$\int_{-\infty}^{\infty}\frac{\sin^2 x}{x^2}dx = \pi$$

This gives us

$$\left|a_2(t)\right|^2 = \frac{1}{4\hbar^2}\left(\mu_z\right)_{21}^2 E_{0z}^2\left(\nu_{12}\right)t$$

One can easily show that for isotropic radiation, the *z*-component of the electric field is related to the radiation density by

$$E_{0z}^2(\nu) = \frac{2}{3\varepsilon_0}\rho(\nu)$$

The probability of finding the system at time t in level 2 is then given by:

$$\left|a_2(t)\right|^2 = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho\left(\nu_{12}\right)t$$

The average transition rate is the probability of making the transition during the time interval t during which the perturbation exists.

Thus we can write

$$\text{transition rate } = \frac{\left|a_2(t)\right|^2}{t} = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho\left(\nu_{12}\right)$$

But recall that the rate of making an upward transition is related to the Einstein B coefficient

$$\text{transition rate} = B_{12}\rho(\nu_{12}) = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2 \rho(\nu_{12})$$

Therefore

$$B_{12} = \frac{1}{6\hbar^2\varepsilon_0}\left(\mu_z\right)_{21}^2$$

Remember that we treated only polarized light in the z-direction. The expressions for the x and y-directions are completely analogous. We therefore have in general

$$B_{12} = \frac{1}{6\hbar^2\varepsilon_0}\left[\left(\mu_x\right)_{21}^2 + \left(\mu_y\right)_{21}^2 + \left(\mu_z\right)_{21}^2\right]$$

Thus, we have related the absorption strength directly to the dipole moment matrix elements (or transition moments)

$$\left(\mu_z\right)_{21} = \int \psi_2^*(\mathbf{r})\hat{\mu}_z \psi_1(\mathbf{r})d\mathbf{r}$$

and likewise for the x and y components. If we have an expression for the dipole moment of a molecule, we can calculate the intensity of its spectroscopic transitions. Selection rules arise because in certain situations, these integrals become identically zero.

It is important to realize that dipole moment matrix elements such as these play an extremely important role in spectroscopy! The two most important features in a spectrum are the frequency and the intensity of the transitions. The frequencies tell us about the spacing of the energy levels and ultimately about the potential energy surface. The intensities are related to properties of the wave functions through this dipole moment integral.

I would now like to discuss some general considerations in evaluating the spectroscopic selection rules for different kinds of spectroscopy.

2.4.3 Spectroscopic Selection Rules

I have just shown that the transition probability or transition rate $B_{12}\rho$ is proportional to the square of the dipole moment matrix elements. This gives us a measure of the relative strength or intensity of a spectroscopic transition.

I have frequently used the term *selection rules* in discussing spectroscopic transitions but I haven't clearly defined what I mean. Selection rules are restrictions on the changes in quantum numbers between the initial and final state in a spectroscopic transition.

In other words, transitions are only allowed for certain changes in the quantum numbers. The origin of these rules can be clearly seen by considering the integral of the dipole moment operator that we had to perform to determine the Einstein coefficient.

That integral will be non-zero for only certain allowed changes in the quantum numbers during a transition. From a practical point of view, the fact that transitions are not allowed between all levels is extremely important. If all possibilities were allowed, it might be hopeless to understand the pattern of transitions that one observes in a spectrum. However, the fact that only a restricted number of transitions occur makes the pattern of lines simpler.

Let us go back and consider the transition moment integral and see how it gives rise to several different types of selection rules.

For plane polarized light in the *z*-direction,

$$B_{12} \propto \left(\mu_z\right)_{21}^2 = \left(\int \psi_2^* \hat{\mu}_z \psi_1 d\tau\right)^2$$

where $\hat{\mu}_z$ is the dipole moment operator.

For any kind of dipole-induced transition between two states (*i.e.*, rotational, vibrational, electronic) we can write to a first approximation:

$$\int \psi_2^* \hat{\mu}_z \psi_1 d\tau = \int \psi_{2el}^* \psi_{2vib}^* \psi_{2rot}^* \hat{\mu}_z \psi_{1el} \psi_{1vib} \psi_{1rot} d\tau_{el} d\tau_{vib} d\tau_{rot}$$

$\hat{\mu}_z$ is the dipole moment operator in the lab fixed frame.

From the point of view of intensities, the rigid rotor and harmonic oscillator wave functions are good enough to use in these integrals. However, the breakdown of these approximations will lead to certain “forbidden” transitions having small intensities.

When one thinks of dipole moments, one usually thinks in the molecular frame. For a diatomic molecule, we can relate the *z* component of the dipole moment in the lab fixed frame to that in the molecule fixed frame by:

$$\mu_z = \mu_\eta \cos\theta$$

where μ_η is the dipole moment in the molecule fixed frame and θ is the angle between the lab and molecule fixed *z*-axis (*z* and η axes)). The $\cos\theta$ is the direction cosine for the *z*-component. If we were to use the *x* or *y* component, this factor would be the corresponding direction cosine. (For *x*: $\sin\theta\cos\varphi$ and for *y*: $\sin\theta\cos\varphi$)

It is important to realize that μ_η depends on the position of the electrons and nuclei and therefore on the electronic and vibrational coordinates.

We can substitute the above expression for μ_z into the integral to get:

$$\left(\mu_z\right)_{21} = \int\int \psi_{2el}^* \psi_{2vib}^* \hat{\mu}_\eta \psi_{1el} \psi_{1vib} d\tau_{el} d\tau_{vib} \int \psi_{2rot}^* \cos\theta \psi_{1rot} d\tau_{rot}$$

The first integral of this expression will give us the selection rules for electronic and vibrational transitions. The second integral will give us the same rotational selection rules for all types of transitions (between rotational states, vibrational states, electronic states). We can evaluate this integral by putting in the eigenfunctions for the rigid rotor, *i.e.* the spherical harmonics.

You can see that to determine spectroscopic intensities one must evaluate these integrals for different types of molecules in particular quantum states.

As we discuss each type of spectroscopy in more detail, we will evaluate these integrals to determine the selection rules in a particular type of situation. We will also see that there are other factors that can determine whether the transition moment integral is non-zero or not. In particular, the symmetry of the integrand (and hence the symmetry of the wave functions) will often determine that the integral is equal to zero.

2.4.4 State Populations

An additional factor that clearly must affect the intensities of spectroscopic transitions is the number of molecules in the state from which the transition originates. In the limit that there are no molecules in the initial state, the number of molecules that absorb a photon and make a transition from that state to some higher state (and hence the intensity of the transition) must clearly equal zero.

Thus, we have to incorporate what we know about the populations of quantum states at a particular temperature into our analysis of molecular spectra.

The populations of quantized energy levels can be determined using ***statistical mechanics.*** I will only briefly discuss the results.

If we have a set of quantized energy levels of a molecule, we need to know how many molecules are in level 1, how many are in level 2, etc..., at a particular temperature.

This number of molecules in the i^{th} level is given by statistical mechanics to be:

$$N_i = c g_i e^{-\frac{E_i}{k_b T}}$$

where c is a proportionality constant, g_i is the degeneracy of the i^{th} level, E_i is the energy of the i^{th} level, k_b is the Boltzmann constant, and T is the temperature.

We can determine the proportionality constant by summing over both sides of this equation and noting that

$$\sum_i N_i = N$$

Thus

$$\sum_i N_i = N = c \sum_i g_i e^{-\frac{E_i}{k_b T}}$$

or

$$c = \frac{N}{\sum_i g_i e^{-\frac{E_i}{k_b T}}}$$

The result is

$$N_i = N \frac{g_i e^{-\frac{E_i}{k_b T}}}{\sum_i g_i e^{-\frac{E_i}{k_b T}}}$$

We can express the fraction of molecules in a particular state as

$$f_i = \frac{N_i}{N} = \frac{g_i e^{-\frac{E_i}{k_bT}}}{\sum_i g_i e^{-\frac{E_i}{k_bT}}}$$

The denominator of this expression, is called the ***partition function***, and is given the symbol Q

$$Q = \sum_i g_i e^{-\frac{E_i}{k_bT}}$$

The partition function is a constant for a molecule at a certain temperature. Thus, at a given temperature, the fractional population of the i^{th} state will decrease as the energy of that state increases.

To evaluate this expression, one must evaluate the partition function *Q* for the system of interest. You can see that if the energy of the system (molecule) can be written as a sum of energies (*e.g.*, electronic + vibrational + rotational), the total partition function will be a product of partition functions for each type of motion (since the exponential of a sum is a product of exponentials).

If you have an explicit expression for the energies, then one can evaluate the sum. Otherwise one can do it numerically.

Let me have a look at two examples in which I calculate the fraction of diatomic molecules in a particular vibrational state assuming harmonic oscillator energy levels and a particular rotational state assuming rigid rotor energy levels.

First for the vibrational level. The energy is given by:

$$E_{\mathrm{v}} = \left(\mathrm{v} + \frac{1}{2}\right)h\nu$$

Since it is a diatomic, the vibrational levels are non-degenerate. We can therefore write:

$$f_{\mathrm{v}} = \frac{e^{-\frac{\left(\mathrm{v}+\frac{1}{2}\right)h\nu}{k_bT}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\left(\mathrm{v}+\frac{1}{2}\right)h\nu}{k_bT}}} = \frac{e^{-\frac{\frac{1}{2}h\nu}{k_bT}}}{e^{-\frac{\frac{1}{2}h\nu}{k_bT}}} \frac{e^{-\frac{\mathrm{v}h\nu}{k_bT}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_bT}}} = \frac{e^{-\frac{\mathrm{v}h\nu}{k_bT}}}{\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_bT}}}$$

The denominator of this expression can be evaluated by recognizing it to be a geometric series

$$\sum_{\mathrm{v}=0}^{\infty} x^{\mathrm{v}} = \frac{1}{1-x}$$

where $x = e^{-\frac{h\nu}{k_bT}}$

We can therefore write

$$\sum_{\mathrm{v}=0}^{\infty} e^{-\frac{\mathrm{v}h\nu}{k_bT}} = \frac{1}{1 - e^{-\frac{h\nu}{k_bT}}}$$

Putting this into the expression for the fraction of molecules in the v^{th} state gives

$$f_{\mathrm{v}} = \left(1 - e^{-\frac{h\nu}{k_b T}}\right) e^{-\mathrm{v}\frac{h\nu}{k_b T}}$$

To find the fraction of molecules in the lowest level, we just let v=0.

$$f_0 = 1 - e^{-\frac{h\nu}{k_b T}}$$

A typical frequency for a diatomic molecule is 2000 cm^{-1}.

Note: Rather than using $h\nu$, if we express k_bT in cm^{-1}, we can just use the wavenumber in cm^{-1}.

$$k_b = 0.69509\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1}$$

so $$k_bT = (0.69509\ \mathrm{cm}^{-1}\ \mathrm{K}^{-1})(298\ \mathrm{K}) = 207.1\ \mathrm{cm}^{-1}$$

Thus we have: $$f_0 = 1 - e^{-2000/207} = 0.99994$$

Essentially, all the molecules will be in their lowest vibrational state at room temperature. This is usually the case unless either the vibrational frequency is very low or the temperature is very high.

Let us now do the same for the rotational levels. The energy of the rigid rotor is given by:

$$E_J = BJ(J+1)$$

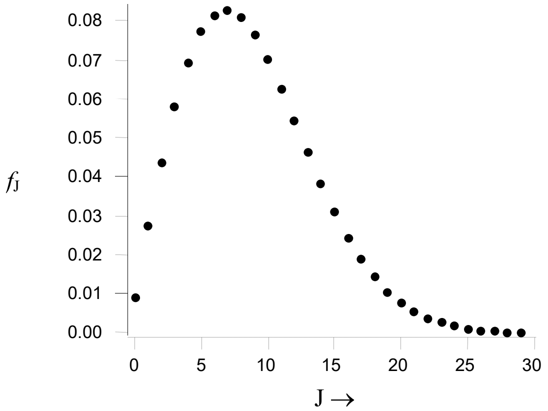
The fraction of molecules in a particular rotational state J given by

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

where

$$Q_{Rot} = \sum_J (2J+1)e^{-\frac{BJ(J+1)}{k_b T}} \approx \frac{k_b T}{B}$$

Note that the 2J+1 factor comes from the m degeneracy, as m can take values from m=-J, -J+1, …, 0,…,J-1, J
The probability distribution as a function of J is plotted below for the CO molecule (B = 1.9225 cm^{-1}) at 300K.



In contrast to vibrations, this function peaks away from zero. This is caused by the (2*J* + 1) degeneracy factor which is increasing with *J* and at low *J* it dominates. At higher *J*, the exponential factor wins and causes the probability to decrease with *J*.

As the energies for electronic states are in general much larger than the thermal energy only the lowest state electronic states will be populated at room temperature.

It is important to realize that the intensity of the transition depends on the difference in populations between the upper and lower states. This is because the probability of making a transition from the upper state down to the lower state is the same as the upward transition. The downward transition results in the emission of two photons (the original one and the one due to stimulated emission). If there were equal populations in both states, there would be no net absorption. Clearly, this will only be a problem for low energy transitions (*i.e.*, those in which the upper state is low enough in energy to be thermally populated). Thus, it will never be a problem in electronic or vibrational spectroscopy, but may be in rotational spectroscopy.

2.4.5 Nuclear Spin Statistics

There is one more factor that affects the intensities of spectroscopic transitions that I have not yet mentioned related to the degeneracy, g_I, in the expression for the state populations. It arises from the treatment of indistinguishable particles in quantum mechanics. During the Quantum chemistry course the topic of the Pauli Principle was extensively discussed. I will briefly review the major conclusions and then apply it to linear molecules. Similar arguments can be made for nonlinear polyatomics.

The interchange of identical particles cannot affect the properties of a molecule. Because all observable properties are related to the square of the wave function, $\psi\psi^*$ cannot change when identical particles are exchanged. This implies that the wave function ψ can either remain unchanged or change sign upon interchange of indistinguishable particles.

All known particles in nature can be divided into two groups:

- Particles whose wave functions are **symmetric**with respect to interchange (+ sign) are called **Bosons**.
- Particles whose wave functions are **antisymmetric** (- sign) are called **Fermions**.

According to the spin statistics theorem:

- half integral spin particles (electrons, positrons, neutrons, protons) are Fermions
- integral spin particles (photons, mesons) are Bosons

Now let us consider what effect this has on the intensities of spectroscopic transitions. Consider a homonuclear diatomic molecule. This discussion below is valid for any linear molecule with indistinguishable nuclei (*i.e.*, HCCH, OCO, etc.), but for simplicity, we will treat a diatomic.

Depending upon whether the indistinguishable particles are Fermions or Bosons, the wave functions must be either antisymmetric or symmetric with respect to interchange. Because rotation of a molecule can interchange two nuclei, one must consider the symmetry properties of the rotational wave functions.

The overall wave function for a molecule can be written as a product of electronic (spatial + spin), rotational, and nuclear spin parts.
Thus

$$\psi_{Total} = \psi_{el}\psi_{vib}\psi_{rot}\psi_{ns}$$

It is the overall wave function that must be symmetric or antisymmetric. Assume for the moment that the electronic part of the wave function is symmetric with respect to interchange of the nuclei. This need not be the case, but our conclusion will just be reversed for the case of an antisymmetric electronic wave function.

The vibrational part of the wave function will be symmetric since the potential only depends upon the absolute value of the internuclear separation.

For a given electronic state, the symmetry of the overall wave function will therefore be controlled by the rotational and nuclear spin parts.

Interchanging identical nuclei in a diatomic can be brought about by rotating the molecule by 180°. One can verify by examining the rigid rotor wave functions that changing θ and φ by 180° multiplies the function by $(-1)^J$.

This means that

- *for even J, the rotational wave function is symmetric* with respect to particle interchange
- *for odd J, the rotational wave function is antisymmetric* with respect to particle interchange

The general phenomenon holds true for any molecule with indistinguishable particles. Moreover, nuclear spin statistics affect all types of spectroscopy insofar as it modifies the expected populations of states.

Let us consider the simple case of the H_2 molecule.
A hydrogen atom has a nuclear spin $I = 1/2$. This makes it a Fermion. Thus, the overall wave functions of H_2 must be antisymmetric.

This introduces the requirement that even J levels (symmetric) must be paired with antisymmetric nuclear spin wave functions and odd J levels (antisymmetric) must be paired with symmetric wave functions.
Let us think about nuclear spin wave functions in the same way as we think about electronic spin wave functions. With $I = 1/2$, one has a possibility of one of two spin states for each nuclei, each representing different orientations of the angular momentum vector in space.

Each nucleus can have either spin up ($M_I = 1/2$) represented by α, or spin down $M_I = -1/2$) represented by β.

This leads to 4 possibilities for combination of the two, 3 of which are symmetric, and one antisymmetric:

$$\left.\begin{array}{c} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\beta(1)\alpha(2)\right] \end{array}\right\} \qquad \text{symmetric, 3 with odd } J\text{'s}$$

$$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right] \qquad \text{antisymmetric, 1 with even } J\text{'s}$$

To result in an overall wave function that is antisymmetric, the odd J states must be paired with one of the three symmetric nuclear spin functions and the even J states must be paired with the antisymmetric wave function. You can see that there will be 3 times as many odd J states as there will be even J states. In the absence of a magnetic field, the nuclear spin doesn't affect the energy. So the odd states are 3-fold degenerate compared to the even states.

This means that the odd J states will have 3 times the statistical weight as even J states. This will be reflected in a spectrum as a 3:1 intensity alternation between even and odd states.

In general, the levels with the higher statistical weight are designated ***ortho*** and the states with the lower statistical weight is designated ***para***.

Hydrogen comes in two forms: **ortho-Hydrogen** (odd *J* states) and **para-Hydrogen** (even *J* states).
The three nuclear spin states of ortho-hydrogen correspond to having both nuclear spins parallel. That would give a net nuclear spin of 1 with projections 1, 0, -1.

Para-hydrogen has the two nuclear spins anti parallel giving a net spin of 0.

It turns out that it is *very difficult to interchange between ortho and para forms*, not only spectroscopically, but by collisions or other means. If one starts out with pure para-hydrogen, for example, and leaves it in a bulb, it can take weeks or months for a significant amount to convert to ortho.

These two forms of hydrogen are basically *different molecules*. They have different heat capacities at low temperature and can be isolated. One method to convert ortho to para hydrogen is to use a charcoal catalyst at very low temperature. In this way one can produce pure para-hydrogen. Once taken off the catalyst, this will remain in the para form for a long time, and one can measure its properties.

Now consider the case of D_2:

Deuterium atoms have a nuclear spin I=1 and hence are Bosons. For the exchange of identical Bosons, the total wave function must be symmetric. Therefore, odd *J* states go with antisymmetric spin functions and even *J* states go with symmetric spin functions (the opposite of the case of H_2).

Because I=1, there are now three orientations of the angular momentum vector and three possible spin functions corresponding to M_I = -1, 0, 1

I will call the three spin functions α, β, and γ. There will be six symmetric spin functions and three antisymmetric functions.

symmetric	**antisymmetric**
$\alpha(1)\alpha(2)$	
$\beta(1)\beta(2)$	
$\gamma(1)\gamma(2)$	$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right]$
$\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right]$	$\frac{1}{\sqrt{2}}\left[\alpha(1)\gamma(2)-\alpha(2)\gamma(1)\right]$
$\frac{1}{\sqrt{2}}\left[\alpha(1)\gamma(2)+\alpha(2)\gamma(1)\right]$	$\frac{1}{\sqrt{2}}\left[\beta(1)\gamma(2)-\beta(2)\gamma(1)\right]$
$\frac{1}{\sqrt{2}}\left[\beta(1)\gamma(2)+\beta(2)\gamma(1)\right]$	
6 with even *J*'s	**3 with odd *J*'s**

Thus, there are twice as many molecules in even *J* states as in odd *J* states. This will give rise to a 2:1 intensity alternation in the spectra.

General Case:

In general, the number of orientations, or spin wave functions, for a specific nucleus of spin I is $(2I+1)^2$.

- The number of symmetric spin functions for two particles will always be $(I+1)(2I+1)$
- The number of antisymmetric functions will be $I(2I+1)$.

The ratio of antisymmetric functions to symmetric functions is therefore: $\frac{I}{I+1}$

It is this factor that determines the intensity ratio.

Note what happens when $I = 0$. If I=0, the number of antisymmetric spin functions = 0. Since an $I = 0$ particle is a Boson, the total wave function must be symmetric. Since there are no antisymmetric spin functions to combine with the odd number J levels, which are antisymmetric, ***it is impossible to construct a satisfactory wave function with odd J values!!***

CO_2 is an example. Oxygen is an $I = 0$ particle. This means that there are no odd J values in CO_2. As we will see shortly, the vibration-rotation spectrum shows that ***all the odd J values are missing!!***

Nuclear spin statistics affect all kind of spectra, and are not limited to diatomic or linear molecules. For example, the hydrogen atoms in NH_3 are indistinguishable and give rise to certain levels having higher statistical weight than others.

I will not discuss these slightly more complicated situations, but I will refer to nuclear spin statistics and expect that you can appreciate the physical origin of these effects.

2.5 Spectral Line Broadening

There are several effects that give rise to a finite width in the spectral lines that one measures. I would like to briefly comment on three of them.

2.5.1 Natural Line Broadening

I pointed out previously that the lifetime of a molecule in a particular state (in the absence of radiation to cause stimulated emission) is inversely proportional to the Einstein A coefficient.

$$\tau = \frac{1}{A}$$

This is the average time that a molecule remains in a particular level before it undergoes spontaneous emission, making a transition to a lower energy state. For this reason it is called the ***radiative lifetime.***

Analogous to the position-momentum uncertainty principle there is also a time-energy uncertainty principle. Although the origin of this uncertainty principle is different from that of the position-momentum uncertainty principle, it has a similar form:

$$\Delta E \Delta t \geq \hbar$$

Because a molecule remains in a particular state for a finite amount of time, τ, there will be an uncertainty to the energy of that state. If we associate the lifetime, τ, with Δt, then we can write

$$\Delta E \tau \geq \hbar \qquad \text{or} \qquad \Delta E \geq \hbar A$$

This energy uncertainty will appear as a broadening of the spectral line that one measures.

If we write $\Delta E = h \Delta \nu$

then

$$h\Delta\nu \geq \frac{h}{2\pi}A \qquad \rightarrow \qquad \Delta\nu \geq \frac{1}{2\pi}A \qquad \rightarrow \qquad \Delta\nu \geq \frac{1}{2\pi\tau}$$

or in units of cm^{-1}

$$\Delta\tilde{\nu} \geq \frac{1}{2\pi c\tau}$$

This is a fundamental limit to the line width of a spectral transition and is called the **natural linewidth**. There is nothing one can do to remove or reduce it.

In practice, because vibrational and rotational levels have long lifetimes, the natural linewidth is often much smaller than one's ability to measure it.

However, recall that the Einstein A coefficient increases as ν^3. Electronically excited states, which are at much higher energies, have short lifetimes. In this case, transitions to these states can be significantly broadened.

This type of spectral broadening gives rise to a *Lorentzian* line shape:

$$g(\nu) = \frac{\Delta\nu}{\left(\nu - \nu_0\right)^2 + \left(\frac{\Delta\nu}{2}\right)^2}$$

2.5.2 Other Types of Lifetime Broadening

There are other mechanisms that can shorten the time a molecule remains in an particular quantum state, and each of these will give rise to *lifetime broadening* as determined by the time-energy uncertainty principle.

The expression $\Delta\nu \geq \frac{1}{2\pi\tau}$ holds in general, although the details of the proportionality constant may differ depending upon the form of the decay in time (*i.e.*, exponential, square wave, etc.)

For example, molecules can change quantum states as the result of a collision with another molecule or atom. If the frequency of collisions is sufficiently high, the average time between collisions can be short enough to broaden the energy levels. This type of spectral broadening is called ***pressure broadening*** since it increases with increasing pressure.

We saw before that

$$\Delta\nu \propto \frac{1}{\tau_{coll}}$$

And since

$$\tau_{coll} \propto \frac{1}{P}$$

We find

$$\Delta\nu = bP$$

where *b* is a pressure broadening coefficient and *P* is the pressure. The value of *b* can vary greatly, depending upon the type of molecule and the type of energy level. A typical value, assuming the collisions between molecules are like those of hard spheres, is about

$b \sim 10$ MHz per mBar

As in the case of natural line broadening, pressure broadening gives rise to a Lorentzian line shape.

Pressure broadening can be eliminated by working at low enough pressure to make the average time between collisions very long.

Another type of lifetime broadening is called ***power broadening***. If one uses an intense light source such as a laser, one can pump a molecule up to the excited state and then stimulate it back down to the ground state. The rate at which a molecule performs this cycle limits its lifetime in any one state and hence gives rise to spectral broadening.

A fourth type of lifetime broadening is ***transit time broadening***. This comes from the fact that a molecule may only be exposed to a light source for a finite amount of time due to its flight through the beam. In the reference frame of the molecule, the light source seems pulsed, and hence has a limited linewidth by the time-energy uncertainty principle.

In this case, the broadening is actually the broadening of the laser in the reference frame of the molecule and not actually a broadening of the levels. But the measured transition will be nonetheless broadened.

With reasonable molecular velocities, the amount of transit time broadening it is usually very small. However, it must be taken into account when performing very high-resolution measurements.

Other processes that shorten a molecule's lifetime can also give rise to broadening. If in the excited state the molecule dissociates (*i.e.*, breaks a chemical bond), this will also broaden the molecular energy levels.

Lifetime broadened line widths can often provide important information on the rates of certain processes such as chemical reactions and collisional energy transfer.
Natural line broadening, pressure broadening, power broadening, and transit time broadening are considered ***homogeneous*** types of broadening. This means that if you were to take the spectrum of different individual molecules, they would all show the same spectral width.

This is to be contrasted with ***inhomogeneous*** types of broadening which arise from different molecules having slightly different frequencies. Each individual transition may be sharp, but the collection together result in a broad spectral feature.

Doppler Broadening and Other Types of Inhomogeneous Broadening
The frequency at which radiation is absorbed or emitted depends upon the velocity of the atom or molecule relative to the source or detector. It is for this very same reason that a train whistle sounds to be at a higher pitch when it is approaching you and at a lower one as it moves away. This is known as the ***Doppler effect***.

If an atom or molecule is traveling towards the light source with a velocity v_a, then the frequency ν_a at which a transition is observed to occur is related to the frequency ν_0 in a stationary atom or molecule by

$$\nu_a = \nu_0 \left(1 - \frac{\mathrm{v}_a}{c}\right)^{-1}$$

where *c* is the speed of light.

Because there is usually a spread of molecular velocities v_a in a sample, there will be a corresponding spread in the absorption frequencies. At thermal equilibrium, the velocity distribution in one dimension is given by

$$P(\mathrm{v}) = \sqrt{\frac{m}{2\pi k_b T}}\, e^{-\frac{m\mathrm{v}^2}{2k_b T}}$$

This Gaussian velocity distribution gives rise to a Gaussian frequency distribution for the spectral transition

$$g_D(\nu) = \frac{1}{\nu_0}\sqrt{\frac{mc^2}{2\pi k_b T}}\, e^{-\frac{mc^2(\nu-\nu_0)^2}{2k_b T \nu_0^2}}$$

This is characteristically different than the Lorentzian that one obtains for lifetime broadening. One can easily show that the width of the transition is given by

$$\Delta\nu = \frac{2\nu_0}{c}\sqrt{\frac{2k_b T \ln 2}{m}}$$

where *m* is the mass of the atom or molecule.

We have

$$\Delta\nu = 7.1\cdot 10^{-7}\nu_0\sqrt{\frac{T}{M}}$$

where M is in amu and T in Kelvin.

Note the linear dependence on the frequency (or wavenumber). This means that microwave and infrared spectra will have much less Doppler broadening than electronic spectroscopy in the visible or UV region.

Doppler broadening is a major source of spectral broadening and is usually far greater than the natural line width.

This type of broadening is inhomogeneous, since not all atoms or molecules have the same spectrum. Doppler broadening can be greatly reduced using one of several clever experimental techniques.

If the molecules are not isolated, but rather solvated in a liquid or embedded in a solid (matrix) the transitions are often significantly broadened. This line broadening can be caused by several effects. For example due to the interaction of the molecule with the environment, the excited state lifetime might be significantly reduced, giving rise to homogeneous lifetime broadening. The transition frequencies are also weakly modified due to the interaction of the molecule with the environment. Since the environment seen by the molecule is not isotropic, especially in solids, inhomogeneous line broadening results. Of course, both effects are generally present. Which one is the most important depends on the system.

3 Rotational Spectroscopy

3.1 Classifications of Rotors

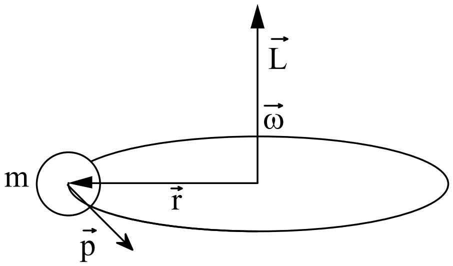
I will begin this subject by looking at the rotational motion of molecules in general. I will first classify molecules into different types according to the nature of their rotational motion. We will then look at a few of these types in somewhat more detail.

Last semester, I discussed the quantum mechanics of the Rigid Rotor. During that discussion, I made a brief digression comparing linear and rotational motion.

Linear Motion	**Rotational Motion**
x	θ
m	I
$v= dx/dt$	$\omega=d\theta/dt$
$\mathbf{p} = m\mathbf{v}$	$\mathbf{L} = I\omega$

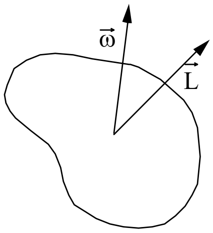
The expression for angular momentum, $\mathbf{L} = \mathbf{I}\omega$, in rotational motion is analogous to $\mathbf{p}=m\mathbf{v}$ in linear motion.

For the rotational motion of a single particle about a point, both ω and **L** are vectors which point out of the plane of rotation in the same direction.



This will be true for a diatomic molecule if one neglects any angular momentum of the electrons.

For an extended object however (which includes non-linear polyatomic molecules), ω and **L** need not point in the same direction.



You can see in this case, rather than being a single number, **I** must be represented by a 3 × 3 matrix

$$\mathbf{L} = \mathbf{I}\boldsymbol{\omega}$$

written explicitly as

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{xy} & I_{yy} & I_{yz} \\ I_{xz} & I_{yz} & I_{zz} \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

I is called the moment of inertia tensor.

One can derive the form of the moment of inertia tensor for a collection of nuclei rotating in space using the definition of angular momentum.

Consider a collection of nuclei of mass m_α located at positions $\mathbf{r}_\alpha$ relative to the origin in a Cartesian coordinate system. The collection of nuclei is rotating with angular velocity $\boldsymbol{\omega}$.

The angular momentum is given by

$$\mathbf{L} = \sum_\alpha \mathbf{r}_\alpha \times \mathbf{p}_\alpha = \sum_\alpha m_\alpha \mathbf{r}_\alpha \times \left(\boldsymbol{\omega} \times \mathbf{r}_\alpha\right)$$

Where we used that:

$$\mathbf{p}_\alpha = m_\alpha \mathbf{v}_\alpha = m_\alpha \left(\boldsymbol{\omega} \times \mathbf{r}_\alpha\right)$$

To simplify this, we need to use the cross product identity

$$\mathbf{P} \times \left(\mathbf{Q} \times \mathbf{R}\right) = \mathbf{Q}\left(\mathbf{P} \cdot \mathbf{R}\right) - \mathbf{R}\left(\mathbf{P} \cdot \mathbf{Q}\right)$$

This gives

$$\begin{aligned}\mathbf{L} &= \sum_\alpha m_\alpha \left(\boldsymbol{\omega}\left(\mathbf{r}_\alpha \cdot \mathbf{r}_\alpha\right) - \mathbf{r}_\alpha \left(\mathbf{r}_\alpha \cdot \boldsymbol{\omega}\right)\right) \\ &= \sum_\alpha m_\alpha \left(\boldsymbol{\omega}\left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right) - \mathbf{r}_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\right)\end{aligned}$$

Writing out the vector components gives

$$\begin{aligned}L = \sum_\alpha m_\alpha \Big[&\omega_x \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{e}_1 + \omega_y \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{e}_2 + \omega_z \left(x_\alpha^2 + y_\alpha^2 + z_\alpha^2\right)\hat{e}_3 \\ &- x_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{e}_1 - y_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{e}_2 - z_\alpha \left(x_\alpha \omega_x + y_\alpha \omega_y + z_\alpha \omega_z\right)\hat{e}_3 \Big]\end{aligned}$$

This can be written in matrix form as:

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} \sum_\alpha m_\alpha \left(y_\alpha^2 + z_\alpha^2\right) & -\sum_\alpha m_\alpha x_\alpha y_\alpha & -\sum_\alpha m_\alpha x_\alpha z_\alpha \\ -\sum_\alpha m_\alpha y_\alpha x_\alpha & \sum_\alpha m_\alpha \left(x_\alpha^2 + z_\alpha^2\right) & -\sum_\alpha m_\alpha y_\alpha z_\alpha \\ -\sum_\alpha m_\alpha z_\alpha x_\alpha & -\sum_\alpha m_\alpha z_\alpha y_\alpha & \sum_\alpha m_\alpha \left(x_\alpha^2 + y_\alpha^2\right) \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

The diagonal elements of this matrix are referred to as the **moments of inertia**

$$I_{xx} = \sum_\alpha m_\alpha \left(y_\alpha^2 + z_\alpha^2\right) = \sum_\alpha m_\alpha r_{x\perp}^2$$

$$I_{yy} = \sum_\alpha m_\alpha \left(x_\alpha^2 + z_\alpha^2\right) = \sum_\alpha m_\alpha r_{y\perp}^2$$

$$I_{zz} = \sum_\alpha m_\alpha \left(x_\alpha^2 + y_\alpha^2\right) = \sum_\alpha m_\alpha r_{z\perp}^2$$

Note that the moment of inertia with respect to an axis involves the squares of the perpendicular distances of the masses from that axis (*e.g.*, $r_{x\perp}^2$ from the *x*-axis).

The off-diagonal terms in this matrix are called the **products of inertia**:

$$I_{xy} = -\sum_\alpha m_\alpha x_\alpha y_\alpha$$

$$I_{xz} = -\sum_\alpha m_\alpha x_\alpha z_\alpha$$

$$I_{yz} = -\sum_\alpha m_\alpha y_\alpha z_\alpha$$

The matrix is called the **moment of inertia tensor**.

Because the moment of inertia tensor is a real symmetric matrix, one can prove that it is always possible to find an orthogonal transformation matrix **X** that transforms the moment of inertia tensor **I** into diagonal form.

$$\mathbf{I}' = \mathbf{X}^{-1}\mathbf{I}\mathbf{X}$$

The matrix **X** represents a rotation of the coordinate system, which can be written as

$$\mathbf{r}' = \mathbf{X}^{-1}\mathbf{r} \text{ or } \qquad \mathbf{r} = \mathbf{X}\mathbf{r}'$$

(One can show that the columns of the matrix **X** are made up of the normalized eigenvectors of **I**).

The new coordinate system is called the ***principle axis system*** and the **I'** matrix is a diagonal matrix given by

$$\mathbf{I}' = \begin{pmatrix} I_{x'x'} & 0 & 0 \\ 0 & I_{y'y'} & 0 \\ 0 & 0 & I_{z'z'} \end{pmatrix}$$

Usually the use of the principle axis system is assumed, so the primes are dropped and

$$I_x = I_{x'x'} \quad I_y = I_{y'y'} \quad I_z = I_{z'z'}$$

In the principle axis system one can always write

$$\begin{pmatrix} L_x \\ L_y \\ L_z \end{pmatrix} = \begin{pmatrix} I_x & 0 & 0 \\ 0 & I_y & 0 \\ 0 & 0 & I_z \end{pmatrix} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \end{pmatrix}$$

Which axis is labeled *x*, *y*, and *z* is chosen by a set of geometrical conventions. For example, the *z*-axis is always chosen to be the highest order axis of rotational symmetry, and the *x*-axis is out of the plane for a planar molecule.

With the moment of inertia tensor in diagonal form like this, the different components of the angular momentum can simply be written

$$L_x = I_x\omega_x \qquad L_y = I_y\omega_y \qquad L_z = I_z\omega_z$$

The total angular momentum vector can be constructed from these three projections on the principle axes.

The rotational kinetic energy can be written as:

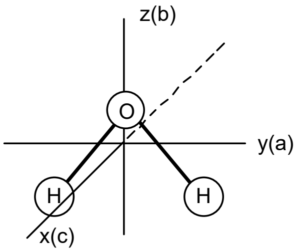
$$E_{rot} = \frac{1}{2}\left[I_x \omega_x^2 + I_y \omega_y^2 + I_z \omega_z^2 \right]$$

$$= \frac{L_x^2}{2I_x} + \frac{L_y^2}{2I_y} + \frac{L_z^2}{2I_z}$$

An alternative labeling scheme for the principal axes is based upon the magnitudes of the moments of inertia. In this case, the axes are labeled *A*, *B*, and *C* according to the requirement that

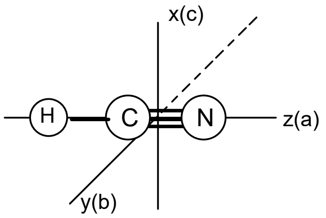
$$I_A \le I_B \le I_C$$

It is not obvious in this case which one is *A*, *B*, and *C* from simply looking at the molecule. One must calculate the moments of inertia. It is important to realize that this is simply another way of labeling the axes. They are the same set of three axes, however.

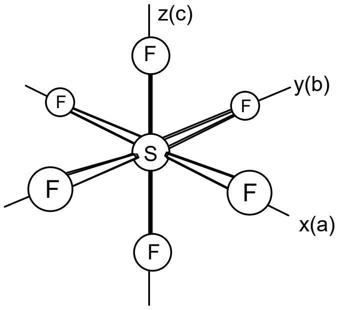


All molecules can be classified on the basis of their three moments of inertia. There are 5 different cases:

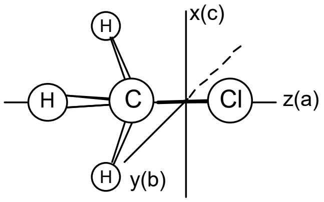
1. **Linear Molecules**, $I_A = 0$, $I_B = I_C$ *e.g.*, HCN



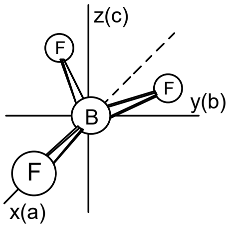
2. **Spherical Tops**, $I_A = I_B = I_C$ *e.g.*, SF_6 and CH_4



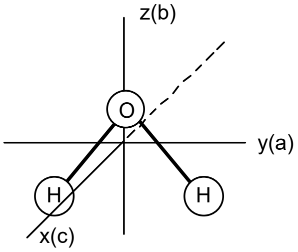
3. **Prolate Symmetric Tops**, $I_A < I_B = I_C$ *e.g.*, CH_3Cl



4. **Oblate Symmetric Tops**, $I_A = I_B < I_C$ *e.g.*, BF_3



5. **Asymmetric Tops,** $I_A < I_B < I_C$ *e.g.*, H_2O



Group theory can be used to classify the rotational properties of molecules. There are three important rules to remember:

- Molecules in the groups O_h, T_d, and I_h are spherical tops.
- Molecules in $C_{\infty v}$ and $D_{\infty h}$ are linear.
- All symmetric top molecules must have a C_n axis with $n>2$.

You can see that H_2O only has a C_2 axis and is an asymmetric top.

3.2 Linear Molecules

I have already laid much of the foundation for discussing rotational spectroscopy of diatomic molecules, and linear molecule rotation is essentially the same as that of diatomic rotation.

3.2.1 Level Spacing

In general, we write the ***classical*** expression for the kinetic energy as

$$E_K = \frac{1}{2} I_A \omega_A^2 + \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

Recall that in a diatomic molecule, $I_A = 0$ and $I_B = I_C = I$. We can therefore write

$$E_K = \frac{1}{2} I_B \omega_B^2 + \frac{1}{2} I_C \omega_C^2$$

$$= \frac{J_B^2}{2I} + \frac{J_C^2}{2I} = \frac{J^2}{2I}$$

The quantum mechanical Hamiltonian for a linear rigid rotor is just

$$\hat{H} = \frac{\hat{J}^2}{2I}$$

We have already solved this problem:

$$\hat{H} Y_J^m(\theta,\varphi) = \frac{\hat{J}^2}{2I} Y_J^m(\theta,\varphi) = E\, Y_J^m(\theta,\varphi)$$

$$= \frac{\hbar^2}{2I} J(J+1) Y_J^m(\theta,\varphi) = BJ(J+1) Y_J^m(\theta,\varphi)$$

where

$$B = \frac{\hbar^2}{2I} = \frac{h^2}{8\pi^2 I} \qquad \text{(in Joules)}$$

Often spectroscopists use *F*(*J*) to express the rotational energy levels as a function of the quantum number *J* in units of MHz or in cm^{-1}.

$$F(J) = BJ(J+1)$$

Unfortunately, the same symbol *B* is used whether expressed in Joules, MHz, or cm^{-1}.

Remember that for a linear molecule, $I_A = 0$ and $I_B = I_C = I$. The moment of inertia, *I*, will simply be

$$I = \sum_\alpha m_\alpha r^2$$

where *r* is the distance of the atom from the center of mass.

3.2.2 Selection Rules

In our earlier discussion of selection rules for a diatomic, we started with the transition moment integral

$$Intensity \propto \left(\int \psi_2^* \, \hat{\mu}_z \psi_1 d\tau \right)^2 \qquad \text{(or the equivalent with } \mu_x \text{ or } \mu_y\text{)}$$

After putting in the wave functions as products of vibrational, rotational and electronic parts, we get that the integral can be written as:

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

Where q_i are the electron coordinates and R the distance between the nuclei. The dipole moment which is given in the laboratory frame of reference as $\mu_z(q_i, R)$ and depends on both the electron and the nuclear positions can be written in the molecular frame of reference as

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

Rearranging terms and grouping them together gives:

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

If we now realize that for pure rotational transitions we do not change electronic or vibrational level we can rewrite this as:

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

This double integral gives the mean value of the dipole moment, averaged over the electronic and nuclear coordinates. This is also known as the permanent dipole moment, μ_e, of the molecule. We can thus write:

$$\mu_e \int \psi^*_{2rot}(\theta,\varphi)\cos\theta\psi_{1rot}(\theta,\varphi)\;d\tau_{\theta,\varphi}$$

You can see that one requirement for pure rotational transitions is that the molecule has a permanent dipole moment, μ_e.

Thus, molecules such as O=C=O, Cl – Cl, H-C≡C-H which have no dipole moment, have no pure rotational spectra.

The other requirement is that the integral is non-zero. We can use rigid rotor wave functions for evaluating this integral.

Recall that:

$$\psi_{RR} = Y_J^m(\theta,\varphi) = N_{Jm}P_J^{|m|}(\cos\theta)e^{im\varphi}$$

where

$$N_{Jm} = \left[\frac{(2J+1)}{4\pi}\frac{(J-|m|)!}{(J+|m|)!}\right]^{\frac{1}{2}}$$

Remember that the $P_J^{|m|}(\cos\theta)$ are the associated Legendre polynomials.

Putting this into the integral yields

$$\begin{aligned}\int \psi^*_{2rot}(\theta,\varphi)\cos\theta\psi_{1rot}(\theta,\varphi)\;d\tau_{\theta,\varphi} &= \int N_{J'm'}P_{J'}^{|m'|}(\cos\theta)e^{-im'\varphi}\cos\theta N_{J''m''}P_{J''}^{|m''|}(\cos\theta)e^{im''\varphi}d\tau_{\theta,\varphi}\\ &= N_{J'm'}N_{J''m''}\int P_{J'}^{|m'|}(\cos\theta)\cos\theta P_{J''}^{|m''|}(\cos\theta)d\tau_\theta \int e^{-im'\varphi}e^{im''\varphi}d\tau_\varphi\end{aligned}$$

Note: It is spectroscopic convention to label the upper state quantum number by a single prime and the lower state quantum number by a double prime. When indicating a transition between two states, the convention is to write the upper state first and the lower state second. An arrow is used to indicate absorption, *J*'←*J*'' or emission, *J*'→*J*''. When no prime is indicated, the quantum number refers to the lower state.

The integral over φ will be zero unless $m'' = m'$ in which case it will be 2π. This gives rise to the *m* selection rule **Δ*m* = 0.** This Δ*m* selection rule results from our choice of radiation along the *z*-direction. If we chose the *x* or *y* component, we could get **Δ*m* = ±1.** This arises from the relation between the molecule fixed dipole moment and the projection on the different axes. We know that

$$\mu_z = \mu_\eta \cos\theta$$

$$\mu_y = \mu_\eta \sin\theta \sin\varphi$$

$$\mu_x = \mu_\eta \sin\theta \cos\varphi$$

If you used one of the latter two components, you would get a $\sin\varphi$ or $\cos\varphi$ in the φ integral, and this would give $\Delta m = \pm 1$.

To help evaluate the integral over θ which gives the *J* selection rules, one can make use of a recursion formula that relates different Legendre polynomials to one another.

$$\cos\theta P_J^{|m|}(\cos\theta) = \frac{J+|m|}{2J+1} P_{J-1}^{|m|}(\cos\theta) + \frac{J-|m|+1}{2J+1} P_{J+1}^{|m|}(\cos\theta)$$

Using this recursion relation in the θ part of the integral gives

$$\int P_{J'}^{|m'|}(\cos\theta)\cos\theta P_{J''}^{|m''|}(\cos\theta) d\tau_\theta = \left(\frac{J''+|m''|}{2J+1}\right)\int P_{J'}^{|m'|}(\cos\theta) P_{J''-1}^{|m''|}(\cos\theta) d\tau_\theta + \left(\frac{J''-|m''|+1}{2J+1}\right)\int P_{J'}^{|m'|}(\cos\theta) P_{J''+1}^{|m''|}(\cos\theta) d\tau_\theta$$

Remember that the eigenfunctions of a Hermitian operator form a complete orthonormal set. This means that eigenfunctions corresponding to different eigenvalues are orthogonal.

Thus, the first integral on the right will be zero unless $J' = J'' - 1$ or $J' - J'' = -1$. This gives rise to the selection rule that $\Delta J = -1$.

Once can see that the second integral will be equal to zero unless $J' = J''+1$. This gives rise to the selection rule that $\Delta J = 1$

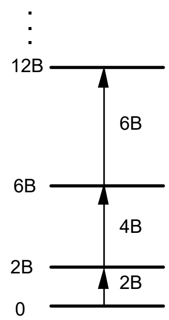
Together we have: **Δ*J* = ± 1 Δ*m* = 0, ±1**

So in addition to the requirement of a permanent dipole moment for pure rotational transitions, the rotational selection rules require that $\Delta J = \pm 1$ and $\Delta m = 0, \pm 1$. Because in the absence of a magnetic field the states of different *m* are degenerate, the $\Delta m = 0, \pm 1$ selection rule has no effect on the energies of the transitions in the spectrum. We will therefore ignore it for the moment.

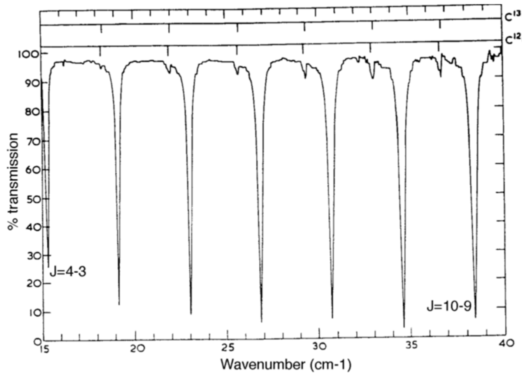
The selection rule $\Delta J = \pm 1$ results in the following transition frequencies:

$$\begin{aligned} \nu_{J+1\leftarrow J} &= F(J') - F(J'') = F(J+1) - F(J) \\ &= B(J+1)(J+2) - BJ(J+1) \\ &= 2B(J+1) \end{aligned}$$

Thus, the first transition, $J = 1 \leftarrow 0$, occurs at $2B$. The others are spaced at multiples of $2B$.



Example: Rotational Spectrum of CO.



Note the isotope peaks; different isotopes have different rotational constants. From analysis of this spectrum, one could get the rotational constant *B*, which gives the moment of inertia, *I*, which in turn will provide r_e. This is the most accurate way to determine bond lengths.

The expression that we derived for the energies of the rotational levels was in the rigid rotor approximation where we have neglected vibration rotation interaction and centrifugal distortion.
Recall our general expression for the energy levels of a diatomic:

$$F(\mathrm{v},J)=\frac{E_{\mathrm{v}J}}{hc}=\omega_e\left(\mathrm{v}+\frac{1}{2}\right)+B_eJ(J+1)-\omega_ex_e\left(\mathrm{v}+\frac{1}{2}\right)^2-\alpha\left(\mathrm{v}+\frac{1}{2}\right)J(J+1)-DJ^2(J+1)^2$$

It is important to note that the number of terms here is simply determined by how many terms we carry in the perturbation theory treatment to derive it. One can take this out to higher order terms if one likes.

One can rewrite this expression in the following way

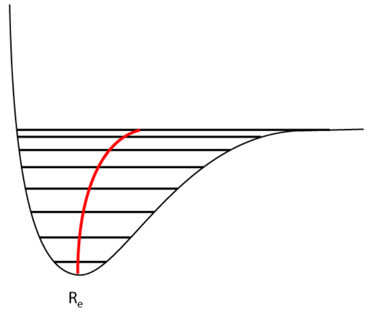
$$F(\mathrm{v},J)=\omega_e\left(\mathrm{v}+\frac{1}{2}\right)-\omega_ex_e\left(\mathrm{v}+\frac{1}{2}\right)^2+B_{\mathrm{v}}J(J+1)-DJ^2(J+1)^2$$

where

$$B_{\mathrm{v}}=B_e-\alpha\left(\mathrm{v}+\frac{1}{2}\right)$$

One can have pure rotational transitions in excited vibrational states, and this expression accounts for the change in the *B* rotational constant with increasing vibrational quantum number as well as the effects of centrifugal distortion. (Higher order treatments include the vibrational dependence of *D* as well).

As we discussed earlier in the course, the fact that the rotational constant is dependent on the vibrational level reflects the fact that there is anharmonicity in the potential that makes the average bond length increase with increasing vibrational quantum number. This makes the effective rotational constant depend upon the vibrational quantum number, v.



The frequency for a pure rotational transition comes from taking the difference in energy levels:

$$
\begin{aligned}
\nu_{J+1\leftarrow J} &= F(J') - F(J'') = F(J+1) - F(J) \\
&= B_v(J+1)(J+2) - D(J+1)^2(J+2)^2 - B_vJ(J+1) + DJ^2(J+1)^2 \\
&= 2B_v(J+1) - 4D(J+1)^3
\end{aligned}
$$

You can see that the transition frequencies are slightly lowered by centrifugal distortion.

Using this more accurate expression, one can now obtain not only the rotational constant *B*, but also the vibration rotation interaction constant α and the centrifugal distortion constant *D*.

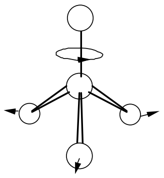
3.3 Spherical Tops

In general, one would expect spherical top molecules not to show any pure rotational transitions because they do not have any permanent dipole moment (which is a requirement for having a pure rotational spectrum).

You can see this by simply looking at the character tables for the point groups T_d, and O_h. There is no translational coordinate (*i.e.*, *x*, *y*, or *z*) which belongs to the totally symmetric representation. Remember, that the symmetry of different components of the dipole moment are the same as a translation in that direction. Thus we would not expect there to be any dipole moment and hence no rotational spectrum.

However, for spherical top molecules which have only C_3 axes of symmetry, there can be a slight dipole moment induced by centrifugal distortion.

Consider the molecule CH_4 for example. Rotation about any of the 4 C_3 axes will push out the off axis hydrogens slightly but does not effect the hydrogen that is on the axis. This results in a very small dipole moment and hence a weak rotational spectrum. I will not take the time to discuss this in detail.



3.4 Symmetric Tops

Now let's turn to the more complex problem of symmetric top rotational motion. Although more complex than that of linear molecules, among polyatomics the rotational motion of symmetric tops is the simplest to understand. My discussion will focus on ***prolate symmetric tops***, although I will mention oblate tops at several points.

Recall that in a prolate symmetric top, $I_A < I_B = I_C$. The two identical moments are usually called I_B. We call the axis of highest symmetry in a symmetric top, the ***figure axis.***

In the quantum mechanical picture of symmetric top rotation, one has to consider which operators commute with each other, since this determines which quantities can be simultaneously well defined. Moreover, the quantities whose operators commute with the Hamiltonian will be independent of time and will be represented by "good" quantum numbers.

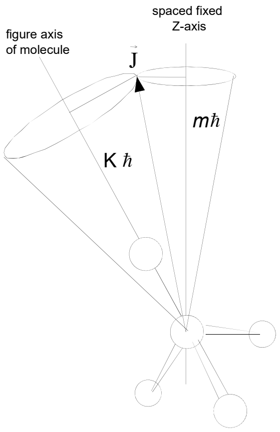
Recall that for rigid diatomic molecules, the operators $\hat{H},\hat{J}^2,\hat{J}_z$ all commute with each other. Remember that J_Z represents the projection of **J** on the spaced fixed *z*-axis. We therefore had two good rotational quantum numbers *J*, and *m*, although the energy depends only on *J*.

For a symmetric top molecule we will find that there is another operator that commutes with these three, *i.e.* the operator representing the projection of *J* on the figure axis. This operator is given the symbol J_z (lower case *z*) or J_a.

Thus, there will be an additional good quantum number, which is denoted *K*, that represents a constant projection of the total angular momentum on the figure axis of the molecule.

In the quantum mechanical problem of the symmetric top, the total angular momentum of the molecule must simultaneously maintain a constant projection on the spaced fixed *z*-axis as well as on the figure axis of the molecule.

We therefore have the following picture:



We get two cones, constrained by the need to have constant projections of *J*. The relative sizes of these cones are simply related to the projection quantum numbers *K* and *m*. We should realize that the ***J*** vector is not fixed in space, it simply has a fixed length and a fixed projection on the space fixed *z*-axis.

In a symmetric top, we will see that the energy now depends upon two of the three good quantum numbers, *i.e*. *J*, which corresponds to the total angular momentum, and *K*, which corresponds to the projection of *J* on the figure axis. It is still true that in the absence of magnetic fields, the energy doesn't depend upon *m* since space is isotropic. The fact that the molecule is not isotropic means that the energy will depend upon *K*. If the molecule was isotropic (*i.e.*, a spherical top) the energy would not depend upon *K*.

3.4.1 Hamiltonian and Energy Levels

To treat the quantum mechanical problem of the symmetric top, one has to write down the classical expression for the total energy and then substitute the corresponding operators to get the Hamiltonian. One must then find the eigenvalues and eigenfunctions of the Hamiltonian.

The classical expression for the energy of a rigid prolate symmetric top is:

$$E = \frac{J_A^2}{2I_A} + \frac{J_B^2}{2I_B} + \frac{J_C^2}{2I_C}$$

$$= \frac{J_A^2}{2I_A} + \frac{1}{2I_B}\left(J_B^2 + J_C^2\right)$$

Since $I_B = I_C$

We could also write this

$$E = \frac{J_z^2}{2I_A} + \frac{1}{2I_B}\left(J_x^2 + J_y^2\right)$$

since for a prolate symmetric top, $a \leftrightarrow z$, $b \leftrightarrow x$, and $c \leftrightarrow y$.

(Remember that lower case *x*, *y*, *z* are molecule fixed coordinates, uppercase *X*, *Y*, *Z* are spaced fixed coordinates)

We know that

$$J_x^2 + J_y^2 + J_z^2 = J^2 \qquad \text{or} \qquad J_x^2 + J_y^2 = J^2 - J_z^2$$

We can therefore write

$$E = \frac{J_z^2}{2I_A} + \frac{1}{2I_B}\left(J^2 - J_z^2\right)$$

Rearranging this gives

$$E = \frac{J^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)J_z^2$$

The corresponding quantum mechanical Hamiltonian is therefore:

$$\hat{H} = \frac{\hat{J}^2}{2I_B} + \left(\frac{1}{2I_A} - \frac{1}{2I_B}\right)\hat{J}_z^2$$

Because we are dealing with non-linear molecules, the eigenfunctions of this Hamiltonian will depend upon three angles, the so-called Euler angles θ, φ, and χ. The first two are those of a spherical polar coordinate system that describe the orientation of the figure axis (which is fixed in the molecule) with respect to the space-fixed *X*, *Y*, and *Z* axes. Another angle, χ, is needed, to describe the orientation of the molecule about its figure axis. (The spinning motion of a symmetric top about its top axis involves a change in χ.)

Thus $\psi = \psi(\theta, \varphi, \chi)$

These eigenfunctions will be simultaneous eigenfunctions of $\hat{H}, \hat{J}^2, \hat{J}_Z$ and $\hat{J}_z$ since these operators commute. In addition to representing states having a fixed value of the energy, these eigenfunctions can be characterized by 3 rotational quantum numbers, *J*, *m*, and *K*. The first two have their usual meaning, while the third represents the projection of *J* on the figure axis.

It is important to note the analogy between $\hat{J}_Z$ and $\hat{J}_z$. Recall that the operator for J_Z is given by

$$\hat{J}_Z = -i\hbar \frac{\partial}{\partial \varphi}$$

One could show that

$$\hat{J}_z = -i\hbar \frac{\partial}{\partial \chi}$$

If we substituted into the Hamiltonian the $\hat{J}^2$ and $\hat{J}_z$ operators, we would find that we could separate the Hamiltonian into separate parts that depend upon θ, φ, and χ. Thus the eigenfunctions will be products of separate functions of θ, φ, and χ.

We already know what the solutions to the φ and χ parts are. Remember that the eigenfunctions for

$$\hat{J}_Z = -i\hbar \frac{\partial}{\partial \varphi} \qquad \text{are simply} \qquad \psi(\varphi) = e^{im\varphi}$$

In the same way, the eigenfunctions of

$$\hat{J}_z = -i\hbar \frac{\partial}{\partial \chi} \qquad \text{are} \qquad \psi(\chi) = e^{iK\chi}$$

This set of eigenfunctions will therefore have the form

$$\psi_{J,K,m}(\theta, \varphi, \chi) = \left(\frac{2J+1}{8\pi^2} \right)^{\frac{1}{2}} e^{im\varphi} d^J_{mK}(\theta) e^{iK\chi}$$

It is clear that these functions are eigenfunctions of J_Z and J_z since multiplication by a function of θ will not affect the eigenvalue equation for these operators.

The functions $d^J_{mK}(\theta)$ are hypergeometric functions of $\sin^2(\theta/2)$. They are rarely listed explicitly since the actual functions are usually not needed for calculations. It is sufficient to know the eigenvalues for each of the angular momentum operators with these functions.

Although I haven't given you expressions for these functions $d^J_{mK}(\theta)$ it is important to know that if one sets *K*=0, these functions simply become the spherical harmonics. This makes physical sense in that if there is no rotation about the figure axis, the system behaves just like a diatomic molecule.

The important thing to realize is that the wave functions for a symmetric top depend upon 3 rotational quantum numbers (rather than two for linear molecules).

- ***J*** is the total angular momentum quantum number as in the case of linear molecules.
- ***m*** is the quantum number for the projection of the total angular momentum on the spaced fixed Z-axis (as before).
- ***K*** is quantum number for the projection of the total angular momentum on the figure axis of the molecule.

We already know what the eigenvalues are for the $\hat{J}^2$ and $\hat{J}_Z$ operators. Because $\hat{J}_z$ is also a projection operator, one can treat it in an analogous manner to $\hat{J}_Z$.

We will have the following set of eigenvalue equations:

$$
\begin{aligned}
&\hat{H}\,\psi_{J,K,m}(\theta,\varphi,\chi)=E\,\psi_{J,K,m}(\theta,\varphi,\chi)\\
&\hat{J}^2\,\psi_{J,K,m}(\theta,\varphi,\chi)=\hbar^2 J(J+1)\,\psi_{J,K,m}(\theta,\varphi,\chi)\\
&\hat{J}_Z\,\psi_{J,K,m}(\theta,\varphi,\chi)=\hbar m\,\psi_{J,K,m}(\theta,\varphi,\chi)\\
&\hat{J}_z\,\psi_{J,K,m}(\theta,\varphi,\chi)=\hbar K\,\psi_{J,K,m}(\theta,\varphi,\chi)
\end{aligned}
$$

where $\hbar K$ is the projection of *J* on the figure axis.

Given the expressions for the eigenvalues of the angular momentum operators for a symmetric top, it is simple to determine the expression for the energy levels.

$$
\begin{aligned}
\hat{H}\,\psi_{J,K,m}(\theta,\varphi,\chi)&=\left[\frac{\hat{J}^2}{2I_B}+\left(\frac{1}{2I_A}-\frac{1}{2I_B}\right)\hat{J}_z^2\right]\psi_{J,K,m}(\theta,\varphi,\chi)\\
&=\left[\frac{\hbar^2}{2I_B}J(J+1)+\left(\frac{\hbar^2}{2I_A}-\frac{\hbar^2}{2I_B}\right)K^2\right]\psi_{J,K,m}(\theta,\varphi,\chi)
\end{aligned}
$$

In units of cm^{-1}, the energy levels for a ***prolate*** symmetric top are given by

$$E=BJ(J+1)+(A-B)K^2$$

The corresponding levels of an ***oblate*** symmetric top can be obtained by simply substituting *C* for *A*:

$$E=BJ(J+1)+(C-B)K^2$$

The rotational constants *A*, *B*, and *C*, in units of cm^{-1}, are defined by:

$$A=\frac{h}{8\pi^2 cI_A}\qquad B=\frac{h}{8\pi^2 cI_B}\qquad C=\frac{h}{8\pi^2 cI_C}$$

Remember that the convention in labeling the axes was that $I_A<I_B<I_C$. Because the rotational constants *A*, *B*, and *C* are inversely proportional to the moments of inertia I_A, I_B, I_C their ordering is reversed

$$A\ge B\ge C$$

Since the *K* quantum number is a projection of *J*, it can only take on the values

K = -*J*, -*J*+1, . . .-1, 0, 1, . . . *J*-1, *J*

Another way to look at this is that $J\ge|K|$

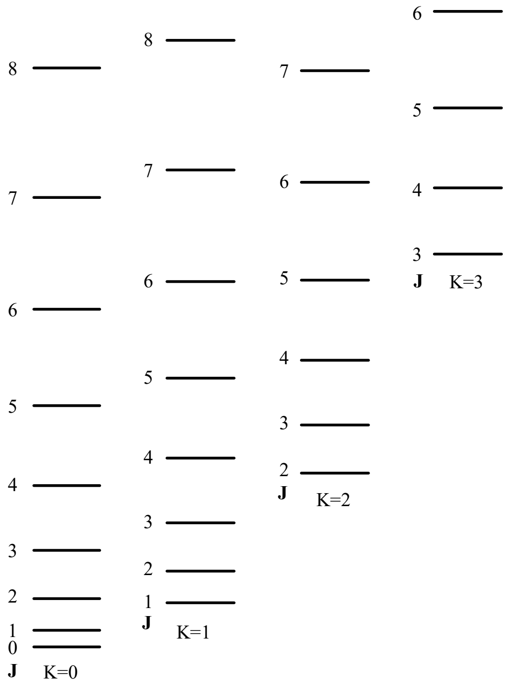
Notice that in the energy levels expressions above, the *K* quantum number enters in as K^2. This means that the +*K* and the -*K* levels with the same |*K*| have the same energy (*i.e.*, the direction of rotation doesn't affect the energy). For this reason one usually leaves off the sign designation.

Note also that *m* does not enter into the energy level expression. This is because J_Z did not appear in the Hamiltonian. In the absence of an external field, there is nothing to make the energy different in one direction in space than in another, thus there is a 2*J*+1 fold degeneracy with respect to the *m* quantum number (*i.e*. the *Z*-projection in space). However, if one puts a molecule in an electric or magnetic field, the degeneracy would split and states with different *m* would have different energies.

The pattern of energy levels of a symmetric top is fairly simple. For a given value of *K*, the energy level structure looks like that of a linear molecule apart from an offset of $(A-B)K^2$ for a prolate top and $(C-B)K^2$ of an oblate top. This is shown in the figure below.

You can see that each value of *K* has its own stack of energy levels, the spacing of which is just $BJ(J+1)$, which is the same as a linear molecule. Notice that each stack starts at successively higher values of *J.* This is because of the restriction that $J \geq K$. Also note that because $(A-B)$ is a positive value (by definition of the ordering of the rotational constants), the offset of each successive *K* stack (*i.e*., increasing *K*) is positive. That means for fixed *J*, the levels increase with *K*.

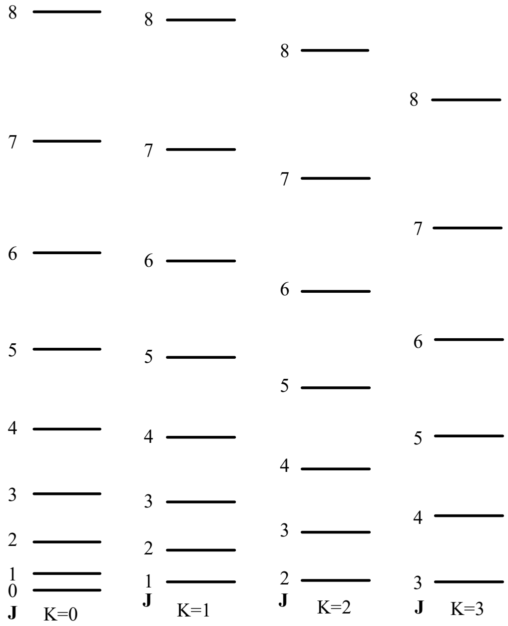
The major difference in the oblate top is that because $(C-B)$ is negative, each successive *K* stack is lower in energy. You might not see this immediately from looking at the diagram above since each stack starts at a higher *J* level (since *K* must be greater than or equal to *J*). Nevertheless, you can see that for fixed *J*, the levels get lower in energy with increasing *K*.



Prolate Symmetric Top Energy Levels

$$E = BJ(J+1) + (A-B)K^2$$

The levels of an oblate symmetric top are shown in the figure below:



Oblate Symmetric Top Energy Levels

$$E = BJ(J+1) + (C-B)K^2$$

3.4.2 Selection Rules and Spectra

I will not derive the selection rules for symmetric tops, but in principle it is no different than for a diatomic molecule. One has to evaluate the transition moment integral using the appropriate eigenfunctions.

The result is $\Delta J = \pm 1 \qquad \Delta m = 0, \pm 1 \qquad \Delta K = 0$

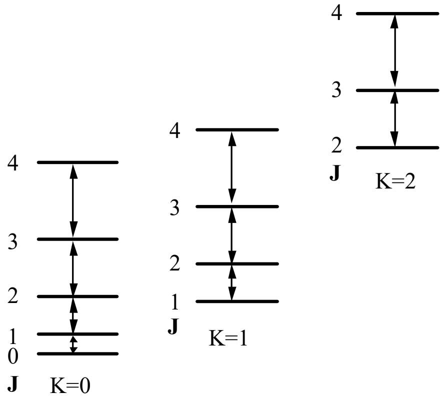
This is for pure rotational spectra. We will soon see that the rotational selection rules will be different for vibration-rotation spectra.

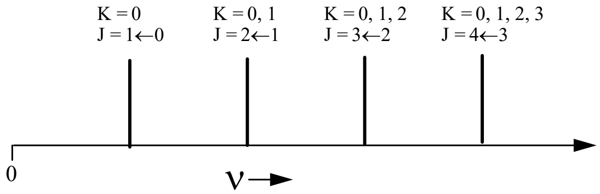
- The ΔJ selection rule is the same as a linear molecule.
- The Δm selection rule has no effect on the spectra since the *m* levels are all degenerate.
- The ΔK selection rule restricts transitions to states within the same *K* stack. From a physical point of view, the ΔK selection rule comes from the fact that because there is no dipole moment perpendicular to the axis, you cannot induce any angular momentum parallel to the axis (which is what is needed to change *K*).

Neglecting centrifugal distortion, the transition frequencies are simply given by

$$\begin{aligned} v_{J+1,K\leftarrow J,K} &= F(J+1,K) - F(J,K) \\ &= B(J+1)(J+2) + (A-B)K^2 - BJ(J+1) - (A-B)K^2 \\ &= 2B(J+1) \end{aligned}$$

This is shown schematically below.





Note the superposition of several transitions at the same frequency. This is because the *B* constant is independent of the value of *K*. If one takes into consideration centrifugal distortion, the overlapping transitions will be shifted from one another.

3.4.3 Effects of Centrifugal Distortion

If we include the effects of centrifugal distortion of a symmetric top, the energy level expression becomes

$$F(J,K) = BJ(J+1) - D_J J^2 (J+1)^2 + (A-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$$

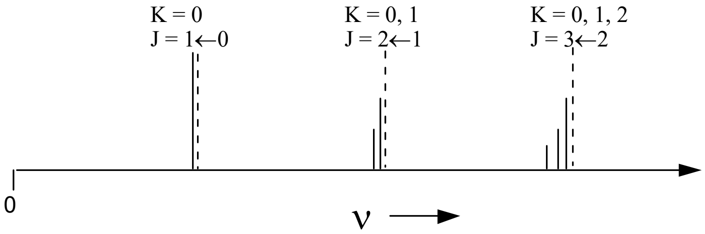
There are now 3 centrifugal distortion constants, D_J, D_K, and D_{JK}.

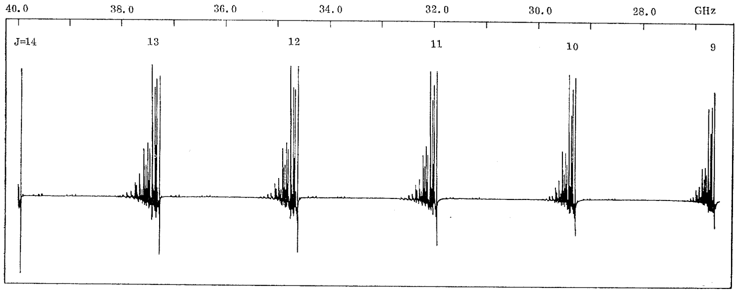
You can see that because of the selection rule $\Delta K = 0$, all of the terms which depend only on *K* will drop out when one takes the difference in energy levels. The transition frequencies are given by

$$\nu_{J+1,K\leftarrow J,K} = F(J+1,K) - F(J,K)$$

$$= 2B(J+1) - 4D_J (J+1)^3 - 2D_{JK} (J+1)K^2$$

The constant D_{JK} splits out the transitions with different *K* for a given $J+1 \leftarrow J$ which in the absence of centrifugal distortion would fall on top of one another.





Part of the microwave spectrum of cyanodiacetylne

3.5 Asymmetric Tops

Asymmetric top molecules have $I_A < I_B < I_C$ with no two moments equal to one another.

The rigid rotor Hamiltonian can be written:

$$\hat{H} = \frac{\hat{J}_A^2}{2I_A} + \frac{\hat{J}_B^2}{2I_B} + \frac{\hat{J}_C^2}{2I_C}$$

The Schrödinger equation for the asymmetric top has no general analytical solutions and must be solved numerically.

If two of the rotational constants are nearly equal, the spectrum will resemble that of a symmetric top with some of the lines split due to asymmetry. One way to think of an asymmetric top is that the quantum numbers corresponding to the +*K* and -*K* levels that were degenerate in the symmetric top are no longer degenerate.

The degree of asymmetry can be quantified by an asymmetry parameter, called "Ray's asymmetry parameter", κ, which can take values from -1 to +1. The asymmetry parameter is defined as

$$\kappa = \frac{2B - A - C}{A - C}$$

You can see from this definition that for a: **prolate top:** $B = C$ and $\kappa = -1$
oblate top: $A = B$ and $\kappa = +1$

For a slightly asymmetric top the splitting between these levels is given by

$$\Delta E = \frac{b^K (J+K)!}{8^{K-1}(J-K)!\left[(K-1)!\right]^2}$$

With for a slightly asymmetric prolate top:

$$b_p = \frac{\kappa + 1}{\kappa - 3}$$

Note that b_p is zero for a prolate symmetric top and increases as the molecule becomes more asymmetric.

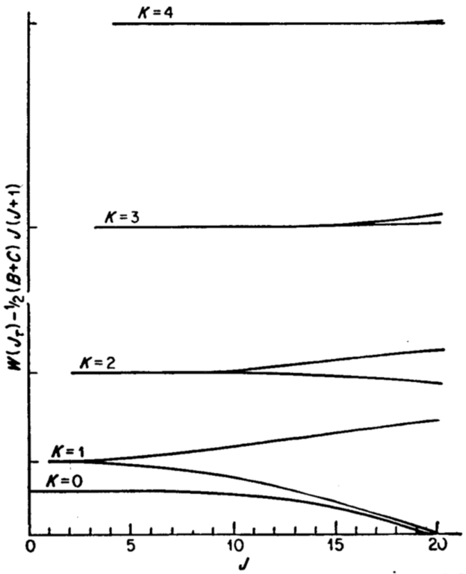
The corresponding definition for an oblate top is:

$$b_o = \frac{\kappa - 1}{\kappa + 3}$$

If the asymmetry is somewhat small, the spectrum can be analyzed as a symmetric top spectrum taking the asymmetry splitting into account.

The figure below shows this splitting for a slightly asymmetric prolate top (b_p = 0.01). Here the energy levels are plotted with the pure *J* contribution to the energy subtracted off.
There is no analytical formula, however, to relate the energies of the levels to the *J* and *K* quantum numbers.

Rotational levels of asymmetric tops only have only two "good" quantum numbers (that is quantum numbers that correspond to conserved quantities), and that is the total angular momentum quantum number, *J* and the projection of *J* on the space fixed *z*-axis, *m*.



Rotational energy of a slightly asymmetric top (b about 0.01) as a function of J. [The term $\frac{1}{2}(B + C)J(J + 1)$ is subtracted from the energy, *i.e.*, the deviations of the curves from horizontal lines represent the deviations from the levels of the symmetric top.] *(From Dieke and Kistiakowsky)*

The quantum number *K* is no longer a good quantum number insofar as the projection of *J* on the principal axis is no longer a conserved quantity. However, the levels of an asymmetric top are often labeled by the *K* quantum numbers corresponding to the levels of a prolate or oblate symmetric top, K_A, and K_C.

A notation that you will often see is J_{K_A,K_C} to designate the rotational levels of an asymmetric top.

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:

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

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 $\text{⍰}_{\text{⍰}el} = \text{⍰}_{\text{⍰}el}$. 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 $x = R - R_e$.

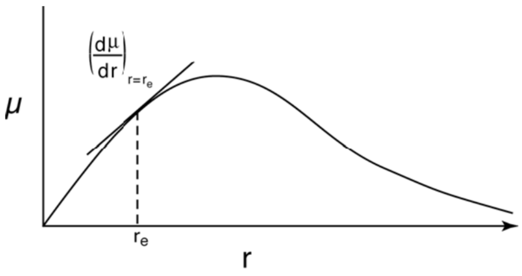
$$\mu(x) = \mu_0 + \left.\frac{d\mu}{dx}\right|_{x=0} x + \frac{1}{2}\left.\frac{d^2\mu}{dx^2}\right|_{x=0} x^2 + \ldots$$

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

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

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

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

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:

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

Using the fact that

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

we have

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

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

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

together with the $\Delta\mathrm{v}$ = ±1 and ΔJ = ±1 selection rules to see what the spectrum will look like.

$$\begin{aligned}\nu&=F(\mathrm{v}',J')-F(\mathrm{v}'',J'')\\&=T_e+\omega_e\left(\mathrm{v}'+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}'+\frac{1}{2}\right)^2+B_{\mathrm{v}'}J'(J'+1)-D_{\mathrm{v}'}J'^2(J'+1)^2\\&\quad-T_e+\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2+B_{\mathrm{v}''}J''(J''+1)-D_{\mathrm{v}''}J''^2(J''+1)^2\end{aligned}$$

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

$$\begin{aligned}\nu_0&=\omega_e\left(\mathrm{v}''+1+\frac{1}{2}\right)-\omega_e x_e\left(\mathrm{v}''+1+\frac{1}{2}\right)^2-\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)+\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2\\&=\omega_e\left(\mathrm{v}''+\frac{3}{2}\right)-\omega_e x_e\left(\mathrm{v}''+\frac{3}{2}\right)^2-\omega_e\left(\mathrm{v}''+\frac{1}{2}\right)+\omega_e x_e\left(\mathrm{v}''+\frac{1}{2}\right)^2\\&=\omega_e-\omega_e x_e\left[\left(\mathrm{v}''^2+3\mathrm{v}''+\frac{9}{4}\right)-\left(\mathrm{v}''^2+\mathrm{v}''+\frac{1}{4}\right)\right]\\&=\omega_e-\omega_e x_e(2\mathrm{v}''+2)\\&=\omega_e-2\omega_e x_e(\mathrm{v}''+1)\end{aligned}$$

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

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

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

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

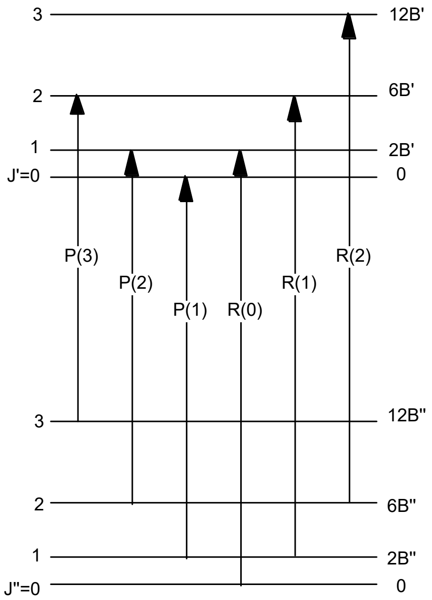
I will neglect the centrifugal distortion part for now. Rearranging, we get

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

<u>*P* Branch:</u> **(Δ*J* = -1)** *J'* = *J''* - 1

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

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.

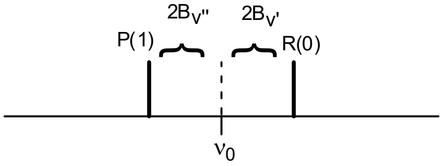
<u>First</u>, notice that there is no transition right at the band origin, ν_0. You can see that by letting *J''* = 0, the first transition in the *R* branch is:

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

The first in the *P* branch is:

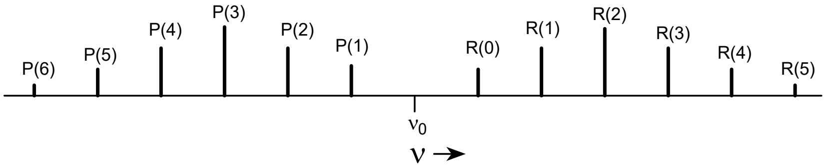
$$P(1) = \nu_0 - 2B_{v''}$$

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



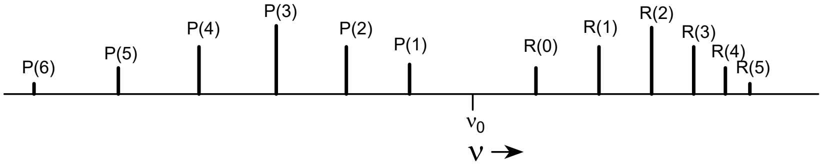
The spacing between $R(0)$ and $P(1)$ is $2(B_{v'} + B_{v''})$. If $B_{v'}$ and $B_{v''}$ were equal, this would be a gap of $4B$. This gap is called the ***null gap.*** The band origin, ν_0, is approximately in the center.

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 $2B$.



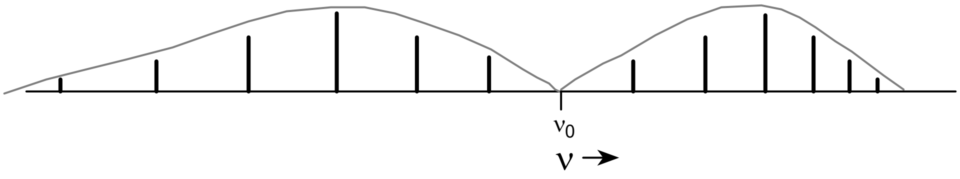
The inclusion of this second term will shift the levels in each branch by an amount that depends upon J''^2. For the infrared spectrum of a diatomic molecule, $B_{v'}$ is always less than $B_{v''}$. This is because of anharmonicity in the potential. The average bond length is always a bit longer in a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

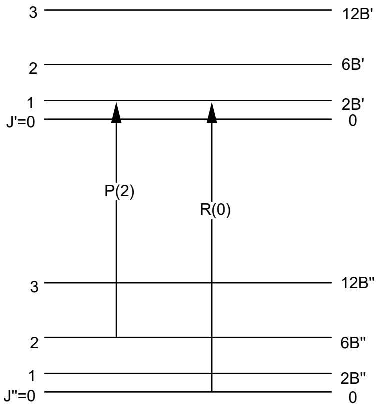
$$f_J = \frac{(2J+1)e^{-\frac{BJ(J+1)}{k_bT}}}{Q_{Rot}}$$

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

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

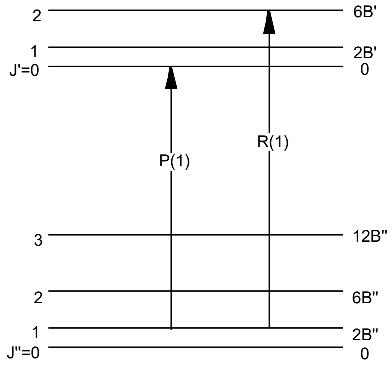
In general, one can write

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

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

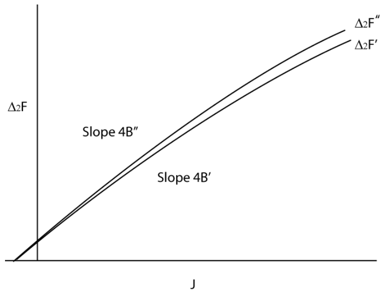
$$\Delta_2 F' = R(J) - P(J) = 4B_{v'}\left(J + \frac{1}{2}\right)$$

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*.

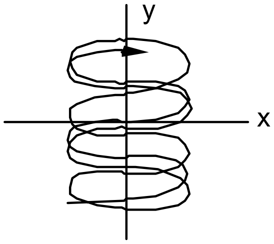
4.2 Polyatomic Vibration

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 ***<u>normal vibration or a normal mode.</u>*** 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.

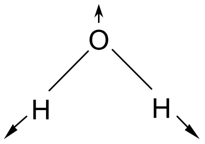
The number of normal mode for a molecule can be derived by considering the degrees of freedom. For a molecule consisting of N atoms the total number of degrees of freedom equals $3N$. To describe the position of the molecule 3 degrees of freedom are required. The orientation in space of a molecule is 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 $3N$-6 for a non-linear molecule and $3N$-5 for a linear molecule.

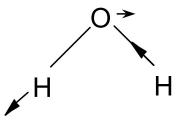
As the number of normal modes equals the number of vibrational degrees of freedom we find for the number of normal modes:

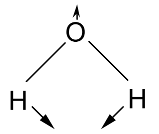
$3N$-6	for a non linear molecule
$3N$-5	for a linear molecule

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.

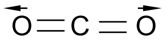
In water, as we will see later these normal vibrations are:

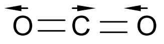

Symmetric Stretch

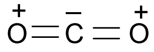

Antisymmetric Stretch

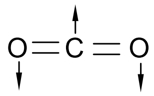

Bend

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:

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

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:

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

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

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

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.

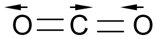
$$\psi_0 = N_{01} e^{-\frac{\alpha_1 Q_1^2}{2}} N_{02} e^{-\frac{\alpha_2 Q_2^2}{2}} N_{03} e^{-\frac{\alpha_3 Q_3^2}{2}} \ldots$$

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



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

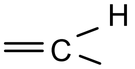
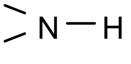
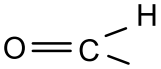
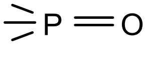
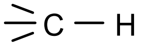
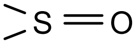
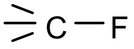
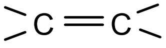
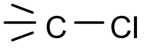
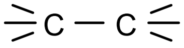
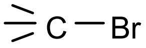
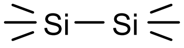
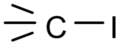
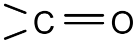
The normal modes of a molecule involve movements of essentially all the atoms (except in cases in which by symmetry a central atom must remained fixed). The normal mode is a global molecular motion in which all the atoms move in phase and at the same frequency.

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		
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Angle bending | **Angle bending**

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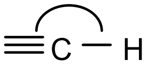
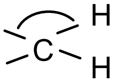
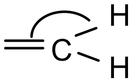
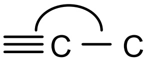
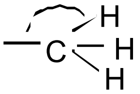
	700		1450
	1100		300
	1000		

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.

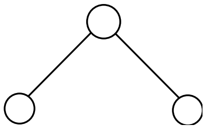
If one knows the displacement vectors corresponding to a normal mode, one can find the symmetry properties of that mode by noting the effect of the symmetry operations on these vectors. (This works well with non-degenerate vibrations but is more complex with degenerate vibrations.)

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.

$\chi(E) = 3N-6$ (or $3N-5$)	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.

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_j. 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

$$\psi_{1vib} = \psi''_{\mathrm{v}1}\,\psi''_{\mathrm{v}2}\,\psi''_{\mathrm{v}3}\cdots\psi''_{\mathrm{v}(3N-6)}$$

where $\psi''_{\mathrm{v}1}, \psi''_{\mathrm{v}2}$, etc. represent the different normal modes for the lower state. The final state we write as:

$$\psi_{2vib} = \psi'_{\mathrm{v}1}\,\psi'_{\mathrm{v}2}\,\psi'_{\mathrm{v}3}\cdots\psi'_{\mathrm{v}(3N-6)}$$

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), and B_1 (polarized along the *x*-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,

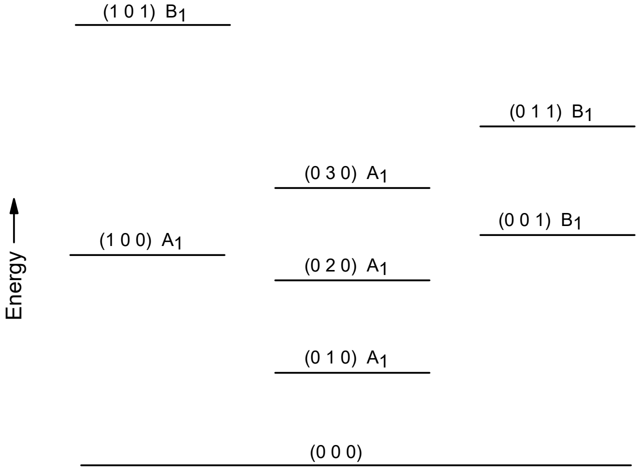
$$\Gamma\left(\psi_{\mathrm{v}=2}\right)=\left(E\right)^{2}\neq E\otimes E$$

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 ΔK=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):

$\Delta K = 0,\ \Delta J = \pm1$ if $K = 0$
$\Delta K = 0,\ \Delta J = 0, \pm1$ if $K \neq 0$

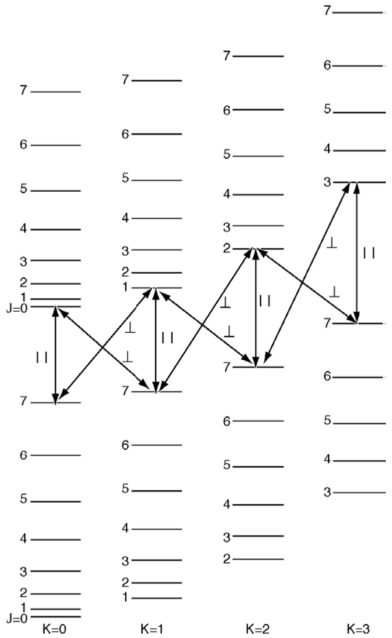
- If the change in dipole moment is perpendicular to the top axis (perpendicular band):

$\Delta K = \pm1,\ \Delta J = 0, \pm1$

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.



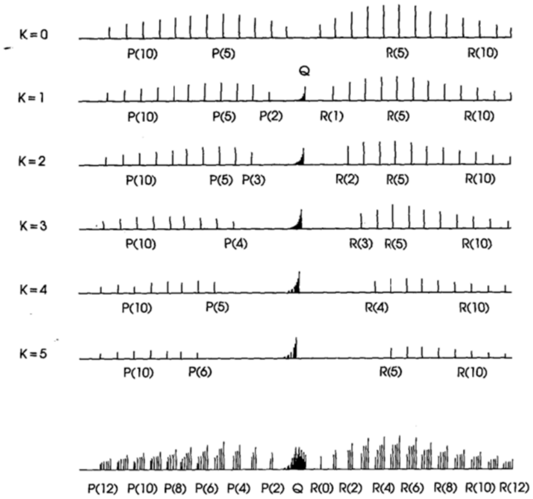
(Note that the arrows indicate only the change in K, not the change in J)

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.

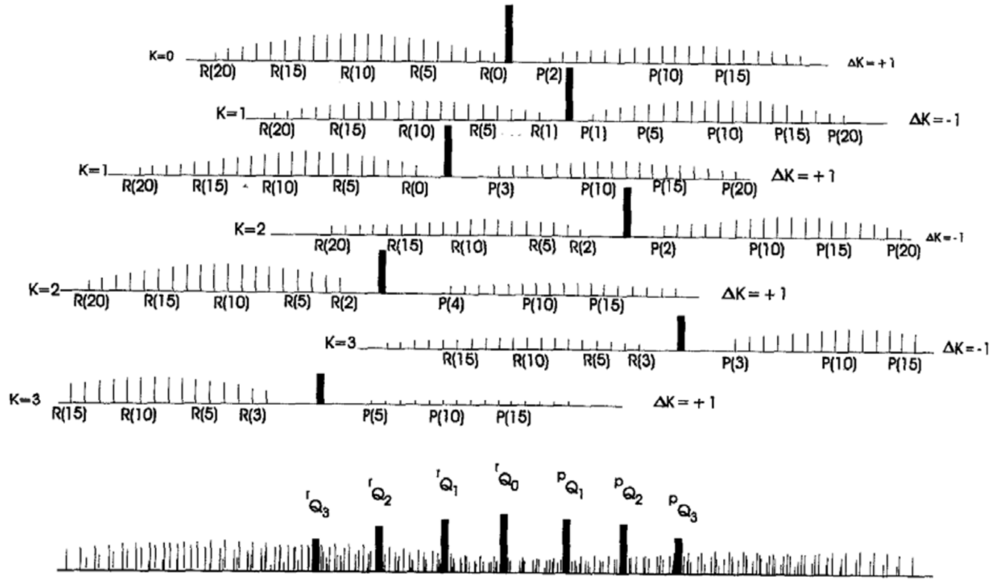


Perpendicular bands

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 $\Delta J = \pm 1$ 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 ΔK or ΔJ is indicated by the *P Q R* notation.

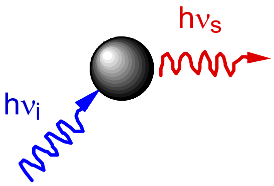
Thus, if one writes $^{Q}P_2(3)$ this means a transition that starts with *K*=2 and *J*=3 in the lower vibrational state and goes to *K*=2 and *J*=2 in the upper vibrational state.

4.4 Raman Spectroscopy

4.4.1 Introduction

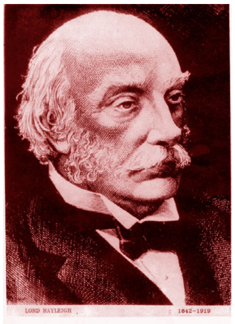
Now I would like to address the subject of Raman Spectroscopy. Although one cannot truly do justice to this subject in the time we have, I will try to give you an appreciation for its important features.

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).

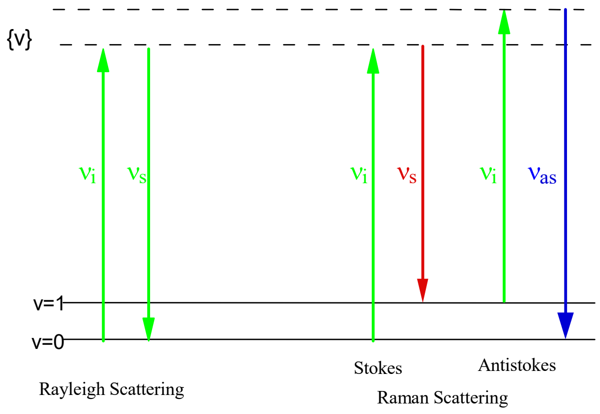


Lord Rayleigh

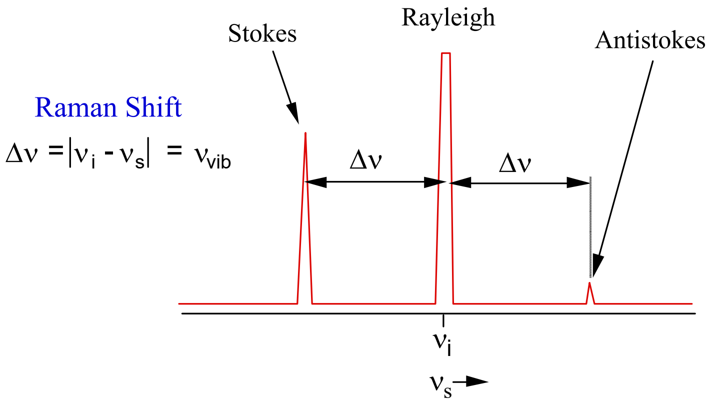
Chandrasekhara Raman

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**.

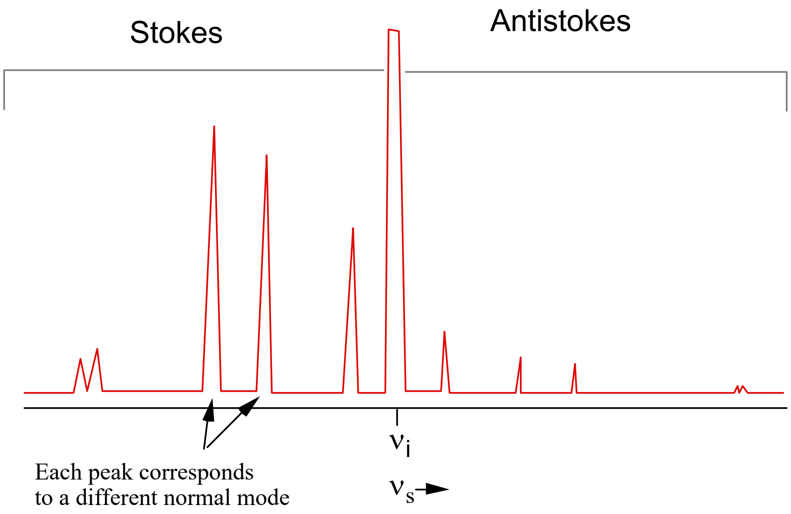


In Raman Scattering, information is contained in the difference in frequency between the incident and scattered photons, for this corresponds to vibrational and rotational energy level spacings of the molecule. This difference, $\Delta\nu$, is called the **Raman Shift.**

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

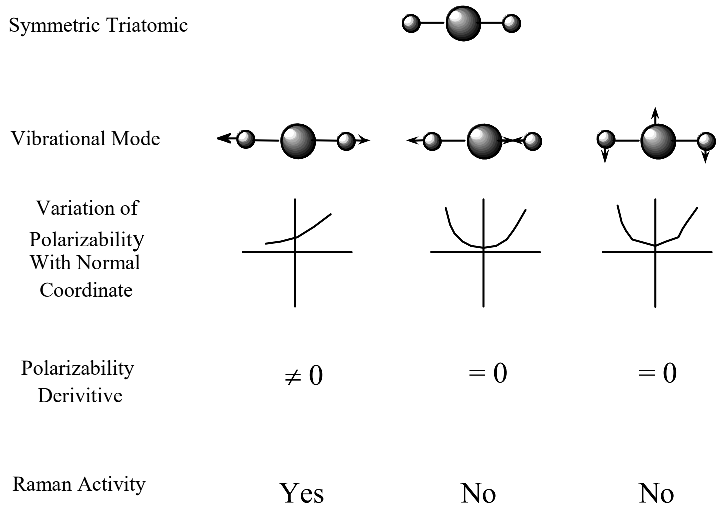
$$\Gamma\left(\psi_2^*\right) = \Gamma\left(\alpha_{ij}\right)$$

One simply looks in the character table for the different components of α. 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.

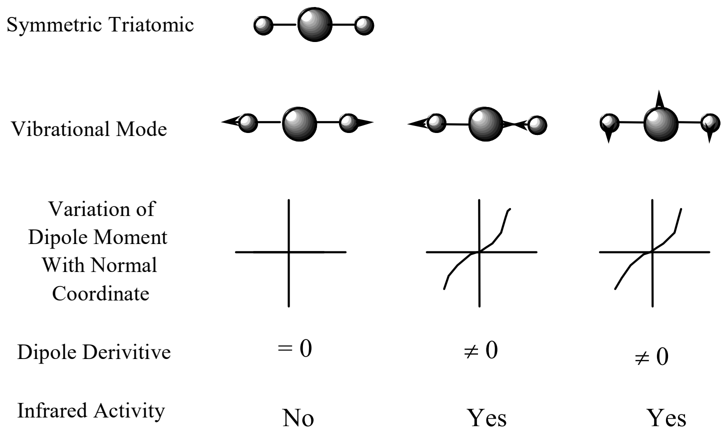
There is one important to thing to notice. If you look at character tables for a group in which there is a center of inversion, you will find that the symmetry species that contain the translations in the *x*, *y*, and *z* directions will be mutually exclusive from those that have the components of the 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.

5 Electronic Spectroscopy

Electronic spectroscopy involves transitions in which the electronic state changes. In case of molecules the vibrational state and rotational state will change in addition.

We will begin our treatment of this subject with atoms. Electronic spectroscopy of atoms is a powerful spectroscopic tool and is often used in analytical chemistry to determine the atomic composition of a substance. Next we will move on to diatomic molecules. Some of the important principles that we will find will be equally applicable to polyatomics. It is not clear how much time we will have left to much time to spend on electronic spectroscopy of polyatomics themselves, but I will at least highlight some of the most important points.

For diatomic molecules that have no unpaired electrons and no net electronic orbital angular momentum in the initial or final electronic state, electronic spectroscopy can be no more complex that rotation-vibration spectroscopy of diatomics. However, once one involves states in which one has either net orbital or spin angular momentum in one of the two electronic states involved in the transition, the rotational structure of the electronic transition becomes more complex.

5.1 Atomic Spectroscopy

In our discussion on spectroscopy up to now we have only looked at molecules since atoms do not have vibrational and rotational degrees of freedom. However, as we have seen before atoms do possess electronic structure. We will start our discussion on electronic spectroscopy with atoms, more specifically with the hydrogen atom.

5.1.1 Hydrogen atom

We have seen before that the energy levels of the hydrogen atom are given by:

$$E_n = -\frac{\mu e^4}{8\varepsilon_0^2 h^2 n^2} \qquad n = 1,2,3,\ldots$$

whereas the eigenfunctions are given by:

$$\psi_{nlm}(r,\theta,\varphi) = R_{nl}(r) Y_l^m(\theta,\varphi)$$

Here $R_{nl}(r)$ are the associated Laguerre functions and $Y_l^m(\theta,\varphi)$ the well-known spherical harmonics.

Although the energy is solely determined by the principle *n* quantum number one should realize that the levels are described by two additional quantum numbers, being *l* the total angular momentum and *m* the projection of *l* onto the space fixed *z*-axis. When discussing the selection rules for electronic transitions in hydrogen and other atoms one has to take these quantum numbers into account.

As we have seen before in our discussion of rotational and vibrational spectroscopy the intensity of a transition is related to:

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

In case of a hydrogen atom the total wavefunctions are simply the electronic wavefunctions, *i.e.*

$$\psi_2 = \psi_{2elec} \qquad \text{and} \qquad \psi_1 = \psi_{1elec}$$

and equal

$$\psi_{2elec}(r,\theta,\varphi) = R_{n'l'}(r)Y_{l'}^{m'}(\theta,\varphi)$$

and

$$\psi_{1elec}(r,\theta,\varphi) = R_{n''l''}(r)Y_{l''}^{m''}(\theta,\varphi)$$

In the expression above for the transition intensity μ is again the dipole moment ***operator*** (it is obvious that an atom does not have a permanent dipole moment but one can readily define the dipole moment operator) which is defined as

$$\boldsymbol{\mu} = \sum_j q_j \mathbf{r}_j$$

where *j* represents the summation over all charges, *i.e*. nuclei and electrons.

In the case of atoms where the center of gravity is located on the nucleus this expression simplifies to a sum over electrons:

$$\boldsymbol{\mu} = -\sum_i e\mathbf{r}_i$$

This expression simplifies even further in the case of a hydrogen atom where there is only one single electron.

$$\boldsymbol{\mu} = -e\mathbf{r}$$

Because of the spherical symmetry of the hydrogen atom it is convenient to write the dipole moment in spherical coordinates.

$$\mu_x = -er\sin\theta\cos\varphi$$

$$\mu_y = -er\sin\theta\sin\varphi$$

$$\mu_z = -er\cos\theta$$

Making use of these expression, the intensity for transitions between states in the hydrogen atom is now determined by the integral:

$$\int \left(R_{n'l'}(r)Y_{l'}^{m'}(\theta,\varphi)\right)^{*} -er\cos\theta\left(R_{n''l''}(r)Y_{l''}^{m''}(\theta,\varphi)\right)d\tau$$

Again we can separate the variables to rewrite this as:

$$-e\int R_{n'l'}^{*}(r)rR_{n''l''}(r)d\tau_r \int Y_{l'}^{m'*}(\theta,\varphi)\cos\theta Y_{l''}^{m''}(\theta,\varphi)d\tau_{\theta\varphi}$$

The second part of the expression we have already evaluated before in our discussion on rotational and vibrational spectroscopy and yields the selection rules:

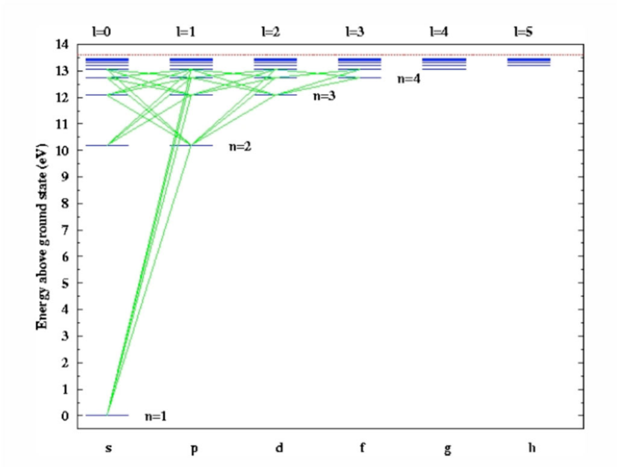
$l' - l'' = \Delta l = \pm 1$ and $m' - m' = \Delta m = 0$

In case one not only considers the μ_z component but also the μ_x and μ_y components on finds for the selection rules:

$\Delta l = \pm 1$ and $\Delta m = 0, \pm 1$

Evaluation of the first integral in the expression above shows that the value of this integral is generally non-zero independent of the quantum numbers *n* and *l*.

We can now plot the allowed transition of the hydrogen atom in a so called Grotrian diagram. We observe the well-known transitions (Lynmann, Balmer and Paschen series) in the hydrogen atom that we have already encountered before. At that time we did not concern ourselves with the selection rules, we simply said that we could change the *n* quantum number in an arbitrary way and did not discuss the selection rules for the *l* and *m* quantum numbers. Now we see that these can only change by certain amounts. Since the energy levels do not depend on these quantum numbers the spectrum is identical to that without considering the selection rules for the *l* and *m* quantum numbers.



5.1.2 Helium Atom

When discussing the electronic structure of the helium atom we saw that the electronic repulsion between the two electrons prevented us from solving this problem exactly. In the absence of this interaction we could write the Hamiltonian as the sum of two hydrogen atom Hamiltonians. In this case we could write the total wavefunction as the product of two hydrogen atom wavefunctions. If we where to use these wavefunctions in the expression to evaluate the selection rules we would find the same selection rules as for the hydrogen atom.

However, we already saw that the presence of this inter-electronic repulsion makes that the angular momentum of individual electrons, l_i , is not a conserved quantity. We did see that the total angular momentum

$$L = \sum_i l_i$$

is a conserved quantity. This has also an effect on the selection rules. Whereas for the hydrogen atom we found that the angular momentum of the electron has to change by one quantum we now could show that the total angular momentum has to change by one quantum:

$$\Delta L = \pm 1$$

In our discussion of the electronic structure of atoms we also saw that we had to include the spin of the electron for a proper description. We found that in the case of the helium atom we could write the total wavefunction as the product of a spatial and a spin wavefunction:

$$\psi_{Total} = \psi_{spatial}\psi_{spin}$$

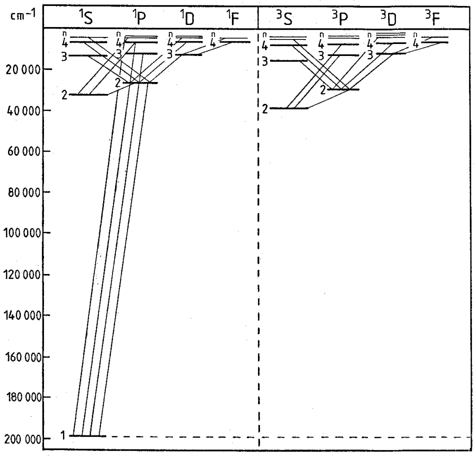
We just saw that the dipole moment acts only on the spatial coordinates and not on the spin coordinates. This implies that we can now write the transition probability integral as:

$$\int \left(\psi_{2spatial}\psi_{2spin}\right)^{*} \hat{\mu}\psi_{1spatial}\psi_{1spin}\, d\tau = \int \psi_{2spatial}^{*}\hat{\mu}\psi_{1spatial}\, d\tau_{spatial} \int \psi_{2spin}^{*}\psi_{1spin} d\tau_{spin}$$

The first integral on the right hand side gives the selection rules discussed above. The second integral will give the selection rules for the spin quantum numbers. Since we know that the eigenfunction of an operator form a complete orthonormal set we find that the spin wavefunctions have to be equal in both states for this integral to be non-zero. Consequently we have the selection rule:

$$\Delta S = 0$$

We saw that the application of the Pauli principle to the helium atom implied that for the ground state of the helium atom where both electrons reside in the same spatial orbital, the spin wavefunction has to be antisymmetric. This in turn implied that the total spin *S* equaled zero and that the ground state corresponded to a singlet state. This has not to be true for excited states where the electrons occupy different spatial orbitals. For excited states therefore both singlet and triplet states exist which have nearly the same energy, the triplet states being slightly lower in energy in accordance with Hund's rules. Since transitions between the singlet and triplet states are forbidden by the selection rules one often shows the singlet and triplet systems separately in the Grortian diagrams.



5.1.3 Multi-electron Atoms

The treatment of atoms consisting of more than 2 electrons is not very different from that of helium. We saw before that we can use the Russell-Sanders coupling approximation to derive the states (designated by term symbols, $^{2S+1}L_J$) from any electron configuration. One can now derive the following general selection rules.

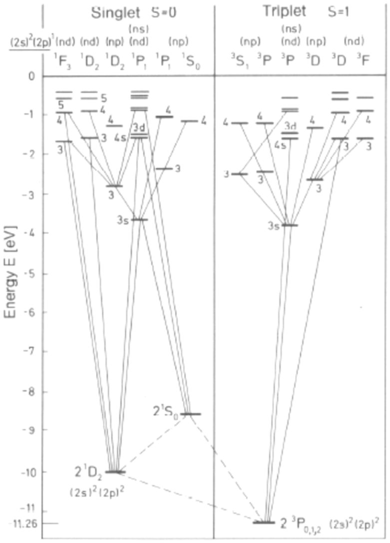
1. $\Delta L = 0, \pm 1$
   The selection rule $\Delta L = 0$ is not valid for states having *L*=0

2. $even \not\leftrightarrow even, \quad odd \not\leftrightarrow odd, \quad even \leftrightarrow odd$
   Here even and odd refer to the arithmetic sum $\sum_i l_i$ over all the electrons. This selection rule is called the ***Laporte*** rule. An important result of this rule is that transitions between states arising from the same electron configuration are forbidden. This has important consequences. For example transitions between the ^1P state and ^1D states of carbon which both arise from the excited $1s^2 2s^2 2p^1 3d^1$ configuration are forbidden by the Laporte rule (but not forbidden by rule 1).

3. $\Delta J = 0, \pm 1$
   The selection rule $\Delta J = 0$ is not valid for states having *J*=0

4. $\Delta S = 0$
   This selection rule is only valid if the spin-orbit coupling is small. It is therefore only applicable for those atomic systems that can be accurately described by the Russell-Sanders coupling scheme.

As an illustration of these selection rules let us have a look at the Grotrain diagram for carbon shown below. Transitions between states derived from the ground state electron configuration are not allowed based on the ΔL and ΔS selection rules. From the diagram it is clear that even for a relative simple atom as carbon many electronic transitions are possible. We also see that the transitions between the ^1P state and ^1D states that both arise from the $1s^22s^22p^13d^1$ configuration are forbidden by the Laporte rule. For atoms containing a much larger number of electrons, the number of states and thus transitions increases dramatically which makes the resulting spectra rather complex and difficult to analyze.



5.2 Vibrational structure of electronic bands

In contrast to atoms, electronic transitions in molecules can be accompanied by changes in vibrational and rotational states. It is therefore that by an electronic band I refer to the entire spectrum including all the transitions between one electronic state and another.

To get an overview of what an electronic band will look like, consider the following. In each electronic state we have electronic, vibrational, and rotational energy. I will use the notation T_e for electronic energy in cm^{-1}, G(v) for the vibrational energy, and F(J) for the rotational energy.

For the upper state of the electronic band we can therefore write

$$E' = T_e' + G' + F'$$

and for the lower state

$$E'' = T_e'' + G'' + F''$$

This neglects the interaction of rotation and vibration, however this simple treatment will allow us to see the overall structure of the band. We can look at the details later.

Neglecting vibration-rotation interaction, the frequencies of the transitions in a given electronic band can therefore be written:

$$\begin{aligned}\nu = E' - E'' &= \left(T_e' - T_e''\right) + \left(G' - G''\right) + \left(F' - F''\right)\\ &= \quad \nu_e \quad + \quad \nu_{vib} \quad + \quad \nu_{rot}\end{aligned}$$

The first part is simply the difference in energy between the bottoms of the two electronic potential curves and has a fixed value for a particular electronic band.

The second two parts give the vibrational and rotational structure respectively. Because the rotational energies are small with respect to the vibrational energies, the rotational structure will appear as fine structure on each vibrational band but will not alter the overall appearance of the band.

I will first focus on the vibrational structure of the electronic band to get some idea of the overall shape of the spectrum. I will then go on to discuss the rotational structure of the electronic band.

As we will see in the next section, there are no strict rules that govern the change in vibrational quantum number that accompanies an electronic transition. The Franck-Condon Principle, which we will discuss shortly, determines the intensities of the transitions for different values of Δv. Because of the lack of a strict Δv selection rule, there is potentially much information in an electronic transition.

I will talk separately about two different types of electronic spectra: ***absorption spectra*** and ***emission spectra.***

Absorption spectra are caused by molecules in the lower electronic state that make a transition to the upper state upon absorbing a photon. Emission spectra are caused by molecules in the upper electronic state spontaneously make a downward transition and in doing so, emit light.

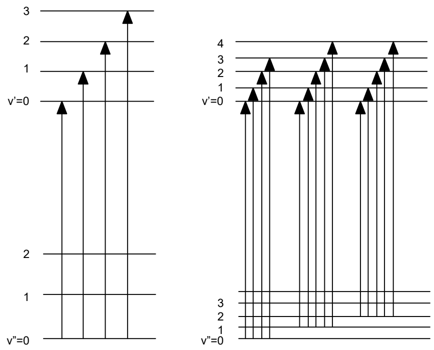
In our discussions of other types of spectroscopy, we have considered only absorption spectra. That is because the lifetimes of vibrational and rotational states are sufficiently long that molecules will more often than not collide with other molecules and give their energy off through the collision before they have the chance to emit a photon. While one can observe infrared and even microwave emission, one must look at samples at very low pressure where the collision frequency is low. Moreover, detectors that operate in this frequency range are not so sensitive.

In electronic spectroscopy, the radiative lifetimes are sufficiently short that molecules can easily emit before they undergo a collision. In addition, detectors for visible and ultraviolet light can be very sensitive.

Let us first consider absorption spectra.

The overall appearance of an electronic absorption band depends upon the vibrational spacings and the temperature of the sample. If the vibrational spacing in the lower state is high, most of the population will be in the ground vibrational state. Thus, the spectrum will contain a single ***progression*** of vibrational transitions, all of which originate in the ground vibrational state of the lower electronic state and go to different vibrational states in the upper electronic manifold (as shown on the left in the figure below).

Note that we are not applying a Δv=±1 selection rule here. The vibrational selection rules are given by the Franck-Condon principle, which we will consider shortly. This principle allows for larger changes in vibrational quantum number.



However if the vibrational spacings in the lower electronic state are small (as in the right part of the figure above), there may be significant population in several vibrational states. In this case there will be a series of vibrational progressions originating from different initial states. If the vibrational spacing of the upper and lower electronic states is similar, many of these transitions will be very close in frequency and may overlap.

For example, in the right hand side of the figure, notice that the 0-0 band will be similar in energy to the 1-1 band and the 2-2 band. This ***sequence*** of bands that differ by one vibrational quantum number in both the lower and upper electronic manifolds are called ***sequence bands.***

Any band that originates from a vibrational state other than $v''=0$ is also called a ***hot band.***

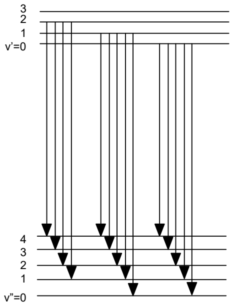
Electronic spectra can be greatly simplified by cooling the sample and getting rid of population in higher vibrational states. Normally one can only do this until the point at which the molecule condenses and becomes a liquid (at which point the spectrum changes fairly radically). There are some tricks, however, to cool molecules to a few degrees Kelvin and keep them in the gas phase. This dramatically reduces the complexity of a spectrum.

You can see that on the left-hand side of the above figure, the spacing of the members of the vibrational progression reflects the vibrational spacing in the upper electronic state. This provides information that allows one to find the shape of the potential curve in the excited electronic state.

On the right hand side of the figure, you can find transitions that go to the same final state but originate in different initial states. One can use these transitions in a manner similar to the method of combination differences to find the vibrational spacings in the lower electronic state.

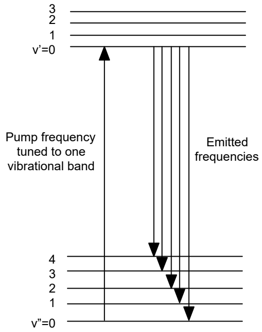
<u>Now let us consider emission spectra.</u>

The picture for emission spectra is almost the inverse of that for absorption spectra:



You can see that by choosing transitions that begin in the same upper state, one can get information on the vibrational spacing in the lower electronic state.

One important difference from absorption spectra, however, is that that molecules produced in an excited electronic state are often formed in more than one vibrational level (for example in an electrical discharge or in a flame), and this means that there will be several progressions in the emission spectrum. It is possible, if one uses optical excitation to populate a single level in absorption, to look at a single progression in the emission spectrum.



To summarize, from absorption and/or emission spectra between two different electronic states one can get information on the vibrational spacings in each electronic state and from this derive the potential. As we will see in a moment, even in a broad overview spectrum of the vibrational bands (without the rotational fine structure), the intensities will tell us something about the geometry change upon electronic transition. If one can go high enough in the upper electronic state, one can even determine the dissociation energy of the molecule.

Let us now look a little more deeply into the question of intensities and selection rules for the vibrational quantum numbers.

5.2.1 Vibrational selection rules

Recall that selection rules for all types of *dipole induced* transitions arise from the dipole moment integral:

$$(\mu_z)_{12} = \int \psi_2^* \, \hat{\mu}_z \, \psi_1 \, d\tau$$

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

where μ_z is dipole moment in lab fixed frame.

The first thing we have to do is to convert the dipole moment into the molecule fixed frame:

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

where μ_η is the dipole moment in the molecule fixed frame and θ is the angle between the lab and molecule fixed *z*-axis.

It is important to realize $\mu_\eta(q_i,R)$ depends on electronic and vibrational coordinates

We can then write our integral:

$$(\mu_z)_{12} = \left[\iint \psi_{2el}^*(q_i;R)\psi_{2vib}^*(R)\;\hat{\mu}_\eta(q_i,R)\psi_{1el}(q_i;R)\psi_{1vib}(R)\;d\tau_{q_i}\;d\tau_R\right]\times\left[\int \psi_{2rot}^*(\theta,\varphi)\cos\vartheta\,\psi_{1rot}(\theta,\varphi)d\tau_{\theta,\varphi}\right]$$

The second part gives the rotational selection rules. These are independent of the electronic or vibrational state and will give the usual selection rules:

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

We can rewrite the first part of the expression as:

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

The integral over the electronic coordinates defines what is known as the electronic transition dipole moment function:

$$\mu_e(R) = \int \psi_{2el}^*(q_i;R)\hat{\mu}_\eta(q_i,R)\psi_{1el}(q_i;R)d\tau_{q_i}$$

Note the differences between the electronic transition dipole moment function and the dipole moment function we defined when discussing vibrational spectroscopy. The transition dipole moment function is defined as the integral using $\psi_{2el}^*(q_i;R)$ and $\psi_{1el}(q_i;R)$ whereas for the evaluation of the dipole moment function the electronic wavefunctions are for the same electronic state, *i.e.* $\psi_{1el}^*(q_i;R)$ and $\psi_{1el}(q_i;R)$
We get various restrictions for electronic transitions from this factor $\mu_e(R)$.

1. One restriction, which we have already discussed in vibrational spectroscopy, comes from symmetry considerations. If we know the symmetries of the electronic states, one has to simply look in the character tables to find which components of the dipole moment have the proper symmetry to make the direct product in the integrand totally symmetric.

2. A second restriction comes if we write the electronic state as a function of spatial and spin coordinates. In this case, like for atoms there is a restriction that the spin state must not change during an electronic transition. This means that a singlet must go to a singlet and a triplet to a triplet, etc. This rule can break down due to spin-orbit coupling terms in the Hamiltonian. The breakdown is more severe if there are atoms of high atomic number.

The intensities for the vibronic transitions are then deduced from:

$$\int \psi_{2vib}^*(R)\ \mu_e(R)\,\psi_{1vib}(R)d\tau_R$$

Analogous to our discussion of vibrational spectroscopy we can expand the transition dipole moment as function of *R*.

$$\mu_e(R) = \mu_e(R_e) + \left(\frac{d\mu_e(R)}{dR}\right)_{R_e}\left(R - R_e\right) + \dots$$

As the first term will generally be the largest the integral for the transition dipole moment can be approximated as:

$$\int \psi_{2vib}^*(R)\ \mu_e(R)\,\psi_{1vib}(R)d\tau_R \cong \mu_e(R_e)\int \psi_{2vib}^*(R)\,\psi_{1vib}(R)d\tau_R$$

This approximation is equivalent to saying that the electronic transition moment is constant for all vibrational levels.

The intensity of an electronic transition, I, is therefore proportional to

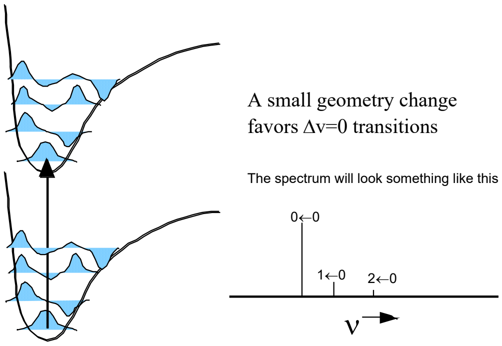
$$I \propto \mu_e(R_e)^2\left[\int \psi_{2vib}^*(R)\,\psi_{1vib}(R)d\tau_R\right]^2$$

The overlap integral of the vibrational wave functions, which is called a ***Franck-Condon factor,*** determines the strength of the transitions. It is important to realize that since the vibrational wavefunctions belong to different electronic states the vibrational integral is not equal to zero.

5.2.2 Franck-Condon Principle

The Franck-Condon Principle states that the intensities are given by the vibrational overlap integral, and this gives a simple yet powerful picture for interpreting electronic spectra. Note that there is overlap with the wave function of more than one vibrational level in the excited electronic state.

We can look at this integral graphically in the following manner:



Consider two nearly identical potential curves as sketched above:

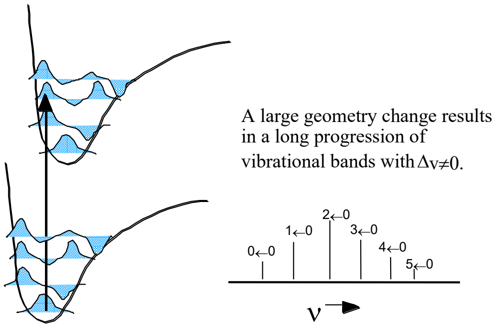
If the two curves lie right above each other (same equilibrium internuclear separation or same geometry), then the best overlap will be for final states with the same number of vibrational quanta as the initial state (Δv=0). You can see that all transitions with Δv not equal to zero will be small. In the limit that the two potential curves are exactly the same shape and have exactly the same equilibrium geometry, there will be a strict Δv=0 selection rule, since the eigenfunctions will be strictly orthonormal.

In this case where Δv=0 transitions dominate, the spectrum will consist of as strong 0-0 band and very weak 1-0 and 2-0 bands.

If the vibrational frequency is sufficiently low, there may be population in more than one initial level. In this case, there will also be sequence bands with Δv=0 such as a 1-1 or a 2-2 band. However, if the vibrational frequencies are not very different in the two electronic states, these will fall very close to the 0-0 band and will not change the overall appearance of the band structure.

Consider now the case in which the two potentials are shifted. This means that the molecule has a different geometry in the excited electronic state than the ground electronic state (different *R* for the case of a diatomic). You can see that in this case, shown below, the best overlap with the ground state wave function will be to states that have larger numbers of vibrational quanta. The overlap persists over a number of vibrational levels, thus giving rise to a ***vibrational progression***.

In general, long vibrational progressions in electronic spectra indicate an appreciable change in geometry in the excited electronic state. (*i.e.* shift in equilibrium positions of the potential wells).



This general principle holds for polyatomic molecules as well as for diatomics. Remember when we treated vibrational motion of polyatomics, the use of normal modes allowed us to treat a polyatomic molecule as a collection of harmonic oscillators. The same is true here. One can consider each vibrational mode separately. If there is a large change in geometry along a particular normal coordinate, then there will be a progression of

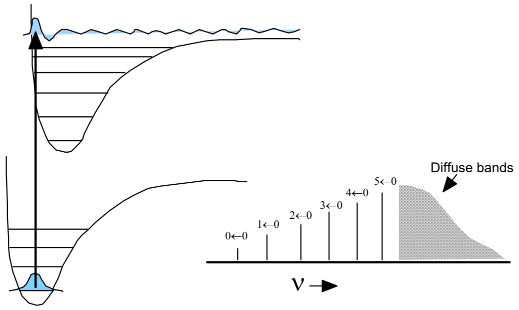
bands in that particular mode in the electronic spectrum. If the geometry doesn't change, then the most intense peak will be for $\Delta v=0$ for that mode.
Thus, one can look at an electronic spectrum and get an idea immediately about what the difference in geometry will be for the excited electronic state. However, what one sees in the spectrum are the geometry changes projected onto the normal modes of the molecule. We usually think of geometry changes in terms of bond length and angle changes. Because more than one normal mode can involve a particular bond vibration or angle bending motion, a change in a particular geometrical feature could cause a progression in more than one normal mode.

5.3 The FC principle and diffuse spectra

Recall that our discussion of the Franck-Condon principle considered two general cases.

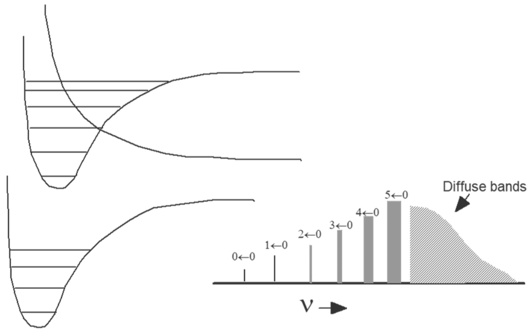
In one case, the excited state potential is very much like the ground state potential with little shift in the equilibrium bond distance. In this case, the strongest feature in the spectrum is the 0-0 band.

In a second case, there is a strong geometry shift that causes a long progression of vibrational bands. Let us now consider an extreme case of the second type. The best Franck-Condon factors might be for states that are actually above the dissociation threshold on the upper surface. Since the levels are not quantized at this energy, the bands will become diffuse (*i.e.,* continuous), although they will still show the same overall bandshape. This comes from the overlap with the continuum wave functions.



In this case, excitation of the bands higher than v=5 causes the molecule to dissociate. The energy of the photongoes into breaking the chemical bond, and thus no light can be re-emitted. This is one example of a *non-radiative process*.

Another scenario can be the following, see figure below.



In this case, a purely dissociative state crosses the upper bound state. Molecules excited to levels above the crossing point could potentially cross over and dissociate rather than radiate. This is called *predissociation*.

The levels are broadened by the time-energy uncertainty principle, and as the dissociation becomes faster, the possibility of light re-emission decreases.

These are two examples of non-radiative processes in diatomic molecules that are fairly common. These and other such processes are also common in polyatomics. I will briefly describe them in the following section.

5.4 Non-radiative processes

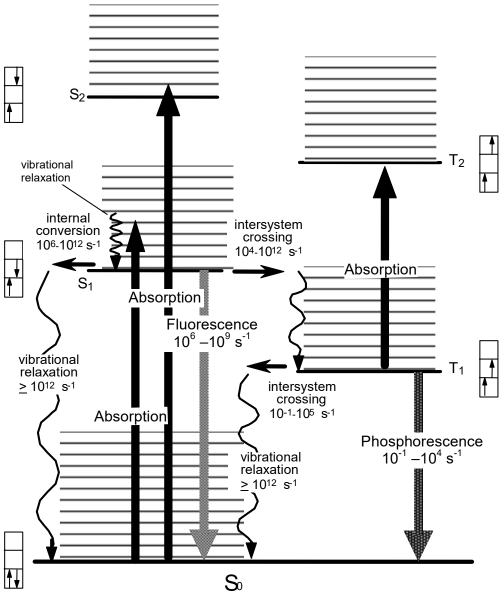
Think back to our treatment of the vibrational states of polyatomic molecules. Recall the complications that can arise when we have two vibrational states that are close in energy—in a perturbation theory picture the wave functions can "mix", which means that they have some character of each of the two near-resonant states. A similar situation occurs in electronic spectroscopy because there can be different energy levels at the same energy. As we will see in a moment, this kind of mixing represents a type of "non-radiative" energy transfer from one state to another.

One typically describes non-radiative processes in excited electronic states by the use of a *Jablonski diagram.* In this picture I no longer show potential curves since, for polyatomics there are too many dimensions. I will simply draw the levels.

Let me simply define the different terms that are used in this figure.

The significations S and T indicate singlet and triplet states (electronic states with paired and unpaired spins respectively).

Vibrational relaxation – the loss of vibrational energy through collisions with other molecules. This will happen both in the gas phase and in condensed phases, although generally much faster in the latter.



Internal conversion – a non-radiative process by which a molecule changes from one electronic state to another of the same multiplicity (i.e., singlet to singlet or triplet to triplet). It is a problem of mixing between electronic states that occurs due to terms in the electronic Hamiltonian that we neglected when we made the Born-Oppenheimer approximation.

Intersystem crossing- a non-radiative process by which a molecule changes from one electronic state to another of different multiplicity (i.e., singlet to triplet or triplet to singlet). It is a problem of mixing between electronic states that occurs due to spin-orbit terms in the electronic Hamiltonian.

Absorption – the absorption of a photon, causing a change in electronic state.

Fluorescence – the emission of a photon, causing a change from one electronic state to another of the same multiplicity.

Phosphorescence - the emission of a photon, causing a change from one electronic state to another of different multiplicity. Because this is formally forbidden by the electronic selection rules, it tends to be very weak and hence have a very long lifetime.

The numbers given in the figure are typical values for the rates of these various processes for a polyatomic molecule in solution. The situation is somewhat different for an isolated gas phase molecule.

In an isolated molecule, the only way to change energy is to radiate, and thus vibrational relaxation cannot occur. However, one can still have intersystem crossing and internal conversion as well as *redistribution* of energy between different vibrational modes. This latter process is called *intramolecuar vibrational energy redistribution* and is abbreviated *IVR*.

In the condensed phase, vibrational relaxation is very fast, and this means that very quickly a molecule moves to the lowest vibrational level of whatever electronic state it is in. One typically observes fluorescence (or phosphorescence) from these lowest vibrational levels.

It is important to have this picture in mind and to know the difference between what happens in the gas phase and what happens in the condensed phase.

5.5 Rotational structure of electronic transitions

Recall that when discussing diatomic molecules during the Quantum Chemistry course we introduced the concept of term symbols to describe electronic states of molecules.

Term symbols are denoted as:

$$^{2S+1}\Lambda_{\Omega}$$

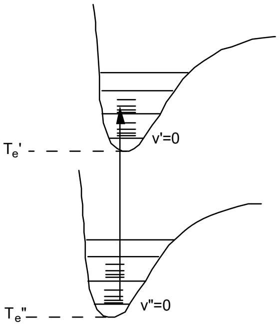
where, $2S+1$ is the spin multiplicity, Λ the projection of the total electronic orbital angular momentum *L* onto the bond axis and Ω the projection of the total angular momentum (including spin angular momentum) onto the bond axis. For Λ = 0, 1, 2 . . the states are designated as Σ, Π, Δ . . .

For the moment, we will consider only $\Sigma - \Sigma$ transitions. Other types of transitions will have similar overall properties, but the details will be different.

The rotational selection rule for diatomics with no electronic angular momentum, *i.e*. Σ states, is simply $\Delta J = \pm 1$. Since there is no electronic angular momentum, the change in angular momentum due to the absorption of the photon must go into a change in the mechanical rotation of the nuclei.

This case is similar to the rotational structure of infrared spectra. One observes two rotational branches in the electronic spectrum: a *P*-branch and an *R*-branch.

To see what the spectrum would look like, we simply have to take the difference in the energy level expression consistent with the rotational selection rules.



The transition frequency comes from the difference between these when you apply the selection rules.

In a manner analogous to that for infrared spectroscopy, we can define the part corresponding to the rotationally independent part of this expression as the **band origin.**

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

This represents the difference in electronic and vibrational energy of the two states (*i.e.*, the difference in energy of the two vibrational levels of the different electronic states).

The vibrational frequencies ω_e' and ω'' as well as the anharmonicities are completely unrelated because they refer to different potential curves (different electronic states).

We can then write

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

If we neglect the centrifugal distortion terms we have

$$\nu_{transition} = \nu_0 + B_\mathrm{v}' J'\left(J'+1\right) - B_\mathrm{v}'' J''\left(J''+1\right)$$

It is important to note here that these rotational constants are unrelated since they correspond to different electronic potential curves.

If we now apply the selection rules, we get *P* and *R* branches analogous to vibration-rotation spectroscopy

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

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

You can see that the overall pattern of rotational lines will be the same as in vibrational spectroscopy. There will be a *null gap* in the area around ν_0 where there is no transition, and then transitions spaced by approximately 2*B*.

The big difference here, however, is that the two rotational constants can now differ much more because the geometry of the molecule can be very different in the ground and excited electronic states.

If the *B*'s differ widely enough, then at high *J*, the last term in the above expressions can be larger that the first and cause the rotational transitions in the spectrum to go the other direction. The point at which the transition frequencies turn around and go in the other direction is called a ***band head.***

Case (1) $r_e' > r_e'' \Rightarrow B_v' < B_v''$ and $(B_v' - B_v'') < 0$

In this case, the *R* branch transitions, which initially go to higher wave number with increasing *J* will turn around and go to lower wave number at sufficiently high *J*. This causes a band head in the *R* branch.

Case (2) $r_e' < r_e'' \Rightarrow B_v' > B_v''$ and $(B_v' - B_v'') > 0$

In this case, the P branch transitions, which initially go to lower wave number with increasing *J* will turn around and go to higher wave number at sufficiently high *J*. This causes a band head in the *P* branch.

You can see that there will be a correlation between the vibrational structure of an electronic spectrum and the rotational structure in the following sense. If there is a large change in geometry between the ground and excited electronic state, this will result in Franck-Condon factors that favor a large change in the vibrational quantum number v.

At the same time, the change in geometry will mean the rotational constant will be different for the two states, and this may lead to a band head in one branch or the other. Thus, the strong change in geometry has important consequences both for the overall vibrational structure as well as for the rotational structure of the each vibrational band.

5.6 Electronic Spectroscopy of polyatomics

We have already discussed many topics associated with the electronic spectroscopy of polyatomic molecules. Although our discussion of the vibrational structure of electronic bands was focused on diatomics, the principles hold for each normal mode of a polyatomic molecule. The same is true for the Franck-Condon principle—one can take a cut through the potential curve in each normal coordinate, and everything that we discussed about the FC principle would hold for each coordinate. This implies that depending upon the geometry change of the molecule upon electronic excitation some normal modes show long progressions whereas others show no progressions at all.

In the electronic spectroscopy of polyatomic molecules one often uses the following notation to indicate the change in vibrational quantum numbers.

$$\nu_i{}^{v'}_{v''}$$

here ⍰$_i$ indicates the i^{th} normal mode, v" is the vibrational quantum number in the lower electronic state and v' that of the upper electronic state.

Some examples:

1_0^2	Normal mode 1 changes vibrational quantum number from 0 in the lower electronic state to 2 in the upper state.
3_1^2	Normal mode 3 changes vibrational quantum number from 1 in the lower electronic state to 2 in the upper state. This is a hot band transition (start from excited vibrational level).
$2_0^1 4_1^0$	Normal mode 2 changes vibrational quantum number from 0 in the lower electronic state to 1 in the upper state and at the same time normal mode 4 changes vibrational quantum number from 1 to 0. This is combination band transition (2 modes are involved) and a hot band transition (start from excited vibrational level)..

The transition from the vibrational ground state (vibrational quantum number of all normal modes equal zero) in the lower electronic state to the vibrational ground state of the upper electronic state is called the band origin and has the special notation.

$$0_0^0$$

Depending on the number of normal modes and whether they form long progression upon electronic excitation the spectrum can become very complicated. Let's have a look at an example. Assume we have a molecule with 3 normal modes that have the following frequencies.

	Vibrational frequencies Lower electronic state	Vibrational frequencies Upper electronic state
ν_1	2900 cm^{-1}	3000 cm^{-1}
ν_2	2200 cm^{-1}	2100 cm^{-1}
ν_3	800 cm^{-1}	600 cm^{-1}

Assuming that the ν_3 vibration forms a long progression the electronic spectrum might than look as in the figure indicated below.

The zero frequency in this figure corresponds to the frequency of the band origin, ν_0