

# The Franck-Condon Factors ©

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## Goal

The goal of this document is to introduce the mathematical models that are used to describe vibronic spectra (vibration-electronic spectra) of molecules. This document focuses on the computation and simulation of spectra in terms of the Franck-Condon factors.

## Prerequisites

1. Experience with harmonic oscillator wave functions.
2. Moderate skill with Mathcad.
3. Ability to use a full set of orthonormal functions in a linear combination to represent some other well behaved function over the same interval, e.g. Fourier Series expansions.
4. The introduction to Franck Condon Factors document, **FranckCondonBackground.mcd** should be studied prior to using this document. The background document also contains a list of prerequisites, objectives, and preliminary tasks to facilitate learning when using the more quantitative and interactive material presented here.

## Performance Objectives

At the end of this exercise you will be able to:

1. describe the relationship between Franck Condon factors and vibronic spectra;
2. explain the key ideas determining the magnitude of the Franck Condon factors;
3. compute Franck Condon factors;
4. construct a vibronic spectrum for a molecule from a knowledge of the wavelength of the electronic transition, the number of vibronic peaks, and the relative intensity of the vibronic peaks.

## Introduction

During a molecular electronic transition from the ground electronic state to an excited electronic state, the vibrational wave functions of the ground state overlap with the vibrational wave functions of the excited state. The degree of overlap between the ground and excited state vibrational functions determines the shape and structure of the electronic spectrum that is observed.

In this document we treat the overlap between the ground and excited vibrational states by projecting the ground state vibrational wave function onto the excited state vibrational wave functions. Mathematically this is equivalent to writing the ground state vibrational wave function as a linear combination of excited state vibrational wave functions. The harmonic oscillator wave functions will be used for both the ground state and excited state vibrational energy levels. Both the ground state and excited state have a full set of wave functions characterized by the quantum numbers,  $v''$  and  $v'$ .  $v''$  is used to identify the ground state wave functions and  $v'$  is used for the excited state wave functions. For iodine the ground electronic state,  $v'' = 0$ , has the greatest population. The interaction of this vibrational level of the ground electronic state with the excited electronic state via an electronic transition can be with any of the excited state vibrational energy levels characterized by vibrational quantum number  $v'$ . The most intense interaction will occur when there is a maximum overlap between the ground state vibrational wave function and an excited state vibrational wave function. Smaller peaks will be observed when the overlap between the ground state and excited state wave function is less. In general the transition from  $v'' = 0$  to  $v' = 0$  (commonly called the 0-0 transition) is unlikely because the equilibrium bond length of the ground state and excited state are expected to be different and this leads to a very small overlap between the wave functions for these two states.

For determining the degree of interaction between the two electronic states we will use the harmonic oscillator wave functions because these functions form a complete orthonormal set of functions. The linear combination process itself is the same as using a Fourier series for some arbitrary function. Furthermore, as when using the Fourier series, weighting factors (the coefficients in the linear expansion) determine how much of each member in the series is used in the expansion that is made for a particular ground state wave function. These weighting factors are given the symbol ' $c_i$ '.

The square of the coefficients used in the linear combination tells us about the degree of overlap between the excited state wave functions and the ground state wave function. The square of the coefficients are the Franck Condon factors. The larger the square of the coefficient the more intense the peak observed in the electronic spectrum. Since several excited state vibronic wave functions can have significant values for their coefficient in the linear combination, the electronic spectrum can contain several overlapping bands. This contributes to the complexity of the electronic spectra.

Consider the excited state as defining the coordinate system for the vibrating bond in a molecule and then, for the excited state, call the displacement of the bond from its equilibrium position  $x$ . The equilibrium bond length of the excited state is at  $x=0$ . The ground state equilibrium bond length is at  $x=a$ , where ' $a$ ' is the difference in equilibrium bond length between the ground state and the excited state. This choice of the coordinate system for the excited state and ground state presents the situation where the ground state equilibrium displacement is longer than that found in the excited state. This is typical of transitions from antibonding to nonbonding molecular orbitals. To see this more clearly draw the potential energy function for the ground state and excited state and locate the minimum in each curve. Place the minimum for the excited state at  $x = 0$  and label the difference in the minima of the curves ' $a$ '.

The approach taken in this document will be to first set up the set of wave functions to be used in the linear combination. Specifically we will create a set of seven harmonic oscillator wave functions for the excited state. Then the ground electronic state vibrational wave function, quantum number  $v=0$ , will be written as a linear combination of the excited state wave functions. The coefficients of the linear combination will be determined by applying the same techniques used to do Fourier series expansions. Next the fitted function and the given function will be compared. Changes in the goodness of fit will be explored by systematically removing one term after the other from the expansion. Finally, a spectrum for vibronic transitions will be simulated. Along the way you will be provided with opportunities to interact with the material by completing calculations, recording and writing about your observations, and given ideas for creating your own mathematical models.

## Setting up the worksheet:

### A. First we define some equations and variables that we will use later.

$$v := 0..6$$

$v$  is highest vibrational quantum number to be used in the expansion used to write the ground state function. The number of terms in the expansion will be  $v + 1$ . To use more terms you must modify this document to include additional Hermite polynomials on the next page.

$$(1) \quad \Psi(v, x) := N_v \cdot H_v \left( \frac{1}{\alpha^2} \cdot x \right) \cdot e^{-\frac{\alpha \cdot x^2}{2}}$$

This equation defines the form for the wave function of a harmonic oscillator with quantum number  $v$ . Note that this equation is toggled off. The rectangular box to the right of the equation is the toggle equation off indicator. Although equation (1) is not a valid Mathcad equation, it is given here to remind you of the explicit form of the wave function.

### Exercise 1. Identify each part of equation (1). With what mathematical concept is $v$ associated?

$$N_v := \frac{1}{\sqrt{2^v \cdot v! \cdot \sqrt{\pi}}}$$

$$\alpha := \frac{k \cdot \mu \cdot (4 \cdot \pi)^2}{h^2}$$

Identify each term in  $\alpha$ .

$$\alpha := 1$$

Here we let  $\alpha = 1$  to simplify the following discussion and calculations. What physically relevant molecular property are we neglecting with this assumption?

$$x_{\min} := -10 \quad x_{\max} := 10 \quad x_{\text{incr}} := .01$$

$$x := x_{\min}, x_{\min} + x_{\text{incr}}, \dots, x_{\max}$$

This sets the range for calculating the harmonic wave functions in this exercise. If necessary review the harmonic oscillator section of your notes especially any work done with Mathcad on this topic.

Mathcad Note: these literal subscripts are made with periods. Active vector indices are made with the open square bracket key ( [ ). See pp 161 & 187 in the manual that accompanies the Mathcad 6.0+ software.

## B. Bring in the Hermite polynomials.

$$H_0(x) := 1$$

$$H_1(x) := 2 \cdot x$$

$$H_2(x) := -2 + 4 \cdot x^2$$

$$H_3(x) := -12 \cdot x + 8 \cdot x^3$$

$$H_4(x) := 12 - 48 \cdot x^2 + 16 \cdot x^4$$

$$H_5(x) := 120 \cdot x - 160 \cdot x^3 + 32 \cdot x^5$$

$$H_6(x) := -120 + 720 \cdot x^2 - 480 \cdot x^4 + 64 \cdot x^6$$

$$H_7(x) := -1680 \cdot x + 3360 \cdot x^3 - 1344 \cdot x^5 + 128 \cdot x^7$$

These are the first few Hermite polynomials. You may expand this document by typing in other polynomials or using a generating function for them.

Mathcad Note: Notice the form for naming the functions used here. The subscripts are made using the period. They are literal subscripts, i.e. they are part of the variable name. They are not subscripts that identify elements in a vector array.

### C. Systematically create the required excited state wave functions:

$$\psi_0(x) := N_0 \cdot (H_0(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_1(x) := N_1 \cdot (H_1(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_2(x) := N_2 \cdot (H_2(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_3(x) := N_3 \cdot (H_3(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_4(x) := N_4 \cdot (H_4(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_5(x) := N_5 \cdot (H_5(x)) \cdot e^{-\frac{x^2}{2}}$$

$$\psi_6(x) := N_6 \cdot (H_6(x)) \cdot e^{-\frac{x^2}{2}}$$

Remember  $\alpha$  was set = to 1.0. You may put in the full expression for  $\alpha$  but this requires defining any parameters that appear in  $\alpha$  and rewriting the functions shown here on the left.

The Hermite polynomials and the general form of the wave function are used here to create the first seven excited state harmonic oscillator wave functions we will use for the linear combination expression for the ground state function.

$x$  is the displacement of the bond from equilibrium in the excited state coordinate system. It is the excited state wave functions that will be used to expand the ground state function to calculate the Franck-Condon factors later in this document.

**Note to the Instructor:** The last four functions may be eliminated to permit students to learn the topic interactively. In this case the students should be explicitly instructed to construct these missing functions.

**Note to Student:** You can practice the concept on this page by creating the  $\psi_7(x)$  wave function and carrying it through to the end of the document to determine its significance in the linear combination of functions representation of the ground state function.

What is the Franck-Condon factor for  $\psi_7$ ? Will this factor contribute significantly to the observed spectrum?

## Interlude

### Examining the ground state wave function in the excited state coordinate system.

An electronic transition is most likely to originate in the lowest vibrational state of the ground state. Other choices for the origin of the excitation can be made but they are much less likely to occur.

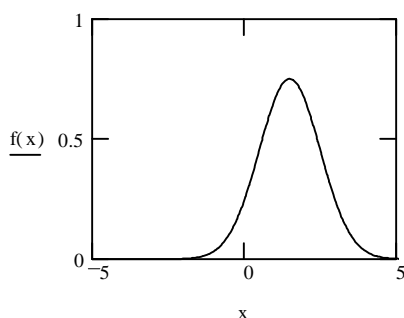
Why is this so? Explain.

The ground state wave function in the excited state coordinate system is shown below this paragraph. Here the excited state bond length is shorter than the ground state bond length. The equilibrium bond length for the ground state ( $x = 0$ ) is found at  $x' = a$  in the excited state coordinate system. Explain. ( $x' = x - a$  translates the origin in the ground state coordinate system to the origin in the excited state coordinate system.)

$$a := 1.5$$

$$f(x) := N_0 \cdot \exp\left[-\frac{(x - a)^2}{2}\right]$$

Note:  $a$  and  $\alpha$  are different.  $a$  is the difference between the excited and ground state coordinate systems while  $\alpha$  is the drop-off rate for the exponential function.



To the left we write the ground state wave function in simplified form but use the excited state coordinate system. It is this function that will be expanded as a linear combination of the excited state functions given on the previous page.  $a=1.5$  is an arbitrary choice at this point. Actual equilibrium ground state bond lengths would be used for real molecular systems. Try several different values for 'a' and record your observations for the graph immediately below. How would you change the equation to represent an excited state bond that is longer than the ground state bond? Summarize the various conditions under which you would find the excited state bond length longer or shorter than the ground state bond length. Return the value of 'a' to 1.5 before going on to the next section of this document.

**Exercise 2.** Examine the curve shown here. The x axis corresponds to the displacement from equilibrium for the excited state. Notice that the ground state wave function has become very small by  $x = +5$  and  $-2$ . What is the significance of this? The maximum in the ground state wave function occurs at what value in the excited state coordinate system shown here? By how much would the ground state wave function overlap with the excited state wave function? What is the significance of this?

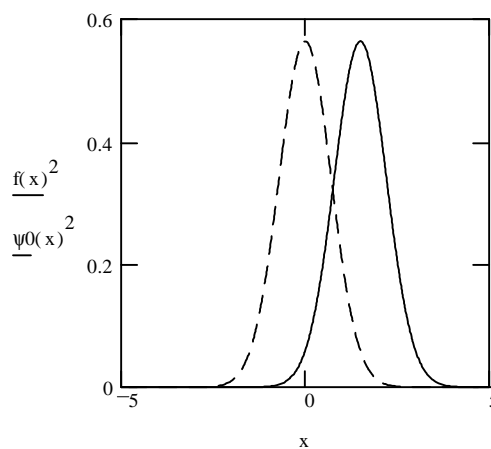
How does your answer compare to what you expect for the equilibrium bond length of the ground state with respect to the excited state? Which should be shorter and does this figure agree with your choice? Refer to the diagrams you prepared using the FranckCondonBackground.mcd document.

Change the  $x-a$  in the exponential of the function to an  $x+a$  and see what happens to the curve. What is the significance of this with respect to the relative interatomic distances expected in the excited state and the ground state? Explain.

## End of Interlude

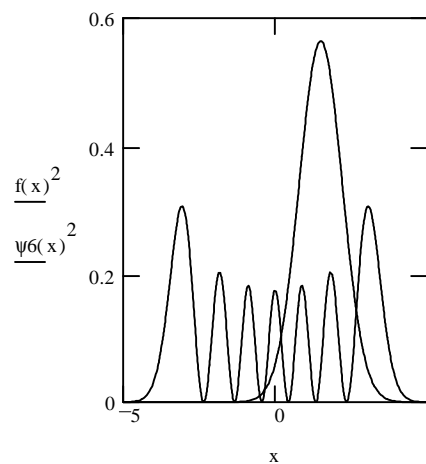
### The probability density for the ground and excited states.

Here on the right we see the probability density function for the excited state lowest vibrational level in blue (dashed) and the probability density function for the ground state lowest vibrational level using the excited state coordinate system in red (solid). Notice how each curve is situated with respect to the other.



On the right we see a similar curve but this time we use a higher excited state vibrational energy level.

**Exercise 3.** Vary the function used in the figure on the right to examine all 7 vibrational levels in the excited state that are included in this document. First plot only the two functions and then plot the probability density functions. From the graphs predict which excited state functions would be most important in the linear combination representation of the ground state function. Record your results and compare your observations to the computed Franck-Condon factors you will obtain on the next page.



## Computing the Franck Condon factors: determining the coefficients for the linear combination of excited state vibrational wave functions used to write the ground state wave function.

The ground state wave function will be written as a linear combination of excited state functions:

$$f(x) = \sum_n c_n \cdot \psi_n$$

The coefficients for this linear expansion are given by the integral over all space for

the product of the target function and each of the basis set functions taken one at a time

$$c_n = \int f(x) \cdot \psi_n \, dx$$

This is shown here for the seven basis set functions from the excited state. The

method is the same as when evaluating the coefficients in a Fourier series expansion. Note how each coefficient is obtained. Obtain the coefficient for one more term in the linear combination. Explain why each integral can be called an overlap integral.

**Exercise 4.** Fill in the coefficient and coefficient squared columns below. Check for completeness, i.e. that the sum of the coefficients squared is close to one.

Integral	Coefficient	Coefficient Squared
$c_0 := \int_{-2}^5 f(x) \cdot \psi_0(x) \, dx$	$c_0 = 0.57$	$(c_0)^2 = 0.325$
$c_1 := \int_{-2}^5 f(x) \cdot \psi_1(x) \, dx$		
$c_2 := \int_{-2}^5 f(x) \cdot \psi_2(x) \, dx$		
$c_3 := \int_{-2}^5 f(x) \cdot \psi_3(x) \, dx$		
$c_4 := \int_{-2}^5 f(x) \cdot \psi_4(x) \, dx$		
$c_5 := \int_{-2}^5 f(x) \cdot \psi_5(x) \, dx$		
$c_6 := \int_{-2}^5 f(x) \cdot \psi_6(x) \, dx$		

**Exercise 5.** Given the data accumulated above identify the most important excited state wave functions in the expansion. Explain why you made these choices. Explain the significance of this with respect to observable spectroscopic transitions. What do you expect the observed spectrum to look like? How far apart would the peaks be? What instrument resolution would you need to resolve the peaks? Make sketches to show what would happen to the spectrum as you reduced resolution from high to low?

**Exercise 6.** Review the plots you prepared above in Exercise 3. Do the graphs qualitatively agree with your computed Franck-Condon factors in Exercise 4 and your choices of the most important excited state wave functions in the expansion? Which type of plot, the wave function or probability function plot, enabled you to most easily predict the importance of a wave function in a linear combination? Explain.

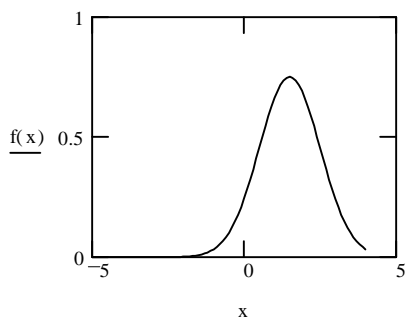
### Writing out the expansion function and plotting both the expansion function and the original function.

The expansion of the function is shown here with all six terms. If you successfully completed the previous page then you should see two graphs below. The one on the left shows the original function and the one on the right shows the linear expansion fit to the function. How do the graphs look?

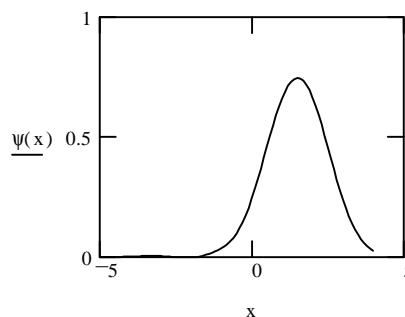
$x := -5, -4.9..4$

$x$  sets the range for the plot

$$\psi(x) := c_0 \cdot \psi_0(x) + c_1 \cdot \psi_1(x) + c_2 \cdot \psi_2(x) + c_3 \cdot \psi_3(x) + c_4 \cdot \psi_4(x) + c_5 \cdot \psi_5(x) + c_6 \cdot \psi_6(x)$$



Original Function Plot



The Linear Expansion Function Plot

**Exercise 7.** Duplicate the Linear Expansion function (copy and paste) immediately below the original function.

Use this new copy of the function to systematically remove terms from the sum starting with the  $c_6$  term. Record in your notebook the behavior of the Linear Expansion Function Plot as each term is removed.

Estimate the goodness of fit by determining the standard deviation of the fitted function from the original function. This is shown below (on the next page) for the full fitted function. Explain each step leading to the calculation of the standard deviation.

Repeat for a fit that uses only the first three terms in the sum. Discuss the significance of the difference in the standard deviations. Remove this extra work before proceeding to the next page.

### Estimating the goodness of fit.

pmax := 150

The number of computed points can be varied by changing pmax

i := 1 .. pmax

$x_1 := -5$  Value of  $x_1$

$x_i := x_{i-1} + .1$  Value of x for point i

$$fx_i := N_0 \cdot \exp\left[-\frac{(x_i - a)^2}{2}\right]$$

Here we are computing 150 points for the original function. This function was called f(x) in the Interlude.

Next we compute 150 points for the fitted function

$$\psi x_i := c_0 \cdot \psi 0(x_i) + c_1 \cdot \psi 1(x_i) + c_2 \cdot \psi 2(x_i) + c_3 \cdot \psi 3(x_i) + c_4 \cdot \psi 4(x_i) + c_5 \cdot \psi 5(x_i) + c_6 \cdot \psi 6(x_i)$$

$$SD := \sqrt{\sum_i^{pmax} (fx_i - \psi x_i)^2}$$

The standard deviation between the function and the fitted function is computed to the left.

$$SD = 2.857 \cdot 10^{-3}$$

**Exercise 8.** Examine the standard deviation as the number of terms in the fitting is reduced one by one starting with  $\psi 6(x_i)$ . You can do this by copying (duplicating) the  $\psi x_i$  equation into a space just above the definition of SS and then reducing the number of terms in  $\psi x_i$  systematically.

Make a table of the standard deviations and write an explanation of your observations. What number of terms in the linear expansion would adequately represent the original function? Explain.

## Creating a Spectrum

In this section we will create a vibronic spectrum and study the concepts that permit this.

To plot a vibronic spectrum, we need to have the energy of the electronic transition, the vibrational energy, the shape and width of the spectral peak, and the intensity. The energy is given by  $\Delta E = hv = hc/\lambda$  and the relative intensity is given by the Franck-Condon coefficients,  $c_n^2$ .

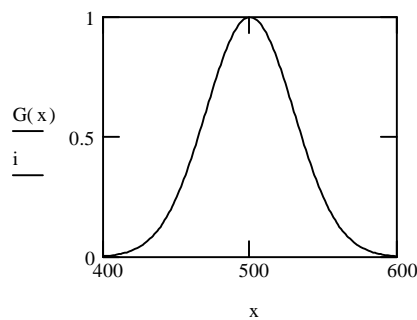
Many spectral peaks can be represented by Gaussian functions,  $G(x) := e^{-\frac{(x-x_0)^2}{2s^2}}$ . These functions are characterized by a standard deviation,  $s$ . In spectroscopic measurements, the full width at half maximum (FWHM) height is a standard measure of peak width. The FWHM is related to the standard deviation,  $s$ , by  $\text{FWHM} = 2.35s$ .

As an example, consider a peak centered at 500 nm with a standard deviation of 30. The FWHM should be 70.5. Let's see....

range for x       $x := 400..600$       peak center       $x_0 := 500$

standard deviation       $s := 30$        $i := .5$

$$G(x) := e^{-\frac{(x-x_0)^2}{2s^2}}$$



A line has been drawn for you at the half maximum.

**Exercise 9.** Select the graph and use the trace command to check on the FWHM. What do you observe? Change the FWHM. What happens to the curve? Record your observations in your notebook.

## Back to the Franck-Condon factors.

Here we will actually use the Franck-Condon Factors to draw an electronic spectrum for a molecule. Consider an electronic transition for an alkene at 250 nm with a vibrational component of  $1200 \text{ cm}^{-1}$ . The transition wavelength at 250 nm is assumed to be the adiabatic or 0 - 0 transition.

We choose a transition wavelength in nm  $\lambda := 250$

The required constants are  $h := 6.62 \cdot 10^{-34}$   $c_{\text{light}} := 3 \cdot 10^8$

A suitable wavelength range for the graph of the spectrum is :  $\lambda_{\text{min}} := 200$   $\lambda_{\text{max}} := 300$

Vibrational frequency  $\nu := 1200 \text{ cm}^{-1}$  Here we are using the C=C vibrational mode in alkene.

Earlier we computed seven Franck-Condon factors. Recall that these factors depend on 'a', the displacement of the excited state relative to the ground state coordinate system. Each of these corresponds to the probability of a transition between the ground electronic state's lowest vibrational energy level and one of the vibrational energy levels of the excited state. These seven vibrational transitions are superimposed on the electronic transition. Let's look at these seven vibrational components using the seven Franck-Condon factors that you computed in this document.

We have seven peaks, so  $k := 0..6$

First, give each peak a FWHM,  $\Delta\lambda$  of 5 nm. You can change this later and observe the results.

$$\Delta\lambda := 5 \quad s := \frac{\Delta\lambda}{2.35}$$

Next, calculate the energies and wavelengths:

$$E_{\text{min}} := \frac{h \cdot c_{\text{light}} \cdot 10^9}{\lambda_{\text{max}}} \quad E_{\text{max}} := \frac{h \cdot c_{\text{light}} \cdot 10^9}{\lambda_{\text{min}}} \quad E := \frac{h \cdot c_{\text{light}} \cdot 10^9}{\lambda}$$

$E_{\text{vib}} := h \cdot c_{\text{light}} \cdot \nu \cdot 100$  The energy of each vibrational transition.

$E_k := E + k \cdot E_{\text{vib}}$   $E_k$  is the energy of each peak relative to the energy for the electronic transition.

What specific transition is being considered when  $k = 0$  ?

$$\lambda_{\text{center}_k} := \frac{h \cdot c \cdot \text{light} \cdot 10^9}{E_k}$$

This gives each peak's center.

**Exercise 10. Check the units for each of the last three equations.**

**Now calculate 200 data points in the spectrum. You may calculate more or less points depending on the speed of your computer. 200 points gives a nice spectrum.**

$$\text{maxpts} := 200 \quad i := 0.. \text{maxpts} \quad \lambda_{\text{incr}} := \frac{\lambda_{\text{max}} - \lambda_{\text{min}}}{\text{maxpts}} \quad \lambda_i := \lambda_{\text{min}} + i \cdot \lambda_{\text{incr}}$$

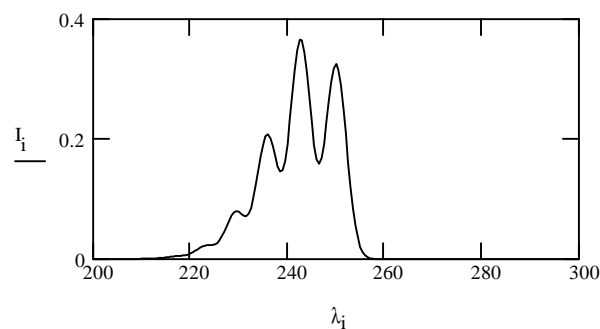
Notice how the range, just above, for the calculation is designed.

each peak is a Gaussian  
with width  $\Delta\lambda$  specified earlier

$$f_{i,k} := \exp \left[ -\frac{(\lambda_i - \lambda_{\text{center}_k})^2}{2 \cdot s^2} \right]$$

sum over all seven peaks to  
generate spectrum ----->

$$I_i := \sum_{k=0}^6 f_{i,k} \cdot (c_k)^2$$



### Exercise 11.

- a. Systematically vary the parameters used to produce the spectrum.
- b. What is the effect of the vibrational frequency?
- c. What effect does the FWHM have?
- d. Change the distance "a" on page 6. This will change the distance between the ground state and excited state equilibrium extensions.
- e. What effect does this have on the Franck-Condon factors?
- f. How does it change the spectrum? This exercise can be facilitated by declaring 'a' as a global variable and moving it next to the graph. Toggle the equation for 'a' on page 6 to off to do this.

### Exercise 12.

An observed alkene spectrum has five vibrational peaks from about 262 nm to 237 nm. The ratios of intensities are (starting at 262) : 1.7, 2.7, 2.3, 1.7, 1. Vary 'a' on page 6 to try to match the alkene spectrum. Again the global variable declaration is useful here. If you use the global variable declaration then you must toggle the equation defining 'a' on page 6 to off and remove the global declaration for 'a' used in Exercise 11. Only one global declaration is allowed for a variable in a document.

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