



IN MEMORIAM

Theodor Förster, 1910-1974

Theodor Förster was born on May 15, 1910 in Frankfurt, Germany and died of a heart attack on the 20th of May 1974 at the age of 64.

In view of his numerous important and fundamental contributions to photochemistry, it is indeed appropriate to pay honour to the man and his work on the occasion of the seventieth anniversary of this birthday.

He went to school in Frankfurt and after completing his Abitur in 1929, he became a student of physics and mathematics at Frankfurt University.

At that time there was very little red tape at German Universities. It was for instance possible to study physics and/or mathematics without an examination except for the final oral examination after having finished the Ph.D. thesis. As a consequence the good student, in general, was able to finish the University in surprisingly short time; and so in 1933, at the age of 23, after 4 years of study Theodor Förster was promoted to Dr. phil. with a thesis entitled *Zur Polarisation von Elektronen durch Reflexion* [1] under the tutelage of *E. Madelung*.

Still before having finished his thesis he had become an Assistent (scientific coworker) of Professor *Karl-Friedrich Bonhoeffer*. They were all quite young at that time: the Professor 34, his Assistent 23 and the university (founded in 1974) 19 years old. In 1934 Bonhoeffer accepted an offer from the University of Leipzig to become full professor of Physical Chemistry and director of the famous Institute of Physical Chemistry, the first of its kind, which had been founded by *Wilhelm Ostwald*. Leipzig at that time with men such as *Peter Debye*, *Werner Heisenberg*, and *Hans Kautsky* had one of the most outstanding Physics and Chemistry Departments of Germany.

Förster went with Bonhoeffer, so to speak as his house-theoretician, and between the age of 25 and 30 he published those theoretical studies about valences on the carbon atom [5,7,10] and the light absorption of organic compounds [6,8,11,12,13] which got him

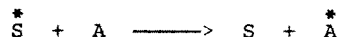
a name and a full professorship at the age of 32.

In his theoretical works he wanted to make the foundations and results of quantum mechanics understandable and useful to the chemist. It was this aim which determined his choice of using the valence bond method in which valence functions are correlated with valence structures.

There are no publications from the three years 1942 - 1945 when Förster was professor at Posen University. However, he was married during that time. But, although (or because) this marriage was a very happy one from the beginning and for more than thirty years, there is no reason for us to believe that this event could have diverted him from science. No, it must have been the demands of his new professorship which together with the hardships of the war prevented him from working in the laboratory. Actually it was during that seemingly unproductive time that he got the idea of writing a book on absorption and fluorescence of organic compounds. He evidently had already collected a wealth of knowledge on this subject when the war was over and he became Abteilungsleiter (head of a department) at the Max-Planck-Institut für Physikalische Chemie at Göttingen.

The town of Göttingen with its well-known university located in the British occupied zone had survived the war intact and attracted a great number of scientists especially from the many destroyed cities and the more eastern parts of Germany. Among them were Max Planck (who died in 1947), Otto Hahn, Max von Laue, Werner Heisenberg and many others. It is, therefore, not surprising that in 1948, as soon as the Max-Planck-Gesellschaft was established as successor of the former Kaiser-Wilhelm-Gesellschaft, two new Max-Planck-Institutes were founded in Göttingen, one for physics under Werner Heisenberg and one for physical chemistry under Karl-Friedrich Bonhoeffer.

Besides some theoretical spectroscopic work [15,18], e.g. about the absorption spectra of substituted benzenes (where Förster introduced the idea of the *spectroscopic moments*), he published his theoretical and experimental studies on *energy transfer*. In these papers [14,17,21,24] he describes and evaluates the kinetics and mechanism of the reaction:



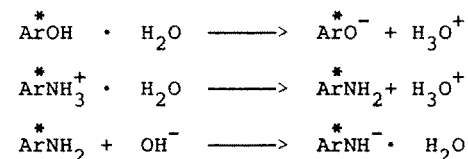
where the electronic excitation energy is transferred from the sensitizer S to the acceptor A over distances of up to 100 Å. Already in the very first paper on this subject [14], published in 1946, Förster points out the importance of energy transfer in biological systems such as in photosynthesis or in the cellular nucleic acid material [16]. And, indeed, the Förster-mechanism of energy transfer has become an important concept in molecular biology. His later works on this subject in which he extends and refines the theory [41,43,44], or as in the Spiers-Memorial Lecture during the Faraday Discussions in 1959 [40], where he brings applications and presents the theory in a digestible form to

chemists and biochemists, culminate in the 1965 publication *Delocalized Excitation and Excitation Transfer* [56] which for anybody who has an understanding of the fundamental ideas is an intellectual enjoyment to read. It is here where he fully develops and evaluates the important differentiation of the strong, weak, and very weak coupling cases on the basis of the following inequalities concerning the coupling energy U

$$\begin{array}{l} U \gg \Delta\epsilon_{el} \gg \Delta\epsilon_{vib} \quad (\text{strong coupling}) \\ \Delta\epsilon_{el} \gg U \gg \Delta\epsilon_{vib} \quad (\text{weak coupling}) \\ \Delta\epsilon_{el} \gg \Delta\epsilon_{vib} \gg U \quad (\text{very weak coupling}) \end{array}$$

where $\Delta\epsilon_{el}$ and $\Delta\epsilon_{vib}$ are the electronic and vibrational band widths, respectively.

Also from these five years after the war stem his first works on the *protolytic reactions* of electronically excited aromatic hydroxy- and aminocompounds [26,27,28]:



The fruitful union of theory and experiment which characterizes all of Förster's work and his ability to see, brilliantly and appropriately, both the shape of the forest and the details of the trees are properly revealed in the first and last sentences of his paper entitled *Elektrolytische Dissoziation angeregter Moleküle* [27]:

The modern valence theory has led us to interpret the acidity and basicity of the aromatic acids and bases as properties of the electronic structure. For that reason we expect that the transition of a molecule into an excited state alters substantially its acidity or basicity"

And in closing he writes:

..... One can infer from these investigations that an excited electronic state of an aromatic molecule is more resistant to certain chemical reactions than it hitherto had appeared. An excited molecule can give off or take on a proton without thereby becoming automatically deactivated. The transfer of a proton evidently can occur so mildly that it does not perturb the electronic systems of the molecules involved. This seems to be the case only in those more energetic events which bring about fluorescence quenching.

Furthermore, the observations at hand allow statements about the time required to reach electrolytic dissociation equilibria. Since the lifetimes of the excited molecules lie between 10^{-8} and 10^{-7} seconds, the elementary reaction of the proton transfer must proceed in still shorter times. By continuation of the quantitative investigations a further improvement of this estimate should be possible.

This was five years before Eigen's measurements of these "unmeasurably" fast reactions.

These papers on proton transfer reactions in the excited state opened up the new field of investigations on reactions of excited molecules which provided the foundation of the Förster school in Stuttgart.

In 1951 Förster accepted a chair offered to him by the University of Stuttgart and an important contribution to the new field came in 1954 when Förster discovered that pyrene shows different fluorescence spectra in concentrated and in dilute solutions [32]. The effect, he showed, was due to dimer formation between excited and ground state molecules:



So originated the concept of *excimers* which already Förster had proposed as intermediates in photochemical dimerization reactions in 1952 [31], two years before their actual discovery. Ten years later the concept was extended to *exciplexes* which are now regarded as essential intermediates in bimolecular photochemical reactions.

Förster described the phenomenon connected with excimer formation as *Konzentrationsumschlag* of the fluorescence. This term which could be translated as *concentration induced transformation* became the misleading phrase "*concentration reversal*" of fluorescence in Chemical Abstracts.

Four years earlier, in analogy to the well-known *Farbumschlag*, the colour change which occurs in indicator dyes when passing through the p_H -scale, Förster coined the term *Fluoreszenzumschlag* in order to describe the fluorescence transformation accompanying protolytic reactions in the excited state. In a literal but wrong translation this became "*fluorescence envelope*" in Chemical Abstracts.

However, in spite of these minor mishaps, Förster's work was definitely more appreciated abroad, both in East and West, than at home. Already in his first work on protolytic reactions in the excited state [27], he suggested an energy-cycle for the calculation of the corresponding dissociation enthalpies which has long since been known in the Anglo-Saxon literature as the *Förster-cycle*. Also the term *excimer* condensed from the words excited dimer will always be connected with his name [62].

During his last five years Förster became interested in a hitherto completely neglected aspect of photochemistry: the differentiation between *diabatic* and *adiabatic* reactions [64,65]. He designed and carried out experiments which made a quantitative distinction possible [66,70,72], and he worked on a theory of diabatic reactions which also included *radiationless transitions* [67,73].

This evaluation of Förster's scientific achievements would be incomplete without mentioning his special ability to provide overviews and to write summarizing articles. Last but not least there is his book entitled *Fluoreszenz organischer Verbindungen* [29] which he wrote in the "golden" Göttingen years and which received worldwide attention. For Förster's disciples in Stuttgart the book for many years was the so-called Home Bible - 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.

There is a great number of papers not appearing on Förster's publication list which were either inspired by him or received his energetic support and guidance. He was a modest man, and his successes in science were primarily due to two of his qualities - his intuition how to undertake new investigations and his feeling for where the heart of a problem lies which he shared generously with his colleagues and coworkers in illuminating small group and blackboard discussions.

His life was exemplified by his serenity and unpretentiousness which allowed him to always put the task before the man. Beyond his scientific achievements we shall always remember the teacher, the colleague, the friend.

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Professor Theodor Förster

List of Publications

- 1) *Zur Polarisierung von Elektronen durch Reflexion*
(Dissertation), Z. Physik 85, (1933) 514.
- 2) *Die theoretische Behandlung chemischer Reaktionen in strömenden Systemen*,
(with K.H. Geib), Ann. Physik [5] 20 (1934) 250.
- 3) *Die Gleichgewichtskonstante der Reaktion $HDO+H_2 \rightleftharpoons H_2O+HD$*
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- 4) *Über die experimentelle Bestimmung der linearen Kristallisationsgeschwindigkeit*,
Z. physikal. Chemie (A) 175 (1935) 177.
- 5) *Valenzwinkelung und Bindungsfestigkeit am Kohlenstoffatom*
a) Naturwiss. 25 (1937) 366;
b) Verh. Dt. Physik. Ges. (3) 18 (1937) 52.
- 6) *Die Ultraviolettabsorptionsspektren deuteriumsubstituierter Methylamine*
(with J.C. Jungers),
a) Z. physikal. Chem. (B) 36 (1937) 387;
b) Physik. Z. 38 (1937) 140;
c) Verh. Dt. Physik. Ges. [3] 18 (1937) 37.
- 7) *Der Einfluß einer Doppelbindung auf die Festigkeit in der Nähe befindlicher Einfachbindungen*
Z. Elektrochem. 43 (1937) 667.
- 8) *Die Lichtabsorption aromatischer Kohlenwasserstoffe*
a) Z. physikal. Chemie (B) 41 (1938) 287;
b) Z. techn. Physik 19 (1938) 611;
c) Physik. Z. 39 (1938) 925;
d) Verh. Dt. Physik. Ges. [3] 19 (1938) 132.
- 9) *Über die Lage der ersten Oberschwingung der Wasserstoffbindung*
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- 10) *Die gegenseitige Beeinflussung der Valenzen im Kohlenstoffatom*
(Habilitationsschrift),
Z. physikal. Chemie (B) 43 (1939) 58.
- 11) *Farbe und Konstitution organischer Verbindungen vom Standpunkt der modernen physikalischen Theorie*
Z. Elektrochem. 45 (1939) 548.
- 12) *Die Lichtabsorption organischer Moleküle und Ionen nach der Quantenmechanik*
Z. Elektrochem. 47 (1941) 52.
- 13) *Quantenmechanische Rechnungen zur Theorie der organischen Farbstoffe*
I, Z. physikal. Chem. (B) 47 (1940) 245;
II, Z. physikal. Chem. (B) 48 (1940) 12.
- 14) *Energiewanderung und Fluoreszenz*
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- 15) *Zur Deutung der Regelmäßigkeiten in den Spektren substituierter Benzole*
Z. Naturforsch. 2a (1947) 149.
- 16) *Ein Beitrag zur Theorie der Photosynthese*
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- 17) *Zwischenmolekulare Energiewanderung und Fluoreszenz*
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- 18) *Elektronensprungsspektren*
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- 19) *Das Fluoreszenzvermögen organischer Farbstoffe*
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- 20) *Assoziation und Fluoreszenz von Farbstoffen*
Angew. Chemie 59 (1947) 27.
- 21) *Versuche zum zwischenmolekularen Übergang von Elektronen-
anregungsenergie*
Z. Elektrochem. 53 (1949) 93.
- 22) *Quantentheorie und chemische Bindung*
Angew. Chem. 61 (1949) 144.
- 23) *Dispersionskräfte*
in Zwischenmolekulare Kräfte (Hrsg. H. Friedrich-Freska,
B. Rajewsky, M. Schön) Braun, Karlsruhe 1949, p. 62.
- 24) *Experimentelle und theoretische Untersuchung des zwischen-
molekularen Übergangs von Elektronenanregungsenergie*
Z. Naturforsch. 4a (1949) 321.
- 25) *Neuere Untersuchungen über die Phosphoreszenz organischer
Stoffe in festen Lösungen*
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- 26) *Fluoreszenzspektrum und Wasserstoffionenkonzentration*
Naturwiss. 36 (1949) 186.
- 27) *Elektrolytische Dissoziation angeregter Moleküle*
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- 28) *Die p_H -Abhängigkeit der Fluoreszenz von Naphthalinderivaten*
Z. Elektrochem. 54 (1950) 531.
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Vandenhoeck & Ruprecht, Göttingen, 1951.
- 30) *Lichtabsorption und Fluoreszenz aromatischer Amine in
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(with E. Bonitz), Z. Elektrochem. 56 (1952) 137.
- 31) *Photochemische Primärprozesse bei mehratomigen Molekülen*
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- 32) *Ein Konzentrationsumschlag der Fluoreszenz des Pyrens*
(with K. Kasper),
a) Z. physikal. Chem. N.F. 1 (1954) 275;
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- 33) *Untersuchungen über Löschung und Polarisationsgrad der
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- 34) *Fluoreszenz und Phosphoreszenz*
in Methoden der Organischen Chemie (Houben-Weyl),
4. Auflage, Stuttgart 1955, Bd. III/2, p. 477.
- 35) *Absorptionsspektroskopischer Nachweis der elektrolytischen
Dissoziation angeregter Molekeln*
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- 36) *Absorptionsspektren und Fluoreszenzeigenschaften konzen-
trierter Lösungen organischer Farbstoffe*
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- 37) *Absorptions- und Fluoreszenzspektren von Aryl-Alkalamiden*
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- 38) *Molecular Electronic Spectroscopy*
Ann. Rev. Phys. Chem. 8 (1957) 331.
- 39) *Regelmäßigkeiten in den Absorptionsspektren von Aryl-Alkali-
amiden und anderen einfach substituierten Aromaten*
(with E. Döllner and H. Renner),
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- 40) *Transfer Mechanisms of Electronic Excitation*
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- 41) *Zwischenmolekularer Übergang von Elektronenanregungsenergie*
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- 42) *Elementary Photoprocesses in Solution*
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- 43) *Transfer Mechanisms of Electronic Excitation Energy*
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- 44) *Excitation Transfer*
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- 45) *Elektronenspektren gekoppelter Moleküle*
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- 47) *Der Konzentrationsumschlag der Fluoreszenz des Pyrens*
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- 48) *Der Konzentrationsumschlag der Fluoreszenz des Naphthalins*
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- 51) *Proposal for Standardization of Methods of Reporting Fluorescence Emission Spectra*
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- 56) *Delocalized Excitation and Excitation Transfer*
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- 57) *Die Druckabhängigkeit des Konzentrationsumschlages der Fluoreszenz*
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- 66) *Die Viskositätsabhängigkeit der Fluoreszenzquantenausbeuten einiger Farbstoffsysteme*
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- 67) *Excitation Transfer and Internal Conversion*
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- 73) *Primary Photophysical Processes*
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