Teaching Nonradiative Transitions with MATLAB and Python

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Abstract

Nonradiative transitions are changes in energy states in atoms, ions or molecules that do not involve the emission or absorption of photons. Despite their importance in understanding luminescent properties and photochemical reaction mechanisms, nonradiative transitions are rarely given more than a qualitative overview in undergraduate and even graduate physical chemistry curricula. To supplement the coverage of nonradiative transition topics, we provide here a set of active learning exercises to help students develop an intuitive understanding of the factors that determine the rate of nonradiative transitions. We start by outlining the theoretical background through the formulation of the Franck-Condon factor and its relation to the rate of nonradiative transition. We then introduce three teaching modules, with associated MATLAB and Python codes, to explore how 1) the excited state nuclear displacement, 2) the electronic energy gap between excited and ground state, and 3) the excited/ground state vibrational mode frequencies affect the magnitude of the Franck-Condon factor and thereby the rate of nonradiative transitions. The wavefunction overlap plots that accompany all teaching modules provide direct visualization of the effect of input parameters on the magnitude of Franck-Condon overlap integral.

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Introduction

Absorption of photons by molecules is accompanied by a large and sudden increase in the molecule's energy (e.g., by 170 - 300 kJ/mol upon absorption of visible light). The molecule typically dissipates this energy through radiative (RT) and/or nonradiative (non-RT) transitions.¹ Non-RTs are described by two fundamental steps, as illustrated by wavy arrows in Scheme 1. The steps represented by horizontal arrows involve transitions between electronic states of either same or different spin, defining internal conversion (IC) and intersystem crossing (ISC), respectively. Those are shown as green and orange arrows, respectively. The steps represented by vertical red arrows represent the vibrational relaxation (VR) of the molecule within the same electronic state. These non-RTs distribute the excitation energy into different vibrational modes of the molecule (intramolecular dissipation) and, in the condensed phase, the vibrational modes of the surrounding bath (intermolecular dissipation), effectively converting the absorbed photon's energy into heat. We focus here on the electronic transitions IC and ISC, processes that typically involve a conversion from the lowest vibrational level of one electronic state (such as S₁ state in Scheme 1) to the manifold of vibrationally "hot" states of another electronic state (such as T₁ states in Scheme 1).



Scheme 1. Jablonski diagram summarizing radiative (absorption, fluorescence and phosphorescence) and nonradiative (vibrational relaxation, internal conversion and intersystem crossing) transitions.

Even though non-RTs are spectroscopically silent, they indirectly influence the spectroscopy of emissive molecules. The dynamic competition between RTs and non-RTs shapes the energies and lifetimes of emissive states. For example, the absorption of light generates an electronically excited state whenever the photon energy matches its resonant frequency and the transition dipole moment is nonzero. However, fluorescence and phosphorescence typically occur only from the lowest electronic excited states, leading to the well-known insensitivity of emission spectra to the excitation wavelength known as Kasha's rule.² These observations are a result of fast IC that occurs

between closely spaced high-energy electronic states and outcompetes radiative processes from higher electronic excited state. The increased IC rate between two close-lying electronic states is a result of the "energy gap law" (EGL), which is responsible for the experimental observation that the excited state lifetime decreases as the emission energy of the chromophore moves towards longer wavelengths.³⁻⁴ The EGL, derived by Englman and Jortner⁴ and Fischer,⁵ describes an exponential increase the in the rate of non-RT between two electronic states as the energy gap between them decreases. Faster non-RT competes with emission and therefore shortens the excited state lifetimes at small energy gaps.

Non-RTs can also affect the emission in chemiluminescence and bioluminescence.⁶ One example is bacterial bioluminescence, where a flavin cofactor, noncovalently bound to a luciferase protein, reacts with molecular oxygen to non-radiatively populate an emissive electronic excited state.⁷ The blue emission from bacterial luciferase is strong enough to be detectable by satellites in space.⁸ However, when the same chemical modification of the flavin cofactor occurs outside the rigid protein environment, the chemically generated excited state is not emissive due to a competing non-RT pathway accompanying excited-state distortion of the flavin.⁹⁻¹⁰ This example illustrates the ongoing competition between RTs and non-RTs and its sensitivity to factors such as the solvent or protein environment.

Understanding non-RTs is a pre-requisite to understanding the mechanisms of chemical reactions initiated by light (photochemistry).¹¹⁻¹³ Non-RTs can either compete with the photochemical reaction, reducing the quantum yield of the product formation, or enhance the reaction by quickly funneling the excited state population to the electronic state on which the reaction occurs. In the primary step of vision, for instance, the absorption of light by the retinal protonated Schiff base of rhodopsin generates a singlet excited state that undergoes non-RT to the ground state via a conical intersection that is located along the *cis*- to *trans* reaction coordinate.¹⁴⁻¹⁶ This photoisomerization initiates signaling cascades in the retina of our eyes that ultimately leads to an electrical impulse in the optic nerve connecting our eyes to our brain. The highly efficient non-RT in rhodopsin is critical to visual sensitivity, enabling our eyes to detect even a single photon.¹⁷ Non-RTs also affect the photocatalytic performance of transition metal complexes: the excited state lifetimes of 3dmetal complexes are often shorter than those of 4d and 5d metal analogs.¹⁸ This arises from the smaller ligand-field splitting of 3d metals that lower the energy of metal-centered (³MC) ligandfield states below the long-lived metal-to-ligand charge transfer triplet (³MLCT) state. Since ³MC tend to undergo fast non-RT deactivation pathways, 3d metal complexes have short-lived excited states, which undermines their utility in photoinduced charge separation.¹⁸

The rates of non-RTs are controlled by, among other parameters, an overlap integral between the vibrational wavefunctions of the initial and final states. The square of this overlap integral is called the Franck-Condon factor (FCF), a concept formulated by James Franck and Edward U. Condon¹⁹⁻²¹ to calculate the intensities of absorption bands from vibronic transitions that are concomitant with electronic transitions. FCFs, in the context of non-RTs, will be the focus of this technology report. Although the overlap integral itself is occasionally referred to as the FCF,²² we will keep consistent with the definition given by many contemporary textbooks^{2, 23-27} and articles²⁸⁻³⁵ and define the overlap integral as the FC overlap and the square of the overlap integral as the FCF. The

FCF is a dimensionless parameter that has a value in the range of 0 to 1. The rate of IC is slow for FCF values close to 0 and is fast for FCF values close to 1. The value of the FCF is sensitive to the structural distortion (Δx) and the energy gap (ΔE) between the states involved in the transition, as shown in Scheme 2. It is also dependent on the curvatures (vibrational frequencies or wavenumbers, $\tilde{\nu}$) of the potential energy surfaces of the two electronic states.

Despite their importance in molecular spectroscopy and photochemistry, the fundamentals of non-RTs are generally not covered in undergraduate curricula.³⁶⁻³⁹ Most undergraduate textbooks describe RTs involving the absorption and emission of light. Physical chemistry textbooks by Atkins and de Paula, Engel and MacQuarrie briefly describe non-RTs such as IC and ISC, but only introduce FCF within the context of vibrational structure in electronic spectra,⁴⁰⁻⁴¹ while other physical chemistry textbooks by Levine and Duffey do not cover non-RTs.⁴²⁻⁴⁵ Quantum chemistry textbooks such as those by Levine, McOuarrie and McIntyre derive Fermi's golden rule in chapters on time-dependent perturbation theory but limit the application of the golden rule to electric dipole interactions. Many graduate-level textbooks also focus on RTs while giving brief introductions of non-RTs and only invoke FCFs to explain the intensities of vibrational bands in molecular electronic spectra.^{22-23, 25, 46-50} In Levine's Molecular Spectroscopy, RTs are covered quantitatively and at length, while non-RTs are introduced briefly and qualitatively in a section on collisions of the first kind and the second kind.²³ In Banwell's Fundamentals of Molecular Spectroscopy non-RT is briefly covered in vibrational cross-overs of predissociation and collision-induced ISC in phosphorescence.⁵⁰ In Harris and Bertolucci's Symmetry and Spectroscopy, non-RTs are covered qualitatively and FCFs are introduced to explain the probability of IC.²² In Bernath's Spectra of Atoms and Molecules, non-RTs are covered briefly in sections on Jablonski diagrams and breakdown of Born-Oppenheimer approximation in conical intersections and Jahn-Teller effects.²⁵ In McHale's Molecular Spectroscopy, non-RTs are covered in a section on emission spectroscopy of polyatomic molecules.⁴⁹ A few experimental physical chemistry or computational chemistry textbooks provide more mathematical treatment of Franck-Condon analyses.⁵¹⁻⁵²

FCFs are often introduced in the context of RTs because they can be intuitively connected to the line shapes of absorption and emission spectra. Non-RTs do not produce spectroscopic signals that can be correlated to FCFs. Therefore, there is a need to develop alternative visual aids and tools to help students learn about non-RTs. Only in highly specialized textbooks do we begin to see an indepth, physical description of non-RTs.^{2, 24-26, 53-54} However, these chemical physics books are not accessible to many chemistry students who do not have the pre-requisite mathematics background to describe the underlining quantum phenomena. Thus, there is a need for teaching tools that can introduce the concepts behind non-RTs to chemistry students.

Here, we provide teaching modules that can be used in undergraduate and graduate physical chemistry classrooms to help students develop intuition for factors that control non-RTs. We provide a set of codes, written in MATLAB and Python, to enable direct visualization of these factors and to complement the theoretical aspects learned in the classroom. MATLAB and Python were selected due to their versatility at illustrating topics in chemical education⁵⁵⁻⁶⁶ and because they are readily available to students. The Background section of the article provides a brief description of IC and ISC through the framework of perturbation theory. The Modules section provides a description of three teaching modules that illustrate how IC is affected by the parameters that describe molecular potential energy surfaces.



Scheme 2. Potential energy diagram illustrating important factors that control the rate of IC between two vibronic states, namely the initial vibronic state composed of the zeroth vibrational level ($QN_{ES} = 0$) of an electronic excited state (ES) and the final vibronic state composed of the fourth vibrational level ($QN_{GS} = 4$) of the electronic ground state (GS): the structural distortion between energy minima (Δx) and the energy gap between the two electronic states (ΔE).

Background

Non-RTs are composed of two fundamental steps: the horizontal (isoenergetic) IC/ISC processes that involve a conversion from one electronic state to another, and vertical VR processes that dissipate excess energy into the vibrational modes of the solute and solvent (Scheme 1). A theoretical description of IC/ISC is often presented within the framework of perturbation theory, where the stationary-state solutions to molecular Hamiltonians are used to derive the rates of transitions caused by a weak perturbation.⁶⁷ The rate $\Gamma_{i\to f}$ for the non-RT from the initial eigenstate *i* to a density of final eigenstates *f* that are close in energy to state *i* can be expressed using Fermi's Golden Rule as shown in eq 1:

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \rho_f(E_f) \left(\int \Psi_i \widehat{H}_{i \to f} \Psi_f d\tau \right)^2 \tag{1}$$

Here, Ψ_i and Ψ_f are the stationary-state solutions for the initial and final states of the molecular Hamiltonian, respectively. For example, if we are interested in non-RT from the excited electronic state S₁ to the ground electronic state S₀ (e.g., the IC shown in Scheme 2), the initial eigenstate Ψ_i is typically the lowest vibrational level of an electronically excited S₁ state, while Ψ_f represents the eigenstates of the vibrationally "hot" electronic S₀ state. $\rho_f(E_f)$ represents the density of acceptor states that are close in energy to initial state (namely, they satisfy the energetic criterium $E_f \approx E_i$). For simplicity, we focus here on the transition involving a single final state and assume the value of $\rho_f(E_f)$ is 1 J⁻¹. Here, the J⁻¹ unit is necessary for balancing units, with the understanding that the total transition probability must usually be obtained by integrating over all possible transitions in the relevant energy range. For non-RT processes, $H_{i\to f}$ is a kinetic energy operator for nuclear motion:

$$\widehat{H}_{i \to f} = -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2$$
⁽²⁾

The operator $\hat{H}_{i \to f}$ perturbatively couples nuclear and electronic motion, which are otherwise assumed to be separable within the Born-Oppenheimer approximation. Electronic and nuclear motion can be strongly coupled during non-RTs, which is why non-RTs are often described as nonadiabatic.

In the context of the Born-Oppenheimer approximation and assuming weak spin-orbit coupling, we introduce below a zeroth-order approximation where we write the molecular wavefunctions, Ψ_i and Ψ_f , as a product of fundamental electronic (ψ_i and ψ_f), nuclear (χ_i and χ_f) and spin (S_i and S_f) wavefunctions, as shown in eq 3. This equation follows the approach used by Turro et al.²

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar} \left(\int \psi_i \widehat{H}_{i\to f} \psi_f d\tau \right)^2 \left(\int \chi_i \chi_f d\tau \right)^2 \left(\int S_i S_f d\tau \right)^2$$
(3)

The first square term in eq 3 represents the electronic coupling matrix $|V_k|^2$. For non-RTs, this parameter will be large for nuclear motion that promotes the mixing of the initial and final states. For example, consider an electronic transition that transforms a *p*-like orbital of the carbon atom to a hybrid *sp*ⁿ orbital. In this case, out-of-plane bending vibrations involving that carbon atom have a strong effect on the electronic coupling matrix values and allow transitions between orbitals of different symmetry.² In contrast, the in-plane vibrations will have a small value of $|V_k|^2$ and will not significantly encourage the electronic transition.²

The second squared term in eq 3 is called the Franck-Condon factor (FCF), a dimensionless parameter that ranges from 0 to 1. In polyatomic molecules with N atoms, the molecular vibrational wavefunction is represented as a product of wavefunctions of 3N-6 (or 3N-5 for linear molecules) vibrational modes. Here, we will assume that a molecule contains only one promoting and one accepting vibrational mode, which is a suitable model for describing a diatomic molecule. Alternatively, the one-dimensional model used here can represent a critical mode of a polyatomic molecule that is effective at causing IC, while all remaining modes are assumed not to participate in IC. In the MATLAB/Python code provided here, the FCF is calculated by squaring the integral of the product of the nuclear wavefunction of the initial zero vibrational level ($QN_{ES} = 0$) of electronic excited state, χ_i , and the nuclear wavefunction of the final vibrationally "hot" level (QN_{GS}) of the electronic ground state, χ_f . Both nuclear wavefunctions are treated as normalized harmonic oscillator wavefunctions. The integration is over the full range of displacement [$-\infty$, $+\infty$], but in practice is carried out over a defined region [x_{min} , x_{max}] around the origin, which is where the minimum of the potential energy well of the ground electronic state is located and where the nuclear wavefunctions have significant amplitudes (eq 4).

$$FCF = \left[\int_{-\infty}^{+\infty} \chi_i \chi_f dx\right]^2 \approx \left[\int_{-x_{\min}}^{x_{\max}} \psi_{ES,0}(\alpha_{ES}, x - \Delta x)\psi_{GS,QN}(\alpha_{GS}, x)dx\right]^2$$
(4)

Here, Δx represents the distortion, i.e., a displacement between the potential energy surface minima of the initial and final state (Scheme 2). This parameter will be varied by students to derive an intuitive understanding of how it affects rates of IC. The normalized quantum harmonic oscillator wavefunctions, $\psi_{\text{ES},0}(\alpha_{\text{ES}}, x - \Delta x)$ and $\psi_{\text{GS},\text{QN}}(\alpha_{\text{GS}}, x)$ are written using Hermite polynomials,⁶⁸ as shown in eq 5a-c:

$$\psi_{\rm QN}(x) = (2^{\rm QN} {\rm QN!})^{-1/2} (\alpha/\pi)^{1/4} e^{-\alpha x^2/2} H_{\rm QN}(\alpha^{1/2} x)$$
(5a)

where the Hermite polynomials are defined as shown in eq 5b

$$H_{\rm QN}(\alpha^{1/2}x) = (-1)^{\rm QN} e^{(\alpha^{1/2}x)^2} \frac{d^{\rm QN} e^{-(\alpha^{1/2}x)^2}}{d(\alpha^{1/2}x)^{\rm QN}}$$
(5b)

and the simplifying frequency parameter, α , is defined as

$$\alpha = 2\pi\nu\mu/\hbar \tag{5c}$$

where ν is the vibrational frequency and μ is the reduced mass.

The value QN_{GS} is obtained from the energy gap ΔE , as shown in eq 6 and illustrated in Scheme 2. Students will be able to change the value of ΔE , to learn how the optical gap affects the rates of non-RTs. Unlike the decreasing Morse potential level spacing approaching the dissociation energy illustrated in Scheme 2, energy levels in our simple quantum harmonic oscillator model are evenly spaced:

$$E_{\rm QN} = \left({\rm QN} + \frac{1}{2}\right)hv = \left({\rm QN} + \frac{1}{2}\right)hc\,\tilde{v}, {\rm QN} = 0, 1, 2, \dots$$
(6a)

where \tilde{v} is the user-defined vibrational wavenumber. To determine the quantum number of the final vibrational level in the electronic ground state, QN_{GS} , that is energetically accessible from $QN_{ES} = 0$ of the electronic excited state, we divide the energy gap ΔE by the quantized energy interval of the ground state $hc\tilde{v}_{GS}$ (or hv_{GS}) and round to the nearest integer:

$$QN_{GS} = \left[\frac{\Delta E}{hc\tilde{\nu}_{GS}}\right]$$
(6b)

The rounding to the nearest integer is done using the "round" functions both in MATLAB⁶⁹ and in the Python NumPy library.⁷⁰

The third square term in eq 3 introduces the spin and distinguishes between IC and ISC. Formally, when $S_i = S_f$, then $\int S_i S_f d\tau = 1$ and the process is considered IC and is spin-allowed, thus occurring at relatively fast rates. When $S_i \neq S_f$, $\int S_i S_f d\tau \sim 0$ and the process is formally spin-forbidden and corresponds to ISC. The "forbidden" spin factor results in a rate of ISC that is orders of magnitude slower than IC unless sufficiently strong spin-orbit coupling takes place. In this teaching module, we consider IC processes, where the spin integral is equal to 1. Therefore, eq 3 can be rewritten for the rate of non-RT, k_{nr} , as

$$k_{\rm nr} = \Gamma_{i \to f} = \frac{2\pi}{\hbar} (1 \, {\rm J}^{-1}) (h c V_k)^2 ({\rm FCF}) (1)^2 \tag{7}$$

This technology report focuses on how FCFs from eq 4 affect the rate of IC. While V_k will be a parameter entered by the user and can be computed using electronic structure software, for the purpose of the modules presented here, we will keep V_k constant at 750 cm⁻¹, which needs to be converted into energy by $E = hc\tilde{v} = hcV_k$ as shown in eq 7. As stated above, we also assume that only a single vibrationally hot electronic ground state contributes to the overall transition probability and leave out the density of states term to avoid summing or integrating over several states that may be energetically accessibility in an ensemble of molecules. The goal is to provide students with an intuition of how structural distortion (Δx), the energy gap (ΔE) and vibrational wavenumbers (\tilde{v}_{ES} and \tilde{v}_{GS}) affect the rate of IC, as shown in Scheme 2.

Modules

The teaching modules reported here utilize eqs 3-7 to generate an output, as illustrated in Figure 1. The MATLAB/Python code allows students to input values for excited-state displacement from the ground state equilibrium (Δx), electronic energy gap between excited state and ground state (ΔE), the electronic coupling matrix element V_k , and the ground and excited state vibrational wavenumbers (\tilde{v}_{GS} and \tilde{v}_{ES}). The output contains a graphical representation of harmonic PESs associated with the relevant vibrational modes. For example, Figure 1 illustrates that Δx and ΔE control the relative horizontal and vertical positions of potential energy surfaces (PESs), respectively. The wavenumbers (\tilde{v}_{GS} and \tilde{v}_{ES}) control the curvature of the PES. The numerical output is shown as a text inset and provides the QN_{GS} values derived using eq 6, the values for FCF calculated using eqs 4 and 5, and the estimated rate of IC non-RT, $k_{nr} = \Gamma_{i\to f}$ calculated using eq 7, assuming the spin factor is unity and using the V_k provided by the user (here 750 cm⁻¹).



Figure 1. Example outputs of (A) the MATLAB code for Modules 1 and 2 and (B) the Python code for Module 3 that plots the overlap between the excited state and ground state harmonic oscillator wavefunctions. The input parameters are based on a ${}^{12}C{}^{-12}C$ bond, which has a reduced mass of 6 g/mol, ground state vibrational wavenumber (\tilde{v}_{GS}) of 1700 cm⁻¹, excited state vibrational wavenumber (\tilde{v}_{GS}) of 1000 cm⁻¹ for (A) and a constant V_k value of 750 cm⁻¹. The *x*-range and number of plot points within defined *x*-range can also be adjusted by the user.

Three teaching modules are provided, as summarized in **Table 1**. In addition to the direct visualization of the overlap between the excited state and ground state harmonic oscillator wavefunctions shown in **Figure 1**, additional MATLAB and Python codes, as well as slides summarizing code outputs for each Module, are provided to show how FCF is affected by excited state displacement from ground state (Δx , Module 1), electronic energy gap between excited state and ground state (ΔE , Module 2) and the ground and excited state vibrational frequency or wavenumber (\tilde{v}_{GS} and \tilde{v}_{ES} , Module 3). Module 1 can be used as the introductory module to familiarize students with the code, the visualization of overlap between vibrational wavefunctions, and the proportional relationship between k_{nr} and FCF. Module 2 can be used to illustrate the EGL and exceptions to the EGL at larger excited state displacement from ground state. In addition to demonstrating the effect of vibrational frequencies (wavenumbers) on the FCF, Module 3 can be used to illustrate how the symmetry and orthogonality of quantum harmonic oscillator wavefunctions determine FCF.

Teaching Module Number	Teaching Module Title	Parameters to Change	Output	Learning Objectives
1	FCF versus displacement	Excited state displacement from ground state	Graph illustrating overlap between vibrational wavefunctions with values for FCF and k_{nr} Graphs showing the change of FCF with	 Overlap between vibrational wavefunctions <i>k</i>_{nr} is proportional to FCF Effect of displacement on FCF and <i>k</i>_{nr}

Table 1. Teaching Modules and Their Input/Output Parameters and Learning Objectives

			displacement at different energy gaps	
2	FCF versus energy gap	Electronic energy gap between excited state and ground state	Graph illustrating overlap between vibrational wavefunctions with values for FCF and k_{nr} Graphs showing the change of FCF with energy gap at different displacements	 Effect of energy gap on FCF and k_{nr} The energy gap law (EGL) and exceptions to the law
3	FCF versus excited state vibrational mode frequencies	Excited state vibrational mode frequencies	Graph illustrating overlap between vibrational wavefunctions with values for FCF and k_{nr} Graphs showing the change of FCF with excited state vibrational frequencies at different displacements or energy gaps	 Effect of excited state vibrational mode frequencies on FCF and <i>k</i>_{nr}. Effect of orthogonality and symmetry (parity) in determining overlap integrals.

<u>Teaching Module 1: FCF versus displacement (Δx).</u> The first module is designed to teach students about the effect of the horizontal geometric displacement (Δx) between the excited state and ground state equilibrium structures on the FCF. For this module, students can change the Δx input parameter to see how the FCF, and thereby k_{nr} , changes with displacement (**Figure 2**), using the "FCF vs Displacement" MATLAB/Python code. For transitions involving higher vibrational levels of the ground electronic state (ground state vibrational quantum number QN_{GS} > 0), students will see that FCF increases and then decreases as Δx increases (See **Figure 2A**). This is due to increasing wavefunction overlap at values of *x* farther from equilibrium with increasing vibrational quantum number. FCF then decreases exponentially at larger Δx as the wavefunction overlap decreases while the wavefunctions move further apart. When Δx is 0 Å, FC overlap will be 0 for any non-zero energy gap, since the harmonic oscillator wavefunctions are orthogonal. Due to the orthonormality of the harmonic oscillator wave functions at $\Delta x = 0$ Å, the FCF is 1 when QN_{GS} = 0 and 0 when the QN_{GS} > 0, which can be emphasized to students.

At small displacements, the FCF increases with displacement for $QN_{GS} > 0$. This means that if a molecule undergoes excited-state distortion, it is less likely to exhibit photoemission due to the competing non-RT that occurs at faster rate due to the large FCF. Such excited-state distortions have been shown in many cases to decrease excited state lifetimes.⁷¹⁻⁷⁵ For instance, ruthenium(II) bipyridine (bpy) complexes are known to exhibit long-lived excited states with triplet $d_{\pi}(Ru) \rightarrow \pi^*(bpy)$ metal-to-ligand charge transfer character (³MLCT). However, when one of bpy ligands is replaced with cyclometalating phenylpyridine, only very weak emission in the 700-800 nm near infrared range is observed at room temperature.⁷⁵ In this case, the non-emissive pathway dominates

excited state deactivation from the ³MLCT state due to large Franck-Condon overlap of the vibronic wavefunctions of the ground state ¹GS and ³MLCT states that arises due to significant distortion of the ³MLCT excited state compared to the ¹GS ground state geometry. The distortion mainly manifests in the elongation of Ru-N bonds of the bipyridine ligand *trans* to the Ru-C bond due to formal oxidation of ruthenium to +3 in the ³MLCT state and the cyclometalating phenyl ring.⁷⁵ Reducing the excited state distortion by making the cyclometalating phenylpyridine ligand a stronger π -acceptor ligand or by introducing tridentate ligands has been shown to effectively improve the phosphorescence quantum yields of such complexes.⁷⁴⁻⁷⁵



Figure 2. (A) Plots of FCF as a function of Δx for several ground state QN (QN_{GS}) values: 0 (gray), 1 (blue), 2 (green), 3 (red), and 4 (purple). (B) For QN_{GS} = 2, FCF first increases and then decreases as Δx increases. This is demonstrated by the 3 snapshots of the FC overlap for QN_{GS} = 2 at Δx = (i) 0.012 Å, (ii) 0.116 Å and (iii) 0.2 Å.

<u>Teaching Module 2: FCF versus energy gap (ΔE).</u> The second module uses the same MATLAB/Python code as Module 1 to generate the wavefunction overlap plots. For this module, students can change the input for the vertical electronic energy gap (ΔE). The MATLAB code will produce the quantum number for the vibrationally excited electronic ground state wavefunction and illustrate the corresponding harmonic oscillator wavefunction, while the electronic excited state wavefunction remains at the vibrational ground state, represented with the harmonic oscillator

function with quantum number 0. The graph will show the quantum number for the ground state wavefunction along with the FCF and k_{nr} values. Students can vary the electronic energy gap to see how it affects the FCF and k_{nr} values (see **Figure 3** and plot a graph like **Figure 3A**) by using the "FCF vs Energy Gap" MATLAB/Python code. As the energy gap is adjusted by a student, the code will produce the QN for the ground state and FCF values for varying ΔE values.

At displacement smaller than 0.1 Å, we see that the rate of non-RT decreases as the vertical energy gap increases (See Figure 3A). This manifests in the energy gap law (EGL), which was first proposed as an empirical relationship by Robinson and Frosch,⁷⁶ and then given a more theoretical development by Siebrand,⁷⁷ Englman and Jortner,⁴ and Fischer.⁵ The EGL has been observed in many systems. In one case, the non-RT decay rate from the triplet state T₁ of platinum-containing conjugated polymers and monomers was found to decrease exponentially with increasing T₁-S₀ energy gap.⁷⁸ As the phosphorescence from the triplet state becomes partially allowed by the platinum-induced spin-orbit coupling, the decay from the triplet state is dominated by the non-RT pathway, the rate of which was shown to be highly sensitive to the triplet state energy by the EGL.⁷⁸ Because the mechanism of the non-RT was associated with the vibrations of bonds in the conjugated spacer groups in the polymers, designing polymers with high energy triplets was suggested as a way to improve phosphorescence yields.⁷⁸ The EGL was also observed in the nearinfrared phosphorescence for a series of homoleptic chromium(III) complexes with 1,3bis(pyridin-2-ylimino)isoindolin-2-ide (bpi) ligands.⁷⁹ The excited state was found to be metalbased ⁴A₂-²E with ligand-to-metal charge transfer (LMCT) character.⁷⁹ Therefore, tuning the energy of the excited state by varying the electron-donating substituents on the ligand pyridyl groups gave varying emission quantum yields in accordance with the EGL (eq 8).⁷⁹ Early work by Meyer also showed the applicability of the EGL to non-RT from a variety of excited states such as MLCT excited states in osmium and rhenium complexes,^{3, 80} d-d excited states in rhodium complexes, π - π * states in fluorescein and d σ *- σ p excited states of dimeric rhodium complexes.³ The EGL has also been observed in the S₁-S₀ transition of many conjugated organic molecular chromophores that emit in the visible⁸¹ and near and short-wave infrared ranges.⁸²⁻⁸⁴ Although near-infrared and short-wave infrared emitters are relatively rare, they are becoming increasingly valuable for emerging applications in biomedical imaging,⁸⁵⁻⁸⁶ photosensitizers for photodynamic therapy,⁸⁷ organic light-emitting devices,⁸⁸ eye-safe lasers in lidar systems for remote sensing and autonomous vehicle guidance,⁸⁹ etc. The trade-off between fluorescence quantum yields and the HOMO-LUMO gap prescribed by the EGL was applied to a collection of laser dyes and flavylium and chromenylium polymethine chromophores to provide fundamental limits on the quantum yields.⁸³ As the maximum vibrational frequency $\omega_{\rm M}$, which is the alkenyl C-H stretch at 3000 cm⁻¹ in the family of polymethine dyes, plays a larger role in setting k_{nr} (eq 8), substitution of the hydrogen in the alkenyl C-H by deuterium was found to improve the quantum yield by decreasing the maximum vibrational energy to 2200 cm⁻¹, thereby decreasing k_{nr} .⁸³ Later DFT computations of the emission spectra and studies on the mechanism of nonadiabatic S₁-S₀ decay of two flavylium polymethine dyes found that vibrational modes such as the wagging and scissoring motions of H atoms other than the maximum frequency mode also contributes to the $k_{\rm nr}$.⁸² Additionally, based on experimental and theoretical k_{nr} values for fully and partially deuterated dyes, the high frequency C-H stretching mode was found to make only a modest contribution to the total nonadiabatic derivative couplings, which provided the major route for non-RT of these infrared dye molecules.⁸² This "isotope effect" that is dominated by the high-frequency C-H stretch in aromatic hydrocarbons was rationalized in the early text on EGL by Englman and Jortner⁴ and

later explicated with various examples in the review by Avouris, Gelbart and El-Sayed.⁹⁰ The observations of non-RT rate decreases with deuteration have been essential in understanding the non-RT and RT mechanisms in numerous molecular systems such as the anomalous, anti-Kasha $S_2 \rightarrow S_0$ fluorescence of azulene.^{2, 4, 90}

While the EGL rule has been widely reported, it may be violated at larger Δx values, as we see in **Figure 3A**, and even inverted beyond that point, meaning FC overlap increases and then decrease as energy gap increases. While this is rare, this effect has been observed experimentally.⁹¹⁻⁹⁶



Figure 3. (A) Plots of FCF as a function of ΔE for different Δx values. (B) For $\Delta x = 0.2$ Å, FCF first increases and then decreases as ΔE increases. This is demonstrated by the 3 snapshots of the FC overlap for $\Delta x = 0.2$ Å at $\Delta E = (i) 0.1$ eV, (ii) 0.3 eV and (iii) 1.36 eV.

<u>Teaching Module 3: FCF versus excited state vibrational mode frequencies (\tilde{v}_{ES})</u>. The third module uses a different MATLAB/Python code for making the wavefunction overlap plots (Figure 1B) to show the effect of the frequencies of the vibrational modes of the excited on FCF and k_{nr} . Students can set the displacement and electronic energy gap values to the same numbers and change the input values for the excited state vibrational mode wavenumber to see how it affects the FC overlap and k_{nr} values (**Figure 4**).

In Modules 1 and 2, students are working with an ideal scenario where the vibrational mode frequencies for the excited and ground states are the same. However, this is rarely the case in practice.⁹⁷ By plotting FCF versus excited state vibrational wavenumber for various ground state QN values (Figure 4A), it can be seen that the FCF value at $\Delta x = 0$ Å is non-zero only for the even ground state QN values. The excited state wavefunction (QN = 0) has even parity, so without any displacement, multiplying this wavefunction by a wavefunction with odd parity will result in an odd function, which always has an integral of 0. Instructors may use this as an opportunity to discuss the role of parity in overlap integrals with help of this tool that allows students investigate overlaps visually.



Figure 4. (A) Plots of FCF as a function of excited state vibrational wavenumbers \tilde{v}_{ES} when $\tilde{v}_{GS} = 1700 \text{ cm}^{-1}$ for different energy gaps or QN_{GS}. The inset is a zoom-in of the plots of FCF as a function of excited state vibrational wavenumbers for QN_{GS} = 1, 3 and 4. (B) For QN_{GS} = 2, FCF decreases as \tilde{v}_{ES} increases from 1000 cm⁻¹ to 1500 cm⁻¹. This is demonstrated by the 3 snapshots of the FC overlap for $\Delta x = 0$ Å and $\Delta E = 0.3$ eV at $\tilde{v}_{ES} = (i) 1000 \text{ cm}^{-1}$, (ii) 1200 cm⁻¹ and (iii) 1400 cm⁻¹.

Classroom Experience

The modules were introduced to 19 graduate students in a 2-hour lecture as part of a physical chemistry seminar course. After providing the theoretical background on non-RTs, students were asked to make hypotheses regarding the effects of various factors that affect the rate of non-RT. Afterwards, students changed the input parameters, e.g., displacement or energy gap from excited state to ground state, in the MATLAB code, visualized the outcome, and discussed whether the results were consistent with their initial hypotheses. Although only a small percentage of the students that were introduced to the activity-based teaching modules had coding experience with MATLAB or Python, all the students completed the tasks requiring changes of input parameters directly in the code by working either individually or in groups. Overall, feedback provided by the students indicated that they found these modules to be an effective and helpful tool to visualize the quantum chemistry concepts associated with molecular spectroscopy. The fact that the students did not need to perform the calculations themselves alleviated the need for the chemistry students to master the mathematics behind the code, making it easier to grasp the underlying principles.

Conclusions

The direct visualization of changes in Franck-Condon overlaps that result from changing excited state displacement from ground state, electronic energy gap between excited state and ground states, and excited state vibrational mode frequencies helps students develop an intuitive understanding of the factors that affect the rate of non-RTs. Furthermore, the understanding of nonradiative decay principles, their ancillary Kasha's rule, the energy gap law, and their exceptions helps students develop a theoretical framework for interpreting experimental electronic spectra and photochemistry.

Associated Content

Supporting Information

The Supporting Information is available at

MATLAB file for overlap plot for teaching Modules 1 and 2 (TXT) MATLAB file for overlap plot for teaching Module 3 (TXT) MATLAB file for FCF calculation for teaching Module 1 (TXT) MATLAB file for FCF calculation for teaching Module 2 (TXT) MATLAB file for FCF calculation for teaching Module 3 (TXT)

Python file for overlap plot for teaching Modules 1 and 2 (TXT) Python file for overlap plot for teaching Module 3 (TXT) Python file for FCF calculation for teaching Module 1 (TXT) Python file for FCF calculation for teaching Module 2 (TXT) Python file for FCF calculation for teaching Module 3 (TXT)

Slides summarizing MATLAB output for teaching Module 1 (PDF) Slides summarizing MATLAB output for teaching Module 2 (PDF) Slides summarizing MATLAB output for teaching Module 3 (PDF)

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Notes

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