

Introduction to Franck-Condon Factors ©

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Introduction

This document and the accompanying file, FranckCondonComputation.mcd, may be useful to students taking a junior or senior college level course in Quantum Chemistry or Spectroscopy. When using these materials you should first work through this study guide and then proceed to the accompanying computational file. This study guide starts by listing the prerequisite skills and knowledge level required for successful and efficient completion of the computational document which is designed to lead you to an understanding of the role of the Franck-Condon principle in spectroscopy. After reviewing harmonic oscillator concepts you proceed here to a qualitative examination of the Franck-Condon principle. In the accompanying computational document you will practice computing Franck-Condon factors and relating them to the electronic spectra. You will be able to see how the Franck-Condon factors and other experimentally observed properties contribute to the shape of a spectrum. The performance objectives given here identify the essential set of concepts you are to learn. A summative mastery type question may be added to the end of this document by your instructor. This summative exercise will pull together the various concepts you will be studying here.

Goal

The goal of this document is to provide students with an introduction to Franck-Condon Factors and the relationship of these factors to vibronic spectroscopy.

Prerequisites

1. Moderate skill with Mathcad.
2. Knowledge of what orthonormal functions are.
3. Experience with harmonic oscillator wave functions.
4. Some experience with Fourier Series expansions of functions.

Performance Objectives

At the end of both segments of this lesson you should be able to:

1. compute the Franck-Condon factors associated with a given electronic transition;
2. express a ground state vibration wave function as a linear combination of excited state vibration wave functions;
3. describe orally and in writing the relationship between Franck-Condon factors and intensities of observed electronic transitions;
4. draw diagrams and qualitatively estimate the magnitude of the Franck-Condon factors using harmonic oscillator wave functions;
5. predict the spectrum associated with a vibration given the energy of the electronic transition and the vibrational frequency of the bond.

Tasks for achieving the objectives

1. review the harmonic oscillator wave functions and their graphical representations;
2. complete the readings in your text assigned by your instructor;
3. complete the activities described in this document;
4. complete the activities described in the FranckCondonComputation.mcd.

Franck-Condon Principle

When a molecule absorbs visible or ultraviolet light, a new excited state electronic structure is substituted for the original electronic structure. This occurs on such a short time scale that there is no significant change in the position of the nuclei of the molecule. The transition between the two states is vertical. If we examine the vibrational wave functions for the ground and excited states, the overlap of the wave functions between these two states will determine the intensity of the transition. After an electronic transition the excited state then adjusts its equilibrium bond length. The concept of a vertical transition at constant internuclear distance is the Franck-Condon Principle. Mathematically the Franck-Condon Principle means that the transition dipole is independent of nuclear coordinates. The degree of overlap of the wave functions for the ground state and excited state of the oscillator give us the Franck-Condon Factors. The Franck-Condon Principle should not be confused with the Born-Oppenheimer (BO) Approximation although they seem similar. In the Born-Oppenheimer Approximation we consider nuclear motion occurring more slowly than electronic motion because the nuclei have more mass than the electrons. The BO approximation states that the rate of change of nuclear wave functions as the nuclear positions change is much smaller than the change in electronic wave functions. This permits solution of the Schrodinger equation for molecules using a fixed set of nuclear coordinates that define the potential field in which the electrons move.

Exercise 1

At the bottom half of a clean piece of paper draw the potential energy as a function of bond length for the ground state of a bond in a molecule. Sketch in horizontal lines for a few vibrational energy levels. Sketch in the wave functions for the vibrational levels into your diagram.

Exercise 2

On the top half of the same sheet draw the potential energy as a function of bond length for the first excited electronic state, assuming that the excited state bond length is shorter than that in the ground state. In some molecules, excitation is from a nonbonding or antibonding orbital to another orbital further removed from the nuclei. This would cause the bond length to shorten in the excited state. How will the shape of the excited state curve differ from that of the ground state? Draw in the horizontal lines for the vibrational energy levels of the excited state. Sketch in the wave functions for the vibrational levels in your diagram.

Note: The two diagrams should share a common PE axis (y) and bond extension axis (x).

How does the dissociation energy of the excited state compare to that of the ground state?

Where would the excited state potential energy diagram lie with respect to the ground state potential energy diagram if the transition was from a bonding to an antibonding orbital?

Before an electronic transition occurs, most molecules will be in the lowest vibrational level ($v = 0$) of the electronic ground state. Absorption of energy during an electronic transition places the molecule into one of the vibrational levels of a higher electronic state. Such a transition most likely would occur from the most probable (equilibrium) bond length of the ground state vibrational energy level, vertically to various vibrational energy levels of the excited state.

According to the Franck-Condon Principle, the nuclear coordinates change more slowly than the electronic coordinates so that a transition is vertical on an energy vs. bond length diagram. **Draw such a transition on your diagram.** The vertical transition that is most probable is the one that has an excited state vibrational wave function maximum at the same place as the ground state wave function maximum. In other words, the probability of a transition is measured by the overlap between the vibrational wave functions of the ground state and excited states. The greater the overlap the greater the probability of the transition.

To evaluate these probabilities one merely needs to compute the overlap between the vibrational wave functions of the electronic ground state and the vibrational wave functions for the excited state. Many of the overlaps between the ground state vibrational wave function and the excited state vibrational wave functions can be computed. The one with the largest overlap is associated with the most intense peak in the spectrum. Other overlaps are associated with other less intense peaks in the spectrum.

In order to compute the overlap between the vibrational wave function of the ground state and the vibrational wave functions of the excited state, the equilibrium extension of the excited state relative to the equilibrium extension of the ground state is needed. Usually this is not known for new materials. One must make a reasonable guess for the displacement of the excited state relative to that of the ground state. This is 'a' in the FranckCondonComputation.mcd document. To estimate 'a' one must decide if the bond length in the excited state is longer or shorter than the length in the ground state. Then the overlaps, i.e. computed Franck-Condon factors, are tabulated, and compared to the relative intensities of the experimental peaks. By varying 'a' a good match between experimental peak intensities and Franck-Condon factors would provide the researcher with an estimate of r_e for the excited state. For some molecules, excitation from the HOMO to the LUMO will shorten the bond length of the excited state. This occurs because the HOMO is usually nonbonding or slightly antibonding and the LUMO is generally either more diffuse or farther away from the nucleus and thus has less impact on the bond length.

Which of the vibrational levels of the excited state will have the highest probability of being achieved? Which will come next? The answers depend on 1) the extension of the molecule at the instant it experiences an electronic transition and 2) the excited state vibrational wave functions at that extension relative to the initial state vibrational wave function at the instant of the transition. In general we consider the ground state to be at its equilibrium bond length.

The intensities of vibrational transitions are governed by the value of the overlap integral connecting the two vibrational levels. This is shown in equation (1) where the v_p and v subscripts identify the ground state and excited state wave functions respectively.

$$\int \phi_{v_p} \cdot \phi_v \, d\tau = c_{v_p, v} \quad (1)$$

The integral in equation (1) is called the vibrational overlap integral and the integration is over all nuclear coordinates. The square of the overlap value is called the Franck-Condon factor. The larger the factor the larger the peak observed in the UV-vis spectrum.

$$\left(|c_{v_p, v}| \right)^2$$

Franck-Condon factors allow one to estimate estimate the relative intensities of vibrational transitions.

The sum of Franck-Condon factors for transitions from a given vibrational state is equal to 1.0. Verification of this statement is left to the student as a master level exercise.

You will compute Franck-Condon factors in the `FranckCondonComputation.mcd` document.

Note: This is a good time to review the harmonic oscillator wave functions. Where are the maxima as a function of bond extension? What are the implications for the atomic positions of the bonded atoms as the vibration quantum number increases?

Note: Electronic transitions occur from a vibrational state of the ground electronic state to a vibrational state of the excited electronic state.

There is no strict selection rule on vibrational quantum numbers during an electronic transition. There is only Franck-Condon modulation of the transition probability.

Exercise 3

- a. From what internuclear distance of the molecule in the ground state is the transition to the excited state likely to occur?
- b. What excited state vibrational state is most likely to be at the end of the transition? Why? How would you quantify your answer?
- c. Predict the relative intensities of various electronic transitions (from a vibrational level in the ground electronic state to a vibrational level in the excited electronic state) if r_e were the same for each state and sketch them using a qualitative bar graph.

Now proceed to the FranckCondonComputation.mcd document where you will be asked to compute the overlap between a vibrational level in the ground state and a vibrational level in the excited state. In the computational document you will also be able to check the way the Franck-Condon factors along with the full width at half maximum (FWHM) property of a Gaussian function determine the shape of a spectrum consisting of several vibronic transitions.

Mastery Exercise: To be provided by the instructor.

You can demonstrate mastery of the concepts by correctly determining the relative intensity order of peaks in a given simple experimental electronic spectrum. You should also be able to describe your work accurately in writing and/or orally.

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