Literature Study

Vibronic spectra simulations: time-independent methods and Franck-Condon factors

Joachim Galiana
M2 Sciences de la Matière, Modélisation Numérique
ENS de Lyon

Under the supervision of
Benjamin Lasorne
Institut Charles Gerhardt, Montpellier

Abstract:
This report aims to review the developement of time-independent methods for the simulation of vibrationally-resolved electronic spectra. Key steps and approximations for the derivation of the electronic transition dipole moment are presented, highlighting the importance of Franck-Condon factors for the simulation. Issues and techniques for derivating them are presented in the simple case of one-dimensional harmonic oscillators, before exploring the issues the multi-dimensional problem. Finally, the aim of the incoming intership on the understanding of an unusual Stokes shift is presented.

Keywords: Spectroscopy, vibronic transitions, time-independent methods, Franck-Condon factors.

Contents

1 Introduction

1.1 Vibrationally-resolved electronic spectra

Molecular spectroscopy is the study of the interaction between molecules and electromagnetic radiations. Different types of molecular spectroscopies exist: this project treats the case of vibronic spectroscopy, which results from transitions involving changes in electronic and vibrational energy levels of a molecule. Associated spectra, vibronic spectra, are usually band spectra in the range of UV-visible light, in absorption as well as in emission.

Thus, vibronic spectra are important tools for the study of molecules with particular photochemical and photophysical properties, such as dye molecules or contrast agents for example for medical imaging. Experimental routines allow chemists to access these spectra in general. However, spectroscopy simulations can serve several purposes from prediction of properties to interpretation of the experimental results. Prediction and interpretation of experimental results are important because it helps to get better insight the structure of studied molecules.

1.2 Objectives

The aim of this project is to give an overview of the existing methods for simulating vibronic spectra. The different methods can be separated between time-independent methods or time-dependent methods. The latter family of methods is not the one presented here but has been widely studied in recent years, for both spectroscopic and femtochemistry simulations [1, 2, 3]. The main focus of this project is on time-independent, or stationary, methods which are based on the direct calculation of the transition dipole moment.

Having enough knowledge on the state of art of the calculation of transition dipole moment and associated transition probabilities, the project aims to give a glimpse on particular type of systems which will be studied during the incoming internship.

Efforts are made so that the reported studies keep as much as possible a consistent chronology, with harmonized notations. Historical aspects of the simulation of vibronic spectra as well as the most recent implementations are evoked but cannot of course be comprehensive.

2 Theoretical background and approximations

2.1 Absorption and emission spectra

The first objects of interest when one simulates a spectrum are the line intensities which are given by the perturbation theory of quantum mechanics [4]. As absorption involves an incident light and molecules and spontaneous emission involves only molecules, the associated cross-sections, describing the spectra, are not the same. The absorption spectrum is described by the rate of energy absorption by a single molecule per unit radiant energy density:

$$\sigma(\omega)_{\text{abs}} = \frac{4\pi^2\omega}{3c} \sum_{\prime} \rho' \sum_{\prime\prime} \left|\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle\right|^2 \delta(E'' - E' - \hbar\omega), \tag{1}$$

and the emission spectrum is described by the rate of photon emission due to a single molecule:

$$\sigma(\omega)_{\text{emi}} = \frac{4\omega^3}{3\hbar c^3} \sum_{\prime} \rho' \sum_{\prime\prime} |\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle|^2 \, \delta(E'' - E' + \hbar\omega). \tag{2}$$

Notations $'$ and $''$ refer respectively to initial states and final states [5]. ρ' is the BOLTZMANN distribution of each initial state. Ψ is the molecular wavefuntion, with associated total energy E, and $\boldsymbol{\mu}$ is the dipole moment of the molecule.

2.1.1 Experimental aspects

The difference of the pre-factor between equations 1 and 2 is of the same nature as the difference between EINSTEIN coefficients for absorption (C_{if}) and spontaneous emission (A_{if}) with state i and state f:

$$A_{if} = C_{if} \frac{\hbar\omega_{if}^3}{\pi^2 c^3}, \tag{3}$$

where C_{if} is discussed in 2.2 and is another formulation of the transition probability. It illustrates the different frequency dependence of the intensity observed in general for absorption (proportional to ω) and for spontaneous emission (proportional to ω^3) [6] as described in the next paragraph [2, 3].

In the case of absorption, the molar absorption coefficient $\epsilon(\omega)$, involved in UV-Vis experiments, can be linked with the cross-section of 1:

$$\epsilon(\omega) = \frac{5N_A}{2\pi\epsilon_0 \ln 10} \sigma_{\text{abs}}(\omega), \tag{4}$$

where N_A is AVOGADRO's number. BEER-LAMBERT's law then links the molar absorption coefficient with the intensity of absorption spectra, for reasonably small intensities and concentrations of absorbing species. In the case of emission, the experimental object of interest is the the energy emitted by one mole of the emitting species per second, also linked with the corresponding cross-section of 2:

$$\frac{I_{\text{emi}}(\omega)}{N_n} = \frac{N_A \hbar^2 \omega}{2\epsilon_0} \sigma_{\text{emi}}(\omega). \tag{5}$$

It is then of primary interest to evaluate $\sigma(\omega)$ to compare theoretical results with experimental data. To reproduce the shape of experimental spectra, the line intensities in equations 1 and 2, which give stick spectra, can be convoluted with a Lorentzian function or a Gaussian function to simulate the broadening of the sticks. Interestingly enough, the literature sometimes focuses on cross-sections or on intensities. However, the computed intensities are in general simply given relatively to the maximum in terms of arbitrary units.

When looking at absorption and emission spectra, it is interesting to compare the position of the intensity maximum of both spectra. One example is given for anthracene in figure 1, where one can notice a significant difference between the energy (in terms of wavelength here) of both maxima [7]. It is called the STOKES shift. In general, the larger the STOKES shift is, the greater the difference between equilibrium positions of ground and excited states is. Hence, it is an interesting quantity to look at when studying molecules capable of absorption and emission of light.

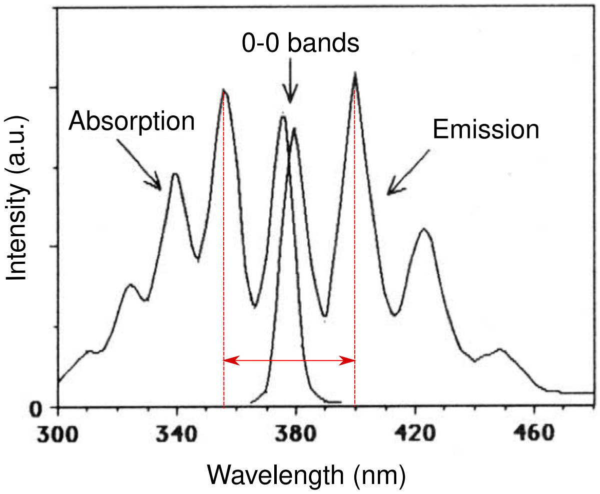


Figure 1: Absorption and emission experimental spectra of anthracene with the associated Stokes shift (red arrow). Adapted from Byron and co-workers, 1991 [7].

The progression seen in absorption spectrum or emission spectrum in figure 1 is given by the study of allowed transitions between ground and excited states.

2.1.2 Quantum description of the transitions

The product of the transition probability $|\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle|^2$ with $\delta(E'' - E' - \hbar\omega)$ in equations 1 and 2 recalls the Fermi's golden rule, giving the transition rate for the one transition between state ' and state ":

$$\gamma = \frac{2\pi}{\hbar} |\langle \Psi' \,|\, \boldsymbol{\mu} \cdot \boldsymbol{E} \,|\, \Psi'' \rangle|^2 \delta(E' - E'' - \hbar\omega), \tag{6}$$

where $\boldsymbol{E}$ is the electric field associated with the incident light for absorption [8, 9]. It means that in order to have a non-zero transition rate, the transition probability should be non-zero and the energy of the absorbed photon or emitted photon should equal the difference of energy between the two considered states. One can already notice that non-zero transition probability is linked with the parity of initial and final wavefunctions as well as the parity of the operator. It leads to selection rules that are evoked in next sections.

The aim of this section will now be focused on establishing an adequate framework for evaluating the transition probability.

2.2 Transition probability and transition dipole moment

The term $|\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle|^2$ in equations 1 and 2 is the transition probability and is simply the square module of the transition dipole moment. The latter is of interest in this section and can be rewritten with the help of the BORN-OPPENHEIMER approximation [10]. Within this approximation, electronic and nuclear variables are separable such that the molecular wavefuntions Ψ can be rewritten as products of the electronic wavefuntions and the nuclear wavefuntions. On the other hand, $\boldsymbol{\mu}$ can be rewritten as the sum of electronic and nuclear contributions, such that the transition dipole moment reads:

$$\begin{aligned} \langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle &\simeq \langle \psi'_e \psi'_n \,|\, \boldsymbol{\mu}_e + \boldsymbol{\mu}_n \,|\, \psi''_e \psi''_n \rangle && \text{(7a)} \\ &= \langle \psi'_e \psi'_n \,|\, \boldsymbol{\mu}_e \,|\, \psi''_e \psi''_n \rangle + \underbrace{\langle \psi'_e \psi'_n \,|\, \boldsymbol{\mu}_n \,|\, \psi''_n \psi''_e \rangle}_{=\,0} . && \text{(7b)} \end{aligned}$$

The first term will be the one of interest as the second term is zero, because of orthogonality properties of electronic wavefunctions. Indeed, we have:

$$\begin{aligned} \langle \psi'_e \psi'_n \,|\, \boldsymbol{\mu}_e \,|\, \psi''_e \psi''_n \rangle &= \int\!\!\int \psi'^*_e(\boldsymbol{r};\boldsymbol{R}) \psi'^*_n(\boldsymbol{R}) \boldsymbol{\mu}_e(\boldsymbol{r}) \psi''_e(\boldsymbol{r};\boldsymbol{R}) \psi''_n(\boldsymbol{R}) \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{R} && \text{(8a)} \\ &= \int \psi'^*_n(\boldsymbol{R}) \underbrace{\left(\int \psi'^*_e(\boldsymbol{r};\boldsymbol{R}) \boldsymbol{\mu}_e(\boldsymbol{r}) \psi''_e(\boldsymbol{r};\boldsymbol{R}) \mathrm{d}\boldsymbol{r} \right)}_{=\,\boldsymbol{\mu}_{if}(\boldsymbol{R})} \psi''_n(\boldsymbol{R}) \mathrm{d}\boldsymbol{R} && \text{(8b)} \end{aligned}$$

and

$$\begin{aligned} \langle \psi'_e \psi'_n \,|\, \boldsymbol{\mu}_n \,|\, \psi''_e \psi''_n \rangle &= \int\!\!\int \psi'^*_e(\boldsymbol{r};\boldsymbol{R}) \psi'^*_n(\boldsymbol{R}) \boldsymbol{\mu}_n(\boldsymbol{R}) \psi''_e(\boldsymbol{r};\boldsymbol{R}) \psi''_n(\boldsymbol{R}) \mathrm{d}\boldsymbol{r} \mathrm{d}\boldsymbol{R} && \text{(9a)} \\ &= \int \psi'^*_n(\boldsymbol{R}) \boldsymbol{\mu}_n(\boldsymbol{R}) \psi''_n(\boldsymbol{R}) \underbrace{\left(\int \psi'^*_e(\boldsymbol{r};\boldsymbol{R}) \psi''_e(\boldsymbol{r};\boldsymbol{R}) \mathrm{d}\boldsymbol{r} \right)}_{=\,0} \mathrm{d}\boldsymbol{R}. && \text{(9b)} \end{aligned}$$

Finally, ECKART & SAYVETZ's conditions are assumed [11], such that the nuclear wavefuntion can be separated into a translational contribution (discarded in this work), a rotation contribution (neglected in this work) and a vibrational contribution, which finally leads to:

$$\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle \simeq \left\langle \psi'_v \,\middle|\, \boldsymbol{\mu}_{if} \,\middle|\, \psi''_v \right\rangle \tag{10}$$

where

$$\boldsymbol{\mu}_{if} = \langle \psi'_e \,|\, \boldsymbol{\mu} \,|\, \psi''_e \rangle \tag{11}$$

is the electronic transition dipole moment, which depends on the nuclear positions of the molecule. In the following, these positions are noted $\boldsymbol{Q}'$ for the initial state and $\boldsymbol{Q}''$ for the final state, and can be expressed in different sets of coordinates.

2.3 The FRANCK-CONDON principle

In the case of small displacement of the position equilibrium between ground state and excited state, one can express the electronic transition dipole moment following the TAYLOR expansion around one of the equilibrium positions (here the excited state):

$$\boldsymbol{\mu}_{if}(\boldsymbol{Q}'') = \boldsymbol{\mu}_{if}(\boldsymbol{Q}_0'') + \sum_{k=1}^{N} \left(\frac{\partial \boldsymbol{\mu}_{if}}{\partial Q_k''} \right)_{\boldsymbol{Q}_0''} Q_k'' + \sum_{k=1}^{N} \sum_{l=1}^{N} \left(\frac{\partial^2 \boldsymbol{\mu_{if}}}{\partial Q_k'' \partial Q_l''} \right)_{\boldsymbol{Q}_0''} Q_k'' Q_l'' + \mathcal{O}(\boldsymbol{Q}''^3). \tag{12}$$

When limited to the first order, equation 12 leads to the well-known Franck-Condon principle. The Franck-Condon principle states that an electronic transition happens in such a short time that the nuclear positions of the molecule stay unchanged during the transition. In other words, the electronic transition dipole moment does not depend on the geometry of the molecule:

$$\boldsymbol{\mu}_{if}(\boldsymbol{Q}'') \simeq \boldsymbol{\mu}_{if}(\boldsymbol{Q}_0''). \tag{13}$$

The contribution of Franck in 1925 was to make the latter statement [12], whereas the contribution of Condon was to link, a few years after, this principle to the fact that some transitions were more likely to occur than others [13, 14].

When including equation 13 into equation 10, the transition amplitude reads:

$$\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle \simeq \boldsymbol{\mu}_{if}(\boldsymbol{Q}_0'') \, \langle \psi_v' \,|\, \psi_v'' \rangle \, . \tag{14}$$

The overlap integral between vibrational wavefunctions of different electronic states appears. It is called the Franck-Condon overlap integral, and the associated Franck-Condon factor is simply $|\langle \psi_v' \,|\, \psi_v'' \rangle|^2$. Selection rules can be expressed for having an electronic transition in this framework of zeroth order: the transition probability is non-zero for non-zero $\boldsymbol{\mu}_{if}$ and non-zero Franck-Condon factors. First, $\boldsymbol{\mu}_{if} \neq \boldsymbol{0}$ if the product of electronic wavefunctions with the transition dipole moment in the $\alpha-$coordinates is even. A practical way of expressing selection rules takes advantage of group theory. A transition occurs between electronic states if the direct product:

$$\Gamma_f \otimes \Gamma_{\boldsymbol{\mu}} \otimes \Gamma_i \tag{15}$$

contains the totally symmetrical representation.

It is the aim of section 3 to review the state of art about computation of the Franck-Condon factors, whereas section 4.1 discusses the validity of zeroth and first orders of equation 12.

2.4 Harmonic approximation and normal coordinates

The harmonic approximation states that the vibrational wavefunction ψ_v is a product of one-dimensional wavefunctions $\psi_{v_i}(Q_i)$ corresponding to one-dimensional harmonic oscillators. Within this approximation, each one-dimensional wavefunction depends only on one of the N normal coordinates, Q_i.

The one-dimensional wavefunction of an harmonic oscillator is:

$$|v\rangle \ \text{ with } \ \langle x \,|\, v \rangle = \psi_v(x) = \frac{1}{\sqrt{2^v v!}} \left(\frac{m\omega}{\pi\hbar} \right)^{\frac{1}{4}} H_v \left(x \sqrt{\frac{m\omega}{\hbar}} \right) \exp\left\{ -\frac{m\omega}{2\hbar} x^2 \right\} \tag{16}$$

where v is the vibrational quantum number, μ the reduced mass of the oscillator, ω the angular frequency of the oscillator and x its equilibrium position. Now, in the frame of spectroscopic studies, oscillators are the vibrational normal modes of the molecule and are computed through diagonalisation of the Hessian matrix for potential energy. The vibrational wavefunction of a vibrational mode i thus depends on the reduced mass μ_i, the angular frequency ω_i also given as a wavenumber $\bar{\nu}_i$ and the normal coordinate Q_i.

Normal coordinates can also be used to describe the dependance of the electronic transition dipole moment on the geometry of the molecule ($\boldsymbol{\mu}_{if} = \boldsymbol{\mu}_{if}(\boldsymbol{Q}'')$). In the case of small displacement of nuclear positions in the molecule during the electronic transition, one can expand the electronic transition dipole moment thanks to the TAYLOR series about the equilibrium geometry of either the initial state or (here) the final state in the same way as in equation 12.

Vibrational modes and thus normal coordinates, reduced masses and angular frequencies have to be computed *ab initio* before ones can compute FRANCK-CONDON factors. The common way to access these quantities is through the diagonalisation of the Hessian matrix, which is implemented for example in the software `Gaussian`. Geometries of the ground state and the excited state and the normal modes have to be computed with the same level of theory. Several *ab initio* methods allow to access optimized excited state or not geometries and to compute the associated potential energy surfaces, but this report does not cover this field.

3 FRANCK-CONDON factors

Thanks to the harmonic approximation, the multi-dimensional vibrational wavefunction can be expressed as the product of one-dimensional vibrational wavefunctions, one for each normal mode of the molecule. In this section, the harmonic character of the normal modes is assumed unless otherwise specified.

In this context, harmonic oscillators from one state and another are said *distorted* if their frequencies are different and *displaced* if their equilibrium positions have changed. It is viewable in the simple case of one dimension for a symmetric diatomic molecule, in figure 2. In one dimension, the normal mode stays the same (elongation of the bond between the two atoms) but can be distorted or displaced.

However, in the case of multiple dimensions (multiple normal modes), a new phenomenon arises. During the transition from one state to another, the normal modes can *mix*. It is known as the DUSCHINSKY effect and it is discussed in section 3.2.

3.1 In one dimension: the case of diatomic molecules

One of the main problem in the field of vibronic spectroscopy and especially the derivation of FRANCK-CONDON factors is the diversity of notations in the literature. Authors have been working on this subject since the emergence of modern quantum chemistry in the 1920' and until now. Hence, notations have evolved between the years but also between the authors depending on their background. The following notations will be used in the current section and the results are adapted according to them. Notations are mostly inspired from the work of CHANG [15], which is discussed in sections 3.1.3 and 3.2.3.

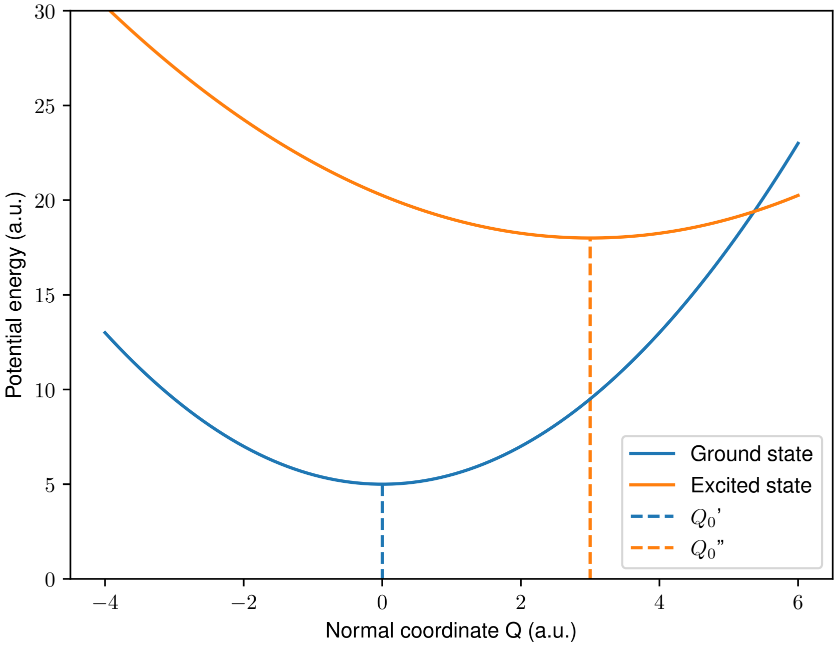


Figure 2: Potential energy profile of a ground state and an excited state in the frame of the harmonic approximation, having different equilibrium positions and different frequencies

In this case, the vibrational wavefunctions of the two states are:

$$|v'\rangle = N_{v'} H_{v'}(\sqrt{\alpha'}x') \exp\left\{-\frac{1}{2}\alpha' x'^2\right\} \text{ and } |v''\rangle = N_{v''} H_{v''}(\sqrt{\alpha''}x'') \exp\left\{-\frac{1}{2}\alpha x''^2\right\} \tag{17}$$

where:

$$N_{v'} = \left(\frac{\sqrt{\alpha}}{2^v v! \sqrt{\pi}}\right)^{\frac{1}{2}}, \tag{18a}$$

$$\alpha' = \frac{\omega'}{\hbar} \text{ and } \alpha'' = \frac{\omega''}{\hbar}. \tag{18b}$$

One should notice that there is no reduced mass in 17 for the harmonic oscillator. It is only because the reduced mass is taken into account in the choice of the coordinates frame, which are here mass-weighted coordinates ($x \longleftrightarrow \sqrt{m}x$). The distortion and the displacement can be respectively characterized by:

$$\beta = \frac{\alpha''}{\alpha'}, \tag{19a}$$

$$x'' = x' + d. \tag{19b}$$

In this framework of approximations and notations, in one dimension, the FRANCK-CONDON integrals are to be evaluated as follows:

$$\langle v' \mid v'' \rangle = \int_{-\infty}^{+\infty} N_{v'} N_{v''} H_{v'}(\sqrt{\alpha'}x') H_{v''}(\sqrt{\alpha''}x'') \exp\left\{-\frac{1}{2}\alpha' x'^2 - \frac{1}{2}\alpha'' x''^2\right\} \mathrm{d}x'. \tag{20}$$

The rest of this section presents different methods to evaluate integrals 20 and associated FRANCK-CONDON factors. One can already notice that there are no easily expressed selection rules additionnally to the rules associated with electronic transitions. However, this is limited to the case of diatomic molecule or totally symmetric normal modes, as it will be discussed in section 3.2.

3.1.1 The generating function method

In 1930, shortly after the works of FRANCK and CONDON, HUTCHISSON first derived analytical formulas to compute the FRANCK-CONDON factors [16]. His work focused on the derivation of FRANCK-CONDON integrals in the case of diatomic molecules, hence in one dimension. The idea was to use one property of the Hermite polynomial regarding the associated generating function, for the initial state:

$$\sum_{v'=0}^{\infty} \frac{H_{v'}(\sqrt{\alpha'}x')}{v'!} s^{v'} = \exp\left\{-s^2 + 2s\sqrt{\alpha'}x'\right\}, \tag{21}$$

with the equivalent property for the final state.

$$\sum_{v''=0}^{\infty} \frac{H_{v''}(\sqrt{\alpha''}x'')}{v''!} t^{v''} = \exp\left\{-t^2 + 2t\sqrt{\alpha''}x''\right\}. \tag{22}$$

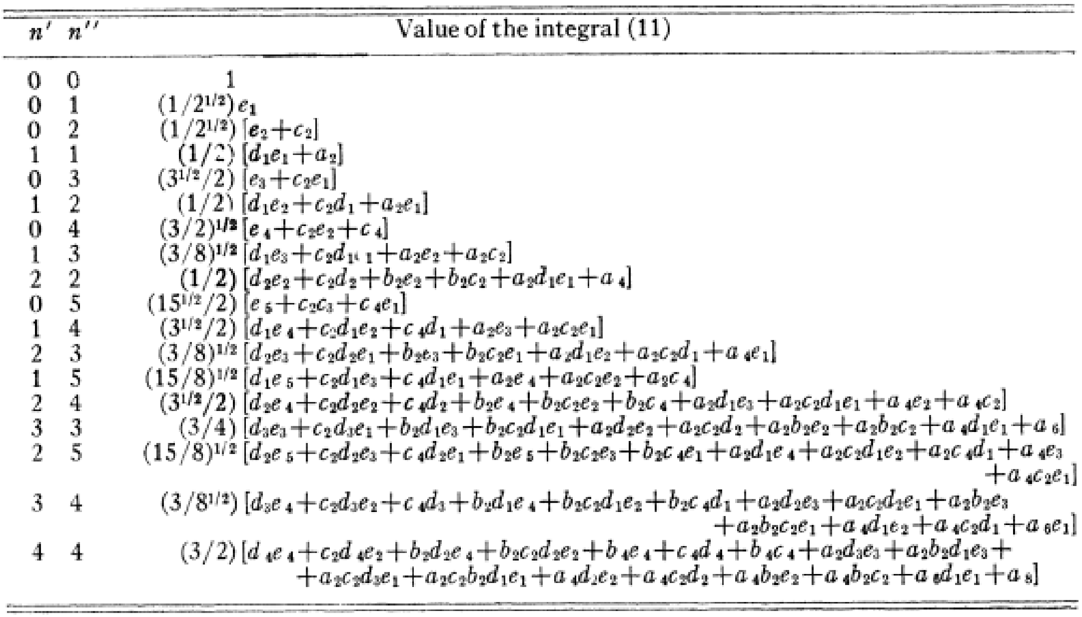
Knowing these sums, one can use the same s and t dummy variables to write a generating function directly with the FRANCK-CONDON integrals 20. After integration of one side of the equation, the generating function reads:

$$\begin{aligned}\sum_{v'=0}^{\infty}\sum_{v''=0}^{\infty} \frac{s^{v'}t^{v''}}{v'!v''!} \langle v' \mid v'' \rangle = \left(\frac{2\pi}{\beta^2+1}\right)^{\frac{1}{2}} \exp\left\{-\frac{d^2}{2(\beta^2+1)}\right\} \\ \times \exp\left\{\frac{(s^2-t^2)(1-\beta^2) - 2\beta d s + 2\beta d t + 4\beta s t}{\beta^2+1}\right\}.\end{aligned} \tag{23}$$

Finally, after the expansion of the last exponential in the powers of s and t, FRANCK-CONDON integrals are reachable by identifying the powers of the variables in both sides of equation 23.

The general results are not reported here, but consists in a triple sum over the quantum vibrational numbers. One can visualize in table 1 the form of the FRANCK-CONDON integrals between vibrational state $v' = n'$ and $v'' = n''$. The coefficients a_{2l}, b_{2i}, c_{2j}, $d_{n'-2i-l}$ and $e_{n''-2j-l}$ depend on their indexes (the vibrational numbers) and the characterization of distorsion (β) and displacement (d) for the harmonic oscillators.

Having this formula for one-dimensional overlap integrals, HUTCHISSON had calculated the intensity of spetral bands in the absorption spectra of Na_2, K_2, I_2 and H_2. When comparing



n'	n''	Value of the integral (11)
0	0	1
0	1	$(1/2^{1/2})e_1$
0	2	$(1/2^{1/2})[e_2+c_2]$
1	1	$(1/2)[d_1e_1+a_2]$
0	3	$(3^{1/2}/2)[e_3+c_2e_1]$
1	2	$(1/2)[d_1e_2+c_2d_1+a_2e_1]$
0	4	$(3/2)^{1/2}[e_4+c_2e_2+c_4]$
1	3	$(3/8)^{1/2}[d_1e_3+c_2d_1e_1+a_2e_2+a_2c_2]$
2	2	$(1/2)[d_2e_2+c_2d_2+b_2e_2+b_2c_2+a_2d_1e_1+a_4]$
0	5	$(15^{1/2}/2)[e_5+c_2c_3+c_4e_1]$
1	4	$(3^{1/2}/2)[d_1e_4+c_2d_1e_2+c_4d_1+a_2e_3+a_2c_2e_1]$
2	3	$(3/8)^{1/2}[d_2e_3+c_2d_2e_1+b_2e_3+b_2c_2e_1+a_2d_1e_2+a_2c_2d_1+a_4e_1]$
1	5	$(15/8)^{1/2}[d_1e_5+c_2d_1e_3+c_4d_1e_1+a_2e_4+a_2c_2e_2+a_2c_4]$
2	4	$(3^{1/2}/2)[d_2e_4+c_2d_2e_2+c_4d_2+b_2e_4+b_2c_2e_2+b_2c_4+a_2d_1e_3+a_2c_2d_1e_1+a_4e_2+a_4c_2]$
3	3	$(3/4)[d_3e_3+c_2d_3e_1+b_2d_1e_3+b_2c_2d_1e_1+a_2d_2e_2+a_2c_2d_2+a_2b_2e_2+a_2b_2c_2+a_4d_1e_1+a_6]$
2	5	$(15/8)^{1/2}[d_2e_5+c_2d_2e_3+c_4d_2e_1+b_2e_5+b_2c_2e_3+b_2c_4e_1+a_2d_1e_4+a_2c_2d_1e_2+a_2c_4d_1+a_4e_3+a_4c_2e_1]$
3	4	$(3/8^{1/2})[d_3e_4+c_2d_3e_2+c_4d_3+b_2d_1e_4+b_2c_2d_1e_2+b_2c_4d_1+a_2d_2e_3+a_2c_2d_2e_1+a_2b_2e_3+a_2b_2c_2e_1+a_4d_1e_2+a_4c_2d_1+a_6e_1]$
4	4	$(3/2)[d_4e_4+c_2d_4e_2+b_2d_2e_4+b_2c_2d_2e_2+b_4e_4+c_4d_4+b_4c_4+a_2d_3e_3+a_2b_2d_1e_3++a_2c_2d_3e_1+a_2c_2b_2d_1e_1+a_4d_2e_2+a_4c_2d_2+a_4b_2e_2+a_4b_2c_2+a_6d_1e_1+a_8]$

Table 1: Expression of the Franck-Condon integrals derived from the generating function method. Taken from Hutchisson, 1930 [16].

these predictions to experimental results, one can see that the general intensity and the number of expected bands agree with the experiment, in spite of mitigated agreement between expected and experimental intensities of individual bands.

Hutchisson's work was later (decades after his article) generalized to an arbitrary number of dimensions, and was implemented in `Gaussian` (see section 3.2). However, this kind of calculations turned out to be computationnally expensive and was predicted not to be efficiently generalized for large molecules, in many dimensions. Indeed, as one can see in table 1, even for diatomic molecules, the 4–4 vibronic transition probability already resulted in a sum of 17 terms. In addition to this problem of efficiency, the formula was not the easiest to generalize as a new formula has to be implemented for each overlap integral. Knowing this problem of implementation, another strategy was explored with the idea to find recursive expressions for the Franck-Condon integrals.

3.1.2 The recursive approach

The derivation was first done by Manneback in 1951 for diatomic molecules, and deviates from Hutchisson's work only when instead of performing the expansion of the exponential, one differentiates the power series with respect to s and t [17]. A more systematic derivation was performed by Lermé in 1990 for one and two dimensional Franck-Condon integrals [18].

The results can be expressed for the one-dimension integral overlap as follows:

$$\begin{aligned}\langle v' \,|\, v'' \rangle = \frac{2\alpha' d\beta}{(1+\beta)\sqrt{2v'}} \langle v'-1 \,|\, v'' \rangle + \frac{1-\beta}{1+\beta} \left(\frac{v'-1}{v'}\right)^{\frac{1}{2}} \langle v'-2 \,|\, v'' \rangle \\ + \frac{2\sqrt{\beta}}{1+\beta} \left(\frac{v''}{v'}\right)^{\frac{1}{2}} \langle v'-1 \,|\, v''-1 \rangle \,.\end{aligned} \tag{24}$$

Like in the previous approach, the integrals depend on the vibrational numbers and the characterization of the involved harmonic oscillators. But, as it was the objective of the recursive approach, integrals of interest are computed from values of the integrals with lower vibrational numbers. Having formula 24, only the first integrals need to be known, and can be computed by analytical formulas before the rest can be deduced.

The accuracy of the recursive approach was studied as well by Lermé. It indicates that the approach is valid for reasonably small vibrational numbers.

3.1.3 A recent straightforward derivation

In 2005, Chang came up with a simple and straightforward derivation of the Franck-Condon factors, without more approximations than the harmonic approximation [15].

Using only simple properties of the Hermite polynomial and of the gaussian integral, without any use of dummy variables, their derivation leads to:

$$\begin{aligned}|\langle v' \,|\, v'' \rangle|^2 = & \frac{A \exp\{-S\}}{2^{v'+v''} v'! v''!} \\ & \times \left[\sum_{k'=0}^{v'} \sum_{k''=0}^{v''} \binom{v'}{k'} \binom{v''}{k''} H_{v'-k'}(b') H_{v''-k''}(b'') (2\sqrt{\alpha'})^{k'} (2\sqrt{\alpha''})^{k''} I(K) \right]^2\end{aligned} \tag{25}$$

with:

$$A = \frac{2\sqrt{\alpha' \alpha''}}{\alpha' + \alpha''}; \tag{26a}$$

$$S = \frac{\alpha' \alpha'' d^2}{\alpha' + \alpha''}; \tag{26b}$$

$$b' = -\frac{\alpha'' \sqrt{\alpha'} d}{\alpha' \alpha''} \text{ and } b'' = \frac{\alpha' \sqrt{\alpha''} d}{\alpha' \alpha''}; \tag{26c}$$

$$K = \frac{k' + k''}{2}; \tag{26d}$$

$$I(K) = 0 \text{ if } k' + k'' \text{ is odd and } = \frac{(2K-1)!!}{(\alpha' + \alpha'')^K} \text{ otherwise;} \tag{26e}$$

$$(2K-1)!! = 1 \times 3 \times 5 \times \cdots \times (2K-1). \tag{26f}$$

The advantage of this derivation is to free the dependance of Hermite polynomials on the coordinates x' and x'', using only the generic property:

$$H_n(x+y) = \sum_{p=0}^{n} \binom{n}{p} H_{n-p}(y)(2x)^p, \tag{27}$$

which allows to factorize the Hermite polynomials outside of the integral, leading to a well-known gaussian integral. The Franck-Condon factors are computed directly knowing the physical parameters of the harmonic oscillators, and there is no need of exponential expansion and identification nor recursive formulas.

Equation 25 represents an improvement compared to the previous approaches. First, an advantage compared to both approaches is that the formula is exact. Then, the formula of Chang can be more easily implemented in future softwares, because there is one formula for all overlap integrals, whereas there was one formula for each overlap integral in Hutchisson's approach.

3.2 A multi-dimensional approach

For the study of molecular spectra beyond diatomic molecules, one has to consider multi-dimensional Franck-Condon integrals and factors. In the framework previously described, the vibrational wavefunction for a system of N atoms depends on $3N$ nuclear coordinates. In the frame of the harmonic approximation, the nuclear coordinates can be taken as normal coordinates gathered in the vector $\boldsymbol{Q}$, each component corresponding to a normal mode of vibration of the molecule. In this case, the vibrational wavefunction can be written as a product of one-dimensional vibrational wavefunctions:

$$|\boldsymbol{v}\rangle = \left|\prod_i v_i\right\rangle. \tag{28}$$

Additional selection rules apply in the case of arbitrary dimensions, because normal modes can either be totally symmetric or not. Potential energy surfaces are indeed even with respect to normal coordinates of non-totally symmetric modes, whereas they are arbitrary with respect to normal coordinates of totally-symmetric modes. It leads to selection rules for having non-zero overlap integrals in the case of non-totally symmetrical modes. Indeed, potential energy surfaces can be displaced between different electronic states for the case of totally symmetric modes but are necessarily centered in zero for every electronic states for non-totally symmetric modes. Thus, in the case of non-totally symmetric modes, overlap integrals are non-zero if the vibrational wavefunctions in the two electronic states have the same parity. It leads to a limited vibronic progression in the spectrum from the 0^{th} initial vibrational state (assuming zero temperature) to the $2^{\text{nd}}, 4^{\text{th}}, 6^{\text{th}}$... where in general, only the first two overlap integrals $\langle 0 \,|\, 0\rangle$ and $\langle 0 \,|\, 2\rangle$ are non-negligible. Selection rules for totally-symmetric modes are unchanged and only concern symmetries of electronic states involved in the vibronic transition. Finally, the entire vibronic progression of a spectrum can be interpreted using these rules. Considering for instance one totally symmetric and one non-totally symmetric modes, the spectrum is expected to show two similar progressions (progression due to totally symmetric mode multiplied by the limited progression due to non-totally symmetric mode), of different intensities.

3.2.1 The Duschinsky effect

In this section, illustrations are given in the case of the two-dimensional derivation. Like in the previous section, each normal mode, each harmonic oscillator, can be either displaced (if totally symmetric) as shows figure 3) or distorted in the transition from one electronic state to another.

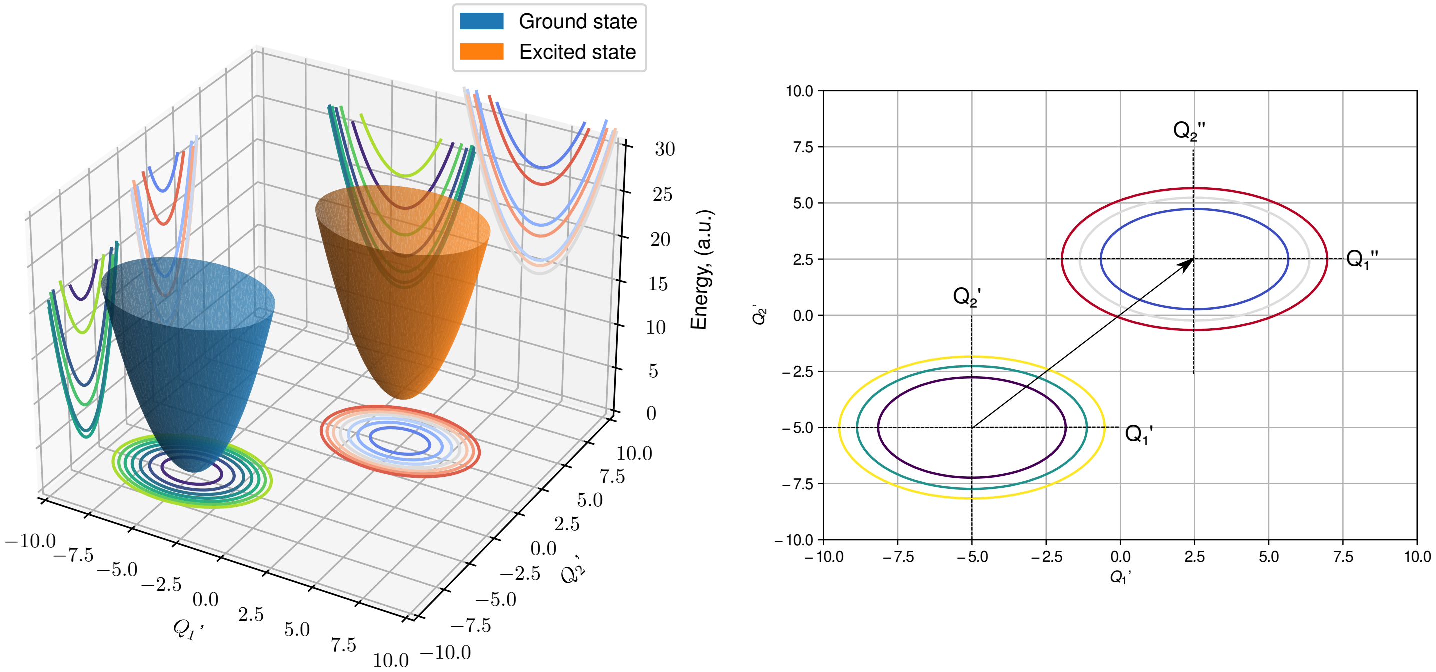


Figure 3: Left, potential energy surfaces of a ground state and an excited state in the frame of the harmonic approximation, having different equilibrium positions, same frequencies. Right, projection of potential energy surfaces in the plane of Q_1'/Q_2'; the straight arrow is the shift in equilibrium position

However, a new problem arises from the multi-dimensional aspect of the situation. Normal modes can be also *mixed* with each other during the transition. This normal mode mixing is related to a change in the character of the normal modes after electronic transition and will be refered as the Duschinsky effect as Duschinsky was the first to describe the phenomenon in 1937 [19]. Indeed, there is no reason for the molecule to have the same normal modes in different electronic states.

Normal mode mixing can be visualized simply as a rotation of the directions associated with the normal modes of the molecule in initial and final states. This rotation is illustrated in two dimensions in figure 4.

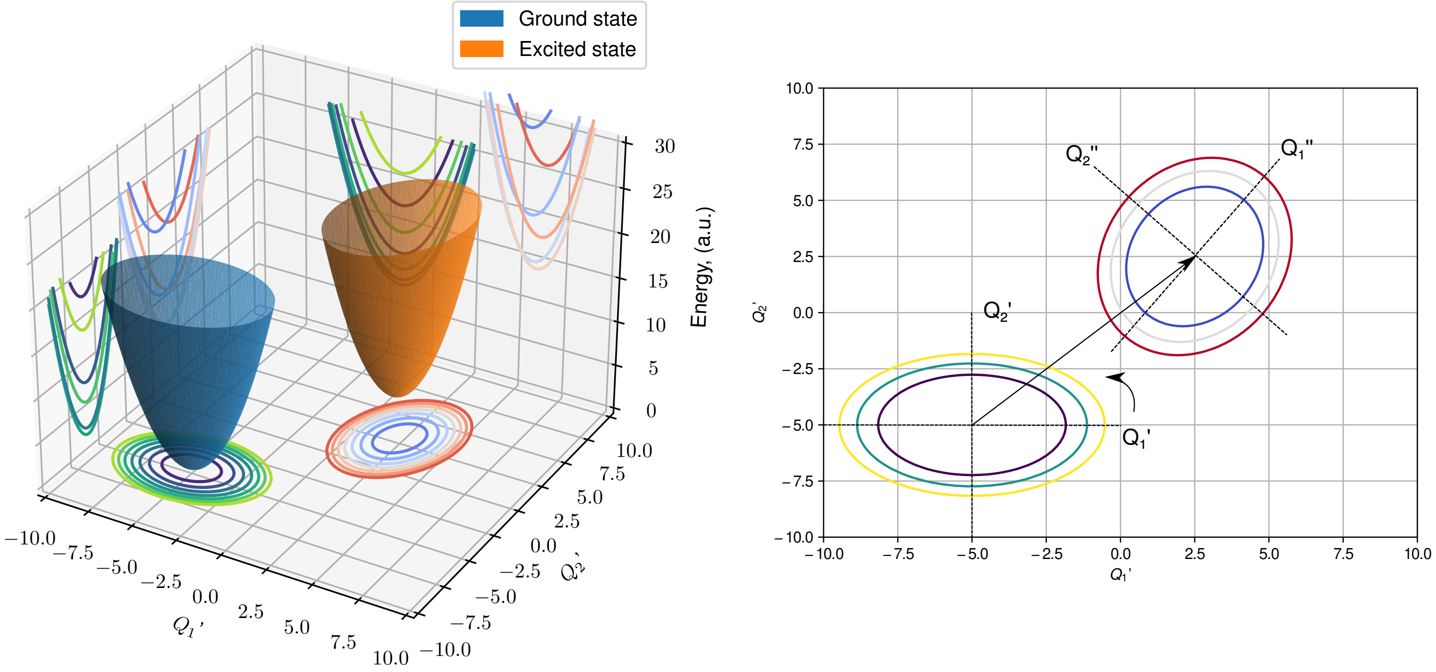


Figure 4: Left, potential energy surfaces of a ground state and an excited state in the frame of the harmonic approximation, having different equilibrium positions, same frequencies and with normal mode mixing. Right, projection of potential energy surfaces in the plane of Q_1'/Q_2'; the straight arrow is the shift in equilibrium position, the curved arrow is the rotation of normal ocordinates.

The mathematical solution to formulate the normal mode mixing was proposed by Duschinsky and explicited by Sharp and Rosenstock [20], is to express the normal coordinates in one state as a linear transformation of the normal coordinates in the other state:

$$\boldsymbol{Q'} = \boldsymbol{J}\boldsymbol{Q''} + \boldsymbol{K}. \tag{29}$$

$\boldsymbol{J}$ is the Duschinsky matrix and $\boldsymbol{K}$ the shift vector due to the changes in geometry between the initial and final states. The role of the Duschinsky effect was extensively studied, for example by Mebel and co-workers in 1999, to evaluate the effect in $\pi - \pi^*$ transitions in small organic molecules [21]. They stated that the displacement played an important role in the broadening or enrichment of the vibronic spectra through Duschinsky effect and thus proposed to look in priority at totally-symmetric modes. Ethylene was studied with a model of two modes mixing among the symmetrical ones, the others being considered as no-mixing. The associated spectra is given 5 and show that takin into account mode mixing brings new non-negligible transisions.

The transformation proposed in equation 29 is valid when the molecule undergoes reasonable distortions and when the symmetry of the molecule stays the same upon transition. Having this transformation, the same methods as the ones used in one dimension can be applied, expressing normal mode coordinates of one state as functions of the normal coordinates of the other when needed.

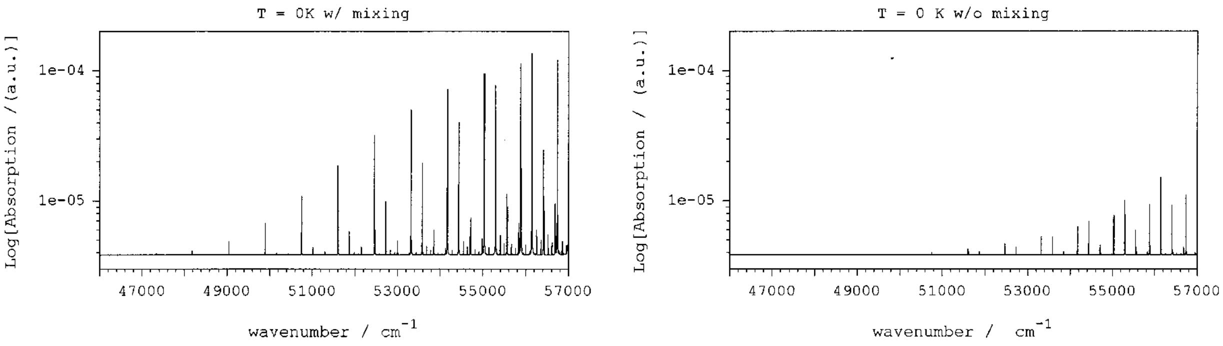


Figure 5: Comparison between mixing (left) and no-mixing (right) cases for the simulation of absorption spectra of ethylene. Extracted from Mebel and co-workers, 1999 [21].

3.2.2 The generating function method and the recursive approach

In 1964, Sharp and Rosenstock directly extended the work of Hutchisson using generating functions and exponential expansion to obtain the Franck-Condon integrals [20]. The integrals are expressed using the elements from matrices **A, C, D** and vectors **b, e**, which correspond to the coefficients defined by Hutchisson in 1930. These matrices and vectors depend on the frequencies of the normal modes, the displacement vector $\boldsymbol{K}$ but also the Duschinsky matrix $\boldsymbol{J}$, respectively corresponding to the distorsion, the displacement and the mixing of the normal modes between initial and final states.

The problem with this method is the same as the one explicited previously section 3.1.1. Each Franck-Condon integral has its expression, and these expressions are complicated, even in simplified cases such as absorption from ground state at zero temperature. For this reason, recursive formulas were derived in 1994 by Ruhoff for an abritrary number of dimensions, following the same procedure as Lermé presented for one dimensional Franck-Condon integrals [22]. An analogous study as the one of Lermé in one dimension was done to investigate the accuracy of this recursive approach. The results suggested that at the time, errors could be propagated leading to a numerical breakdown but that in most applications, computer time could be traded for accuracy.

Interestingly, a derivation of a closed expression was later established by Islampour in 1999 [23], using just one more property of the Gaussian integral. However, because their derivation still uses a Taylor expansion of an exponential, the closed expression of the Franck-Condon integrals is still not exact at the time.

3.2.3 The exact derivation

Like it was previously stated (section 3.1.3), exact derivations of the Franck-Condon integrals were first reported tardily considering the first attempts of calculating them. Chang extended their work in 2008 up to four dimensions and in 2013 for arbitrary dimensions [24, 25]. The derivation is of the same nature of the one used in the one-dimensional case, taking into account the normal mode mixing with Duschinsky's formalism.

Demonstration of the efficiency of their method was showed by Chang and co-workers by applying it to photoelectron spectroscopy [25, 26]. Application for vibronic spectra simulations was recently reported to help interpretation of both theoretical and experimental results for absorption by ethylene [27].

3.3 Implementation of these methods

3.3.1 The `Gaussian` package

All these approaches prepared the development of a solution to an important challenge: simulate spectra of medium-to-large molecules and find a procedure that can be easily used by researchers in spectroscopy without being familiar with neither all the theoretical background nor the computer-related problems. Barone and co-workers proposed such a solution in 2009, a fully integrated approach to compute vibrationally resolved spectra [5], implemented in the software `Gaussian`. Their method takes advantages on both analytical and recursive approaches and addresses an important part of the computer science challenges. Analytical approach allows computation of accurate integrals, but suppose that the program already knows the possible transitions in terms of vibrational quantum numbers to use. However, it is not the case in general and for large systems. Hence, recursive approach is used to compute integrals by needing only the integrals with lower vibrational quantum numbers. The recursive approach has technical drawbacks such that memory use and error propagation, the latter being discussed by Lermé and Ruhoff. The memory use problem recquired an efficient strategy to *a priori* identify relevant transitions between the initial state and the possible final states. Mainly one strategy is implemented, evaluating integrals classes by classes, one class indexed n being the ensemble of integrals having n simultaneously excited normal modes in the final electronic state [28, 29]. Barone and co-workers proposed many applications for their implementation of vibronic spectra simulations, from study of electron photodetachment of simple anions to simulations of vibronic spectra of small organic molecules (anisole, acrolein) or medium-to-large systems (chloropyll, adenin adsorbed on a silicon atoms surface).

3.3.2 Perspectives with recent derivations

One could ask themself if the recent evaluations of Franck-Condon integrals by Chang would represent a more valuable analytical approach than the one previously implemented, being more efficient and accurate than the recursive approach described here. Furthermore, one of the advantages of this formula is that it is the same for all integrals, whereas it was in general not the case for Hutchisson, Sharp and Rosenstock methods.

3.3.3 A word on time-dependent methods

A completely different, time-dependent approach was alternatively developed by Bloino, Baiardi and co-workers for the `Gaussian` software [2, 3]. The method was first described by Heller in 1977 for dynamics of photofragmentation of diatomic molecules [1], and was applied for spectroscopy later and implemented recently for instance in the `Gaussian` software. It requires the potential energy surfaces, which is conceptually and computationnally more advanced than knowing only the normal modes of a molecule in the harmonic framework. The principle is that a wavepacket is propagated in time-dependent simulations, and one can access the vibronic spectra as it is the FOURIER transform of the propagated signal. The time-dependent methods will not be discussed more in this study, because they are part of a completely different domain of its own, quantum dynamics.

4 Beyond the FRANCK-CONDON principle and harmonic approximation

The aim of this section is to give an overview of the first refinements accessible for having a method better suited to real molecules and systems. Indeed, two main approximations are assumed to be valid in the previous studies: the FRANCK-CONDON principle which is a zeroth order approximation of a TAYLOR expansion and the harmonic approximation which is an assumption of small vibrations around equilibrium positions. It is possible to be more precise in the description of real systems, however this section will end up showing that in general, FRANCK-CONDON factors and overlap integrals are the only objects of interest in stationary methods for the simulation of vibronic spectra.

4.1 HERZBERG-TELLER approximation

The FRANCK-CONDON principle can fail to describe vibronic transitions in some cases. Indeed, in the case of dipole-forbidden ($|\boldsymbol{\mu}_{if}(\boldsymbol{Q}''_0)| = 0$) or weakly-allowed electronic transitions ($|\boldsymbol{\mu}_{if}(\boldsymbol{Q}''_0)| \simeq 0$), the zeroth order of expansion in equation 12 can not be used.

This is the case of benzene, of which the absorption spectrum is given figure 6 [30]. According to group theory and selection rules, the only symmetrically allowed transition is the transition $^1\mathrm{A}_{1\mathrm{g}} \rightarrow {}^1\mathrm{E}_{1\mathrm{u}}$. It is indeed the most intense absorption band (spectra are to be read by multiplying constants for scaling) but other non-negligible absorption bands are present, associated with forbidden transisions. The literature often presents this effect as a breakdown of the BORN-OPPENHEIMER approximation. The selection rules for vibronic transitions then apply for the entire transition dipole, with no possible separation of the vibrational part of the wavefunction from the electronic part. In this case, the irreducible representations of vibrational states also participate in the direct product of the previously stated selection rule in equation 15.

Another way to interpret these bands is by taking into account the next orders in the derivation of the transition dipole moment, without directly questionning the BORN-OPPENHEIMER approximation. The extension of FRANCK-CONDON principle to a linear dependance of the electronic transition dipole moment on nuclear coordinates was first proposed by HERZBERG and TELLER in 1933 [31] and is referred as the eponymous approximation in the literature. Indeed, when including first and second orders of equation 12 in equation 10, the probability transition

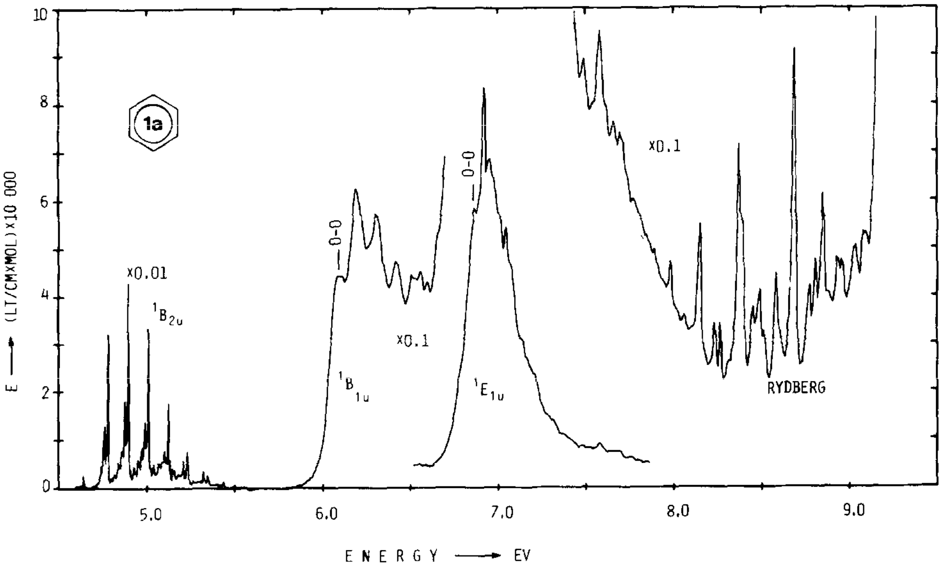


Figure 6: Gas absorption spectrum of benzene. Spectra of different electronic transisions where scaled for readability. Extracted from BOLOVINOS and co-workers, 1984 [30].

reads:

$$\begin{aligned}\langle \Psi' \,|\, \boldsymbol{\mu} \,|\, \Psi'' \rangle \simeq \boldsymbol{\mu}_{if}(\boldsymbol{Q}''_0)\, \langle \boldsymbol{v}' \,|\, \boldsymbol{v}'' \rangle &+ \sum_{k=0}^{N} \left(\frac{\partial \boldsymbol{\mu}_{if}}{\partial Q''_k} \right)_{\boldsymbol{Q}''_0} \langle \boldsymbol{v}' \,|\, Q''_k \,|\, \boldsymbol{v}'' \rangle \\ &+ \frac{1}{2} \sum_{k=0}^{N} \sum_{l=0}^{N} \left(\frac{\partial^2 \boldsymbol{\mu}_{if}}{\partial Q''_k \partial Q''_l} \right)_{\boldsymbol{Q}''_0} \langle \boldsymbol{v}' \,|\, Q''_k Q''_l \,|\, \boldsymbol{v}'' \rangle \,. \end{aligned} \tag{30}$$

In the framework of the previous sections, the second term does not represent a difficulty, as the the integral can be expressed as FRANCK-CONDON integrals. Indeed, with the help of second quantization for the treatment of quantum harmonic oscillators, one can show that:

$$\langle \boldsymbol{v}' \,|\, Q''_k \,|\, \boldsymbol{v}'' \rangle = \sqrt{\frac{\hbar}{2\omega''_k}} \left[\sqrt{v''_k}\, \langle \boldsymbol{v}' \,|\, \boldsymbol{v}'' - \boldsymbol{1}''_k \rangle + \sqrt{v''_k + 1}\, \langle \boldsymbol{v}' \,|\, \boldsymbol{v}'' + \boldsymbol{1}''_k \rangle \right] , \tag{31}$$

where the annihilation and creation operators respectively remove and add a quantum of vibration in the k^{th} dimension of the harmonic oscillator [8]. One can already note that selection rules for vibronic transisions for non-totally symmetrical modes are different in the cas of HERZBERG-TELLER authorized transisions. Indeed, transition between v' and v'' implies integrals in the right-hand side of 31 with ± 1 quatum in the final vibrational function. It leads to opposed selection rules compared to FRANCK-CONDON approximation, with non-zero probability transision for transitions from 0^{th} vibrational state (assuming zero temperature) to $1^{\mathrm{st}}, 3^{\mathrm{rd}}$... vibrational states.

Following the reasoning of Herzberg and Teller, Bloino and co-workers, who implemented the HT approximation in the `Gaussian` software, noticed that one could go beyond the first order in the development of the electronic transition dipole moment [2] by including the diagonal second orders terms. In the end, the main objects of interest are still the Franck-Condon factors and associated integrals, as they are the same integrals used in the simplest, Franck-Condon, approximation as well as in refinements such as Herzberg-Teller approximation. Next orders in the development of the electronic transition dipole moment are in general negligible but would require the exact same integrals.

4.2 Anharmonicity

Previous results are all in the framework of harmonic approximation. It leads to rules of selection as well as rules for evaluating identified integrals (Franck-Condon integrals). However, these rules are necessarily approximations, while real systems are better described by taking into account anharmonicity, usually with Morse's potential. One of the main effect of anharmonicity is the fact that vibrational states are increasingly closer, which leads to a vibronic *packing* progression.

In vibrational spectroscopy, anharmonicity is often taken into account with a development of the vibrational energy in terms of harmonic oscillator numbers:

$$E_v = \hbar\omega\left(v+\frac{1}{2}\right) - x_e\left(v+\frac{1}{2}\right)^2 + \mathcal{O}\left(\left(v+\frac{1}{2}\right)^3\right), \tag{32}$$

where the coefficients of the development are obtained by fitting experimental data. In particular, the anharmonic constant, the first coefficient, is

$$x_e = \frac{\hbar\omega_e}{4D_e} \tag{33}$$

where D_e is the dissociation energy. In vibronic spectra, these effects are often too small to be observable with today's resolution. Implemented packages in `Gaussian` for spectra simulation proposed to apply corrections for anharmonicity by input of anharmonicity coefficients.

Another totally different way for taking into account anharmonicity is to use time-dependent methods evoked in section 3.3.

However, in some cases, anharmonicity may be not caracterized by the usual Morse's potential and may be of a different shape than a simple anharmonic well. Indeed, harmonic double-wells may also be well-suited to describe potential surfaces for some molecules. It is the aim of section 5 to uncover these possibilities and of the internship of the writer to explore them.

5 Conclusion and incoming internship

5.1 Vibronic spectroscopy simulation

In this report, major breakthroughs from Franck statement in 1926 to exact derivation of absorption/emission intensity in the framework of Born-Oppenheimer and harmonic approximations in recent years are discussed. Hopefully the study was large enough to give significant hindsight on the field of theoretical spectroscopy without being too large, allowing to focus on specific issues such as the ones associated with the multi-dimensional aspect of the problem. As stated before, dynamic, time-dependant approaches are no less important for the study of vibronic spectra, but could not be discussed here.

The last part of this reports presents the subject and the aim of the incoming internship.

5.2 Unusual Stokes shift

In recent years, optoelectronics properties of dendrimers have drawn interest on these macromolecules. Since the first synthesis of one of these types of dendrimer (see 7) in 1994 [32], several experimental and theoretical studies explore the properties of their building blocks, as oligo(phenylene ethynylene).

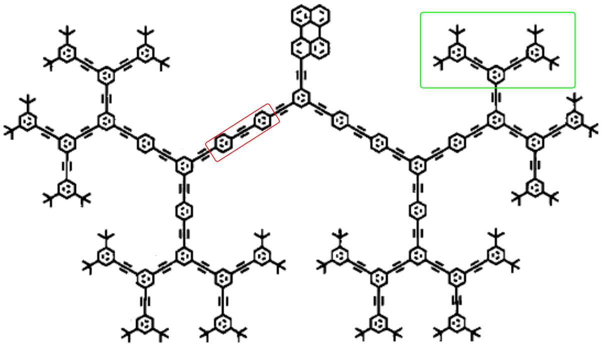


Figure 7: One example of synthetized dendrimer. Extracted from Xu and Moore, 1994 [32].

Two of the most simple yet important building blocks are diphenylacetylene (red in 7) and 1,3-bis(phenylethynyl)benzene (green in 7). In 2004, Chu and Pang studied spectroscopic properties of some of these building blocks for dendrimers [33]. Associated experimental spectra, in both absorption and emission, are given figure 8. Low-temperature data helps noticing a clear vibronic structure, which appears almost identical for both molecules. Within the harmonic approximation, vibrational energies gap are very similar, which suggest that the m-phenylene bridge has little influence on the characteristics of the original chromophores. However, one can notice a significant Stokes shift in the case of 1,3-bis(phenylethynyl)benzene which is not observed in the cas of diphenylacetylene.

Ho and Lasorne rationalized in 2019 the properties of 1,3-bis(phenylethynyl)benzene which were shown to be similar to the one of diphenylacetylene in experimental studies [34]. However the significant Stokes shift has found no satisfactory explanation at the time. One of the aim of the internship is to investigate this unusual Stokes shift, exploring the hypothesis that it is caused by the existence of a double harmonic well in the excited states. The double well in the excited state could help explaining the difference between the most intense transitions in absorption and in emission.

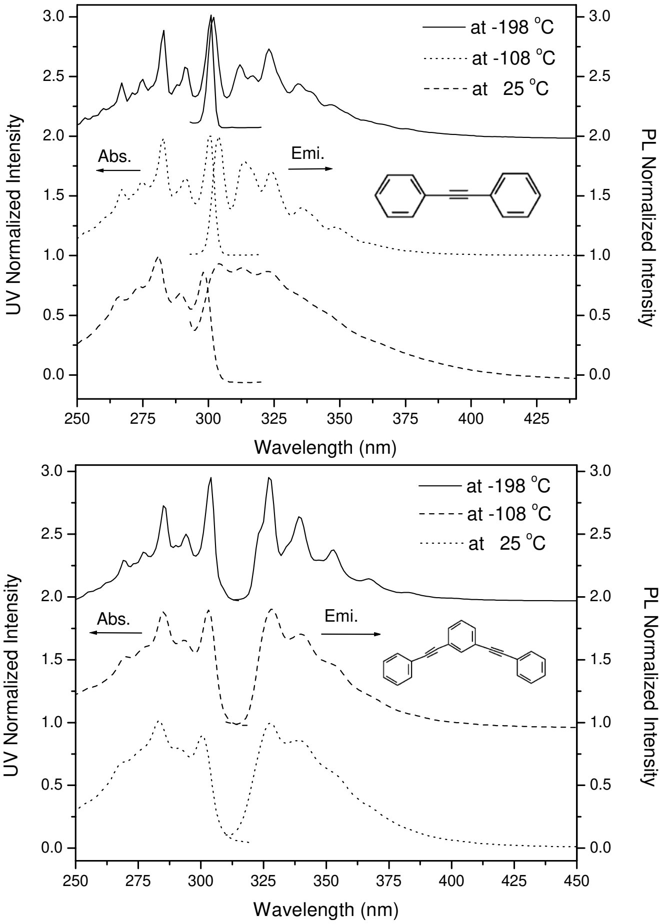


Figure 8: UV-vis absorption and emission spectra of diphenylacetylene (top) and 1,3-bis(phenylethynyl)benzene (bottom). Extracted from Chu and Pang, 2004 [33].

This hypothesis will be studied with a one-dimensional model and *ad hoc* parameters at first, as a unique excited state and as a avoided-crossing between two excited states. Generalization to a two-dimensional model at least could be interesting to explain this avoided-crossing with a conical intersection. The first attempt will be based on a stationary approach like the one described previously, notably the exact and analytical formulas of Franck-Condon factors derived by Chang. If times allows it, the study will be comptleted by a similar study based on time-dependant approach.

References

[1] E. J. Heller, Quantum corrections to classical photodissociation models, *The Journal of Chemical Physics*, **1978**, 68 (5) 2066–2075.

[2] J. Bloino, M. Biczysko, F. Santoro, and V. Barone, General Approach to Compute Vibrationally Resolved One-Photon Electronic Spectra, *Journal of Chemical Theory and Computation*, **2010**, 6 (4) 1256–1274.

[3] A. Baiardi, J. Bloino, and V. Barone, General Time Dependent Approach to Vibronic Spectroscopy Including Franck—Condon, Herzberg—Teller, and Duschinsky Effects, *J. Chem. Theory Comput.*, **2013** 19.

[4] A. Lami, C. Petrongolo, and F. Santoro, Absorption, emission, and photoelectron continuous-wave spectra, in Conical Intersections, vol. Volume 15 of *Advanced Series in Physical Chemistry*, **2004**, 699–738.

[5] V. Barone, J. Bloino, M. Biczysko, and F. Santoro, Fully Integrated Approach to Compute Vibrationally Resolved Optical Spectra: From Small Molecules to Macrosystems, *Journal of Chemical Theory and Computation*, **2009**, 5 (3) 540–554.

[6] J. L. McHale, Molecular spectroscopy, second edition edn., **2017**.

[7] C. M. Byron and T. C. Werner, Experiments in synchronous fluorescence spectroscopy for the undergraduate instrumental chemistry course, *Journal of Chemical Education*, **1991**, 68 (5) 433.

[8] C. Cohen-Tannoudji, B. Diu, and F. Laloë, Mécanique quantique : Tome 1, 2e édition edn., **2018**.

[9] C. Cohen-Tannoudji, B. Diu, and F. Laloë, Mécanique quantique : Tome 2, 2e édition edn., **2018**.

[10] M. Born and R. Oppenheimer, Zur Quantentheorie der Molekeln, *Annalen der Physik*, **1927**, 389 (20) 457–484.

[11] C. Eckart, Some Studies Concerning Rotating Axes and Polyatomic Molecules, *Physical Review*, **1935**, 47 (7) 552–558.

[12] J. Franck and E. G. Dymond, Elementary processes of photochemical reactions, *Transactions of the Faraday Society*, **1926**, 21 (February) 536–542.

[13] E. Condon, A Theory of Intensity Distribution in Band Systems, *Physical Review*, **1926**, 28 (6) 1182–1201.

[14] E. U. Condon, Nuclear Motions Associated with Electron Transitions in Diatomic Molecules, *Physical Review*, **1928**, 32 (6) 858–872.

[15] J.-L. Chang, A new formula to calculate Franck–Condon factors for displaced and distorted harmonic oscillators, *Journal of Molecular Spectroscopy*, **2005**, 232 (1) 102–104.

[16] E. Hutchisson, Band Spectra Intensities for Symmetrical Diatomic Molecules, *Physical Review*, **1930**, 36 (3) 410–420.

[17] C. Manneback, Computation of the intensities of vibrational spectra of electronic bands in diatomic molecules, *Physica*, **1951**, 17 (11) 1001–1010.

[18] J. LERMÉ, Iterative methods to compute one- and two-dimensional Franck-Condon factors. Tests of accuracy and application to study indirect molecular transitions, *Chemical Physics*, **1990**, 145 (1) 67–88.

[19] F. DUSCHINSKY, *Acta Physicochim. (USSR)*, **1937**, 7 551.

[20] T. E. SHARP and H. M. ROSENSTOCK, Franck—Condon Factors for Polyatomic Molecules, *The Journal of Chemical Physics*, **1964**, 41 (11) 3453–3463.

[21] A. M. MEBEL, M. HAYASHI, K. K. LIANG, and S. H. LIN, Ab Initio Calculations of Vibronic Spectra and Dynamics for Small Polyatomic Molecules: Role of Duschinsky Effect, *The Journal of Physical Chemistry A*, **1999**, 103 (50) 10674–10690.

[22] P. T. RUHOFF, Recursion relations for multi-dimensional Franck-Condon overlap integrals, *Chemical Physics*, **1994**, 186 (2) 355–374.

[23] R. ISLAMPOUR, M. DEHESTANI, and S. H. LIN, A New Expression for Multidimensional Franck–Condon Integrals, *Journal of Molecular Spectroscopy*, **1999**, 194 (2) 179–184.

[24] J.-L. CHANG, A new method to calculate Franck–Condon factors of multidimensional harmonic oscillators including the Duschinsky effect, *The Journal of Chemical Physics*, **2008**, 128 (17) 174111.

[25] J.-L. CHANG, C.-H. HUANG, S.-C. CHEN, T.-H. YIN, and Y.-T. CHEN, An analytical approach for computing Franck-Condon integrals of harmonic oscillators with arbitrary dimensions, *Journal of Computational Chemistry*, **2013**, 34 (9) 757–765.

[26] T. SATTASATHUCHANA, R. MURRI, and K. K. BALDRIDGE, An Efficient Analytic Approach for Calculation of Multi-Dimensional Franck–Condon Factors and Associated Photoelectron Spectra, *Journal of Chemical Theory and Computation*, **2017**, 13 (5) 2147–2158.

[27] B. LASORNE, J. JORNET-SOMOZA, H.-D. MEYER *et al.*, Vertical transition energies vs. absorption maxima: Illustration with the UV absorption spectrum of ethylene, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2014**, 119 52–58.

[28] F. SANTORO, R. IMPROTA, A. LAMI, J. BLOINO, and V. BARONE, Effective method to compute Franck-Condon integrals for optical spectra of large molecules in solution, *The Journal of Chemical Physics*, **2007**, 126 (8) 084509.

[29] F. SANTORO, A. LAMI, R. IMPROTA, J. BLOINO, and V. BARONE, Effective method for the computation of optical spectra of large molecules at finite temperature including the Duschinsky and Herzberg–Teller effect: The Qx band of porphyrin as a case study, *The Journal of Chemical Physics*, **2008**, 128 (22) 224311.

[30] A. BOLOVINOS, P. TSEKERIS, J. PHILIS, E. PANTOS, and G. ANDRITSOPOULOS, Absolute vacuum ultraviolet absorption spectra of some gaseous azabenzenes, *Journal of Molecular Spectroscopy*, **1984**, 103 (2) 240–256.

[31] G. Herzberg and E. Teller, Schwingungsstruktur der Elektronenübergänge bei mehratomigen Molekülen, *Zeitschrift für Physikalische Chemie*, **1933**, 21B (1) 410–446.

[32] Z. Xu and J. S. Moore, Design and synthesis of a convergent and directional molecular antenna, *Acta Polymerica*, **1994**, 45 (2) 83–87.

[33] Q. Chu and Y. Pang, Vibronic structures in the electronic spectra of oligo(phenylene ethynylene): effect of m-phenylene to the optical properties of poly(m-phenylene ethynylene), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **2004**, 60 (7) 1459–1467.

[34] E. K. L. Ho and B. Lasorne, Diabatic pseudofragmentation and nonadiabatic excitation-energy transfer in meta-substituted dendrimer building blocks, *Computational and Theoretical Chemistry*, **2019**, 1156 25–36.