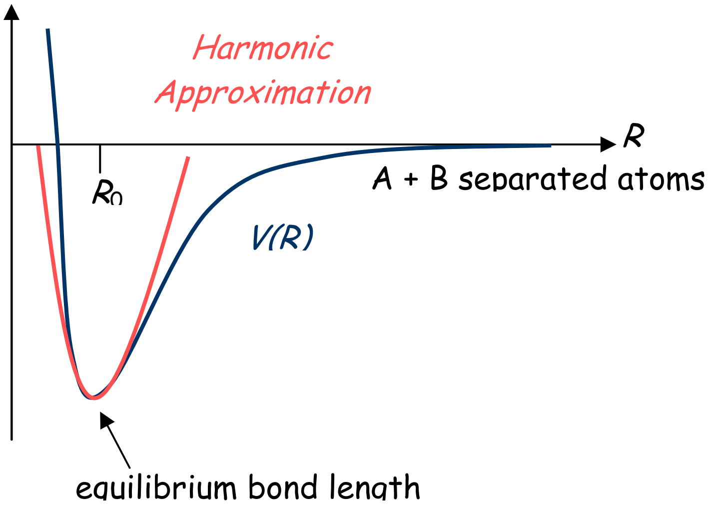
VIBRATIONAL SPECTROSCOPY

As we've emphasized many times in this course, within the Born-Oppenheimer approximation, the nuclei move on a potential energy surface (PES) determined by the electrons. For example, the potential felt by the nuclei in a diatomic molecule is shown in cartoon form at right. At low energies, the molecule will sit near the bottom of this potential energy surface. In this case, no matter what the detailed structure of the potential is, locally the nuclei will "feel" a nearly harmonic potential. Generally, the motion of the nuclei along the PES is called vibrational motion, and clearly at low energies a good model for the nuclear motion is a Harmonic oscillator.



Simple Example: Vibrational Spectroscopy of a Diatomic

If we just have a diatomic molecule, there is only one degree of freedom (the bond length), and so it is reasonable to model diatomic vibrations using a 1D harmonic oscillator:

$$\hat{H} = \frac{\hat{P}^2}{2\mu} + \frac{1}{2}k_o\hat{R}^2 = \frac{\hat{P}^2}{2\mu} + \frac{1}{2}m\omega_o{}^2\hat{R}^2$$

where k_o is a force constant that measures how stiff the bond is and can be approximately related to the second derivative to the true (anharmonic) PES near equilibrium:

$$k_o \approx \left.\frac{\partial^2 V}{\partial R^2}\right|_{R_0}$$

Applying Fermi's Golden Rule, we find that when we irradiate the molecule, the probability of a transition between the ith and fth Harmonic oscialltor states is:

$$W_{fi} \propto \frac{\left|V_{fi}\right|^2}{4\hbar^2}\left[\delta\left(E_i - E_f - \hbar\omega\right) + \delta\left(E_i - E_f + \hbar\omega\right)\right]$$

where ω is the frequency of the light (not to be confused with the frequency of the oscillator, ω_0). Because the vibrational eigenstates involve spatial degrees of freedom and not spin, we immediately recognize that it is the electric field (and not magnetic) that is important here. Thus, we can write the transition matrix element as:

$$\left|V_{fi}\right|^2 = \left|\int \phi_f^{\,*}\hat{\boldsymbol{\mu}}\bullet\mathbf{E_0}\phi_i d\tau\right|^2 = \left|\mathbf{E_0}\bullet\int \phi_f^{\,*}\hat{\boldsymbol{\mu}}\phi_i d\tau\right|^2 = \left|\mathbf{E_0}\bullet\int \phi_f^{\,*}e\hat{R}\phi_i d\tau\right|^2$$

Now, we define the component of the electric field, E_R, that is along the bond axis which gives

$$\left|V_{fi}\right|^2 = \left|E_R\int \phi_f^{\,*}e\hat{R}\phi_i d\tau\right|^2 = e^2\left|E_R\right|^2\left|\int \phi_f^{\,*}\hat{R}\phi_i d\tau\right|^2$$

So the rate of transitions is proportional to the square of the strength of the electric field (first two terms) as well as the square of the transition dipole matrix element (third term). Now, because of what we know about the Harmonic oscillator eigenfunctions, we can simplify this. First, we re-write the position operator, $\boldsymbol{R}$, in terms of raising and lowering operators:

$$\left|V_{fi}\right|^2 = e^2\left|E_R\right|^2\left|\int \phi_f^{\,*}\sqrt{\frac{\hbar}{2\mu\omega}}\left(\hat{a}_+ + \hat{a}_-\right)\phi_i d\tau\right|^2 = \frac{\hbar e^2}{2\mu\omega}\left|E_R\right|^2\left|\int \phi_f^{\,*}\left(\underbrace{\hat{a}_+}_{\sqrt{i+1}\;\phi_{i+1}} + \underbrace{\hat{a}_-}_{\sqrt{i}\phi_{i-1}}\right)\phi_i d\tau\right|^2$$

$$\Rightarrow \left|V_{fi}\right|^2 = \frac{\hbar e^2}{2\mu\omega}\left|E_R\right|^2\left(\left(i+1\right)\delta_{f,i+1} + i\;\delta_{f,i-1}\right)$$

where above it should be clarified that in this expression "i" never refers to √-1 – it always refers to the initial quantum number of the system. Thus, we immediately see that **a transition will be forbidden unless the initial and final states differ by one quantum of excitation**. Further, we see that the transitions become more probable for more highly excited states. That is, V_{fi} gets bigger as i gets bigger.

Combining the explicit expression for the transition matrix element with Fermi's Golden Rule again gives:

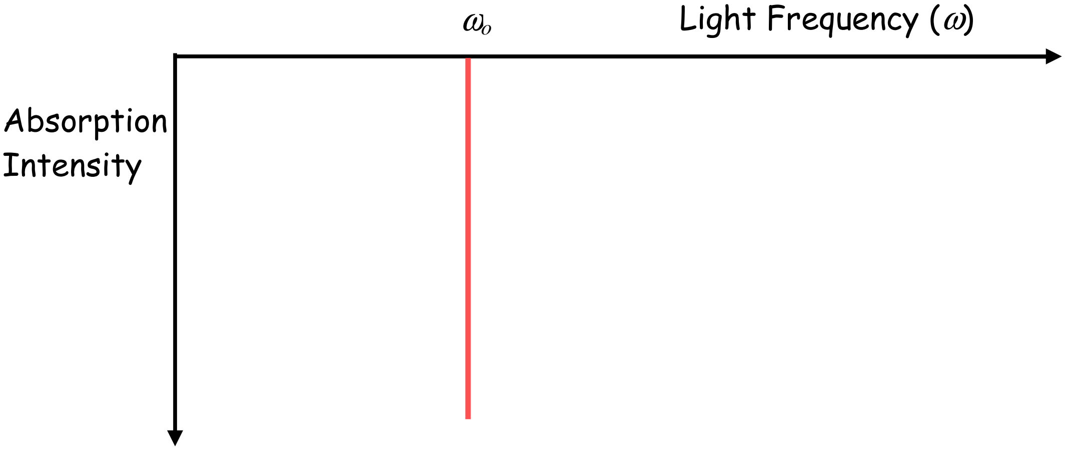
$$W_{fi} \propto \frac{e^2}{8\hbar\mu\omega}\left|E_R\right|^2\left(\left(i+1\right)\delta_{f,i+1} + i\;\delta_{f,i-1}\right)\left[\delta\left(E_i - E_f - \hbar\omega\right) + \delta\left(E_i - E_f + \hbar\omega\right)\right]$$

$$\Rightarrow W_{fi} \propto \left|E_R\right|^2\left\{\left(i+1\right)\delta_{f,i+1}\left[\delta\left(E_i - E_{i+1} - \hbar\omega\right) + \delta\left(E_i - E_{i+1} + \hbar\omega\right)\right]\right.$$
$$\left. + i\;\delta_{f,i-1}\left[\delta\left(E_i - E_{i-1} - \hbar\omega\right) + \delta\left(E_i - E_{i-1} + \hbar\omega\right)\right]\right\}$$

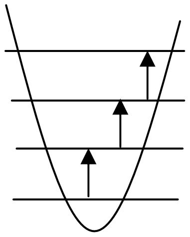
$$\Rightarrow W_{fi} \propto \left|E_R\right|^2 \Big\{ (i+1)\,\delta_{f,i+1}\left[\delta\left(\cancelto{0}{-\hbar\omega_o - \hbar\omega}\right) + \delta\left(-\hbar\omega_o + \hbar\omega\right)\right]$$
$$+ i\;\delta_{f,i-1}\left[\delta\left(\hbar\omega_o - \hbar\omega\right) + \cancelto{0}{\delta\left(\hbar\omega_o + \hbar\omega\right)}\right]\Big\}$$

$$\Rightarrow W_{fi} \propto \left|E_R\right|^2 \left\{(i+1)\,\delta_{f,i+1} + i\;\delta_{f,i-1}\right\}\delta\left(\hbar\omega_o - \hbar\omega\right)$$

Thus, we see that **a harmonic oscillator will only absorb or emit photons of frequency $\hbar\omega_o$, where ω_o is the frequency of the oscillator**. Thus, if we look at the absorption spectrum, for example, we will see absorption at only one frequency:

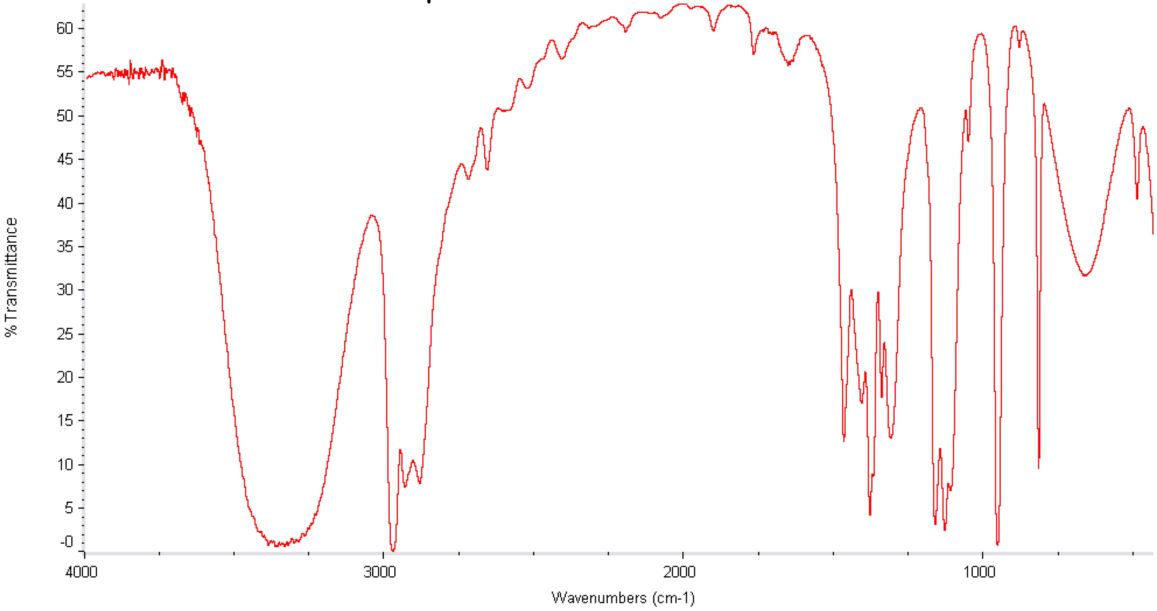


Molecular force constants are typically on the order of an eV per Å, which leads to vibrational frequencies that are typically between 500-3500 cm^{-1} and places these absorption features in the infrared. As a result, this form of spectroscopy is traditionally called IR spectroscopy. We associate the spectrum above as arising from all the n→n+1 transitions in the Harmonic oscillator (see left). Of course, most of the time the molecule will start in its ground state, so that the major contribution comes from the 0→1 transition. However, the other transitions occur at the same frequency and also contribute to the absorption.



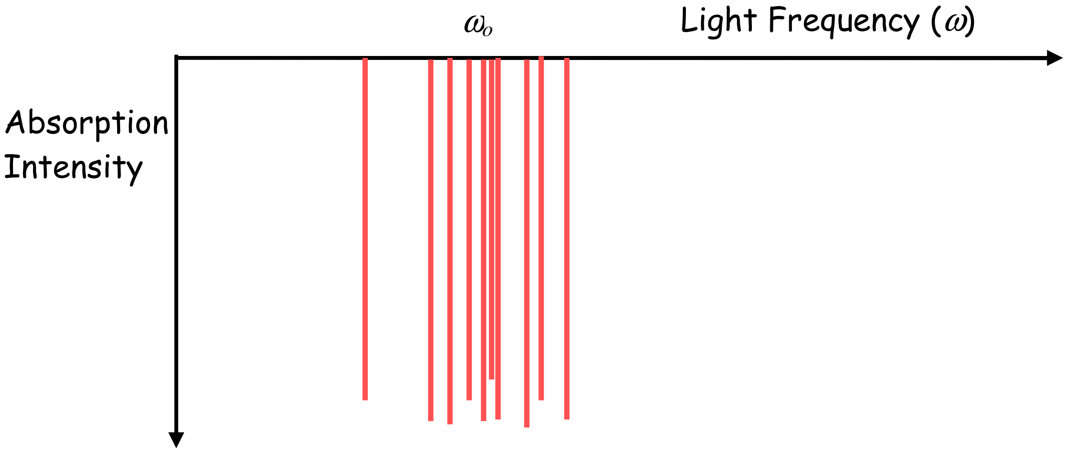
This is the classic paradigm for IR vibrational spectroscopy: each diatomic molecule absorbs radiation only at one frequency that is characteristic of the curvature of the PES near its minimum. Thus, in a collection of different molecules one expects to be able differentiate one from the other by looking for the frequency appropriate to each one. In particular there is a nice correlation between the "strength" of the bond and the frequency at which it will absorb.

Of course, we are not always or even usually interested in diatomics, and even diatomics are not perfect Harmonic oscillators. Thus, there are a number of reasons why IR absorption spectra do not really look like the classic Harmonic oscillator spectrum shown above, but more like:

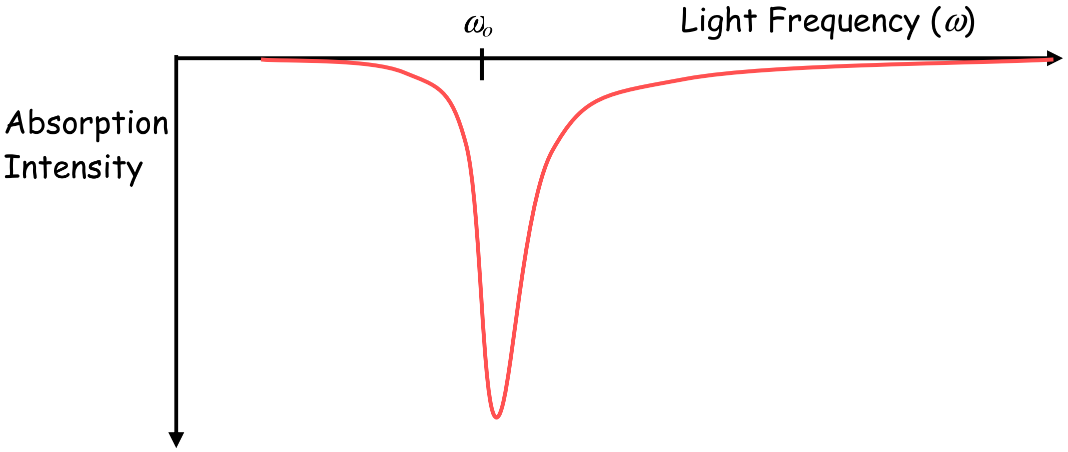


Heterogeneity

The primary reason the real spectrum above looks different than the model is because the real spectrum was taken in solution. The model is correct for a single diatomic, or for many, many copies of identical diatomic molecules. However, in solution, ever molecule is just slightly different, because every molecule has a slightly different arrangement of solvent molecules around it. These solvent molecules subtly change the PES, slightly shifting the vibrational frequency of each molecule and also modifying the transition dipole a bit. Thus, while a single hydrogen fluoride molecule might have a spectrum like the model above, a solution with many HF molecules would look something like:



Going over to the situation where there are 10^{23} HF molecules and recognizing that our spectra will tend to add the intensity of lines that are closer together than our spectrometer can differentiate, we anticipate that for a diatomic molecule in solution, the vibrational spectrum should look something like:



The resulting feature in the spectrum is usually called a lineshape. It primarily reflects the distribution of different environments surrounding your oscillators. Thus, by analyzing the lineshape of a well-known type of vibration (such as a C=O stretch) one can get an idea about the environments those CO groups live in: How polar are the surroundings? Are they near electron withdrawing groups? What conformations give rise to the spectrum? Finally, we should note that vibrational spectra recorded in the gas phase have very narrow linewidths, qualitatively resembling our model above.

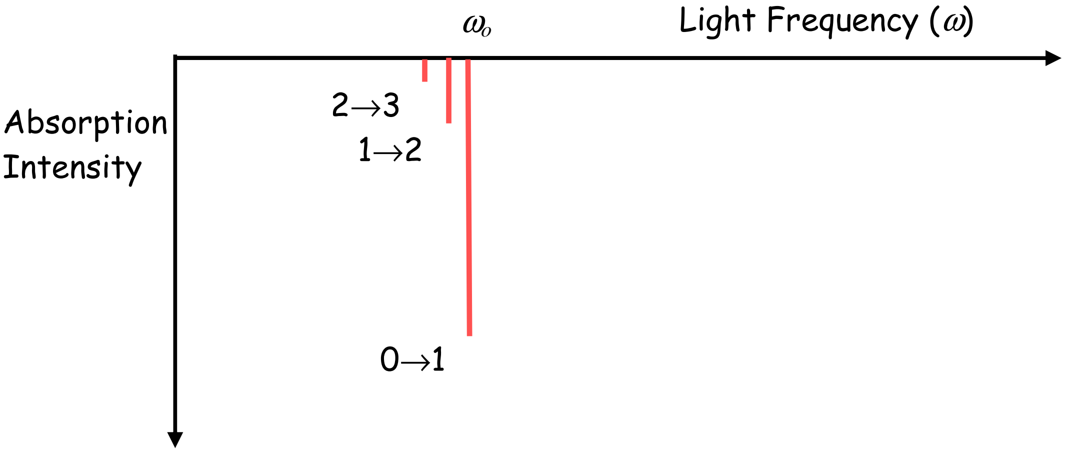
Anharmonicity

Another reason real spectra differ from our model is that assuming the PES is harmonic is only a model. If we want high accuracy, we need to account for anharmonic terms in the potential:

$$V(R)=\frac{1}{2}m\omega_o^2(R-R_0)^2+\frac{1}{6}\alpha(R-R_0)^3+\frac{1}{24}\beta(R-R_0)^4+\ldots$$

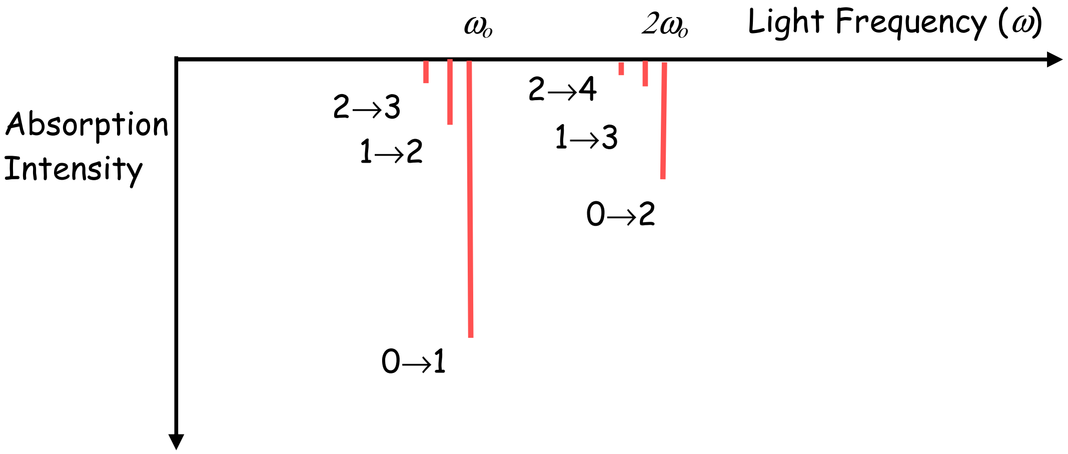
One can investigate the quantitative effects of the anharmonic terms on the spectrum by performing variational calculations. However, at a basic level there are two ways that anharmonic terms impact vibrational spectra:

1) *The energy differences between adjacent states are no longer constant.* Clearly, the eigenvalues of an anharmonic Hamiltonian will not be equally spaced – this was a special feature of the Harmonic system. Thus, for a real system we should expect the 0→1 transition to have a slightly different frequency than 1→2, which in turn will be different that 2→3 …. Generally, the higher transitions have lower (i.e. redshifted) energies because of the shape of the molecular PES – rather than tend toward infinity at large distances as the harmonic potential does, a molecular PES tends toward a constant dissociation limit. Thus, the higher eigenstates are lower in energy than they would be for the corresponding harmonic potential. Taking this information, we would then expect a single anharmonic oscillator to have a spectrum something like:



where we note that while the rate of, say, 1→2 is about twice that of 0→1 (because the transition dipole is twice as big) the *intensity* of 0→1 is greater because the intensity is (Probability of i being occupied)x(Rate of i→f) and at room temperature the system spends most of its time in the ground vibrational state. The 1→2, 2→3 … lines in the spectrum are called **hot bands**.

2) *Anharmonicity relaxes the $\Delta n=\pm1$ selection rule.* Note that the rules we arrived at were based on the fact that $\hat{a}^+\phi_i \propto \phi_{i+1}$. This is only true for the Harmonic oscillator states. For anharmonic eigenstates $\hat{a}^+\phi_i \propto \phi_{i+1}+\varepsilon_1\phi_{i+2}+.....$. Thus transitions with $\Delta n=\pm2,\pm3...$ will no longer be forbidden for anharmonic oscillators. Rather, in the presence of a bit of anharmonicity, they will be *weakly allowed*. Combining this observation with point 1) above results in a more complete picture for what the IR spectrum of an anharmonic oscillator should look like:



The peaks at around $2\omega_o$ are called **overtones**. Meanwhile, those at around ω_o are called **fundamentals**.

Polyatomic Molecules

The final difference between the model above and a general IR spectrum is that in chemistry, we are not always dealing with diatomic molecules. For a polyatomic molecule, we can still think of the potential as a Harmonic potential, but it has to be many-dimensional – it has to depend on several variables R_1, R_2, R_3, …. The most general Harmonic potential we can come up with is then of the form:

$$V(R_1,R_2,R_3,...)=\tfrac{1}{2}k_{11}R_1^{\,2}+\tfrac{1}{2}k_{12}R_1R_2+\tfrac{1}{2}k_{13}R_1R_3+....+\tfrac{1}{2}k_{21}R_2R_1+\tfrac{1}{2}k_{22}R_2^{\,2}+\tfrac{1}{2}k_{23}R_2R_3+....$$
$$+\tfrac{1}{2}k_{31}R_3R_1+\tfrac{1}{2}k_{32}R_3R_2+\tfrac{1}{2}k_{33}R_3^{\,2}+...$$

where it is important to notice the cross terms involving, say R_1 and R_2, which couple the different vibrations. At first sight, it seems like we can't solve this Hamiltonian; the only many-dimensional Harmonic potential we would know how to solve would be one that is separable:

$$\tilde{V}\left(R_1,R_2,R_3,...\right)=\tfrac{1}{2}k_{11}R_1^{\,2}+\tfrac{1}{2}k_{22}R_2^{\,2}+\tfrac{1}{2}k_{33}R_3^{\,2}+...$$

If the Harmonic potential were of this form, we would be able to write down the eigenstates as products of the 1D eigenstates and get the energies as sums of the 1D eigenenergies. As it turns out, by changing coordinates we *can* turn a quadratic system with off-diagonal cross terms (like the first potential) into one with no cross terms (like the second). These new coordinates, in terms of which the Hamiltonian separates, are called **normal modes** and they allow us to reduce a polyatomic molecule to a collection of **independent 1D oscillators**.

First, we note that V can be re-written concisely in matrix notation [Note: it may be useful to consult McQuarrie's supplement on Matrix Eigenvalue problems if the following seems unfamiliar.]:

$$V\left(R_1,R_2,R_3,...\right)=\tfrac{1}{2}\mathbf{R}^T\bullet\mathbf{K}\bullet\mathbf{R}$$

$$\mathbf{R}\equiv\begin{pmatrix}R_1\\R_2\\R_3\\\vdots\end{pmatrix}\qquad\qquad\mathbf{K}\equiv\begin{pmatrix}k_{11}&k_{12}&k_{13}&\cdots\\k_{21}&k_{22}&k_{23}&\cdots\\k_{31}&k_{23}&k_{33}&\cdots\\\vdots&\vdots&\vdots&\ddots\end{pmatrix}$$

Now, the Hamiltonian is of the form:

$$\hat{H}=\sum_i\frac{\hat{P}_i^2}{2\mu_i}+\frac{1}{2}\hat{\mathbf{R}}^T\bullet\mathbf{K}\bullet\hat{\mathbf{R}}$$

It is convenient to first transform to **mass-weighted coordinates**:

$$\hat{p}_i\equiv\frac{\hat{P}_i}{\sqrt{\mu_i}}\qquad\qquad\hat{x}_i\equiv\sqrt{\mu_i}\,\hat{R}_i\qquad\qquad\tilde{k}_{ij}\equiv\frac{k_{ij}}{\sqrt{\mu_i\mu_j}}$$

in terms of which we can write the Hamiltonian:

$$\hat{H}=\sum_i\frac{\hat{p}_i^{\,2}}{2}+\frac{1}{2}\hat{\mathbf{x}}^T\bullet\tilde{\mathbf{K}}\bullet\hat{\mathbf{x}}$$

As is clear from the kinetic energy above, in these coordinates, every degree of freedom has the same reduced mass.

Now we perform the normal mode transformation. We want to write:

$$\hat{\mathbf{x}}^T \bullet \tilde{\mathbf{K}} \bullet \hat{\mathbf{x}} = \hat{\mathbf{y}}^T \bullet \mathbf{K}' \bullet \mathbf{y} \qquad \mathbf{K}' = \begin{pmatrix} k_{11}' & 0 & 0 & \ldots \\ 0 & k_{22}' & 0 & \ldots \\ 0 & 0 & k_{33}' & \ldots \\ \ldots & \ldots & \ldots & \ldots \end{pmatrix}$$

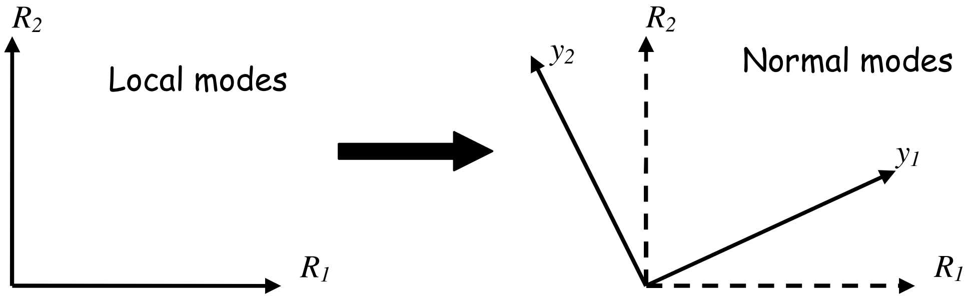
Further, we will assume there is a matrix $\mathbf{U}$ that transforms from $\mathbf{x}$ to $\mathbf{y}$

$$\mathbf{y} = \mathbf{U} \bullet \mathbf{x} \qquad \Rightarrow \qquad \mathbf{y}^T = \mathbf{x}^T \bullet \mathbf{U}^T$$

where in the second equality, we recall the general rule that the transpose of a product is the product of the transposes, but in the opposite order. Combining these two equations:

$$\hat{\mathbf{x}}^T \bullet \tilde{\mathbf{K}} \bullet \hat{\mathbf{x}} = \hat{\mathbf{y}}^T \bullet \mathbf{K}' \bullet \mathbf{y} = \hat{\mathbf{x}}^T \bullet \mathbf{U}^T \bullet \mathbf{K}' \bullet \mathbf{U} \bullet \hat{\mathbf{x}}$$
$$\Rightarrow \tilde{\mathbf{K}} = \mathbf{U}^T \bullet \mathbf{K}' \bullet \mathbf{U}$$

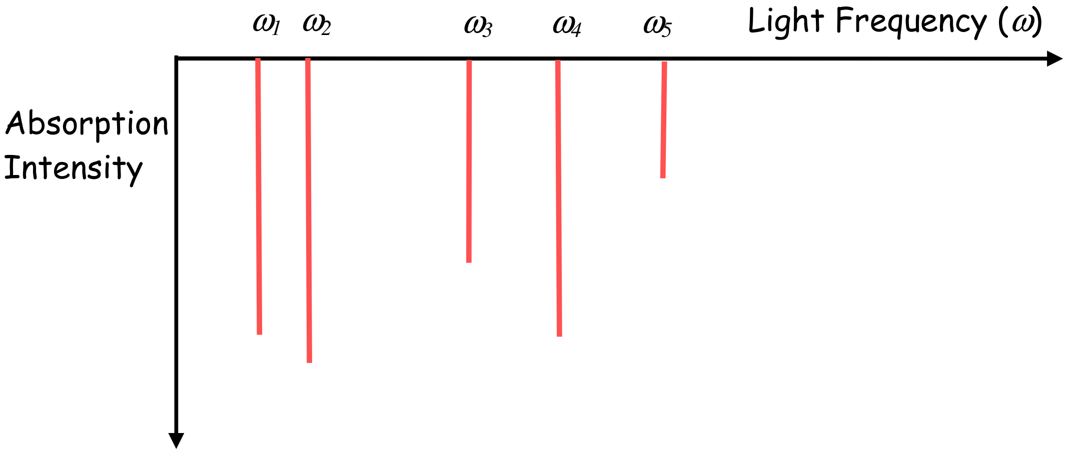
The last equation is a common problem encountered in linear algebra: the quest to take a given matrix ($\tilde{\mathbf{K}}$) and place it in **diagonal form** (the right hand side). For a symmetric matrix like $\tilde{\mathbf{K}}$ the solution to this problem is well known: the diagonal entries of $\mathbf{K}'$ are the eigenvalues of $\tilde{\mathbf{K}}$ and the columns of the transformation matrix $\mathbf{U}$ are the eigenvectors of $\tilde{\mathbf{K}}$. The transformed variables $\mathbf{y}$ are called the **normal modes**. These modes are linear combinations of the local degrees of freedom R_1, R_2, R_3, … that we started out with. Thus, while the initial motions might correspond clearly to local stretching of one bond or bending of an angle, the normal modes will generally be complicated mixtures of different molecular motions. We can visualize this in the simple case of two degrees of freedom. The local modes R_1, R_2 can be thought of as the two orthogonal axes in a plane. Meanwhile, the normal modes y_1, y_2 are also orthogonal axes, but rotated from the original set:



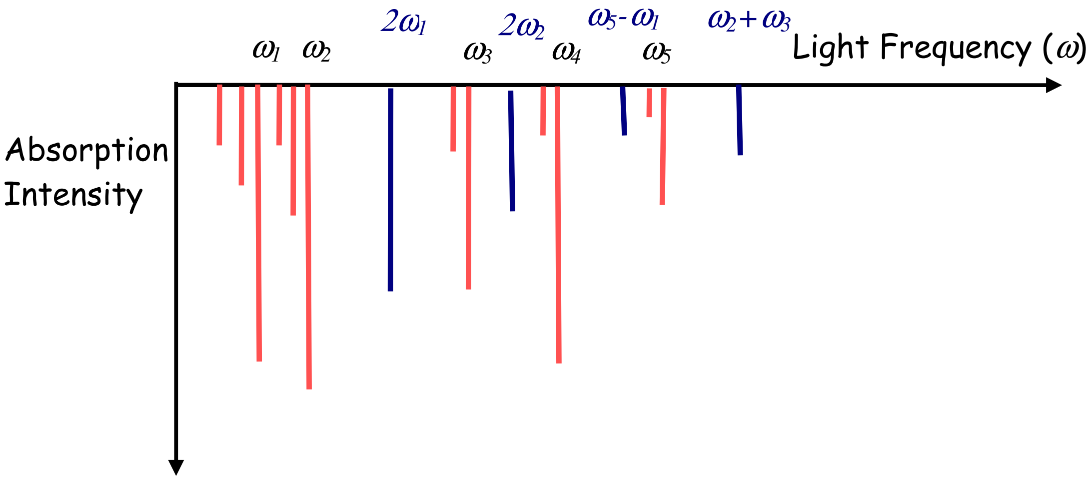
The local modes have interactions between each other: local stretches are coupled to local bends, etc. As a result, **the Hamiltonian is not separable in terms of the local modes** R_1, R_2. However, by design the Hamiltonian ***is*** separable when written in terms of the normal modes:

$$\hat{H} = \sum_i \frac{\hat{p}_i^{\,2}}{2} + \frac{1}{2} k'_{ii} \hat{y}_i^{\,2}$$

The eigenvalues, k_{ii}', tell us the "stiffness" of the PES in the particular direction y_i. Note that **the Hamiltonian above is exactly the same Hamiltonian as the one we started with**. The coupling terms have simply been rotated away by changing the coordinates. As discussed before, we can immediately interpret the spectra of this Hamiltonian in terms of a sum of many independent oscillators. Thus, for a polyatomic molecule within the harmonic approximation we expect to see lines at each of the normal mode frequencies:



Where we have noted that the different oscillators will typically also have different transition dipoles. (For obvious reasons, in vibrational spectroscopy the square of the transition dipole is often called the **oscillator strength**) We can, of course, combine this polyatomic picture with the anharmonicity effects above to get a more general picture that looks like:



where we predict the existence of various hotbands and overtones for each of the normal mode oscillators in the molecule. Note that while the overtones always involve multiple quanta, the quanta need not come from the same normal mode – hence we expect not only overtones at $2\omega_1$, but also a **combination bands** at $\omega_2 + \omega_3$ and $\omega_5 - \omega_1$. The picture above is qualitatively correct for the IR spectrum of a single molecule. In solution, heterogeneity leads to a smearing out and broadening of the peaks, leading to the complex IR fingerprints we are used to.

As should be clear from the above discussion, IR spectra contain a wealth of information about the molecule: the stiffness of each normal mode, the degree of anhormonic effects, the character of the local environment felt by the oscillators …. Of course, in order to extract this information, one must be able to assign the spectrum – i.e. one must be able to distinguish hotbands from overtones and associate the various normal modes (at least qualitatively) with physical motions of the molecule. This task can be extremely challenging – and computation must be used as a guide in many cases – but when it is accomplished, one typically has a very sensitive fingerprint of molecule under consideration.