

Refractive Index Dependence of the Förster Resonance Excitation Transfer Rate

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The rate or yield of resonance electronic excitation transfer is an important tool of biological research, used to estimate distances between chromophores. Besides the interchromophore distance, this rate or yield depends on several other parameters that are clearly important for determining the correct distances. In particular, in a medium characterized by a refractive index n , the expression for the rate contains a factor n^{-4} . We argue here that the correct value for n is that of the donor–acceptor intervening medium, not that of the overall solvent, as has been argued by some. The choice is clearly important to any quantitative application of the theory since the index of typical relevant materials ranges from 1.3 to 1.6. Incidental to our analysis, a certain expression that connects dipole strengths with radiative lifetimes requires correction. This leads to revisions of estimates of the amounts of exciton delocalization in antenna complexes from purple bacteria (downward by 25%). In our analysis we distinguish three physically distinct ways in which refractive index affects the rate and suggest how they should be handled.

1. Introduction

Förster theory^{1–4} explains the process often referred to as “FRET”, fluorescence [with or following] resonance energy transfer. Since its introduction in 1967 by Stryer and Haugland,⁵ excitation transfer has remained a very popular tool for estimating distances in biological macromolecules and their complexes. Determining the distances requires accurate knowledge of fluorescence and absorption spectra of the donor and acceptor, respectively, their orientations with respect to one another, and information about their mutual environment which is usually encapsulated into some index of refraction n . Most importantly for us, the transfer rate contains a factor n^{-4} . The issue motivating our discussion is whether a local environment picture should apply—one in which n is taken as characteristic largely of the medium lying between the two molecules—or a solvent picture, in which n characterizes the solvent associated with the determination of the absorption and emission spectra that appear in the equations. The solvent view has been advocated strongly⁶ and adopted frequently,⁷ but only recently have experiments and structures become sufficiently precise to address the issue experimentally.⁸ These experiments suggest that the local picture applies to the n^{-4} factor. There are, in fact, three different ways in which decisions about n may affect the calculation of the Förster excitation transfer rate. These considerations are of special relevance for chromophores in a protein in a water or lipid environment. Given the popularity and importance of FRET in present research, it is worthwhile to address the unsettled refractive index issues.

The theory of excitation transfer can be approached quite formally, treating the quantum states of the chromophores and their interactions explicitly. Some recent comprehensive calculations are based on determination of both electronic and vibrational states of a bacteriochlorophyll protein *ab initio*.⁹ The present paper addresses problems connected with the familiar phenomenological Förster method in which interaction strengths are derived from spectra of the interacting chromophores. Our results will apply to any theory based on a simple polarizable-medium picture of the chromophores’ environment.

We concentrate on only those aspects of Förster’s theory that depend on the index of refraction. In Sections 2 and 3 we introduce the Coulomb and effective field aspects of the index dependence. In Section 4 we introduce a more elusive aspect, one whose intricacies have led to the controversy. In Section 5 we present a resolution of the n^{-4} index question. In Section 6 we discuss the other important index-dependent factors and summarize the work.

2. The Original Förster Theory and the Coulomb Interaction

The Förster rate of transfer of excitation between two chromophores, one of which is assumed initially excited (the donor D) and the other of which is initially in its ground state (the acceptor A), is given by^{1–4}

$$k = \frac{1}{\tau} \left(\frac{R_0}{R_{DA}} \right)^6 \quad (1)$$

in which τ is the natural radiative lifetime of the donor excited

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state, R_{DA} is the distance between the centers of the molecules, and R_0 is defined through

$$R_0^6 \equiv \frac{9 \ln(10)}{128\pi^5 n^4 N'} \kappa^2 \int \frac{f_D(\tilde{\nu}) \epsilon_A(\tilde{\nu})}{\tilde{\nu}^4} d\tilde{\nu} \quad (2)$$

where $\tilde{\nu}$ is the wavenumber in cm^{-1} , $f_D(\tilde{\nu})$ is the emission spectrum in units such that its integral is unity: $\int f_D(\tilde{\nu}) d\tilde{\nu} = 1$, $\epsilon_A(\tilde{\nu})$ is the molar decadic extinction coefficient in $\text{L}/(\text{mol cm})$ at wavenumber $\tilde{\nu}$, N' is Avogadro's constant divided by 1000, and κ^2 is a factor depending on the relative orientations of the transition dipole moments of the donor and acceptor and their orientations relative to the separation vector. In many applications, κ^2 is replaced by its spatial average over all donor and acceptor orientations, $\kappa^2 = 2/3$. The parameter n is the index of refraction that is the central subject of this paper. The form presented in eq 1, especially the relationship between τ and R_0 , is discussed by one of the authors (ref 3, pp 191–192). The theory was reviewed some time ago by Förster himself.²

The perturbation inducing transfer of electronic excitation between molecules is the Coulomb interaction between them, a sum of many terms proportional to $\pm e^2/r_{ij}$ involving electrons and nuclei in all the atoms of the molecules. Here e is the electronic charge and r_{ij} indicates the distance between any two constituent particles on different molecules. An effective dielectric function is used to modify these interactions to account for the effect of the surrounding medium. Förster replaces each interaction $\pm e^2/r_{ij}$ by $\pm e^2/n^2 r_{ij}$. He says these are “the Coulomb interaction[s] of the moving electronic charges ... wherein the square of the solvent refractive index n serves as the dielectric constant.” (See ref 2, page 99, or ref 4, page 151.) Since Förster was thinking in terms of solute molecules in fluorescing solutions, his word “solvent” has no particular bearing on the present discussion. For him, the local environment was itself the solvent. On the basis of this interaction, he obtained the following rate:

$$k_{DA} = (4\pi^2 \kappa^2 / h^2 c n_{(1)}^4 R_{DA}^6) \int \mu_D^2(\tilde{\nu}) \mu_A^2(\tilde{\nu}) d\tilde{\nu} \quad (3)$$

Many aspects of this rate expression require comment. *First*, in contrast with Förster we retain κ^2 explicitly. *Second*, a subscript “(1)” has been added to the index in order to identify its origin, since we later introduce the index twice again in different contexts. *Third*, eq 3 may be recognized as the usual Fermi golden rule for transition rates induced by a dipole–dipole interaction, with an additional factor $1/(2\pi c)$ that results from wavenumber units. *Fourth*, $\mu_D^2(\tilde{\nu})$ and $\mu_A^2(\tilde{\nu})$ are the squares of transition dipole moments on the donor and acceptor, respectively. They are abbreviations of certain thermal averages of integrals over distributions of vibrational levels^{2,10} and were denoted M^2 by Förster. Because of the energy normalization used in Förster's work, these quantities have units of [(charge \times length)²/wavenumber]. They are therefore dipole strength densities, such that the usual total dipole strengths are given by $\mu_D^2 = \int \mu_D^2(\tilde{\nu}) d\tilde{\nu}$ and similarly for the acceptor. A normalized shape function will be introduced, $\mu^2(\tilde{\nu}) = \mu^2 S(\tilde{\nu})$. *Fifth*, it has recently been found useful^{7,8} to use the normalized functions in the rate expression so that with appropriate constants included the rate becomes

$$k_{DA} = [29.99 \mu_D^2 \mu_A^2 \int S_D(\tilde{\nu}) S_A(\tilde{\nu}) d\tilde{\nu}] \cdot (\kappa^2 / n_{(1)}^4 R_{DA}^6) \\ = C_{DA} \times (\kappa^2 / n_{(1)}^4 R_{DA}^6) \quad (4)$$

with C_{DA} expressed in nm^6/ps . The spectral dependence of the rate is packaged in the parameter C_{DA} . Its value for transfer between isoenergetic chlorophyll-*a* molecules is in the range of 50 to 70 (Knox, unpublished). The functions S integrate to unity and the integral in eq 4 therefore has units $1/\text{wavenumber}$. *Sixth* and finally, the dipole strengths appearing in all the above equations refer to the strengths as measured or calculated *in situ*, that is, they are strengths of the electronic transitions of the entire imbedded chromophore–environment systems, not those of isolated molecules. An important aspect of Förster's theory is his assumption that the spectra appearing in the integral are those measured in precisely the same environment that is involved in the transfer of energy.

3. Effective Field Considerations

In texts and quantitative theoretical work, transition dipole moments are invariably introduced as *vacuum* parameters μ_0 that apply to the totally isolated chromophore. In practice the chromophore's environment is critical and may be thought of as an extension of the chromophore to a system whose transition moment μ (the *in situ* moment) determines its optical and excitation-transfer properties. It is worth reflecting for a moment on this situation because a somewhat different picture is frequently drawn in the literature.

The average electric field E_c of the incident light in the medium acts on the *in situ* transition moment μ and produces the electron–photon interaction proportional to $\mu^* E_c$. This interaction may be written $\mu_0^* f^* E_c$ and can be thought of in one of two ways, as either $(\mu_0^* f)^* E_c$ or $\mu_0^* (f^* E_c)$. In the former case, one has the *in situ* transition moment $\mu = \mu_0^* f$ that interacts with the average field, which is the view of the quantum approach described above. In the latter case, one has the vacuum transition moment interacting with an effective field $E_{\text{eff}} = f^* E_c$, evoking the more classical view that f is an “effective field” factor. The effective increase in field is due to the additional polarization of the environment by the vacuum moment itself.

In this paper we adopt the quantum viewpoint and work with *in situ* dipole moments and strengths $\mu(n_{(2)})$ and $\mu(n_{(2)})^2$, respectively. The argument $n_{(2)}$ serves as a reminder that the strengths in the Förster theory are meant to be *in situ* and it makes a connection with model calculations of the effective field factors. The most familiar connection, related to the Lorentz-sphere treatment of the Clausius-Mossotti equation, is

$$\mu^2(n_{(2)}) = \left(\frac{n_{(2)}^2 + 2}{3} \right)^2 \mu_0^2 = f_L^2 \mu_0^2 \quad (5)$$

An alternative picture is the “empty cavity” treatment of Onsager, which predicts

$$\mu^2(n_{(2)}) = \left(\frac{3n_{(2)}^2}{2n_{(2)}^2 + 1} \right)^2 \mu_0^2 = f_C^2 \mu_0^2 \quad (6)$$

The Lorentz form, eq 5, is reproduced theoretically in lowest order of perturbation for oscillator strengths of imbedded atoms¹¹ and the dipole–dipole interaction in the nondispersive limit in a dielectric.¹² A discussion of these factors may be found in the books by Agranovich and Galanin¹³ and van Amerongen et al.¹⁴ Their application to dipole strength estimates in the chlorophylls is discussed by Alden et al.¹⁵ and by one of the present authors.¹⁶

Up to this point we have introduced the index of refraction in two contexts, $n_{(1)}$ as a representative of the dielectric screening of the Coulomb interaction and $n_{(2)}$ as a single-parameter

surrogate for the effect of the solvent on dipole strengths. These indexes are not necessarily the same, although under very homogeneous conditions they will be identical. In the treatment of Knoester and Mukamel¹² they are explicitly the same in the nondispersive limit and are developed into a scaling factor for the Förster rate, $[(n^2 + 2)/3]^{-4} n^{-4}$. We caution that the use of such a scaling factor assumes the use of vacuum strengths in the Förster rate and therefore the validity of an additional set of theoretical assumptions. As recently noted by one of us,¹⁶ the most reliable assignment of an *in situ* dipole strength index dependence results from correlating dipole strengths in different solvents with the respective refractive indexes, thereby avoiding the effective field factors entirely. Unfortunately, this correlation is not accompanied by guidance as to the value of $n_{(2)}$ to use in a given heterogeneous environment.

4. Spectra and the Refractive Index

In 1984 Moog et al. were applying Förster's theory to chromophores in proteins and proposed⁶ that the index appearing in Förster's equation should be that of the solvent in which the spectra were measured instead of the one corresponding to dielectric screening within the protein. Their view has been rather widely adopted⁷ and since it seems to be in disagreement with Förster's original usage a thorough examination of the issue is in order.

We begin with another look at Förster's paper. Having derived eq 3, he relates the quantities under the integral to the emission and absorption spectra associated with the individual molecules,

$$\epsilon_A(\tilde{\nu}) = \frac{8\pi^3}{3} \frac{N'\tilde{\nu}}{hc n_{(3)} \ln(10)} \mu_A^2(\tilde{\nu}) \quad (7)$$

and

$$A_D(\tilde{\nu}) = \frac{64\pi^4 n_{(3)}^3 \tilde{\nu}^3}{3h} \mu_D^2(\tilde{\nu}) \quad (8)$$

where $\epsilon_A(\tilde{\nu})$ is the molar decadic extinction coefficient of the acceptor (equivalent to a cross section, length²) in the medium characterized by index $n_{(3)}$ and similarly $A_D(\tilde{\nu})$ is the donor's rate of photon emission (per second per wavenumber interval). A_D is converted into the normalized emission spectrum f , $A_D(\tilde{\nu}) = f_D(\tilde{\nu})/\tau$, so that

$$\int A_D(\tilde{\nu}) d\tilde{\nu} = 1/\tau \quad (9)$$

Used in eq 3, the preceding expressions lead directly to the famous formula eq 2, but our interest is in the index $n_{(3)}$. In our context it is an entirely new manifestation of the index. It could be called *elusive* because it canceled out completely in Förster's hands. The product of (7) and (8) does not contain it. It is this $n_{(3)}$ that emerges in the treatment by Moog et al. to take the place of $n_{(1)}$, so we must examine its origin.

The absorption coefficient α (units of inverse length) is defined in terms of the logarithmic decrease of intensity of a beam traversing a medium in (say) the x direction:

$$dI(x) = -\alpha \cdot I(x) dx = -n_0 \sigma \cdot I(x) dx = -\epsilon C \ln(10) \cdot I(x) dx \quad (10)$$

where I is the beam flux (units energy per unit time and per unit area). The second and third forms convert α into absorption cross sections; the concentrations n_0 and C are in particles per unit volume and moles per unit volume, respectively. For a beam

covering an area A , the cross section is extracted and computed as follows:

$$\begin{aligned} n_0 \sigma(\nu) &= \frac{A(-dI)}{I \cdot dx A} \\ &= \frac{\text{energy loss from volume } A \text{ dx per unit time}}{\text{energy traversing volume } A \text{ dx per unit time}} \\ &= \frac{(\text{no. of molecules in } A \text{ dx})(\text{transitions per unit time})(\text{energy per transition})}{(\text{EM wave energy density})(\text{energy velocity})(\text{volume})} \\ &= \frac{CA \text{ dx} \cdot (\text{constant}) \cdot \mu_A^2 E_c^2 \cdot h\nu}{(\epsilon_r E_c^2 / 4\pi) \cdot u_e \cdot A \text{ dx}} \quad (11) \end{aligned}$$

The constant absorbs all factors in the transition rate except the square of the perturbation element, which remains in the form $\mu_A^2 E_c^2$, and the field E_c is the amplitude of the average electric field of the photons in the medium. The parameter ϵ_r is the ratio of the energy density of the electromagnetic wave in the medium to that in a vacuum, and u_e is the energy velocity, which is c in the vacuum. The flux $(\epsilon_r E_c^2 / 4\pi) u_e$ in the denominator of eq 20 derives completely from considerations on the propagation of the electromagnetic field in the medium. In regions of little dispersion, $\epsilon_r = n_{(3)}^2$ and $u_e = c/n_{(3)}$ and the flux becomes simply $n_{(3)} c E_c^2 / 4\pi$. It was pointed out long ago by Brillouin¹⁷ that in dispersive regions of the spectrum, ϵ_r is frequency-dependent, as is the energy velocity u_e , and both depend on the microscopic detail of the model. Using a flux continuity argument he then showed that their product, even in dispersive regions, is nonetheless $\epsilon_r u_e = n_{(3)} c$. This fact must have been clear to Förster. It accounts for the $n_{(3)}$ that appears in eq 7 above. Arguments analogous to those concerning absorption can be made in the case of emission and produce the $n_{(3)}$ in eq 8 when analogous flux arguments are again made.¹⁸

5. Resolution of the Index Question

In their treatment of this problem, Moog et al. replaced eqs 7 and 8 with

$$\epsilon_A(\tilde{\nu}) = \frac{8\pi^3}{3} \frac{N'\tilde{\nu}}{hc \cdot [\epsilon_r / n_{(3)}] \cdot \ln(10)} \mu_A^2(\tilde{\nu}) \quad (7a)$$

and

$$A_D(\tilde{\nu}) = \frac{64\pi^4 \cdot [n_{(3)}^3 / \epsilon_r] \cdot \tilde{\nu}^3}{3h} \mu_D^2(\tilde{\nu}) \quad (8a)$$

respectively. Equations 7a and 8a result from a partial treatment of the flux developed in the preceding paragraph. For example, in the denominator of eq 7a, the approximate energy velocity $c/n_{(3)}$ has been introduced but the energy density parameter ϵ_r has been left undetermined. The reason for this unusual choice is that the authors adopted the formalism of Dexter,¹⁹ who somewhat confusingly associated $1/\epsilon_r$ with a quantity $(E_o/E)^2$ called "the ratio of the field in the [medium] to that in free space," rather than an energy density ratio. By electromagnetic boundary conditions the transverse field of the wave outside the medium is actually the same as that of the average field in the medium, but the energy density does increase, since the medium becomes polarized, and this effect is fully covered by the Brillouin theorem: to complete eqs 7a and 8a one may freely introduce $\epsilon_r = n_{(3)}^2$, regaining the Förster result. Moog et al. chose to interpret ϵ_r as the dielectric constant associated with

the screening of the Coulomb interaction and in our terminology therefore considered it to be $n_{(1)}^2$. This choice turns out to be critical. They assert "...in these equations, as in the excitation transfer equations [emphasis theirs], the ϵ factor [our ϵ_r] reflects predominantly the polarizability of the immediate protein environment ..." No justification is given for this assertion. Gathering together all the medium-dependent quantities under discussion, we find that the Förster equation contains the factor

$$\frac{1}{n_{(1)}^4} \cdot \frac{\epsilon_r}{n_{(3)}} \cdot \frac{\epsilon_r}{n_{(3)}^3} \quad (12)$$

Once the Moog choice has been made, $n_{(1)}^4$ in the denominator is wiped away and replaced by $n_{(3)}^4$. However, on the basis of the Brillouin theorem, the choice $\epsilon_r = n_{(3)}^2$ is not only consistent with the fact that the energy velocity has already been chosen to be $c/n_{(3)}$ but is *required* by it. The second and third factors of expression (eq 12) therefore cancel each other out, as in the original Förster theory. Moreover, since ϵ_r and $n_{(3)}$ are linked through their common electromagnetic origin *it does not even matter to what part of the system they refer*.

Formal analysis of the Coulomb interaction in Förster theory by Dow²⁰ shows that the quantity that we are calling $1/n_{(1)}^2$ approximates the real part of the longitudinal component of the inverse dielectric tensor. As such, it would not naturally be canceled by spectral factors that are related to the transverse components of the electromagnetic field. Moog et al. comment neutrally on a different aspect of Dow's paper, namely, the question of effective local fields, apparently not noticing that Dow disagreed with their own answer to the n^{-4} question.

Because the energy densities of photons in the medium have scale factors of the order of the wavelength of the light, it is likely that the value of $n_{(3)}$, should we need it, refers to a region of the system much wider than the immediate vicinity of the donor and acceptor.

6. Discussion and Summary

As an example of a necessary correction that follows from our observations, consider part of a revision of a major computation of transfer rates in C-phycoyanin.²¹ The reasoning of Moog et al. was used to increase the index-dependent term in the calculated rates by a factor of $(1.54/1.34)^4 = 1.76$. Within the last year or two there has been definite motion toward the acceptance of the use of a local rather than a solvent index. Kleima et al.⁸ showed that an index corresponding to a protein environment is in much better agreement with measurements of transfer rates in a peridinin–chlorophyll protein. Scholes and Fleming²² opted for this view in their estimates of dipole–dipole interactions in the B800–B850 system of purple bacteria and discuss it in the context of Dow's work. Others²³ studying chlorophyll–protein complexes associated with photosystems I and II have employed the local-index view. A protein–environment refractive index is usually estimated in these works by comparing carotenoid level shifts in different environments,²⁴ which is consistent because the shifts are also caused by the Coulomb interaction.

A corollary of the electromagnetic field argument is that no distinction should be made between n and n^3/ϵ_r in the radiative rate. Such a distinction, which would be a necessary consequence of the argument of Moog et al., has been put into practice. Monshouwer et al.²⁵ used n^3/ϵ_r to estimate the differences in the radiative rate for monomeric bacteriochlorophyll *a* (Bchl-*a*) in acetone and coupled Bchl-*a* molecules in various pigment–protein complexes from purple bacteria. For

Bchl-*a* in acetone, $n^3/\epsilon_r = n = 1.36$. For B820, which contains a strongly interacting dimer of Bchl-*a* molecules, n was taken to be 1.33 (water) and for ϵ_r a value of 2.3 was taken. This led to a value of emitting dipole strength 1.3 times as large as that of the monomeric Bchl-*a*, differing significantly from the value 1.9 estimated by Koolhaas et al.²⁶ If in the case of the dimer in water one uses $\epsilon_r = 1.33^2 = 1.77$, or equivalently $[n^3/\epsilon_r] = n = 1.33$, the dipole strength ratio decreases to 0.94, in more serious disagreement with Koolhaas et al. Monshouwer et al. took the same value $\epsilon_r = 2.3$ for LH2 and LH1 complexes, but the temperature dependence of the radiative rate for LH1 could not be satisfactorily fitted with this value. It was stated by the authors that "... a dielectric constant of 1.85 would bring the measured value in better agreement with the simulation..." This is clearly much better in line with the value $\epsilon_r = 1.77$ given above. The latter value would decrease the aggregate/monomer emitting dipole strength ratio for LH2 and LH1 from 2.8 and 3.8, respectively, to 2.1 and 2.9, respectively, at room temperature. This would imply that the amount of delocalization of the excitation would be smaller than calculated in ref 25. The physical delocalization lengths and protein dimensions, of the order of ≤ 10 nm, are still significantly smaller than the wavelength of the light in the medium, justifying the use of the solvent index in calculating these ratios, as discussed above.

Although the propagation-effect $n_{(3)}$ factors cancel in the Förster rate itself, they cannot be ignored during extraction of transition dipole strengths from optical spectra via eqs 7 and 8. On rearranging eq 7 and integrating we obtain the well-known expression for dipole strength

$$\mu_D^2 = 9.186 \times 10^{-3} n_{(3)} \int [\epsilon(\tilde{\nu})/\tilde{\nu}] d\tilde{\nu} \quad (13)$$

Here ϵ is the *in situ* absorption coefficient, and all units are as in previous equations. Occasionally, when attempts have been made to extract vacuum strengths with this equation, the various index contributions have been commingled. For example, in some of the literature^{27,28} the propagation effect (with $n_{(3)}$) and Lorentz local field effect (with $n_{(2)}$) have been combined into a single factor $\theta = n_{(3)}/f_L^2(n_{(2)})$. In other cases²⁵ the Coulomb screening (with $n_{(1)}$) and local field effect (with $n_{(2)}$) have been combined with the dipole strength into a single effective dipole strength scale factor $n_{(1)}^{-2}f_L^2(n_{(2)})$. We recommend against such combinations. The three effects should be kept as distinct as possible because their physical origins are quite distinct.

Merely using an index differing from the bulk solution is far from the final answer to accurate estimates of the Förster rate. Consider first the " $n_{(2)}$ " factors, the effective field factors. We have assumed that *in situ* dipole strengths as measured optically are appropriate, because it has been argued that they are essentially identical for optical processes and the transfer process (see, e.g., refs 13 and 20). This has the consequence that the spectra used in Förster's rate bear yet another burden of environmental information, which will require closer inspection in particular cases. Second, there are dispersive effects, analogous to superexchange effects in electron transfer, as discussed by Dow.²⁰ They will certainly be of importance in many circumstances. Finally, the value of $n_{(1)}$ is rather imprecisely known, especially if the environment of the chromophores is heterogeneous. If the transferring chromophores are situated on separate proteins well separated by the solvent, a solvent index might well be appropriate.

In summary: while pursuing the question of Förster's n^{-4} factor we have identified three roles played by the index of refraction when an energy-transfer process occurs in a polariz-

able medium. We use subscripts (1), (2), and (3) to highlight these roles, not to imply that three different values exist in every case. In particular, the three are identical if all measurements (spectra, transfer rates) are made in the same simple solution. When different media or inhomogeneous media are involved the situation is more complex and is most easily discussed in the context of eq 4. First, dipole strengths are extracted from absorption data in a medium of index $n_{(3)}$ by using eq 13. Then, if transfer is occurring in a different medium, the strengths are revised by using $n_{(2)}$ -dependent effective field factors or (preferably) by a simple mapping procedure.¹⁶ Unfortunately there is no guidance available for the value of $n_{(2)}$ to be used in the effective field or in the mapping procedure when the environment is not a simple solvent. Finally, and this is our principal result, the appropriate index to use in the Förster expression n^{-4} is not that of the spectra-related solvent. Where the donor and acceptor are embedded in a locally heterogeneous region, an index $n_{(1)}$ appropriate to the modification of the Coulomb interaction is required. Recent experimental work appears to support this conclusion.

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References and Notes

- (1) Förster, Th. *Ann. Phys.* [Series 6] **1948**, 2, 55.
- (2) Förster, Th. In *Modern Quantum Chemistry: Istanbul Lectures. Part III, Action of Light and Organic Crystals*; Sinanoglu, O., Ed.; Academic Press: New York, 1965; Part II. B.1, pp 93–137.
- (3) Knox, R. S. In *Bioenergetics of Photosynthesis*; Govindjee, Ed.; Academic Press: New York, 1975; Chapter 4, pp 183–221.
- (4) *Biological Physics*; Mielczarek, E., Knox, R. S., Greenbaum, E., Eds.; American Institute of Physics: New York, 1993; pp 148–160 (translation of ref 1 into English).
- (5) Stryer, L.; Haugland, R. P. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, 58, 719.
- (6) Moog, R. S.; Kuki, A.; Fayer, M. D.; Boxer, S. G. *Biochemistry* **1984**, 23, 1564.
- (7) For example, Eads, D. D.; Castner, E. W., Jr.; Alberte, R. S.; Mets, L.; Fleming, G. R. *J. Phys. Chem.* **1989**, 93, 8271; Debreczeny, M. P.; Sauer, K.; Zhou, J.; Bryant, D. A. *J. Phys. Chem.* **1995**, 99, 8412 and 8420.
- (8) Kleima, F. J.; Hofmann, E.; Gobets, B.; van Stokkum, I. H. M.; van Grondelle, R.; Diederichs, K.; van Amerongen, H. *Biophys. J.* **2000**, 78, 344.
- (9) Damjanovic, A.; Kosztin, I.; Schulten, K. *Phys. Rev. E*, submitted.
- (10) Laible, P. D.; Knox, R. S.; Owens, T. G. *J. Phys. Chem. B* **1998**, 102, 1641.
- (11) Dexter, D. L. *Phys. Rev.* **1956**, 101, 48.
- (12) Knoester J.; Mukamel, S. *Phys. Rev. A* **1989**, 40, 7065.
- (13) Agranovich, V. M.; Galanin, M. D. *Electronic excitation transfer in condensed matter*; transl. by Glebov, O.; North-Holland: Amsterdam, 1982; pp 6–13.
- (14) van Amerongen, H.; Valkunas, L.; van Grondelle, R. *Photosynthetic Excitons*; World Scientific: Singapore, 2000; pp 58–60.
- (15) Alden, R. G.; Johnson, E.; Nagarajan, V.; Parson, W. W.; Law, C. J.; Cogdell, R. J. *J. Phys. Chem.* **1997**, 101, 4667.
- (16) Knox, R. S. In PS2001 Proceedings: 12th Intl. Congr. on Photosynthesis. CSIRO Publishing: Melbourne, paper S2-008. Available at <http://www.publish.csiro.au/ps2001> (posted December 2001, verified April 17, 2002).
- (17) Brillouin, L. Propagation des ondes électromagnétiques dans les milieux matériels. Comptes Rendus du Congrès International d'Electricite, Paris, 1932: Comptes Rendus de la Première Section, v. 2, pp 739–788. See a discussion in Knox, R. S. *Theory of Excitons*; Academic Press: New York, 1963; pp 105–106.
- (18) Fowler, W. B.; Dexter, D. L. *Phys. Rev.* **1962**, 128, 2154, especially section IIIA.
- (19) Dexter, D. L. *J. Chem. Phys.* **1953**, 21, 836.
- (20) Dow, J. D. *Phys. Rev.* **1968**, 74, 962.
- (21) Sauer K.; Scheer, H. *Biochim. Biophys. Acta* **1988**, 936, 157.
- (22) Scholes, G. D.; Fleming, G. R. *J. Phys. Chem. B* **2000**, 104, 1854.
- (23) Trinkunas, G.; Connelly, J. P.; Müller, M. G.; Valkunas, L.; Holzwarth, A. R. *J. Phys. Chem. B* **1997**, 101, 7313; Gradinaru, C.; Ozdemir, S.; Gülen, D.; van Stokkum, I. H. M.; van Grondelle, R.; van Amerongen, H. *Biophys. J.* **1998**, 75, 3064; Gradinaru, C.; Pascal, A.; van Mourik, F.; Robert, B.; Horton, P.; van Grondelle, R.; van Amerongen, H. *Biochemistry* **1998**, 37, 1143.
- (24) Andersson, P.-O.; Gillbro, T.; Ferguson, L.; Cogdell, R. J. *Photochem. Photobiol.* **1991**, 54, 353.
- (25) Monshouwer, R.; Abrahamsson, M.; van Mourik, F.; van Grondelle, R. *J. Phys. Chem. B* **1997**, 101, 7241.
- (26) Koolhaas, M. H. C.; van Mourik, F.; van der Zwaan, G.; and van Grondelle, R. *J. Lumin.* **1994**, 60/61, 515.
- (27) Connolly, J. S.; Janzen, A. F.; Samuel, E. B. *Photochem. Photobiol.* **1982**, 36, 559; Connolly, J. S.; Samuel, E. B.; Janzen, A. F. *Photochem. Photobiol.* **1982**, 36, 565.
- (28) Shipman, L. *Photochem. Photobiol.* **1977**, 26, 287; Shipman, L.; Housman, D. L. *Photochem. Photobiol.* **1979**, 29, 1163.