

THEODOR FÖRSTER 1910 - 1974

MEMORIAL FOR THE LATE PROFESSOR THEODOR FÖRSTER

A. WELLER

Max-Planck-Institut für Biophysikalische Chemie Göttingen, Fed. Rep. Germany

On the 20th of May 1974 Theodor Förster died of a heart attack at the age of 64 while he was on his way to the Institute of Physical Chemistry at the University of Stuttgart whose director he had been for 23 years.

In view of his numerous important and fundamental contributions to almost all aspects of luminescence, it is indeed appropriate to pay honour to the man and his work today.

Theodor Förster was born on May 15, 1910, in Frankfurt, Germany. He went to school there (the same school which about 30 years before Otto Hahn had attended), 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 PhD 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 Theodor Förster was promoted to Dr. phil. with a thesis entitled "Zur Polarisation von Elektronen durch Reflexion" under the tutelage of E. Madelung.

Still before having finished his thesis he had become an Assistant (scientific coworker) of Professor Karl-Friedrich Bonhoeffer. (They were all quite young at that time: the Professor 34, his Assistant 23 and the University (founded in 1914) 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 which had been founded by Wilhelm Ostwald.

Leipzig at that time with men such as Peter Debye, Werner Heisenberg, 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 and the light absorption of organic compounds 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.

10 Memorial

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 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, 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 he describes and evaluates the kinetics and mechanism of the reaction:

$$\overset{*}{S} + A \rightarrow S + \overset{*}{A}$$

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, 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. 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, or as in the Spiers-Memorial Lecture during the Faraday Discussion in 1959, where he brings applications and presents the theory in a digestable form to chemists and biochemists, culminate in the 1964 publication "Delocalized Excitation and Excitation Transfer" which for anybody who has an understanding of the fundamental ideas is an intellectual enjoyment to read. It is here where Förster fully develops and evaluates the important differentiation between

- a) strong coupling, where (coupling energy) $U > \Delta E_{el}$ (electronic band width)
- b) weak coupling, where $\Delta E_{el} > U > \Delta E_{vib}$ (vibrational band width)
- c) very weak coupling, where $\Delta E_{vib} > U$.

Also from these five years after the war stem his first works on the protolytic reactions of excited aromatic hydroxy- and aminocompounds:

Memorial 11

$$Ar^{*}OH \cdot H_{2}O \rightarrow Ar^{*}O^{-} + H_{3}O^{+}$$
 $Ar^{*}NH_{3}^{+} \cdot H_{2}O \rightarrow Ar^{*}NH_{2} + H_{3}O^{+}$
 $Ar^{*}NH_{2} + OH^{-} \rightarrow Ar^{*}NH^{-} \cdot H_{2}O$.

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".

"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 recently initiated 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. The effect, he showed, was due to dimer formation between excited and ground state molecules:

$$\stackrel{*}{P} + P \rightarrow (\stackrel{*}{PP})$$
.

So originated the concept of excimers which already Förster had proposed as intermediates in photochemical dimerization reactions in 1952, two years before their

12 Memorial

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 pH-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, 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.

During the last five years Förster became interested in a hitherto completely neglected aspect of photochemistry: the differentiation between diabatic and adiabatic reactions. He designed and carried out experiments which made a quantitative distinction possible, and he worked on a theory of diabatic reactions which also included radiationless transitions.

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" 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 were the heart of a problem lies which he shared generously with his colleagues and coworkers in illuminating small group and blackbord 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.