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 structure. 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 ⍰ 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:

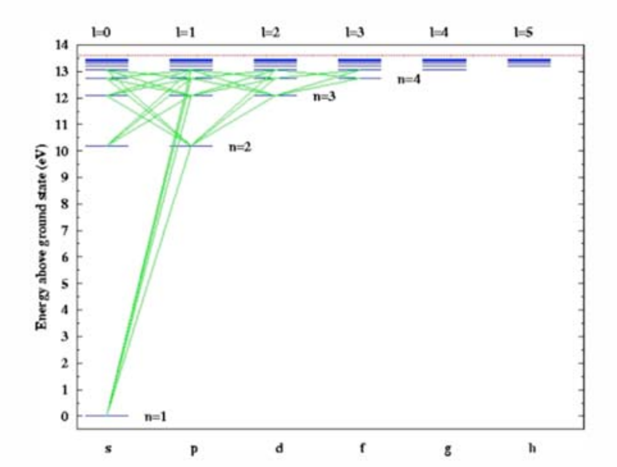
$l' - l'' = \Delta l = \pm 1$ and $m' - m' = \Delta m = 0$

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:

$$\psi_{Total} = \psi_{spatial}\psi_{spin}$$

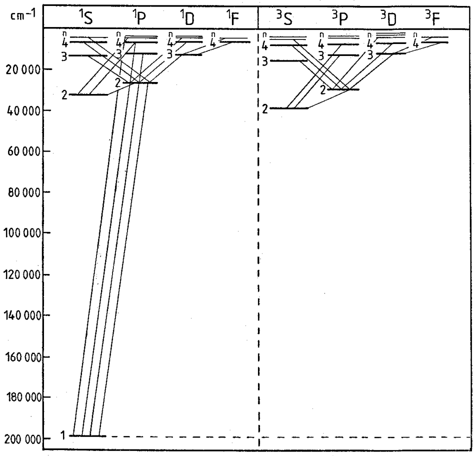
We just saw that the dipole moment acts only on the spatial coordinates and not on the spin coordinates. This implies that we can now write the transition probability integral as:

$$\int \left(\psi_{2spatial}\psi_{2spin}\right)^* \hat{\mu}\psi_{1spatial}\psi_{1spin}\, d\tau = \int \psi_{2spatial}^* \hat{\mu}\psi_{1spatial}\, d\tau_{spatial} \int \psi_{2spin}^* \psi_{1spin} d\tau_{spin}$$

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).

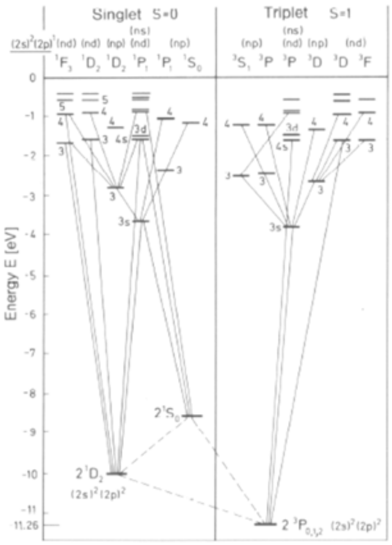
3. $\Delta J = 0, \pm 1$

   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.

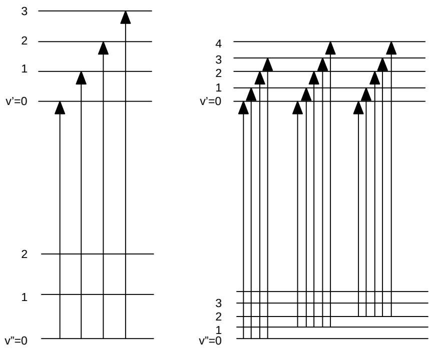
In our discussions of other types of spectroscopy, we have considered only absorption spectra. That is because the lifetimes of vibrational and rotational states are sufficiently long that molecules will more often than not collide with other molecules and give their energy off through the collision 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 $\Delta v = \pm 1$ 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.***

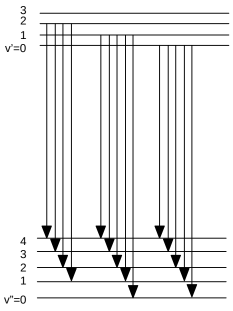
Electronic spectra can be greatly simplified by cooling the sample and getting rid of population in higher vibrational states. Normally one can only do this until the point at which the molecule condenses and becomes a liquid (at which point the spectrum changes fairly radically). There are some tricks, 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.

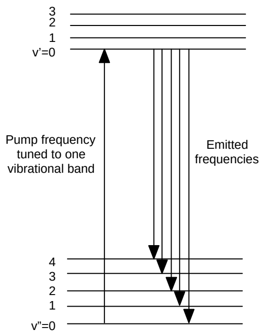
Now let us consider emission spectra.

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

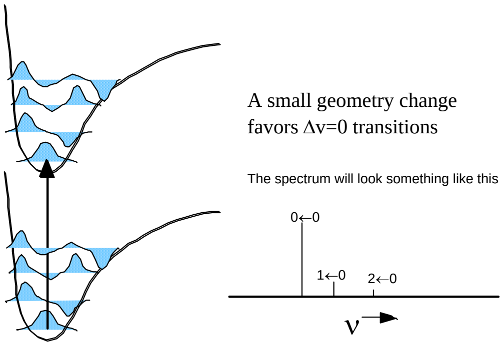
$$I \propto \mu_e(R_e)^2\left[\int \psi^*_{2vib}(R)\,\psi_{1vib}(R)d\tau_R\right]^2$$

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:

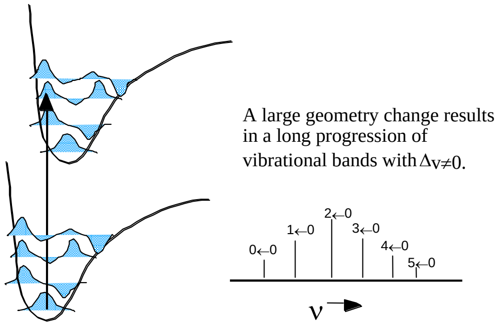
If the two curves lie right above each other (same equilibrium internuclear separation or same geometry), then the best overlap will be for final states with the same number of vibrational quanta as the initial state (Δv=0). You can see that all transitions with Δv not equal to zero will be small. In 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.

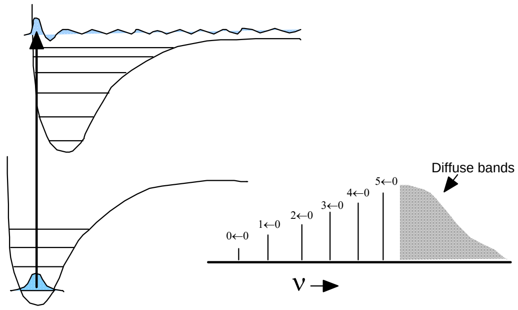
Thus, one can look at an electronic spectrum and get an idea immediately about what the difference in geometry will be for the excited electronic state. However, what one sees in the spectrum are the geometry changes projected onto the normal modes of the molecule. We usually think of geometry changes 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.

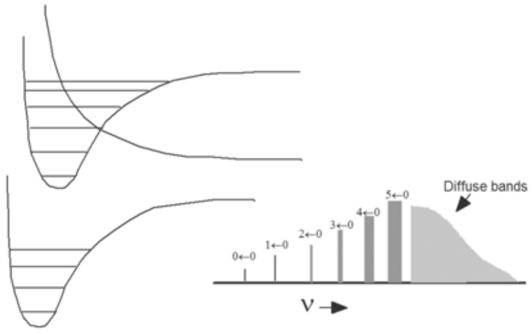
In one case, the excited state potential is very much like the ground state potential with little shift in the equilibrium bond distance. In this case, the strongest feature in the spectrum is the 0-0 band.

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

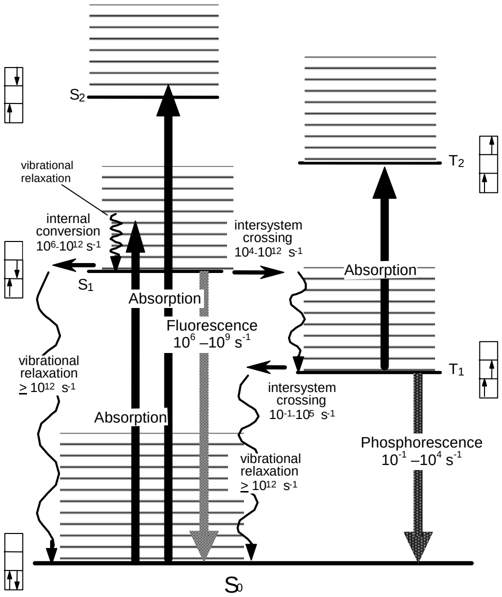
Think back to our treatment of the vibrational states of polyatomic molecules. Recall the complications that can arise when we have two vibrational states that are close in energy—in a perturbation theory picture the wave functions can "mix", which means that they have some character of each of the two 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:

$$^{2S+1}\Lambda_{\Omega}$$

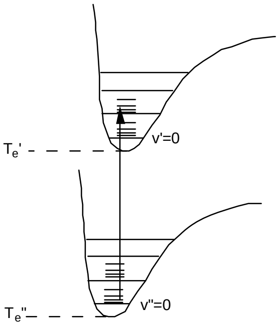
where, $2S+1$ is the spin multiplicity, Λ the projection of the total electronic orbital angular momentum L onto the bond axis and Ω the projection of the total angular momentum (including spin angular momentum) onto the bond axis. For Λ = 0, 1, 2 . . the states are designated as Σ, Π, Δ . . .

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.**

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

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

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

If we neglect the centrifugal distortion terms we have

$$\nu_{transition} = \nu_0 + B_\text{v}' J'(J'+1) - B_\text{v}'' J''(J''+1)$$

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

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

$$P(J) = \nu_0 - (B_\text{v}' + B_\text{v}'')J + (B_\text{v}' - B_\text{v}'')J^2$$

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.

$$\nu_{i\,\mathrm{v''}}^{\;\mathrm{v'}}$$

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.

<u>**Some examples:**</u>

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