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Abstract. After 65 years of increasing scrutiny and application, Theodor Förster's treatment of resonance excitation transfer is widely quoted and has acquired the acronym FRET, in which "F" originally and rather curiously stood for "fluorescence." In this brief and mostly qualitative survey, we review some of its history, mention its important limitations, and relate some personal encounters with Förster. [DOI: 10.1117/1.JBO.17.1.011003]

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1 Introduction

This article originated with an invitation to present an address of the same title to FRET-65, a symposium held at the W. M. Keck Center for Cellular Imaging at the University of Virginia in March 2011. As the symposium was intended to honor Förster and concentrated on current biomedical applications of his theory, I felt free to present an overview of the theory's development and its relation to other work, along with some personal remarks.

Section 2 reviews some of the electronic excitation transfer work preceding Förster's. Section 3 describes the theory's general nature and points out some of its lesser known features. Section 4 briefly discusses developments "beyond Förster" necessitated by increased observational capabilities of modern optics. Section 5 contains a summary and some personal observations.

2 Excitation Transfer, 1930 to 1945

An early indicator of electronic excitation transfer was the concentration quenching of fluorescence polarization. Immediately after excitation by either polarized or unpolarized light, an ensemble of molecules will emit, on average, as a nonisotropic distribution of radiating transition dipoles. A loss of overall polarization in the resulting fluorescence occurs because of excitation transfer to initially unexcited neighbors, whose transition moments are not correlated to those of the donors. When using a viscous solvent, which inhibits actual molecular rotation, the polarization loss can be safely attributed to excitation transfer. At higher concentrations, dimerization occurs, and the intensity itself is quenched. A widely quoted observation of this phenomenon is that of Feofilov and Sveshnikov.[1] As sketched in Fig. 1, a characteristic distance R_0 for transfer can be identified by noting the concentration at which the polarization dropped to 50% of its value at low concentration.

In the early 1930s, the new quantum mechanics was being applied to understand optical properties of solids. Excited states of crystals containing N molecules were described by *excitons*, which were N linear combinations of states of local excitation.[2–4] For just a pair of molecules, a "mini-exciton" theory with $N = 2$ can be written as follows (A and B are of the same species):

$$\psi_+ = \sqrt{\frac{1}{2}}(\psi_A + \psi_B) \tag{1}$$

$$\psi_- = \sqrt{\frac{1}{2}}(\psi_A - \psi_B). \tag{2}$$

By putting the system into states in which these two excitons are equally mixed, one can excite molecule A or molecule B alone. Elementary quantum mechanics tells us that in the presence of an interaction, the excitation moves back and forth between A and B. This is known as "pendulation" and was the basis of an early attempt by Perrin[5] to explain molecular fluorescence depolarization. That attempt failed to explain observed values of R_0, as discussed below.

Interestingly, in the late 1930s, two well-known American physicists, Teller and Oppenheimer, became involved in the interpretation of primary processes in photosynthesis, in quite different ways. It had been found (see, for example, the review by Duysens[6]) that upward of 300 chlorophyll molecules were associated with each photochemical reaction center, raising the question of whether excitation was being transferred within a "photosynthetic unit" over a network of chlorophylls to the center. Teller, working with Franck,[7] made a highly debated attempt to apply exciton theory to the problem, but, as chronicled by Robinson,[8] failed because a linear topological model and an inadvertently too-small assumed transfer rate were used. The excitons would decay before reaching the center, so Franck and Teller concluded that the unit and the participation of excitons could not exist. Work by Bay and Pearlstein[9,10] and by Duysens,[6] relying on Förster's theory that we shall

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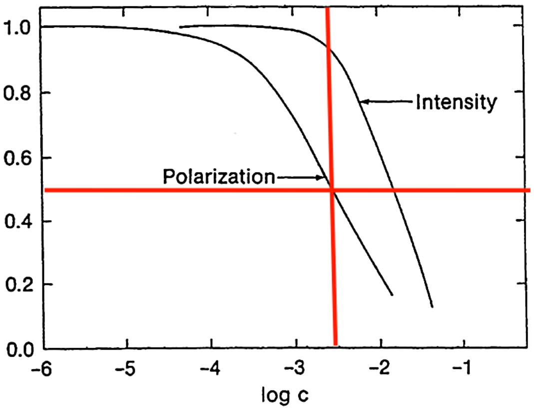

Fig. 1 Concentration quenching of fluorescence anisotropy and yield in fluorescein. Crosshairs indicate the point of 50% reduction of anisotropy and the corresponding concentration $1/(4\pi R_0^3/3)$, which gives R_0 indirectly. (Adapted from Feofilov and Sveshnikov.[1]) (Color online only.)

discuss below, reversed this conclusion. Nowadays, "excitons in photosynthesis" is virtually an industry.[11]

Oppenheimer tackled a completely different excitation transfer problem through his consultation with William Arnold, one of the pioneers of photosynthesis. Oppenheimer questioned how excitation moved from phycocyanin to Chlorophyll, came up with a version of Förster's mechanism that predicted the equivalent of "R^{-6} transfer." The connection has to be carefully gleaned[12] from the Arnold–Oppenheimer papers.[13,14]

In 1947, Förster himself considered the photosynthesis problem,[15] but results of more intensive experimental work of the 1950s were not yet at hand. We turn now to an overview of Förster's theory of excitation transfer.

3 Aspects of Förster's Work on Transfer

Förster's[16,17] first premise, obvious but important, is that the initial excitation is localized. Localized initial excitation is not a problem for heterotransfer, but it can be a problem for homotransfer. For example, it is impossible to localize excitation on one member of an identical pair if the absorption transition moments of the two are parallel. Fortunately, that is not a problem in a random solution, which renders the method exemplified by Fig. 1 successful.

Next, Förster applied stochastic mechanics to the problem, which is where his method differed from Perrin's treatment, in which transfer was essentially characterized as the first half of the pendulation mentioned above.

Finally, as we know, Förster applied his results to the dipole–dipole case, that is, transfer between molecules in which both donor and acceptor transitions are dipole-allowed, arriving at his famous R^{-6} formula. Thus, there are three levels of discourse to consider when analyzing the theory: 1. a Förster *process*, which is the transfer or delocalization of an initially localized excited state, 2. Förster *theory*, which is his selection of a definition of rate of transfer and a method to calculate it, and finally, 3. Förster's *equation* itself, a result of his applying his theory to the dipole–dipole case. In current research, particularly in photosynthesis, the premises for each of these levels are challenged, and the methods are generalized.

Förster's 1948 paper has several noteworthy features. Its principal result was extremely user-friendly, as involvement of transition dipoles on donor and acceptor made it expressible in terms of measured optical spectra. The result was scalable—that is, the transition dipole case was readily generalized to higher multipoles and exchange, as in Dexter's[18] formulation. In this paper, Förster derived the exciton diffusion equation because, although his theory was based on the interaction of a donor and a single acceptor, the case of high concentration required treating competing transfers and eventual motion of excitation over many molecules. Finally, although Förster and others began using the theory for heterotransfer, an application for which it is even more appropriate, that case is never mentioned in the paper.

The basis of, and common form of, Förster's familiar equation for a resonance excitation transfer rate is given by

$$k = \frac{2\pi}{h} \sum_{f,i} |H'_{fi}|^2 \rho(E_f) = \left(\frac{1}{\tau_f}\right)\left(\frac{R_0^6}{R^6}\right), \tag{3}$$

where H'_{fi} is the electronic coupling matrix element between states $|f\rangle$ and $|I\rangle$, the sum stands for a sum over final and average over initial states, ρ is a density of final states, τ_f is the donor excited state lifetime, R_0 is the Förster parameter, and R is the distance between donor and acceptor. (This is meant to be schematic; full details are found in the original paper[17] and reviews.[19,20]) Spectral functions are made explicit in this form of the result:

$$k = \left(\frac{\text{const}}{R^6}\right)\left(\frac{1}{n^4}\right) \int \left[\frac{f_D(\nu)}{n\nu^3}\right]\left[\frac{n\varepsilon_A(\nu)}{\nu}\right] d\nu, \tag{4}$$

where f_D and ε_A are emission and absorption spectra of donor and acceptor, respectively, ν is frequency, n is the index of refraction of the medium in which the spectra were measured, and the constant accounts for a geometrical factor κ^2 and absorbs the donor lifetime. The choice of an index value is not completely straightforward[21] but the value is not usually critical in Förster resonance excitation transfer (FRET). Factors shown separated in the integrand are proportional to the dipole strengths of the emission and absorption transitions, brought out in the following alternative form of the equation:

$$k = \left(\frac{\kappa^2}{R^6}\right)\left(\frac{1}{n^4}\right) \text{const}' \int \mu_D(\nu)^2 \mu_A(\nu)^2 \mathrm{d}\nu. \tag{5}$$

A form used fairly widely in photosynthesis, where the constant and integral in Eq. (5) are combined, is

$$k = \left(\frac{\kappa^2}{R^6}\right)\left(\frac{1}{n^4}\right) \cdot C_{DA} \; (C_{DA} \text{ in nm}^6\,\text{ps}^{-1}). \tag{6}$$

This form enables a clear separation between the spectral properties (in C_{DA}) and the others, which relate to geometry and environment. When R is expressed in nanometers and k in inverse picoseconds, C_{DA} is expressed in $\text{nm}^6\,\text{ps}^{-1}$ with simple numerical values in a range of 10 to 100. C_{DA} is not to be confused with a critical acceptor concentration, sometimes labeled C.

When k is characterized by a parameter R_0 as in Eq. (3), wide disparities in the rate's magnitude can be hidden because of the sixth power. C_{DA} does a much better job of exposing the range of uncertainty in the transfer rate magnitude. For example, in a 1975 compilation (Ref. 22, Table 1), the empirically deduced value of R_0 for chlorophyll-a ranged from 4.4 to 9.6 nm, a factor of two, while the corresponding C_{DA} ranged over two orders of magnitude, from 7 to 700 $\text{nm}^6\,\text{ps}^{-1}$! A survey of more recent literature[23] fortunately produced a much narrower range, and C_{DA} for chlorophyll-a is known to be about 68 ± 4 $\text{nm}^6\,\text{ps}^{-1}$

The Förster rate's strong R-dependence has of course powered its value as a "spectroscopic ruler," a term coined in 1967 by Stryer and Haugland.[24] Because of the importance of R-dependence to FRET, I expand somewhat on it below (Sec. 4.2.).

FRET theory was not without serious criticism of its methodology. Davydov, well known for his treatment of excitation in organic molecular crystals,[25] thought that Förster's application of time-dependent perturbation theory was incorrect for practical purposes and proposed a new version of Perrin's treatment.[26] This was immediately challenged[27] and the FRET theory's validity has stood the test of time.

4 Beyond Förster

4.1 *Strong and Weak Coupling Problem*

Perrin's formulation of the transfer problem was an important stepping stone to Förster's. Clegg[28] has given a detailed description of the relationship between the two formulations. Perrin's pendulation rate, being proportional to the first power of the interaction H'_{fi}, depended on R^{-3} instead of R^{-6}. This rate persisted as a viable alternative for interpreting primary energy transfer in photosynthesis, thanks partly to Förster himself, who showed the curve reproduced in Fig. 2 at a 1960 conference in Puerto Rico,[29] and later wrote about it in his Sinanoglu review.[19] In it, "a" indicates a strong coupling region (R^{-3}, Perrin, coupling larger than spectral width) and "c" a very weak coupling region (R^{-6}, original Förster, coupling smaller than spectral width). He introduced an intermediate "weak" case "b" (R^{-3}, coupling larger than individual vibronic bandwidths but smaller than the entire bandwidth). The short dashed lines connecting the three segments were to indicate a gap in the theoretical explanation of the diagram. Hours of discussion in conferences and many papers were devoted to debate as to which rate was correct for the photosynthesis problem. In 1972, I was fortunate to discuss this with a colleague, V. M. Kenkre, who was familiar with a similar problem in another context and who solved it very quickly.[30] His answer was, "Do not compare apples with oranges." In region "c," the rate is the one usually defined for rate processes, namely, slope of the probability of transfer as a function of time. However, in regions "a" and "b," it is taken to be the inverse of half of an oscillation period. Kenkre introduced a common definition and produced a continuous curve connecting the two extreme cases (Fig. 3). In his treatment, the intermediate-region behavior is analogous to a slightly under-

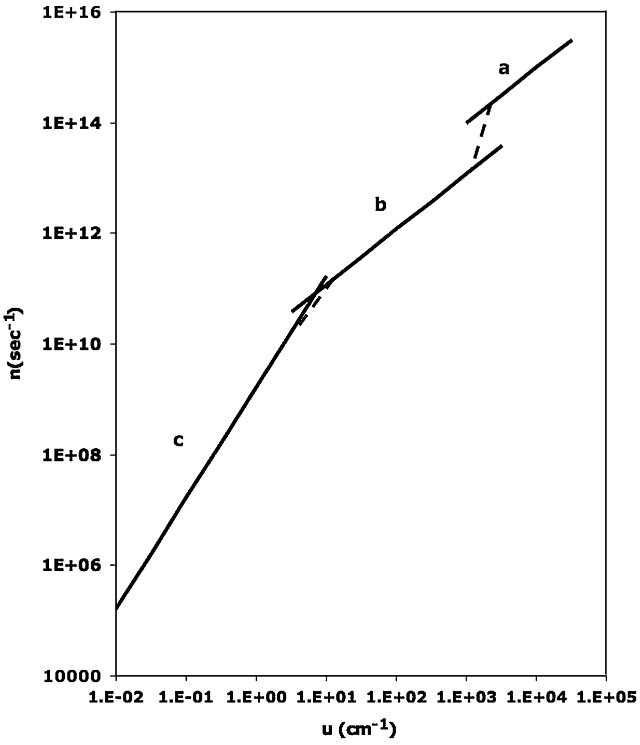

Fig. 2 An attempt by Förster to reconcile "strong coupling" Perrin case (a) with his "very weak coupling" theory (c) by introducing an intermediate case (b), "weak coupling." Vertical axis: transfer rate k (called here n) in s^{-1}. Horizontal axis: magnitude of coupling matrix element H'_{fi} (called here u) in cm^{-1}. (Adapted from Förster[29], Fig. 1.)

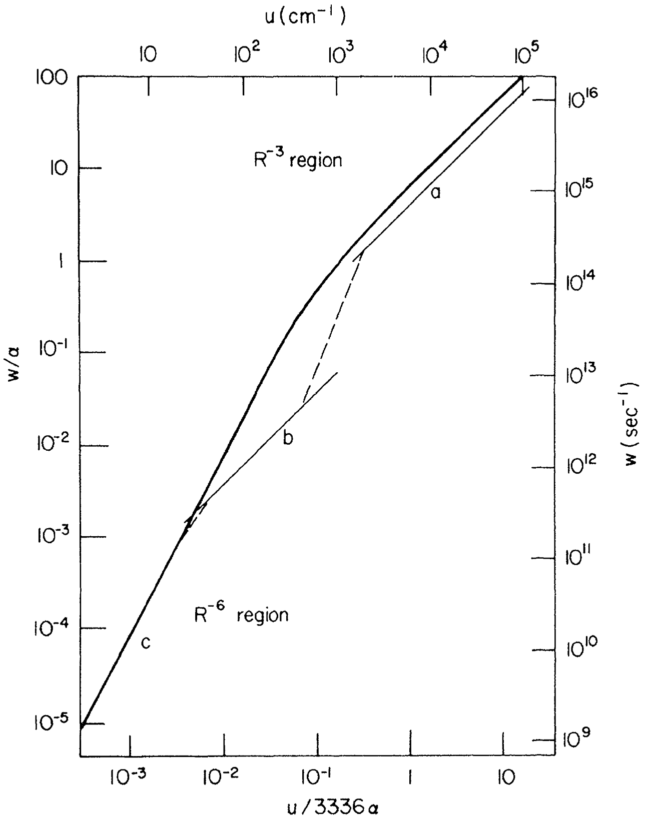

Fig. 3 Kenkre's unification of the weak and strong coupling theories (Ref. 30, Fig. 1). Here, the rate k is called w and the parameter α represents the decay rate of a memory function closely related to the vibrational broadening of the electronic transitions. For the upper and right scales a particular value, $\alpha = 1.8 \times 10^{14}\ \text{s}^{-1}$ was chosen to correspond to Förster's value of 3000 cm^{-1} for the broadening.

damped oscillator where, in modern terms, one sees "quantum beats." A more complete description of this connection is found in Ref. 12. On a personal note, Kenkre and I were able to tell Förster about this result in Rochester, less than a year before his untimely death in 1974.

4.2 *R-Dependence of the Transfer Rate*

Förster theory was developed for more general molecular transitions by Dexter,[18] whose electron exchange term has been widely invoked in interpreting triplet-to-triplet excitation transfer. An exchange term exists as well in the dipole-allowed case. The complete interaction matrix element and resulting R-dependence of its square will lend an R-dependence to k as follows, schematically:

$$k \quad \left|\frac{A}{R^3} + \dots + Be^{-R/a}\right|^2$$
$$= \frac{A^2}{R^6} + \frac{2AB}{R^3}e^{-R/a} + B^2e^{-2R/a} + \dots . \tag{7}$$

Ellipses represent contributions of higher multipole terms. The A^2 term is Förster's dipole–dipole result, the B^2 term is a Dexter exchange contribution, and the AB term, roughly the geometric mean of the others, is new; I have never seen it discussed. Even its algebraic sign is unknown, *a priori*. At close separations of donor and acceptor, it would seem that exchange effects have an especially troublesome effect on the R-dependence.

There are several other reasons to be concerned when relying on R^{-6}. One is the orientation factor κ^2, which may change as R changes in different donor-acceptor configurations. This factor has quite a range and can even be zero. For transition dipoles parallel and in line, k is six times the rate computed with the average κ^2 of $2/3$. An exhaustive study of the effects of rotational depolarization on the determination of R was presented long ago by Dale et al.[31] Another reason for concern is a possible R-dependence of effective refractive index.[11] Finally, there is the "monopole effect," which is due to a breakdown of the dipole approximation when R is close to the dimensions of the chromophores. While this is technically a higher multipole effect, the nature of molecular orbitals makes possible a convenient view in terms of interactions of point monopoles and transition densities.[32,33]

4.3 *Further Developments*

A fascinating possibility, introduced by Kleima and colleagues,[34] is asymmetric transfer between rotationally frozen, identical, and differently oriented chromophores. One can imagine that donor and acceptor transition dipoles have values of κ^2 differing from one transfer direction to the other. This hypothetical transfer condition can be set up when there is a relaxation in which the emission dipole orientation of each fixed molecule is different from that of its absorption dipole. I regret that this proposition came up after I stopped teaching graduate statistical mechanics because it poses a very interesting problem in principle: Can excitation make a unidirectional transit around a circle of three or more molecules (an example posed by Kleima)? I suspect not, but it needs to be subjected to a complete analysis. Kleima et al. propose that κ^2 may itself be a function of transition energy and thus must be placed under the integral sign [see Eq. (5)]. It is clear that even in "standard" Förster theory, there remains interesting work to be done.

Recently, Förster's equation has been found to greatly underestimate rates of transfer in multiporphyrin arrays involving molecular wirelike connectors. "Through-bond transfer" has been invoked to explain rates faster than those predicted by Förster.[35] This appears to be related, in principle, to the Dexter exchange term and other refinements to the simple donor–acceptor matrix element.

In photosynthesis, excitation transfer processes have been subjected to extensive study by modern ultrafast pulse methods. As a result of discovery of the importance of delocalized and coherent states, both Förster's equation and theory have been superseded. The need for this can be appreciated by referring again to the states of Eqs. (1) and (2). In many modern instances, it is found that one can assume neither a purely localized nor a purely delocalized initial state. One must deal with coherences, which means that in addition to probabilities of excitation $|\psi_A|^2$, $|\psi_+|^2$, etc. In the simplest case[36] one must deal with the entire density matrix

$$\begin{bmatrix} |\psi_A|^2 & \psi_A^*\psi_B \\ \psi_A\psi_B^* & |\psi_B|^2 \end{bmatrix} \text{ or } \begin{bmatrix} |\psi_+|^2 & \psi_+^*\psi_- \\ \psi_+|\psi_-^* & |\psi_-|^2 \end{bmatrix}. \tag{8}$$

Many more parameters must be introduced, few of which are as directly related to experiment as in Förster's original case. Förster's rate itself, originally referring to $A \leftrightarrow B$ transfer, becomes part of the rate of decay of $\psi_+^*\psi_-$ in this extended formalism. The density matrix in modern use for photosynthesis is far larger because all relevant vibronic states must be included to describe ultrafast phenomena. Thus, the theory becomes computationally intensive. One finds generalized Förster theory, standard Redfield theory, modified Redfield theory, combined Förster–Redfield theory, and more. See a comprehensive review by Novoderezhkin and van Grondelle.[37]

5 Personal Remarks and Summary

David Dexter had a summer retreat in the southern tier of New York. Förster and his wife Martha visited Rochester in 1973 and attended a picnic there. I believe this was the only personal contact between the two scientists (Fig. 4). At that picnic, I persuaded Förster to try the game of Frisbee, probably for the first time (Fig. 5). I have since then come to think of this as Förster's encounter with mechanical energy transfer.

Less than one year later, it was a shock to receive this message from a former student:

> "Prof. Foerster died on May 20. While returning from a mineral bath he had a heart attack. His car went into the left lane where it was hit by a truck. Apparently he was dead before the truck hit his car."—telegram, Pat Martin, Stuttgart, June 1974.

A few months later, a communication arrived from Martha. "[Thank you for] your translation of Theo's theory. He did this work under the worst conditions: no job, no real housing, no food and no heating! I wonder, how could he do it!?!" And

Fig. 4 D. L. Dexter (left) and Th. Förster in Springwater, New York, August 1973. (Color online only.)

Fig. 5 The author with Förster, in Springwater, where Förster was indulging in a game of Frisbee. (Color online only.)

as to the future, "He just had planned a book on photochemistry and he had so many ideas and he was full of energy and was so happy and felt so well!"—letter, Martha Förster, Stuttgart, November 1974.

We owe Förster much for contributing to our knowledge of the initial steps of photosynthesis, the very top of the food chain, and, now, to making possible a technique to measure many important details of biomolecular structure where x-ray crystallization is not feasible. Where others had developed small parts of the theoretical picture, Förster's exceptionally thorough and focused approach guaranteed a clear, useful, and generalizable formalism. Its content was much more than a formula regarding the dependence of transfer rate on intermolecular distance. One aspect of this richness that we have touched on here cautions that FRET practitioners must always keep in mind limitations on a pure R^{-6} rate dependence.

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