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The Scientific Work of Theodor Förster: A Brief Sketch of his Life and Personality**

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We briefly sketch the academic career and present, in more detail, the most important scientific achievements of Theodor Förster, following a commemorative address presented at the opening of an International Bunsen Discussion Meeting, organized in honor of Theodor Förster by the Deutsche Bunsengesellschaft für Physikalische Chemie, the Section Photochemistry of the GDCh, and the Universität Stuttgart in anticipation of his 100th birthday (Figures 1, 2).



Figure 1. Theodor Förster (1955).

Theodor Förster was born on May 15th, 1910, in Frankfurt am Main. He finished his secondary schooling at the Klinger-Gymnasium in Frankfurt with the abitur in 1929, and then studied



Figure 2. Theodor Förster (1960, characteristically with bow-tie and pipe).

physics and mathematics at the University of his home town. After only four years, at the age of twenty-four, he received his Ph.D. with a dissertation "Zur Polarisation von Elektronen durch Reflexion" under the supervision of Erwin Madelung. Karl-Friedrich Bonhoeffer^[1] offered the young scientist an assistant position, and took Theodor Förster with him when he was offered a chair at the University of Leipzig in 1934. The close contact with other renowned scientists, such as Peter Debye, Werner Heisenberg and Hans Kautzky, during his time as research assistant in Bonhoeffer's laboratory was instrumental in forming Förster's scientific personality. His ability, for instance, to apply theoretical concepts directly to practical problems was probably acquired from Debye.

Theodor Förster's prime scientific concern at that time was introducing the newly formulated principles of quantum mechanics into chemistry. He started theoretical studies on the valence states of carbon atoms in organic structures and on the process of light absorption by organic molecules, that is, the correlation between colour and structure. For this, Förster employed a linear combination of valence functions which can directly be assigned to the relevant valence-dash (Lewis) formulae. His most enviable gift certainly was the ability to marry the rigidity of a physical principle with the visual conception of organic chemists.

His work had a decisive influence on this branch of physical chemistry and earned him, at the age of only 32, an appointment as Full Professor at the University of Posen. During his time in Posen, he developed the revolutionary concept to interpret photochemical reactions in terms of physical principles. He thus taught chemists to formulate photochemical mechanisms in a rigid and systematic manner, and to design new photochemical processes along these lines.

After the war and the flight from the now Polish Posen, he and his family found a new home in Göttingen, where his

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former academic teacher Bonhoeffer in the meantime headed the Max-Planck-Institut für Physikalische Chemie. Theodor Förster worked there as a section head from 1948–1951 when he was appointed Ordinarius, that is, Full Professor of Physical Chemistry at the Technische Hochschule Stuttgart.

During his time at the Max-Planck-Institut in Göttingen, Förster published a series of papers^[2–4] on the *nontrivial* energy transfer from an electronically excited sensitizer molecule S^* to an acceptor molecule A [Eq. (1)]:



This process (Figure 3) does not involve the emission of a photon by S^* and re-absorption of this light quantum by the acceptor A , which would constitute a trivial energy transfer.

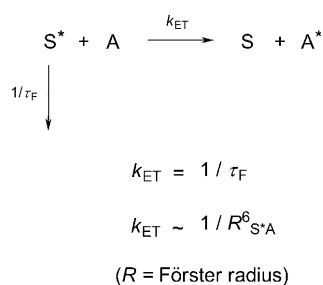


Figure 3. Förster resonance energy transfer (FRET).

Rather, the energy is transmitted by coupling of the two respective oscillating dipoles. Förster therefore called this process *energy transfer by dipole–dipole coupling*, and pointed out the close analogy to mechanically coupled pendula.

In this context, the terminology involved must be briefly addressed. The phenomenon has from the beginning been referred to as Förster Energy Transfer. Recently, though, the term FRET, as acronym for Fluorescence Resonance Energy Transfer, has been employed more and more frequently. Clemens Kaminski who organized the first of the International Theodor Förster Lecture Series (*Quantitative Fluorescence Microscopy*, Cambridge University, 2008) has straightened out this discrepancy in his contribution to the proceedings of this congress.^[5a] He interprets the acronym FRET as *Förster Resonance Energy Transfer*, and points out that the alternative term *Fluorescence Resonance Energy Transfer* is misleading since a proper FRET does by definition not involve emission of a photon from the donor.^[5b] We shall strictly adhere to Kaminski's proposal in the following since it correctly represents the factual state of affairs.

The FRET process is of great importance in biological systems, for instance in photosynthesis. Antennae pigments collect the light and conduct it, by means of Förster energy transfer, to that chlorophyll molecule to which the chemical synthesis apparatus is attached. In the case of chlorophyll, this energy transfer may gap distances of up to 9 nm (90 Å). The Förster radius R_F is defined as that distance between S^* and A at which the rates for the energy transfer and for the deactivation

of S^* are equal. The transfer rate in turn depends on the overlap integral between the emission spectrum of the photosensitizer and the absorption spectrum of the acceptor molecule. It is inversely proportional to the sixth power of the distance between S^* and A [Eq. (2)].^[6]

$$\text{Transfer rate} \sim [1 + (R_{S^*A}/R_F)^6]^{-1} \quad (2)$$

By applying the pair probability method to the Förster Resonance Energy Transfer, the additional effect of diffusion could also be accounted for.^[7–9]

In recent years, Effenberger and his group, as organic chemists, have synthesized specifically tailored compounds and, in collaboration with Wolf and Port from the Stuttgart Physics Department, established Förster energy transfer for these systems. Theodor Förster would have been thrilled if he had lived to see these fascinating experiments from his own university, documented for example on the title page of *Angewandte Chemie*.^[10]

Already in Göttingen, but especially after his move to Stuttgart in 1951, Förster opened up the new field of protolytic reactions in the photoexcited state that likewise bears his name, namely the Förster Cycle (Figure 4). For β -naphthol, he could

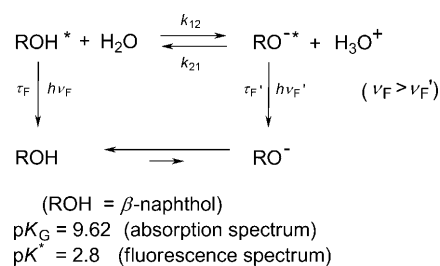


Figure 4. Förster cycle (1950).

demonstrate that, when the undissociated acid is irradiated in the ground state at pH 2–3, the fluorescence of the excited anion is observed. This can only mean that a proton dissociates off the neutral acid molecule upon or after excitation and that the anion, that is, the conjugate base, formed in the excited state, emits the energy absorbed by the neutral. Closer inspection of this process shows the acidity of the neutral to indeed increase by seven pK units upon excitation. Förster explained this in terms of a higher contribution of the polar valence structure in the excited state (Figure 5). Interestingly, amino compounds such as β -naphthylamine also become more acidic upon excitation, heterocyclic structures with an aza nitrogen such as isoquinoline, on the other hand, more basic. Grabowska and her group have verified this for a wide range of aza heterocycles.^[11,12] Grabowski and Rubaszewska have extended the original concept to the Generalized Förster Cycle which combines thermodynamic and non-thermodynamic interrelations between proton transfer, electron transfer, and electronic excitation.^[13]

At the time when the Förster Cycle was discovered, protolytic reactions were still considered as unmeasurably fast. The

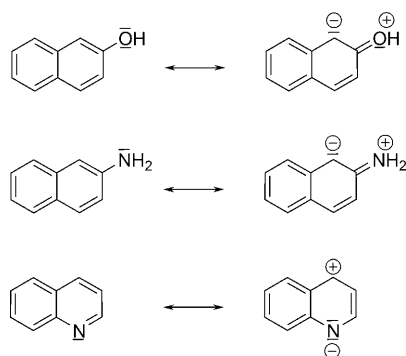


Figure 5. Charge distribution in hydroxy/amino arenes vs aromatic aza compounds.

new system possesses a built-in time scale, in form of the deactivation rate of the undissociated acid in the excited state, $1/\tau_F$. This inner clock could now be used to measure the rate of the competing deprotonation reaction k_{12} (Figure 4). The deactivation rate constant $1/\tau_F$ in turn is directly accessible by measuring fluorescence decay times or can, alternatively, be calculated from the longest wavelength absorption band and the fluorescence yield, according to a method developed by Förster as well. He was thus able to determine true rate constants for both the deprotonation in the excited state and the reverse reaction—four years before Manfred Eigen presented a general methodology for monitoring very fast processes, especially protolytic reactions in the ground state.

1954, now already from the Stuttgart Institute, Förster and Kasper reported on the association of excited pyrene molecules and their fluorescence.^[14–17] The associates between ground and excited state arene were termed excited dimers or, more concisely, excimers. For highly dilute pyrene solutions, only the structured fluorescence spectrum of monomeric pyrene is observed, as expected (Figure 6). With increasing pyrene concentration, though, a new unstructured band appears at longer wavelengths. At the same time, the intensity of the monomer fluorescence band decreases. The appearance of an isostilbic point^[16] constitutes definite proof of an equilibri-

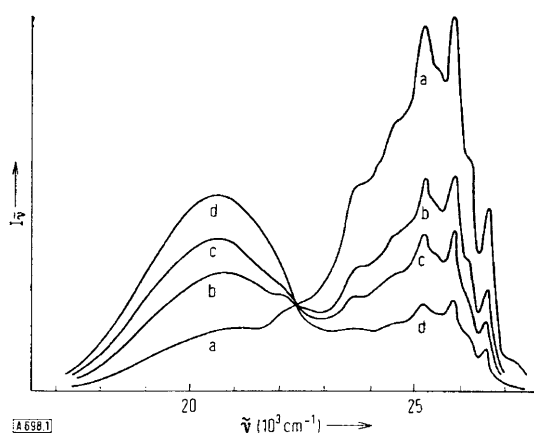


Figure 6. Fluorescence spectrum of pyrene (in *n*-heptane, 20 °C) at different concentrations: a) 5.0×10^{-5} , b) 1.8×10^{-4} , c) 3.1×10^{-4} , d) 7.0×10^{-4} mol L⁻¹ (Reprinted from ref. [16] with permission of Wiley-VCH)

um between two forms in the excited state. For the ground state, this phenomenon is well-established in form of isostilbic points in the absorption spectrum. The absorption spectrum of pyrene, other than the fluorescence spectrum, does not change with higher concentration. Association thence must be limited to the excited state, and the unstructured long-wavelength, that is, lower-energy emission band must originate from the pyrene excimer (Figures 6, 7).^[14–17]

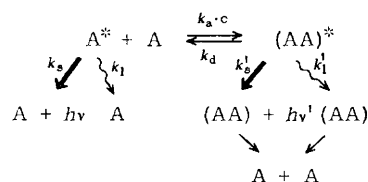


Figure 7. Reaction map for excimer formation and deactivation: → regular (straightforward) reactions (*adiabatic* processes) without change in state of excitation, → radiative processes, ⇌ radiationless (*diabatic*) deactivation processes (Reprinted from ref. [16] with permission of Wiley-VCH)

Both protolytic dissociation reactions in the excited state and excimer formation constitute important cases of so-called adiabatic photochemical reactions where the product is formed in an electronically excited state. From most photochemical reactions, in contrast, the product comes out in the electronic ground state; they are therefore characterized as diabatic—from the Greek διαβαίνω—for transgressing the energy hyperspace from a higher to a lower level, with the opposite (*adiabatic*) meaning staying on the higher level. The photodissociation of di(9-methylanthracene) represents a further example for such an adiabatic process. Both the monomer 9-methylanthracene in its excited state and the corresponding excimer are formed in the course of this reaction, and the product fluorescence spectrum accordingly shows the fluorescence of both species overlaying. This reaction was studied by Julian M. Menter (now at the Morehouse School of Medicine, Atlanta, GA) when he was a post-doc with Förster in the early 1970s.^[18]

In the last years of his life, Theodor Förster was very much concerned with the interrelation and correlation between adiabatic and diabatic photoreactions, and developed a theoretical approach to radiationless deactivation, which can be considered a diabatic process.

Many interesting compounds have become readily available only through photochemical reactions. On the other hand, it often is equally important to *prevent* photochemical processes, such as the photodegradation of polymers, the bleaching of dyestuffs, or formation of skin cancer or light dermatoses by excessive exposure to the sun. Rapid radiationless deactivation presents one solution to reduce the yield of such noxious photoreactions.

No laudation of Theodor Förster's scientific work would be complete without a reference to his book *Die Fluoreszenz organischer Verbindungen* (Vandenhoeck & Ruprecht, Göttingen, 1951) which, though receiving world-wide attention, never was translated into English. In the Stuttgart Institute, it was consid-

ered Scripture; we all called it the *Hausbibel*. There is a touching little story in this context. In 1970, Professor Masao Koizumi, who has more or less single-handedly established photochemistry in Japan, visited Stuttgart. All renowned Japanese photochemists such as Professor Noboru Mataga are his pupils. Professor Förster, who at that time was just recovering from his first heart attack, dragged himself to the lecture of Professor Koizumi out of respect for an esteemed colleague. Professor Koizumi was enchanted to meet his famous colleague, and assured him that *Die Fluoreszenz organischer Verbindungen* always was in front of him on his desk when he was writing a paper or working on his own book. Professor Förster was astonished: "But the book is written in German." Professor Koizumi simply replied: "This I can read."

Albert Weller, in his obituary for Theodor Förster,^[20] stresses his academic teacher's "special ability to provide overviews and to write summarizing articles" and continues, with reference to *Die Fluoreszenz organischer Verbindungen*: "... the *Hausbibel*—a very appropriate name because in the first place this book could open new pathways to knowledge and secondly its concise formulations, in which every word was important, required two or more readings or still better the interpretation of an enlightened mediator before one could comprehend its precious contents. For the non-German speaking people it must have remained a book with seven seals; and since it has not been translated into English it has secured, as many American colleagues more or less have asserted, the German lead in fluorescence spectroscopy for years."

Consequently, the Förster institute became a Mecca for photochemists from all over the world. One of Theodor Förster's most outstanding qualities was that he generously shared his ideas with younger colleagues. Many of his original concepts were later developed in a large number of papers which do not carry Förster's name, for example, exciplexes, charge transfer complexes studied by his coworker Albert Weller.^[19]

Even though he was nominated several times for the Nobel Prize, Theodor Förster has never received the highest scientific honor. He bore this with the equanimity of a stoic philosopher—he well knew the exceptional rank and the far-reaching impact of his scientific work. Therefore, all his students will always remember Theodor Förster not only as an outstanding scientist, but even more so as an exceptional academic teacher, a colleague, some even as a friend.

Keywords: excimers • fluorescence • FRET • scientific biography • Theodor Förster

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