

Fine Structure in Electronic Spectra of Cyanine Dyes: Are Sub-Bands Largely Determined by a Dominant Vibration or a Collection of Singly Excited Vibrations?

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Dedicated to Prof. John Griffiths on the occasion of his 75th birthday

This work critically examines attempts to model the fine structure apparent in electronic spectra of cyanine dyes and their analogues. Numerous computational studies reported over the past decade attribute the origin of sub-bands and their relative intensities to vibronic transitions in which the relevant electronic transition is coupled, irrespective of symmetry, with a collection of vibrations. It is contended that this type of approach is not supported by experimental evidence. An argu-

ment is reiterated for a more appropriate model that adheres closely to fundamental principles and fits the data. It stipulates that essentially just one symmetric vibration, carbon–carbon bond stretching of the cyanine polymethine chain, dominates the coupling and is responsible for the observed fine structure. Furthermore, it is pointed out that the intensities of the sub-bands are readily explained by means of the Franck–Condon principle.

1. Introduction

On August 26th, 1856, William Henry Perkin filed a patent claiming a synthetic dye,^[1] later called Mauveine.^[2] It is often written that his was the first such invention. However, there were earlier colorants of artificial origin, albeit none which enjoyed such phenomenal commercial success, nor sparked the growth of the chemical industry. Nevertheless, on April 7th of that same momentous year for colour chemistry, Charles Greville Williams reported at a meeting of the Royal Society of Edinburgh on the synthesis of beautiful blue dyes,^[3] later called Cyanine, which gave its name to a whole dye class.^[4,5] While not making the swift financial impact that mauveine and its analogues did in textile coloration, Cyanines in time became very important industrially for over a century in the field of image creation.

The first—and for a long time the main—technical application of cyanine dyes was their use as spectral sensitizers in silver halide photography.^[6,7] The commercial introduction of high power laser diodes in the middle of the 1980s opened

the door to numerous new technical applications of cyanine dyes. Among their number were fluorescent probes for biomedical imaging,^[8–13] laser radiation absorbing dyes in CD-R and DVD/R,^[14–16] and sensitizers in computer-to-plate (CtP) lithographic printing plates.^[17,18]


The possibilities of hi-tech applications for these dyes prompted much research directed at developing better understanding of their electronic spectra. Even before such promise was considered, investigation into cyanines formed a major plank of the enquiry into the connection between constitution and colour. Initially, the focus lay on the relationship between the structures of dyes and the wavelengths of their absorption maxima.^[19–23] While the spectra of symmetrical cyanine dyes display fine structure, this aspect received little attention for many years. To the best of our knowledge, in 1960, Werner Maier and Friedrich Dörr were the first to discuss the sub-bands present in cyanine dye spectra in the context of the Franck–Condon principle (FCP) and the coupling of a dominant Raman-active vibration with the electronic transition.^[24] During the next half century or so, the intensity distribution among the sub-bands in cyanine dye spectra was explained by the FCP assuming the sub-bands in cyanine dye spectra are largely determined by coupling of a dominant, totally symmetric vibration with the electronic transition.^[25–34]


In 2007, Guillaume et al. reported the first application of density and time-dependent density functional theory (DFT, TDDFT) in an attempt to simulate the absorption and emission spectra of a cyanine dye.^[35] Based on their findings with such computational tools, they developed a modern model and pointed out:

“Contrary to what is usually assumed when adopting simple schemes such as the Huang–Rhys approximation, the should-

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ers are not determined by a unique, dominant, vibrational normal mode but rather by a collection of singly excited vibrations.”

It is rather surprising to read of the Huang–Rhys (HR) approximation in a paper dealing with molecular spectroscopy, given that its inception was instead related to ionic crystals. In these materials, defects in the regular arrangement of a crystal lattice can produce characteristic colours. Such an imperfection is called an “F-centre”. The term derives from “Farbe”, the German word for colour. Kun Huang and Avril Rhys developed a theory—which will be covered in more detail later—to explain the shapes of the absorption bands originating from F-centres in terms of phonon–exciton coupling.^[36] In molecular spectroscopy, the (intramolecular) vibrational–electronic coupling gives rise to vibrational replicas in the electronic spectra rather than the phonon–exciton coupling in crystalline lattices of the HR approximation.

Therefore, to be more accurate the sentence above should really be paraphrased in the following manner:

“Contrary to what is usually assumed when adopting simple schemes such as the Franck–Condon approximation, the shoulders are not determined by a unique, dominant, vibrational normal mode but rather by a collection of singly excited vibrations.”

The main difference thus boils down to the following dichotomy. The FCP-related model assumes that a dominant, totally symmetric vibration couples with the electronic transition, thereby creating the vibrational–electronic (vibronic) sub-bands (0–0, 0–1, 0–2, ...) observed in electronic spectra. In contrast, the computational model assumes that the appearance of sub-bands is determined by a collection of (symmetric and non-symmetric) singly excited vibrations.

Computational studies like that employed in 2007, which claim a proper theoretical analysis of the sub-bands, continue to appear in the literature. Examples include papers dealing with the electronic spectra of cyanines,^[37–42] merocyanines,^[43] and squaraines^[44] on the basis that the sub-bands are composed of several peaks associated with different vibrations. As noted previously, this type of approach is far from one which relies on the role of a single dominant vibration in the electronic spectrum.

In only one paper among the numerous studies appearing after that of Guillaume et al., and which directly refer to their 2007 paper, can one read a sentiment conveying doubt about sub-band origin:^[45] “The complete rationalization of this transition using theoretical models remains a matter of debate; in particular the clear assignment of the high-energy shoulder remains problematic.”

This statement remains true, but which of the two aforementioned models is more appropriate?

Models are of central importance in linking theory with practice. They aid comprehension of complex experimental data and confer the ability to predict what might happen upon changing something within a system be they constituents or conditions.

In this paper we will argue about the “rightness” of both models outlined above.

Before attempting to answer the above question, we feel it is best to start with a short review of fundamental principles by revisiting the work of those theorists who trail-blazed the field of molecular spectroscopy.

2. The Franck–Condon Principle for Diatomic Molecules

The development of the quantum theory of atoms and molecules can be divided roughly into two periods: the “old” and the “new quantum theory of atoms and molecules”. In 1913, Niels Bohr extended the quantum theory of Max Planck and Albert Einstein to explain the electronic structure of atoms with two postulates:

- (1) the Bohr quantization condition, whereby the electrons move around the nucleus of an atom in definite orbits with an integer quantum number n and a discrete electronic energy, E_a, E_b, E_c, \dots , i.e., the stationary electronic states;
- (2) the Bohr resonance condition, which states that an atom in the initial electronic state with the Energy E_a can absorb or emit a photon of the energy $E = h\nu$ only if there exists a final stationary electronic state with the Energy E_b , whereby the energy difference between E_b and E_a ($\Delta E_{ab} = E_b - E_a = h\nu$) matches the energy of the absorbed or emitted photon.

While involving the mixing of classical physics and quantum ideas, this historical episode is relevant because it marked the start of the development of the “old quantum theory of atoms and molecules”. Within this framework James Franck developed a model to explain the photo-dissociation of diatomic molecules with schematic drawings of potential energy surfaces (PES) of electronic ground and excited states.^[46] Franck postulated that the molecule does not vibrate in its electronic ground state. A consequence of the absence of vibrational states is that the electronic transition originates from the minimum of the PES, since there can be no contribution of vibrational energy to the ground state. We draw attention to this point because the approximation of neglecting the zero-point vibrational energy, and by implication that nuclei are stationary on the minimum of the PES, is still used today in quantum chemistry.^[47]

Edward U. Condon first discussed the coupling of intramolecular bond vibrations with electronic transitions to explain the fine structure of electronic spectra. Building on Franck’s idea, Condon added the element of molecular vibration. He introduced vibrational states to the model in a semi-classical way with the assumption that nuclei are stationary only at the semi-classical turning points of the vibration: these are where vibrational states intersect with the PES.^[48,49] In doing so, Condon developed a theory to explain the intensity distribution of vibronic sub-bands in electronic spectra in the context of the “old quantum theory”.

A new chapter commenced in 1925 with the development of a “new quantum theory of atoms and molecules”. This year

heralded the publication of Louis de Broglie's famous paper "Recherches sur la théorie des Quanta", where he depicted the particle and wave nature of electrons. A year later this proposal led Erwin Schrödinger to describe standing waves of electrons surrounding nuclei. Therefore, this new quantum mechanics is also called wave mechanics of which mathematical relationships such as the one shown below were key:

$$H(r, R) \Psi(r, R) = E \Psi(r, R) \quad (1)$$

Equation (1) represents the time-independent Schrödinger equation with the total Hamiltonian operator $H(r, R)$ and the total wave-function of a molecular state $\Psi(r, R)$ which depends on both the positions of all electrons r and the positions of all nuclei R . Without postulates it follows from the new quantum mechanics that an atom or molecule can exist only in a discrete stationary state (eigenstate), which is characterized by its total molecular wave-function (eigenfunction) $\Psi(r, R)$ and its total energy (eigenvalue) E .

In the context of this new quantum theory Condon modified his initial theoretical framework with the following terms and approximations.^[50–52]

2.1. The First Condon Approximation

Equation (1) can be solved analytically only for a two-body system like the hydrogen atom. To render the task tractable for more complex systems, Condon postulated that electronic and nuclear motions are separable. Neglecting the rotation and translation of a molecule, its total energy is the sum of electronic and vibrational energy. With Condon's postulate the total wave-function of a non-rotating but vibrating molecule $\Psi_{nv}(r, R)$ can be expanded as a product of the electronic wave-function $\psi_n(r, R)$ at fixed nuclear positions and the nuclear vibrational wave-function $\chi_{nv}(R)$ as shown in [Eq. (2)].^[49,50] The quantum number n indicates the electronic state, whereas the quantum number v designates the vibrational state in the electronic state n .

$$\Psi_{nv}(r, R) = \psi_n(r, R) \chi_{nv}(R) \quad (2)$$

In the new quantum theory, nuclei are not stationary, but rather they are delocalized. Their probability distribution is directly related to the square of $\chi_{nv}(R)$.

2.2. The Second Condon Approximation

When the Bohr resonance condition is met, the probability of transition of a molecule from an initial state Ψ_a to a final state Ψ_b depends on the transition moment between the two states \vec{M}_{ab} [Eq. (3)]:

$$\vec{M}_{ab} = \int \Psi_b(r, R) \hat{o}(r, R) \Psi_a(r, R) dr dR \quad (3)$$

The transition moment operator $\hat{o}(r, R)$ is a complex quantity that includes electric dipole, magnetic dipole, electric quadru-

pole, magnetic quadrupole operators, etc. The predominant portion is contributed by the electric dipole operator $\hat{\mu}(r, R)$, so that $\hat{o}(r, R)$ is limited to $\hat{\mu}(r, R)$, which consists of the electronic dipole moment operator $\hat{\mu}(r)$ and the nuclear dipole moment operator $\hat{\mu}(R)$ as shown in [Eq. (4)].

$$\hat{o}(r, R) \approx \hat{\mu}(r, R) = \hat{\mu}(r) + \hat{\mu}(R) = -e \sum_i z_i r_i + e \sum_i z_i R_i \quad (4)$$

Here, $\hat{\mu}(r)$ is the sum of dipole moments of each electron, r_i the coordinates of the i^{th} electron, $\hat{\mu}(R)$ is the sum of dipole moments of each nucleus, z_i the nuclear charge and R_i the coordinates of the i^{th} nucleus. Thus, the electric dipole moment operator becomes the operator of the transition moment, which is therefore called the electric transition dipole moment operator.

Considering an electronic transition from the vibrational state v of the ground electronic state S_0 to the v^{th} vibrational state of the first excited electronic state S_1 the electric transition dipole moment is given as

$$\vec{M}_{0v-1v} = \int \int \psi_1(r, R) \chi_{1v}(R) [\hat{\mu}(r) + \hat{\mu}(R)] \psi_0(r, R) \chi_{0v}(R) dr dR \quad (5)$$

where $\psi_0(r, R)$ is the electronic wave-function for S_0 , $\psi_1(r, R)$ for S_1 , $\chi_{0v}(R)$ is the nuclear vibrational wave-function for S_0 and $\chi_{1v}(R)$ for S_1 . One must keep in mind that the electric transition dipole moment of a molecule is a transient dipole moment which connects two different molecular states: it is not, as is often said, related to the electric permanent dipole moment of a molecular state.

The integral of [Eq. (5)] can be split off and factorized into a product of the electronic transition dipole moment \vec{M}_{01} from S_0 to S_1 and the overlap integral between the wave-functions $\chi_{0v}(R)$ and $\chi_{1v}(R)$ that are involved in the transition:

$$\vec{M}_{0v-1v} = \int \psi_1(r, R) [\hat{\mu}(r)] \psi_0(r, R) dr \int \chi_{1v}(R) [\hat{\mu}(R)] \chi_{0v}(R) dR \quad (6)$$

The electronic transition dipole moment \vec{M}_{01} is a function of the nuclear positions R , which makes calculation very difficult. At this point Condon introduced a second approximation. He considered only $\psi_0(r, R)$ and $\psi_1(r, R)$ at the nuclei equilibrium position R_e of S_0 , enabling the substitution of both $\psi_0(r, R)$ and $\psi_1(r, R)$ in [Eq. (6)] with $\psi_0(r, R_e)$ to give [Eq. (7a)]. As a consequence of this approximation, \vec{M}_{01} is no longer a function of R . It becomes a constant C and can be moved outside the integral to furnish [Eq. (7b)].

$$\vec{M}_{0v-1v} = \int \psi_0(r, R_e) [\hat{\mu}(r)] \psi_0(r, R_e) dr \int \chi_{1v}(R) [\hat{\mu}(R)] \chi_{0v}(R) dR \quad (7a)$$

$$= C \int \chi_{1v}(R) [\hat{\mu}(R)] \chi_{0v}(R) dR \quad (7b)$$

By doing so, the problem reduces to solving the vibrational overlap integral. The square of it, which is called the Franck-Condon factor [see Eq. (8)], is directly related to the relative intensity of the vibronic sub-bands.

$$I_{0v-1v} = \left| \int \chi_{1v}(R) [\hat{\mu}(R)] \chi_{0v}(R) dR \right|^2 \quad (8)$$

2.3. Computation of the Overlap Integral

However, solving this seemingly simple task is not easy. Even with the inclusion of just the quantum harmonic oscillator to model molecular vibration, it is challenging. Both the potential energy V and the wave-function χ_v of the quantum harmonic oscillator in a vibrational state v are functions of the reduced mass m_r , vibrational frequency ν , (force constant $k=4\pi^2 m_r \nu^2$) and the deflection R from the equilibrium position R_e , [Eq. (9),(10)]

$$V = \frac{1}{2} k(R-R_e)^2 = 2\pi^2 m_r \nu^2 (R-R_e)^2 \quad (9)$$

$$\chi_v = N_v H_v [\alpha^{1/2} (R-R_e)] \exp[-\frac{1}{2} \alpha (R-R_e)^2] \quad (10)$$

with the normalization constant [Eq. (11)]

$$N_v = 1/(2^v v! \pi^{1/2})^{1/2} \quad (11)$$

the Hermite polynomials H_v and the coupling parameter α [Eq. (12)]

$$\alpha = 4\pi^2 m_r \nu h^{-1} = k/h\nu \quad (12)$$

Since the coupling parameter α has the dimension of $1/(\text{length unit})^2$, the terms $\alpha^{1/2} (R-R_e)$ and $\frac{1}{2} \alpha (R-R_e)^2$ are dimensionless.

To calculate the intensity distribution of the vibronic sub-bands according to [Eq. (8)], three factors must be taken into consideration:

- 1) a number of vibrational states in S_0 are occupied;
- 2) the vibrational frequencies, that is, the shape of the PES in both states are different [$k(S_0) \neq k(S_1)$; $\alpha(S_0) \neq \alpha(S_1)$];
- 3) the equilibrium bond lengths of the ground and excited electronic state differ [$R_e(S_0) \neq R_e(S_1)$].

These conditions make it difficult to calculate the overlap integrals of two harmonic oscillator wave functions. Therefore, even for diatomic molecules, quite a number of approximations are made to calculate the overlap integrals between the harmonic oscillator wave functions of two electronic states.

Within the harmonic approximation Elmer Hutchisson gave the first evaluation of Franck–Condon overlap integrals based on finite series expansion, which led to rather complicated solutions.^[53] During the following years a lot of papers were published that presented various approaches to evaluate the overlap integrals of harmonic oscillator wave-functions. The most rigorous approximations (4–6 below) were introduced by Carl J. Ballhausen.^[54]

- 4) At typical room temperatures (≈ 290 – 300 K) the vibrational ground state of S_0 is by far the most populated. Only a very small proportion of the molecules will be in anything other

than their vibrational ground state. In this case of negligible population of vibrational excited states in S_0 , the vibronic transitions are considered to take place only from $v=0$ in S_0 to different vibrational states in S_1 .

- 5) Differences in ν in S_0 and S_1 are usually small so the vibrational frequencies in S_0 and S_1 are taken to be equal. A consequence of this assumption is that the shapes of both PES in S_0 and S_1 are the same [$k(S_0)=k(S_1)$; $\alpha(S_0)=\alpha(S_1)$].
- 6) The transition of an electron from S_0 to S_1 leads to an increase of the equilibrium bond length $R_e(S_1)$ in comparison with that of $R_e(S_0)$. Therefore, the two electronic states are described by PES of the same shape but whose minima are in different locations [$R_e(S_0) < R_e(S_1)$]—the “displaced harmonic oscillator approximation”.

Originally, Ballhausen introduced the symbol k for the coupling strength, which led to confusion with the force constant k .^[54] Later he switched to the symbol S , which is more popular today [Eq. (13)].^[55]

$$S = \frac{1}{2} \alpha [R_e(S_1) - R_e(S_0)]^2 = \frac{1}{2} k/h\nu_{vi} [R_e(S_1) - R_e(S_0)]^2 \quad (13)$$

Here, ν_{vi} is the vibrational frequency of the symmetric harmonic valence vibration of a diatomic molecule in S_0 and in S_1 .

Making these approximations rendered it necessary only to consider changes in equilibrium bond length [$R_e(S_1) - R_e(S_0)$] for both electronic states in order to predict the intensity distribution of the vibronic sub-bands in a given electronic transition. They enabled Ballhausen to reduce [Eq. (8)] to [Eq.(14)] for the calculation of the intensities of vibrational-electronic transitions between the vibrational ground state ($v=0$) in S_0 and vibrational states v in S_1 .^[54,55]

$$I_{0-v} = e^{-S} S^v / v! = I_{0-0} S^v / v! \quad (14)$$

[Eq. (14)] makes possible the calculation of the normalised intensity I_{0-v} (transition probability) for a molecule from $v=0$ in S_0 toward the v^{th} vibrational state in S_1 if the coupling strength S is known. Conversely, [Eq. (14)] permits determination of S from the experimental ratio of I_{0-v}/I_{0-0} , i.e., derived from intensities of sub-bands appearing in the fine structure of spectra where one assumes an assignment of sub-bands to particular vibronic transitions. In the case of symmetrical trimethine cyanine dyes, for instance, S falls in the range of 0.44 to 0.68,^[32] whereas for polyenes the value of S lies between 0.92 and 1.29.^[49]

3. The Huang–Rhys Approximation for Diatomic Lattices

Crystallographic defects in the regular arrangement of crystal lattices represent a deviation from ideal colourless ionic crystals, conferring characteristic colours upon them. Such an imperfection is called an F-centre. It constitutes a location within a crystalline lattice where an anion is missing and the vacancy may be occupied by an electron. Light of particular energies excites this electron from the valence band into the conduction band. The resulting localized excited state of a crystal, the

positively charged electron hole and the electron bound together, is called an “exciton”.

One might expect this effect to lead to the appearance of narrow absorption lines, which is not the case in reality. Crystal lattices are not completely rigid. The atoms in the crystal vibrate. The vibrations of the crystalline lattices are called “phonons”. Incorporation of phonon-exciton coupling into the theory of excitons enables a better understanding and description of the shape of exciton absorption bands.

Thus Huang and Rhys developed a theory using FCP as its foundation to explain the shapes of the absorption bands of F-centres present in lattices by invoking the phenomenon of phonon-exciton coupling.^[36] Also here further approximations were introduced to solve the overlap integrals. Melvin Lax extended and formalized the HR approach.^[56] Thomas H. Keil used the harmonic oscillator for the phonons and considered—like Ballhausen—the approximations 4–6 outlined in the previous section and derived a formula, [Eq. (15)], which closely resembles [Eq. (13)].^[57]

$$S = \frac{1}{2} \alpha [R_e(S_1) - R_e(S_0)]^2 = \frac{1}{2} k/h\nu_{\text{ph}} [R_e(S_1) - R_e(S_0)]^2 \quad (15)$$

In the context of [Eq. (15)], the term S is often called the “Huang–Rhys factor”. Despite the form of these equations being similar, the vibrational properties of the systems to which they apply of course are not. One must not forget that in [Eq. (13)] ν_{vi} represents the frequency of the symmetric harmonic valence vibration of the bond in a diatomic molecule, whereas in [Eq. (15)] ν_{ph} symbolises the frequency of the symmetric harmonic phonon of a lattice. The sizes of the coupling strength S for molecular species and the Huang–Rhys factor, as well as the coupling parameter α (and so also the force constant k and vibrational frequency) between [Eq. (13) and (15)], differ substantially.

In summary, S in [Eq. (13)] provides a quantitative description of vibrational-electronic coupling in molecules, whereas in [Eq. (15)], it represents the phonon–exciton coupling property of lattice defects.

4. Applicability of the Franck–Condon Principle to Polyatomic Molecules and Role of Duschinsky Rotation

In the Section 2, we have seen that calculating the intensity distribution of the vibronic sub-bands in a given electronic transition presents a challenge. Several approximations are necessary to arrive at easy-to-handle solutions for diatomic species. Polyatomic entities are of more practical interest to researchers seeking to understand and design organic materials for technological use. These systems of course exhibit far greater complexity owing to the larger set of normal vibrations which their extended molecular skeletons make possible.

In a diatomic molecule, the only vibration is the Raman active symmetric valence vibration, which does not change the symmetry of the molecule. The number of normal vibrations in a polyatomic molecule is $3N-5$ for linear molecules and $3N-6$ for non-linear molecules, where N is the number of atoms in

the molecule. Depending on their symmetry the vibrations can be IR- or Raman-active.

Given the considerable extra permutations, the calculation of multidimensional overlap integrals in polyatomic molecules is demanding and calls for additional approximations. It is therefore worth moving on from a discussion of the applicability of the FCP to diatomic molecules and embarking on one which concerns polyatomic molecules.

The first approach for polyatomic molecules was developed by Gerhard Herzberg and Edward Teller based on Condon’s approximations. They called the first Condon approximation [Eq. (2)] “Vernachlässigung I” and the second Condon approximation [Eq. (7)] “Vernachlässigung II” and discussed [Eq. (8)] based on group theory.^[59]

The wave-function of the vibrational ground state ($v=0$) is totally symmetric. Herzberg and Teller deduced that a) only a totally symmetric vibrational wave-function will have a non-zero overlap integral with it, and b) with any non-totally symmetric vibrational wave-function the overlap integral must be zero. Therefore, within an intense (symmetry allowed; electronic transition dipole moment $\neq 0$) electronic transition in a polyatomic molecule, vibrations can appear as a progression only if the symmetry is the same in the excited electronic state as in the ground state. In other words, the transition can couple only with totally symmetric vibrations, which change the size but not the symmetry of the molecule, just as is the case for a diatomic molecule.

This framework means that IR-active deformation and anti-symmetric valence vibrations cannot couple with the allowed electronic transition. Only Raman active vibrations may do so!

To apply the simple FCP for polyatomic molecules, it is a prerequisite that the intensity distribution of the individual sub-bands must be largely determined by one single generalized parameter of changes in bond length and one dominant, totally symmetric vibration.

Duschinsky has discussed the effect that the normal coordinates of electronic excited states of polyatomic molecules are rotated relative to those of their ground states (Duschinsky rotation).^[58] Contrary to Herzberg and Teller’s model the application of Duschinsky rotation allows the coupling of an intense electronic transition with deformation and anti-symmetric valence vibrations, which change the symmetry of the molecule.

Consequently many quantitative calculations concerning dyes which incorporated the effect of Duschinsky rotation were performed,^[37–44] whose modus operandi are consistent with the conclusion that “...the shoulders are not determined by a unique, dominant, vibrational normal mode but rather by a collection of singly excited vibrations.”^[35]

In the following section we will discuss the “rightness” of both models in light of spectroscopic data obtained from instrumental measurement.

5. Experimental Justification for the Franck–Condon Intensity Distributions in the Electronic Spectra of Cyanine Dyes

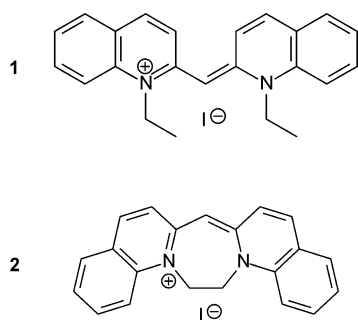
Let us be clear: we will not claim that only one vibration couples with the electronic dipole allowed S_0 – S_1 electronic transition in cyanine dyes. The underlying vibronic transitions will be far more complex owing to the population of vibrational and rotational states of the ground electronic state. Symmetrical vibrations in the region of 30 – 300 cm^{-1} especially will lead to a broadening of the dominant vibronic transitions.

The key question is this: does a dominant vibration give rise to the sub-bands in the electronic spectra of cyanine dyes, or are the sub-bands determined by a collection of singly excited vibrations?

An important prerequisite for discussion of the electronic spectra fine structure in the context of the FCP is that the sub-bands belong to the same electronic transition. Polarisation spectra prove that this applies in the case of cyanine dyes.^[28,29]

To be able to rationalise the intensity distribution of the sub-bands in the electronic spectra of polyatomic molecules via the diatomic Franck–Condon approximation as vibronic sub-bands (0 – 0 , 0 – 1 , 0 – 2 , ...), a specific vibration-related restriction must be imposed: this stipulation is that the sub-bands are mainly determined by a dominant symmetric vibration, just as for a diatomic molecule.

The work-horse of cyanine dye chemists is the pseudoisocyanine **1**, one of the most well-studied cyanine dyes. Its absorption spectrum exhibits a fine structure with a spacing of about $1375 \pm 25\text{ cm}^{-1}$ ^[29] At 77 K , the rigidized derivative **2** possesses a well resolved absorption spectrum whose shape is similar to **1**. The difference between the first four sub-bands of **2** was determined to be 1370 cm^{-1} .^[30]



These regularities, especially the constant difference between the first four sub-bands in the low temperature spectrum, are indicative of the coupling of one dominant vibration having a frequency of about 1370 cm^{-1} in the excited state.

If true, then the next question concerns the identity of this vibration. Jacques Pouradier analysed the absorption spectra of some 90 different cyanine and merocyanine dyes. The energy spacing between the first two sub-bands of all spectra is in the range of $1200\text{ cm}^{-1} \pm 200\text{ cm}^{-1}$,^[25] as illustrated in Figures 1–4. His results support the above conclusion that a dominant vibration, general to these dyes, is the source of the sub-

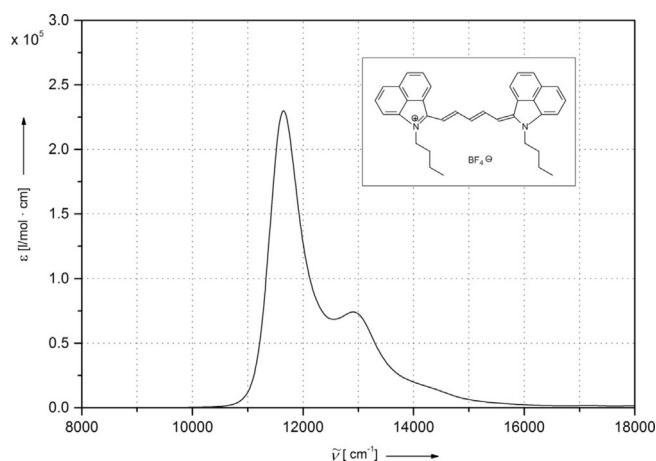


Figure 1. Electronic absorption spectrum in MeOH of a symmetrical red-absorbing cyanine dye.

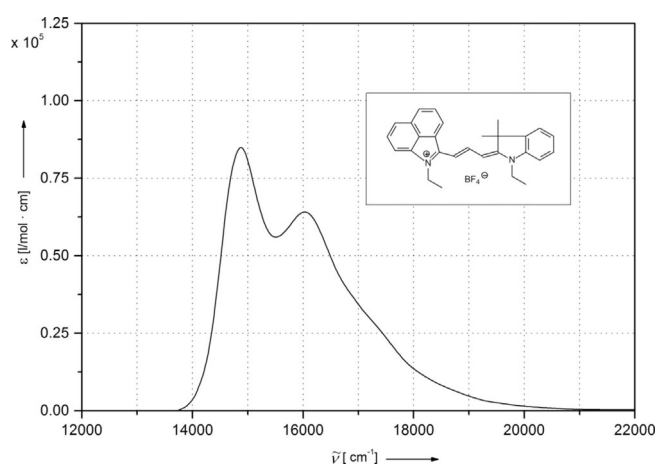


Figure 2. Electronic absorption spectrum in DMSO of an unsymmetrical near-infrared absorbing cyanine dye.

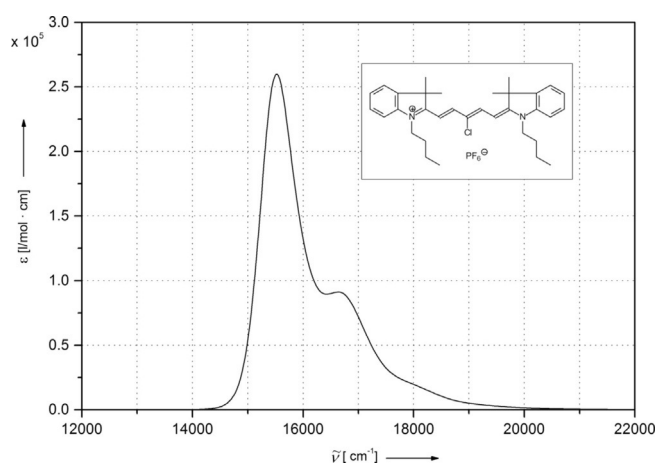


Figure 3. Electronic absorption spectrum in DMSO of a symmetrical cyanine dye.

bands. The single common structural element of the different dyes is the polymethine chain. Because variations in vibrational frequency pertaining to this part of the chromophore induced

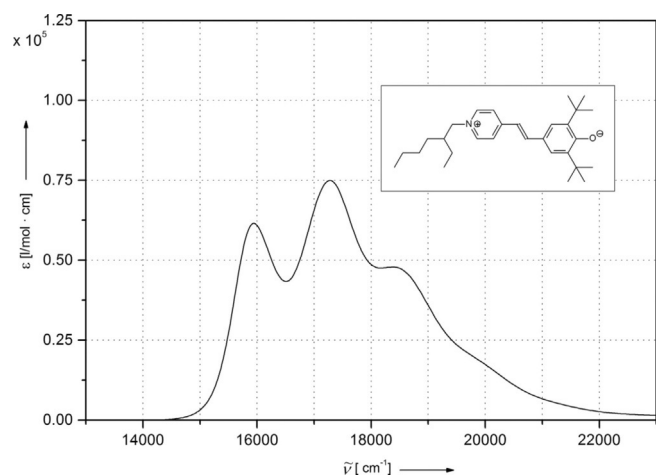


Figure 4. Electronic absorption spectrum in 1,4-dioxane of a merocyanine dye.

by differences in groups at each end of the cyanine dye structure are relatively small, it may be deduced that the sub-bands arise from the coupling of a vibration of the polymethine chain with the S_0 – S_1 electronic transition. It is noteworthy that in Refs. [35, 37–44], Pouradier's work was neither cited, nor was his analysis of experimental spectra discussed.

Maier and Dörr investigated **1** with resonance Raman spectroscopy. They determined that the strongest resonance Raman line in the excited state appeared at 1365 cm^{-1} . This value correlates well with the spacing between the sub-bands in the absorption spectrum. They identified this vibration as the symmetric carbon-carbon valence vibration of the polymethine chain. Subsequent resonance Raman investigations not only confirmed this result for **1**, but did so too for a wide range of cyanine dyes.^[60–62]

All these experimental results are consistent with the interpretation that a dominant, symmetric carbon-carbon valence vibration of the polymethine chain gives rise to the sub-bands in the electronic spectra of cyanine dyes. The observed sub-bands thus correspond mainly to vibronic transitions from $v=0$ in S_0 to $v=0, 1, 2, \dots$ in S_1 , where v is the vibrational quantum number of the respective vibrational state of the symmetric carbon-carbon valence vibration of the polymethine chain.

Courtesy of Ballhausen's approximations it is only necessary to consider the difference $R_e(S_1) - R_e(S_0)$ when modelling sub-band intensity distribution. The S_0 – S_1 electronic transition in cyanine dyes can be ascribed mainly to an electronic transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The HOMO has bonding character whereas the LUMO has antibonding character. It therefore follows that $R_e(S_1)$ is greater than $R_e(S_0)$.

In the fluorescence spectrum of **1** a corresponding main progression appears in approximate mirror symmetry with a spacing between sub-bands of about $1400 \pm 50\text{ cm}^{-1}$.^[29] The well resolved fluorescence spectrum of **2** exhibits a spacing of about 1550 cm^{-1} . The reduction in the vibrational frequency in the excited electronic state, 1370 cm^{-1} , compared to that of the ground state, 1550 cm^{-1} , is consistent with the equilibrium bond length increase upon excitation [$R_e(S_1) > R_e(S_0)$].

Incorporating extra vinylene groups into the polymethine chain increases the total number of π -electrons delocalised across the dye structure. As the amount of π -electrons in the bonding HOMO rises, the influence of an excited electron in the antibonding LUMO decreases. Consequently the difference $R_e(S_1) - R_e(S_0)$ reduces and thus the experimental ratio of I_{0-v}/I_{0-0} decreases as shown in Figure 5 and Table 1.

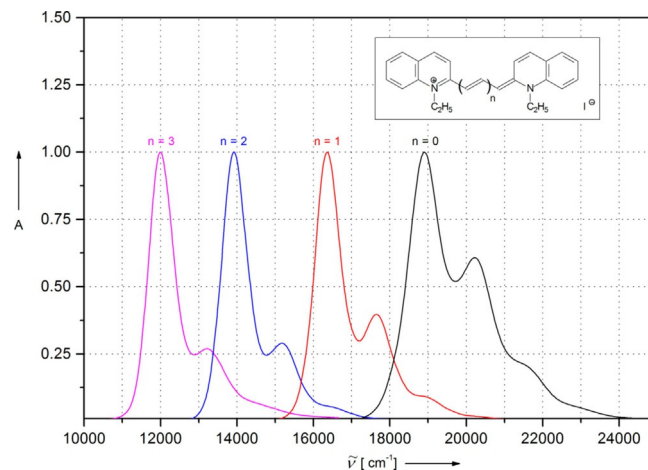


Figure 5. Electronic absorption spectra of 2,2'-carbocyanine dyes in MeOH in dependence on the length of the polymethine chain n .

Table 1. Absorption maxima (λ) and molar absorption coefficients (ϵ) of the 0–0 and 0–1 sub-bands in the electronic absorption spectra of 2,2'-carbocyanine dyes in MeOH and the intensity ratio (I_{0-1}/I_{0-0}) dependence on the length of the polymethine chain (n).

n	$\lambda(0-0)$ [nm]	ϵ [dm ³ mol ⁻¹ cm ⁻¹]	$\lambda(0-1)$ [nm]	ϵ [dm ³ mol ⁻¹ cm ⁻¹]	I_{0-1}/I_{0-0}
0	529	85 000	495	51 600	0.61
1	611	197 000	567	78 300	0.40
2	718	278 000	659	80 700	0.29
3	833	293 000	757	79 000	0.27

All experimental results support the point of view that a dominant vibration gives rise to the sub-bands in the electronic spectra of cyanine dyes and the intensity distribution among the vibronic sub-bands can be explained by the FCP.

To the best of our knowledge, there are no experimental results which justify the conclusion that the sub-bands of cyanine dye electronic spectra are determined by a collection of singly excited vibrations. On the contrary, if many vibrations couple with the electronic transition of a polyatomic molecule, then the various progressions will overlap so that the band envelope will be observed as a smooth absorption curve devoid of significant fine structure.

6. Conclusions

We have presented an answer to the question posed in the title of this article. Our response contrasts with the basis for several computational studies conducted since the turn of the millennium that have been devoted to modelling of fine structure in the electronic spectra of cyanine dyes. These attribute

the position and intensity of sub-bands to vibronic transitions arising from the coupling to electronic transitions of a large array of symmetric and asymmetric vibrations. Notwithstanding any inappropriate invocation of the term Huang–Rhys approximation, their approach diverges from Herzberg and Teller's extension to polyatomic molecules of the Franck–Condon principle in which only symmetric vibrations are of significance to electronic spectra. Even though effects such as Duschinsky rotation provide a mechanism for non-symmetric vibrations to contribute to the vibronic structure of polyatomic compounds, we have demonstrated using literature data that, for a cyanine dye, the spacing of sub-bands in its spectrum is primarily determined by a dominant symmetric vibration associated with its polymethine chain rather than a collection of singly excited vibrations. Furthermore, the observed intensities of these sub-bands can be explained in terms of this dominant vibration by the Franck–Condon principle.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: cyanines · electronic spectra · Franck–Condon principle · molecular modeling · vibronic transitions

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