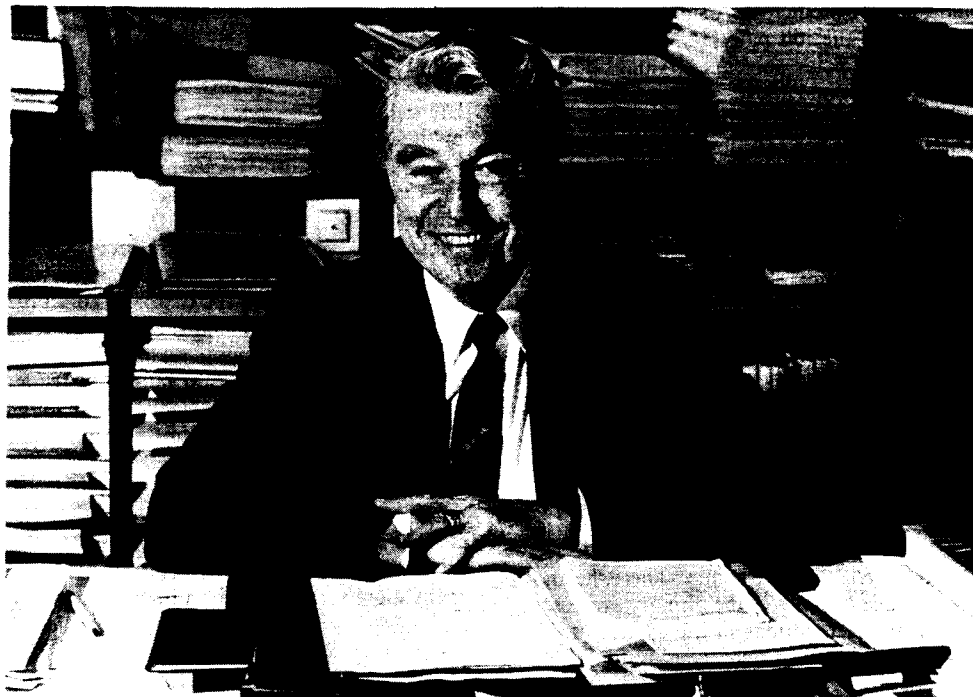


## ALBERT WELLER FESTSCHRIFT

Professor Albert Weller has made many important contributions to chemistry. He has pioneered studies in the field of electron transfer and charge transfer. From the early years of collaboration with Th. Förster in 1950 until now, colleagues in the field have admired his scientific contributions, which are made with style, energy, and enthusiasm.

The contributions in this special issue of *The Journal of Physical Chemistry* by colleagues from around the globe testify to the impact of Weller's research. I am personally delighted to be part of this celebration and to work with Associate Guest Editor Dr. Klaas Zachariasse. To Albert, the colleague and friend, we wish him on this occasion many more years of good health and a continued productive scientific career.—*Ahmed H. Zewail*



Photograph courtesy of Peter Goldmann

Albert Weller was born on April 5, 1922, in Welzheim, Baden-Württemberg, Germany. In 1940 he started his studies in chemistry at the University of Leipzig, where he was exposed to the teachings of K. F. Bonhoeffer, F. Hund, H. Kautsky, and B. van der Waerden. In 1944 he went to the University of Tübingen, where he obtained his Ph.D. degree in 1950 under the electrochemist Gustav Kortüm, with a thesis "On the Solvation of Ions in Water/Ethanol Mixtures". These investigations led to his first two papers, published in 1950. Although Weller does not personally consider himself to be an electrochemist *pur sang*, his strong background in electrochemistry was later to become an important factor in his pioneering studies on electron transfer and exciplex formation.

During the period 1950–1951 he started his cooperation with Th. Förster at the Max-Planck-Institut für physikalische Chemie in Göttingen. In 1951 Weller went to the University of Minnesota in Minneapolis to do postdoctoral work with Robert Livingston,

carrying out spectroscopic investigations on chlorophyll and pheophytin *in vitro*, which resulted in three publications in *The Journal of the American Chemical Society*. He returned to Germany in 1952 to join Förster, who had become Professor of Physical Chemistry at the Technical University of Stuttgart. Weller continued his work, already started in Göttingen, on protolytic reactions of aromatic hydroxy and amino compounds in the excited state. This was "chemistry on a higher level", as Förster's group had established that electronically excited molecules have properties (such as acid–base characteristics,  $pK^*$ ) different from those in the ground state.

Already in 1952 a paper on this subject appeared: "Quantitative Investigations on the Interconversion of Fluorescence in Naphthols". This work was the entry into the realm of fast reactions, employing molecular fluorescence. By use of flash photolysis, the presence of the radical anion of perylene was discovered in the excited-state absorption spectrum of a solution

of perylene and *N,N*-dimethylaniline in acetonitrile (1961). This was the first direct experimental proof that the inner mechanism of fluorescence quenching in such systems involved electron transfer, a notion that had previously been suggested by Baur (1935). After his *Habilitation* in 1957, the Bunsengesellschaft für Physikalische Chemie awarded him the prestigious Bodenstein Prize in 1962.

In the same year, Weller became Professor of Physical Chemistry at the Free University in Amsterdam. From the scientific point of view, emphasis started to shift from proton-transfer toward electron-transfer reactions in the excited state. The first example, found already by him in Stuttgart, of a fluorescing intermediate in such reactions, an "excited charge-transfer complex" or exciplex  $^1(A^{\cdot-}D^+)$ , was reported in 1963 for the system perylene/*N,N*-dimethylaniline in nonpolar solvents such as benzene. The fundamental understanding of these processes came from an analysis based on the electrochemical oxidation/reduction potentials of the reaction partners, which led to the introduction of a semi-empirical formula for the energy of the exciplex (in hexane, as an example, neglecting the interaction of the charge-transfer state with the no-bond ground state and the locally excited states):

$$E^1(A^{\cdot-}D^+) = E_{1/2}(D/D^+) - E_{1/2}(A^-/A) + 0.15 \pm 0.10 \text{ eV}$$

With the aid of this formula, now generally called the Weller equation, the occurrence or nonoccurrence of exciplex formation (i.e.,  $E^1(A^{\cdot-}D^+)$  below or above the energy of the singlet excited state,  $^1A^*$  or  $^1D^*$ ) could easily be predicted. A similar expression was derived for the energy of the ion pair ( $^2A^{\cdot-}\cdots^2D^+$ ), which dominates electron transfer in polar solvents. Alongside the electron-transfer reactions mentioned above, leading to the generation of solvated radical ions  $^2A^{\cdot-}$  and  $^2D^+$  in polar solvents, the reverse process was also studied. Such reactions, taking place on mixing the chemically produced radical anions and cations, could be shown to result in chemiluminescence, coming from a variety of primarily excited species in the triplet and singlet state. Of some importance was the finding that exciplexes  $^1(A^{\cdot-}D^+)$  could be produced directly from the radical ions in solvents of intermediate polarity. Simultaneously, investigations were started on compounds with an electron donor and acceptor linked together by an alkane chain, which were to take a special place in Weller's laboratory and elsewhere. Furthermore, exciplexes in the triplet state  $^3(AD)^*$  were studied, via their luminescence (CT phosphorescence and E-type delayed fluorescence) and also employing ESR.

After three years in Amsterdam, Weller became in 1965 the Director of the Max-Planck-Institut für Spektroskopie in Göttingen, which in 1971 merged into the then newly established Max-Planck-Institut für biophysikalische Chemie. There, he and his co-workers undertook detailed studies of the primary processes connected with electron-transfer reactions in the excited state. Using nano- and picosecond laser flash photolysis systems, the

molecular aspects of exciplex formation and of the dissociation of exciplexes into radical ions were investigated in detail. One of the results of this work was the now famous Rehm-Weller curve (1969), relating the rate constant of electron-transfer reactions to the change in free enthalpy  $\Delta G$ . The inverted chemical effect (the eventual decrease of the rate constant for highly exothermic reactions), as predicted by the Marcus theory, was shown to be absent in electron-transfer reactions in solution starting from uncharged molecules.

Of growing importance became the study of the magnetic field dependence of electron-transfer reactions. The influence of magnetic fields on geminate recombination of radical ion pairs in polar solvents was first established in 1976. It was found that the change in spin multiplicity (singlet to triplet) of a radical ion pair originates from the hyperfine interaction between the nuclear spins and the spins of the unpaired electrons of the radical ions. These studies brought new insights into the influence of the intermolecular distances between the reactants undergoing electron transfer. It now became possible experimentally to distinguish exciplexes (tight ion pairs) from solvent-separated radical ion pairs, an important advance in mechanistic studies, as these species possess very similar absorption spectra. The extension of this research to molecules with linked electron donor and acceptor moieties promises to provide direct access to polymer dynamics.

That Weller is held in high esteem by the scientific community can be seen from numerous invitations as Visiting Professor to Brandeis University (1968/1969), the Lomonossov University of Moscow (1975), the Catholic University of Leuven (1979), the University of Western Ontario (1981), and a sabbatical period at IBM San Jose (1970). He is honorary Professor at the University of Göttingen and has been awarded honorary doctorates by the Universities of Leuven (1983) and of Bayreuth (1987). He is also a member of the Academy of Sciences in Göttingen (1975), the Finnish Academy of Sciences (1984), and the Leopoldina in Halle (1985).

He has served on the advisory editorial boards of *Chemical Physics Letters* (1967-1982) and *Chemical Reviews* (1984-86), and he is currently on the editorial board of the *Zeitschrift für Physikalische Chemie* and the *Berichte der Bunsengesellschaft für Physikalische Chemie*. The pioneering work of Weller on electron and proton transfer in the excited state has had a large impact on many areas of science, of which photosynthesis is not the least, as can be seen from the topics treated in this issue of *The Journal of Physical Chemistry*. His lively contributions to the discussions during scientific meetings are remembered with great pleasure.

The friends and colleagues from all over the world contributing to this Albert Weller Festschrift wish him upon his retirement many more years of good health and productive scientific activity.

Klaas Zachariasse

## Publications of Albert Weller

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