

Title: Intensity distribution in the electronic vibrational structure:

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In lecture-31 we have observed the iodine absorption spectrum. The intensity of the vibrational structure gives a peculiar pattern.

This pattern appears due to the characteristics of the potential curves between the two states.

Franck and Condon gave an explanation about the intensity distribution of the vibrational progression of an electronic transition.

In the lecture, we will learn about the Franck-Condon principle.

The intensity distribution of a particular vibrational structure ν' –progression in the electronic absorption spectrum or ν'' –progression in the electronic emission spectrum displays different kind of pattern.

Let us first discuss the electronic absorption intensity distribution. There are mainly three types of intensity distribution seen in the experiments. In the following we will discuss the nature of these three intensity distributions.

Case-I :

As discussed in the previous lectures that for a ν' –progression with $\nu'' = 0$, the $\nu'' = 0 \rightarrow \nu' = 0$ transition, which is known as the vibration origin transition, is the lowest in energy. This first band is seen to be very intense as shown in the figure-33.1.

Further bands in ν' –progression with $\nu'' = 0$ progression appear with very rapidly decreasing intensities.

This kind of intensity distribution is observed for the atmospheric oxygen in the red part of the solar spectrum.

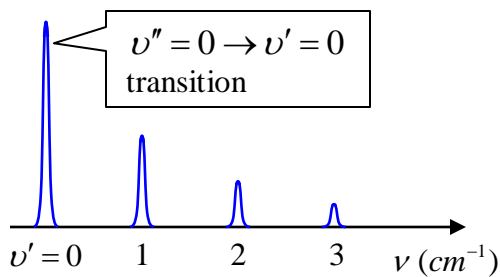


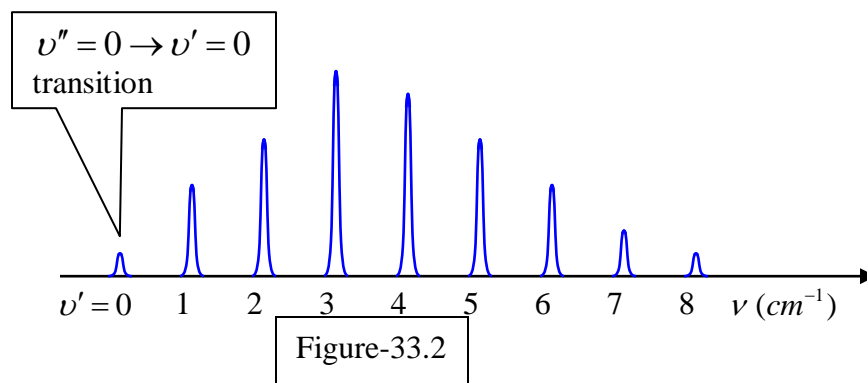
Figure-33.1

Case-II

In this case, the intensity of the bands in the ν' – progression with $\nu'' = 0$ at first increases with increasing in energy. The $\nu'' = 0 \rightarrow \nu' = 0$ transition band is not the intense one.

The intensities of the further bands increase slowly, the intensity reaches to maximum and then decreases slowly with increasing ν' .

This kind of pattern is shown in figure-31.2. The electronic absorption of CO molecule shows this kind of intensity pattern.

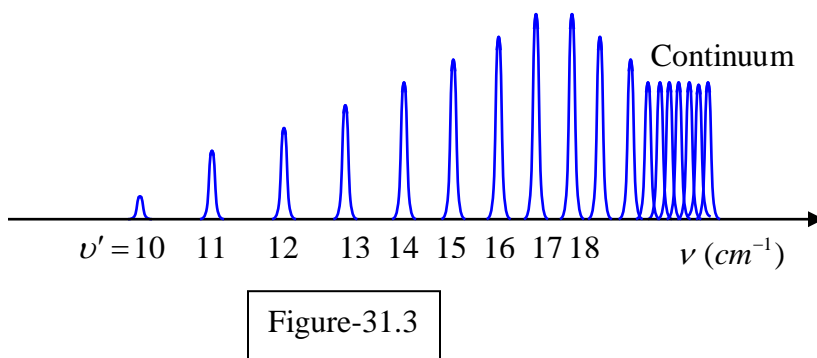


Case-III

In this case, a long progression is seen whose intensity rises gradually and finally reaches a continuum.

Usually, in this type of pattern, the first observe band may not be the $\nu'' = 0 \rightarrow \nu' = 0$ origin band.

The maximum intensity lies either at a very high ν' value as seen in the iodine absorption spectrum (discussed in lecture-31) or possibly be even in the conituum. This pattern is shown in figure-31.3



Franck-Condon principle :

These three different intensity distributions observed in the experiments can be explained by Franck-Condon principle.

J. Franck in 1925 published a paper [Trans. Faraday Soc., Volume-21, Year-1925, Page-536] to describe this phenomenon with simple diagrammatical approach.

Later on, in 1928 Condon gave the wave mechanical formulation on this idea [Physical Review, Volume-54, Year-1928, Page-858].

According to Franck:

“The electron jump in a molecule takes place so rapidly in comparison to the vibrational motion of the nuclei that immediately afterwards the nuclei still have very nearly the same relative position and velocity as before the jump”.

Let us correlate this idea with the intensity three types of intensity pattern discussed before in figure-31.1, 31.2, 31.3.

Case-1

Referring to the figure-31.4, the potential curves of the two electronic states are drawn in such way that their minima lie very nearly one above the other. The physical meaning is that in both the electronic states, the equilibrium internuclear distances are same.

In absorption, the molecule is initially at the minimum vibrational state $\nu'' = 0$. If the transition takes place to $\nu' = 0$ ($A \rightarrow B$), the change of the internuclear distance and momentum is small. The reason is transition is shown as vertical line (same internuclear distance) and both the vibrational levels are at zero point on the potential curve. This satisfies the requirement of the Franck-Condon principle. So, this transition will be highly probable.

On the other hand, a transition from $A \rightarrow C$ is less probable because in this case, the internuclear distance changes after the jump. Further for a vertical transition ($A \rightarrow E$) the velocity or momentum is appreciably changed.

It should be noted that at point E the kinetic energy is EB. At the turning points C and D, the velocity is zero as point A.

Thus, according to Franck-Condon principle, in this situation transition from $\nu'' = 0$ to high ν' levels is less probable or forbidden. For level $\nu' = 1$, the change of the velocity or position is relatively small compared to $\nu' = 2, 3, 4, \dots$ transitions.

Thus, $\nu'' = 0 \rightarrow \nu' = 0$ will be most intense, and highly probable.

$\nu'' = 0 \rightarrow \nu' = 1$ less probable than origin band.

Further transitions to $\nu' = 2, 3, 4, \dots$ will be less probable and the intensity will be rapidly decreased. This explains the intensity pattern described in figure-31.1.

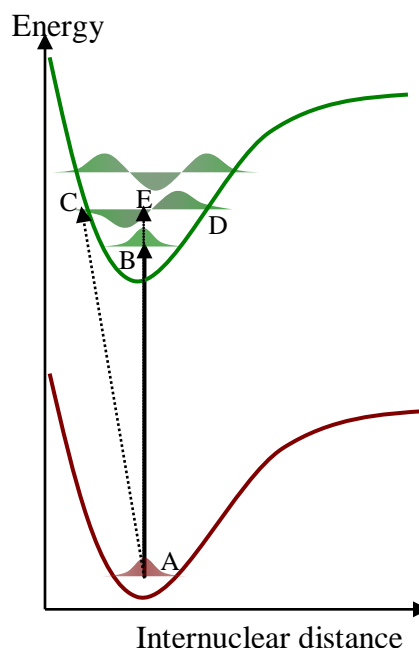


Figure-31.4

Case-II

In figure-31.5, the minimum of the potential curve of the upper electronic state is shifted to higher intermolecular distance than that of the ground state. The physical meaning of this is that the bond length of the upper electronic state at the equilibrium is greater than that of the ground electronic state.

As we can see that the transition from minimum to minimum ($\nu'' = 0 \rightarrow \nu' = 0$) is no longer the most probable because it does not satisfy the requirements of constant position during jump as prescribed by the Franck-Condon principle.

The most probable transition in this case will be from A \rightarrow C. For this transition there is no change of nuclei positions (vertical line on the potential curve) and velocity during jump.

Since the equilibrium internuclear distance is different in this state the nuclei will start vibrating between C and D. So the vibrational state ν' around the point C will have the most intense band.

For the higher and lower vibrational levels with respect to point C, the change will be gradually increase and thus the intensities of these levels will be gradually decreased with respect to the intense band.

It is to be noted that the same intensity distribution will result when the upper potential curve will be shifted to the lower side with respect to the ground state. Thus the intensity pattern seen in figure31.2 can be described.

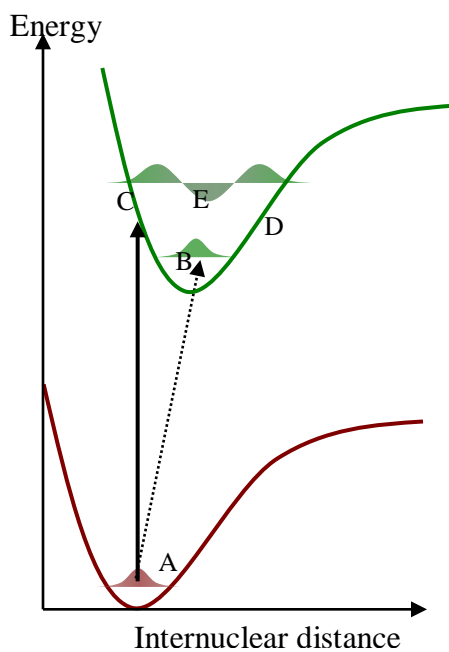
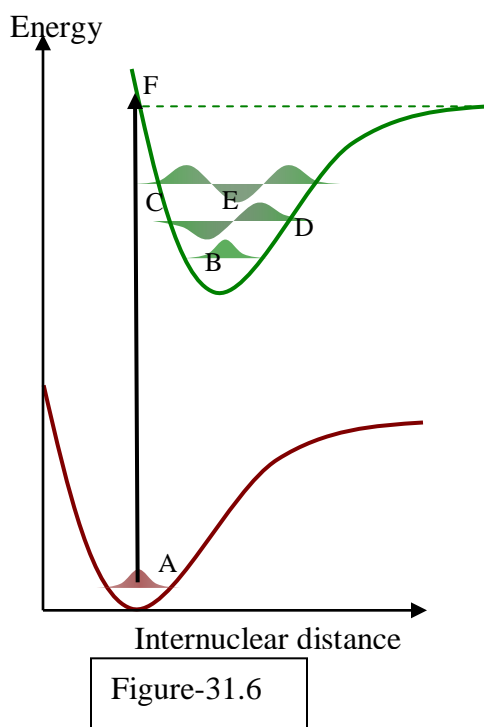


Figure-31.5

Case-III

In figure-31.6, the minimum of the upper electronic potential curve is further shifted to the higher side. In this case the vertical transition for $A \rightarrow F$ lies above the dissociation energy of the upper potential curve. This region F corresponds to the continuous region of the vibrational spectrum. After this transition, molecule will dissociate. However, below the point F, the intensity of the vibrational bands will gradually increase up to the continuum. This is pattern similar to figure-31.3.



In short, in absorption, the most intense band of the transition from $\nu'' = 0$ corresponds to the vibrational level that lies vertically above the minimum of the ground state potential curve.

If $\nu'' = 0 \rightarrow \nu' = 0$ transition is intense, the geometry or the bond length does not change going from ground state to excited electronic state.

Other intensity patterns confirm that there is change in equilibrium intermolecular distance in the excited electronic state.

Emission :

According to the Franck-Condon principle, the intensity distribution in emission of the band ν'' -progression with $\nu' = 0$ corresponds to the same pattern of absorption band progression with $\nu'' = 0$. That means the $\nu'' = 0 \rightarrow \nu' = 0$ origin transition will be most intense and the higher bands will be gradually decreasing in intensity.

However, the intensity distribution is different for the band progression with $\nu' \neq 0$.

Referring to the figure-31.7, the transition from point C, the transition from $C \rightarrow C'$ will be more intense. On the other hand, the transition from D, the transition $D \rightarrow D'$ will be intense.

It is to be noted that, at the turning point i.e. points C and D, the oscillator velocity is zero and it spends most of the time at these turning points. Thus, the probability of the transition from these two points will be more.

Hence, in the emission intensity pattern, the progression with $\nu' \neq 0$ shows two intense bands rather than one as seen in absorption.

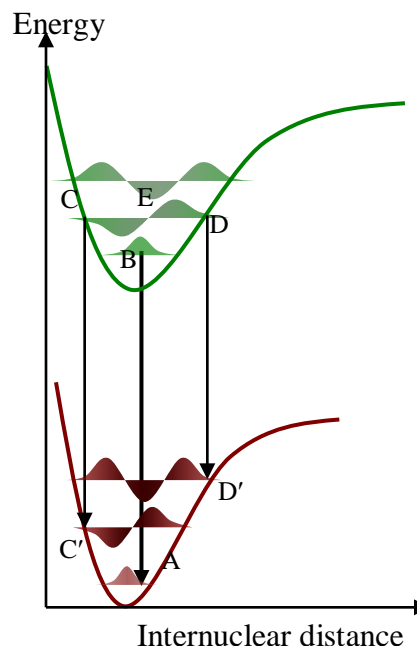


Figure-31.7

Wave-mechanical Formulation of Franck-Condon principle:

As we know that the probability of a transition between the two states is proportional to the square of the matrix element of the electric dipole moment. If ψ' and ψ'' are the total wavefunctions of the upper and lower electronic states, then the transition moment can be written as

$$R = \int \psi'^* M \psi'' d\tau \dots\dots\dots(33.1)$$

Where M is the transition dipole.

Now the total wavefunction is the product of electronic, vibrational and rotational wavefunction and is defined as,

$$\psi = \psi_e \psi_v \psi_r \dots\dots\dots(33.2)$$

Since we are discussing the vibrational structure only, we can drop the rotational wavefunction for this moment, then

$$\psi = \psi_e \psi_v \dots\dots\dots(33.3)$$

The total dipole moment depends on two parts, one the electronic part and the second one originates due to the vibrational motion of the nuclei. Thus, the total dipole can be written as

$$M = M_e + M_n \dots\dots\dots(33.4)$$

Substituting M from equation-33.4 to equation-33.1, we get

$$\begin{aligned} R &= \int \psi_e'^* \psi_v'^* M \psi_e'' \psi_v'' d\tau \\ &= \int \psi_e'^* \psi_v'^* (M_e + M_n) \psi_e'' \psi_v'' d\tau \dots\dots\dots(33.5) \end{aligned}$$

Expanding it,

$$R = \int \psi_e'^* M_e \psi_e'' d\tau_e \int \psi_v'^* \psi_v'' dr + \int \psi_e'^* \psi_e'' d\tau_e \int \psi_v'^* M_n \psi_v'' dr \dots\dots\dots(33.6)$$

Since the electronic wavefunctions are orthogonal to each other, then $\int \psi_e^{*'} \psi_e'' d\tau_e = 0$, and we get from equation 33.6,

$$R = \int \psi_e^{*'} M_e \psi_e'' d\tau_e \int \psi_{v'}^{*'} \psi_{v''}'' dr \dots\dots\dots (33.7)$$

$$= R_e \int \psi_{v'}^{*'} \psi_{v''}'' dr$$

Here $R_e = \int \psi_e^{*'} M_e \psi_e'' d\tau_e$ is the transition moment between the two particular electronic states. Thus the intensity of absorption is

$$I_{abs}^{v',v''} = \frac{8\pi^3}{3hc} I_0 l N_{v''} \nu |R_e|^2 \left| \int \psi_{v'}^{*'} \psi_{v''}'' dr \right|^2$$

Here I_0 and ν are the intensity and the frequency of the incident radiation, l is the length of the absorbing medium and $N_{v''}$ is the number of molecules in the lower electronic state $v'' = 0$.

So the intensity will depend on the overlap integral between the two vibrational states v'' and v' , i.e. $\int \psi_{v'}^{*'} \psi_{v''}'' dr$. Let us understand this vibrational overlap integral with graphical representation.

To proceed, let us first take a look at the vibrational wavefunction.

The vibrational wavefunction is defined as,

$$\psi_v = A_v e^{-\frac{1}{2}\alpha x^2} H_v(\sqrt{\alpha} x)$$

Where A_v is the normalization constant, $A_v = \sqrt{\frac{1}{2^\nu v!}} \sqrt{\frac{\alpha}{\pi}}$.

α is a constant and $H_v(\sqrt{\alpha} x)$ is the Hermite polynomial.

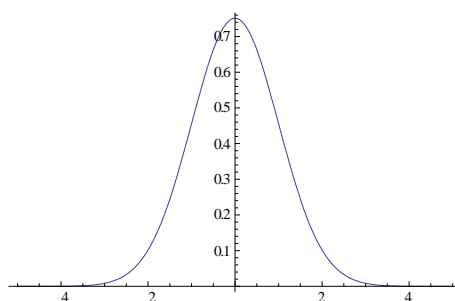
This Hermite polynomial is defined as ($\sqrt{\alpha} x = X$)

$$H_0(X) = 1 \quad H_1(X) = 2X$$

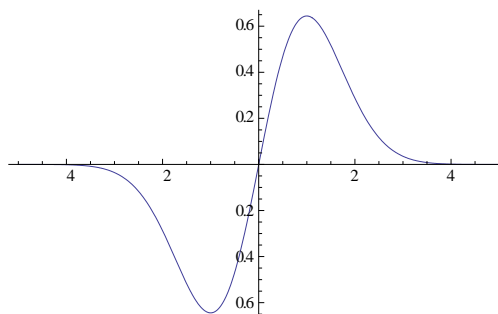
$$H_2(X) = 4X^2 - 2 \quad H_3(X) = 8X^3 - 12X$$

$$H_4(X) = 16X^4 - 48X^2 + 12$$

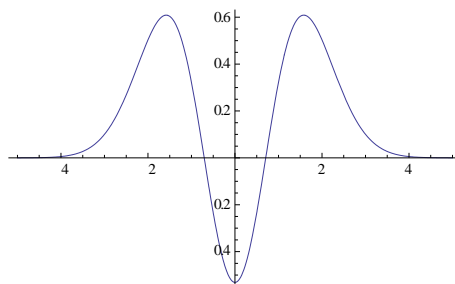
The vibrational wavefunction $\nu = 0$



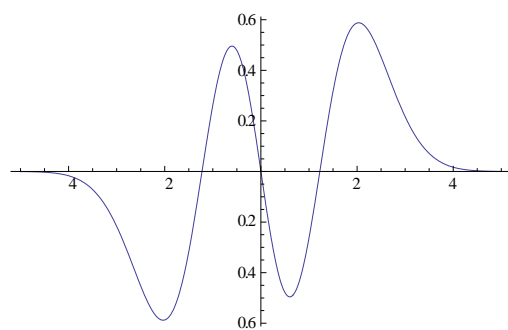
The vibrational wavefunction for $\nu = 1$



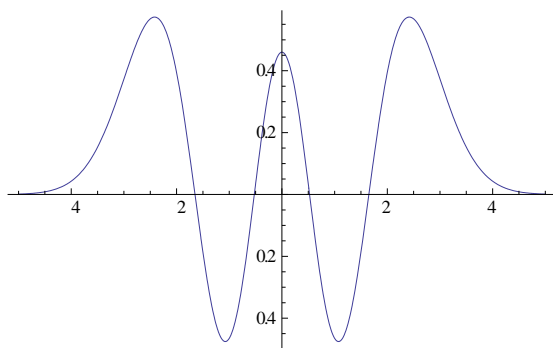
The vibrational wavefunction for $\nu = 2$



The vibrational wavefunction for $\nu = 3$



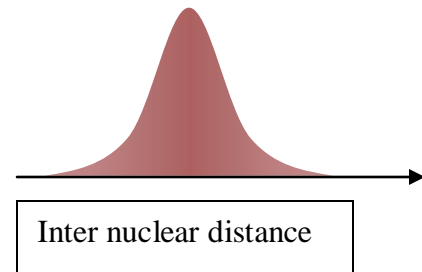
The vibrational wavefunction for $\nu = 4$



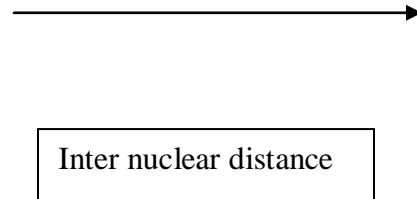
Now we will discuss $\int \psi_{\nu'}^* \psi_{\nu}'' dr$

Case-I

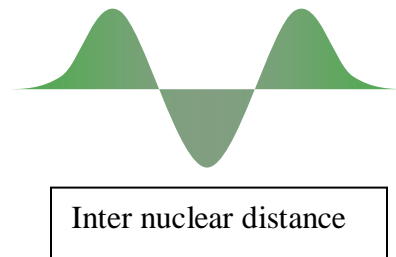
When equilibrium internuclear distances are same for the both the electronic states then the vibrational $\nu'' = 0$ to $\nu' = 0$ transition, the overlap is as shown in the figure. Here the maximum overlap is obtained. So the intensity will be maximum.



For $\nu'' = 0$ to $\nu' = 1$ transition, the overlap is as shown in this figure. Here both the positive and negative overlap reduce the total overlap and is less than the $\nu'' = 0$ to $\nu' = 0$ transition

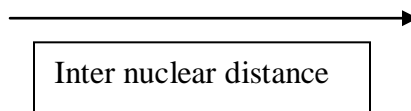


For $\nu'' = 0$ to $\nu' = 2$ transition, the overlap is as shown in this figure. Here both the positive and negative overlap cancel the total overlap and is even less than the $\nu'' = 0$ to $\nu' = 1$ transition
Thus this describes the intensity pattern described in Case-I before.

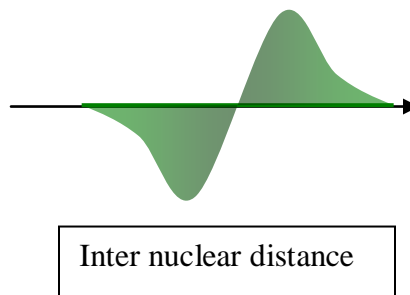


Case-II

When equilibrium internuclear distances are shifted in the upper electronic state than that for the lower electronic state, then the vibrational overlap integrals for $\nu'' = 0$ to $\nu' = 0$ transition, is as shown in the figure. As seen that the overlap is less.

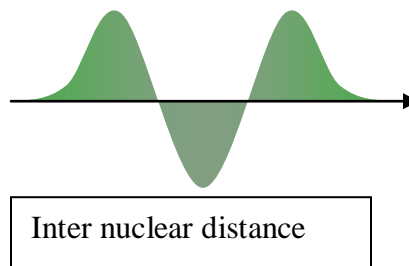


For $\nu'' = 0$ to $\nu' = 1$ transition, the overlap is as shown in this figure. Here the total overlap is more than the $\nu'' = 0$ to $\nu' = 0$ transition. Thus in this case the intensity will be more than the $\nu'' = 0$ to $\nu' = 0$ transition.



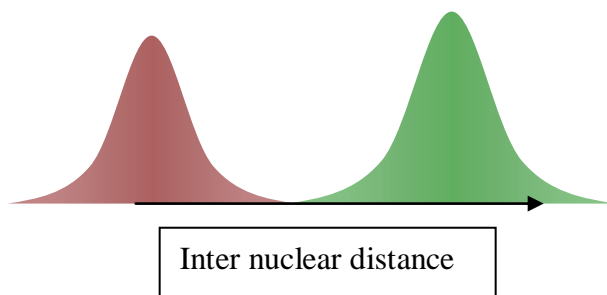
For $\nu'' = 0$ to $\nu' = 2$ transition, the overlap is as shown in this figure. Here both the positive and negative overlap cancel the total overlap and is even less than the $\nu'' = 0$ to $\nu' = 1$ transition.

Thus this describes the intensity pattern described in Case-II before.

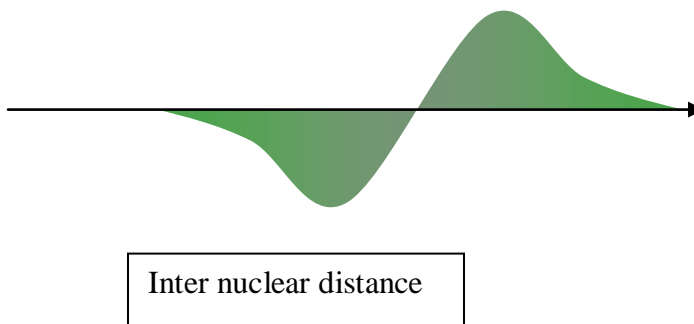


Case-III

When equilibrium internuclear distances are shifted further in the upper electronic state than that for the lower electronic state, then the vibrational overlap integrals for $\nu'' = 0$ to $\nu' = 0$ transition, is as shown in the figure. As seen that the overlap is no more so the intensity will be zero in this case.

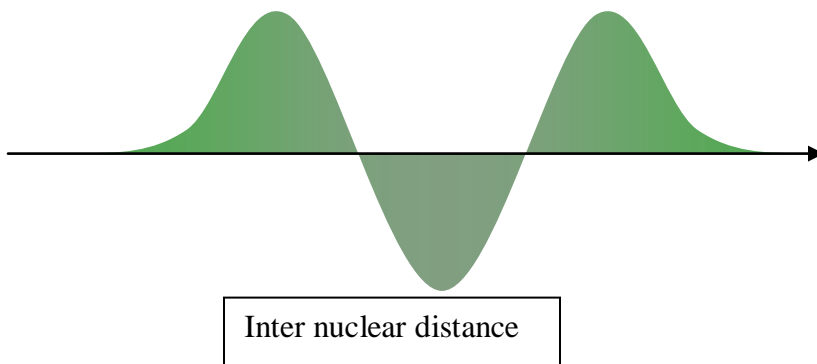


For $\nu'' = 0$ to $\nu' = 1$ transition, the overlap is as shown in this figure. Here the total overlap is more than the $\nu'' = 0$ to $\nu' = 0$ transition. Thus in this case the intensity will be more than the $\nu'' = 0$ to $\nu' = 0$ transition.



For $\nu'' = 0$ to $\nu' = 2$ transition, the overlap is as shown in this figure. Here total overlap and is maximum and thus for this transition the intensity will be more.

Thus this describes the intensity pattern described in Case-III before.



Recap

There are different kind of intensity distribution we observe in the vibrational progression of an electronic transition.

These patterns arises due to the relative position of the upper electronic state with respect to the lower electronic state.

If the origin band is the most intense one, we can conclude that the molecule is not changing its geometry going from lower to upper electronic state.

Any other pattern proves that there is a change in the molecular conformation.