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Tribute

The contributions of James Franck to photosynthesis research: a tribute

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Abstract

The scientific career of James Franck (26 August 1882–21 May 1964) spanned seven decades in which he was preoccupied with understanding the interaction of light with matter, starting with atoms and moving to the photosynthetic apparatus in green plants.

The 1926 Nobel Prize in physics

In a sense, James Franck's (Figures 1 and 2) earliest scientific contributions to photosynthesis were his experimental results that would lead to an understanding of molecular photochemistry, begun almost a century ago. An experimental physicist working in Berlin, Franck published his first papers with Gustav Hertz on the collisions between electrons and gaseous atoms (Franck and Hertz 1914a, b). This work was a demonstration of the existence of discrete energy levels of excited electronic states of atoms and provided confirmation of Niels Bohr's theoretical proposal for the quantization of atomic energy levels. Franck and Hertz were jointly awarded the Nobel Prize for this work in 1926. (For a discussion of the life and major discoveries of Franck, see Kuhn 1965.)

Discovery of sensitized fluorescence and photochemistry and of the Franck–Condon principle

A continuation of these investigations over the following two decades, first at Berlin and later at the University of Göttingen, included an experimental demonstration of the quantization of electronic states in molecules, photodissociation of molecules, the quantization of energy in atomic and molecular fluorescence, and the first demonstration of sensitized fluorescence of an emitting species following absorption of light by a different donor substance (Franck 1923) and of sensitized photochemistry (Cario and Franck 1922). His studies of polarization of fluorescence provided an early experimental method for determining the lifetime of fluorescent states. Other important discoveries of that period which would have an impact on much later work in photosynthesis research included an analysis, supplemented by Edward Condon, of the shape of molecular absorption and fluorescence spectra (Franck 1925; Condon 1926). This is known as the Franck–Condon principle and is based on the rapidity of electronic transitions in contrast to the slower equilibration of the heavier nuclei that follows. Franck originally used this principle to explain the photodissociation of molecules, and Condon extended the principle to rationalize the shapes of absorption and fluorescence bands, including the Stokes shift (named after Sir G.G. Stokes): the red shift of the fluorescence emission from that of the absorption maximum. Other findings of that period included an understanding of competing processes for de-excitation of higher electronic states of molecules,

Figure 1. A photograph of James Franck by Lotte Meitner-Graf, daughter of Lisa Meitner, a colleague of Franck from his German days.

Figure 2. From a portrait of James Franck painted by Martyl from photographs and from memory. The painting, hanging in the James Franck Institute at the University of Chicago, was unveiled in 1983, close to the 100th anniversary of James Franck's birth.

including internal conversion and the role of metastable states. (These Franck publications, mostly in German, are summarized in Kuhn 1965.)

Figure 3. Photograph of the author, Jerry Rosenberg, and his wife Shoshana.

Political dissent in Germany

Franck's 12 productive years at Göttingen ended in 1933 with his forthright entry into the arena of political dissent. His resignation from his professorship as a public protest against emerging Nazism became a cause celebre in Germany. Although his World War I army service would have spared him from dismissal from his post under the new anti-Semitic laws, although only for the short term as we now know, he refused to accept his orders to dismiss many of his faculty, staff, and students under the new edicts dealing with racial and 'politically correct' classifications. Instead, he worked tirelessly as a private citizen from his home in Göttingen to locate scientific employment opportunities throughout the Western world for dozens of his colleagues. One of the beneficiaries of this activity was Eugene Rabinowitch, who spent some time with Niels Bohr (see Bannister 1972).

Transition years

Franck had a brief sojourn in Niels Bohr's laboratory in Copenhagen. One of his important papers from this period was his work with Eugene Rabinowitch (Franck and Rabinowitch 1934) on solution effects in photochemical processes, in which rules for recombination of photodissociation products were worked out. Here, the quantum yield of the photo-dissociation in a liquid may be less than in the gas phase because the primary photodissociation fragments, unable to escape the liquid 'cage' surrounding them, may undergo recombination before the finishing reaction can take place. Franck's modesty did not allow him to refer to this work by its common name, the Franck–Rabinowitch cage effect. Instead, he used the term 'the so-called Franck–Rabinowitch effect,' just as he always referred to his earlier work on the shape of molecular absorption and fluorescence bands in terms of the 'so-called Franck–Condon principle.'

Immigration to the United States and entry into photosynthesis research

Franck came to the United States in 1935, first to Johns Hopkins University in Baltimore, and later, in 1938, to the University of Chicago as Professor of Physical Chemistry. Franck began to think about turning his attention to photosynthesis at the time of his move to the United States. Perhaps he was discouraged about the prospects of setting up a modern laboratory in atomic and molecular physics. A more likely explanation is that in 1938, at the age of 56, he felt challenged to tackle the major problem of photobiology. The Samuel Fels Foundation established a laboratory in photosynthesis for him in 1938 at the University of Chicago, where he became Professor of Physical Chemistry. Within a year he invited Hans Gaffron (for some of the contributions of Gaffron, see Homann 2003) to join him, and the two constituted an interesting complementary pair, one emphasizing physical mechanisms and the other comparative biochemistry and plant physiology.

Collaborators

Franck continued a pattern established in Germany of working with colleagues with whom he could jointly think out a variety of explanations for complex problems. His earliest senior co-workers in the area of photosynthesis in his brief sojourn at Johns Hopkins were physicists – the experimental spectroscopist R.W. Wood and two theoreticians, Karl Herzfeld and Edward Teller. The papers with these three were in the areas of chlorophyll fluorescence (Franck and Wood 1936), general photosynthetic theory (Franck and Herzfeld 1937), and electronic energy migration (Franck and Teller 1938), respectively.

At Chicago, some of his early collaborators were visiting scientists, including the photochemist Robert Livingston, the plant physiologist Allan Brown, and several younger scientists just beginning their research careers, including C. Stacy French and Ted Puck, followed after World War II by Henry Linschitz. I (Figure 3) joined the group in my first postdoctoral position in 1949. Of Franck's graduate students, most continued in scientific careers, including Sol Weller, George Zimmerman, Leonard Tolmach, John Brugger, Frank Allen and Sanford Lipsky. Best known to those in photosynthesis research was Franck's last doctoral student, Warren Butler (see Benson 1998, for Butler's biography).

The Franck Report

Franck's second major foray into the public arena developed from his role as chairman of the Committee on Social and Political Implications of Atomic Energy, a small group of scientists working at the Metallurgical Laboratory, the Chicago arm of the Manhattan Project which was formed by the US government near the beginning of World War II to develop nuclear weapons. This committee issued its findings and recommendations in what came to be known as the Franck Report, delivered personally by Franck to the US Secretary of War Henry Stimson on 11 June 1945, shortly before the detonation of the first nuclear test bomb in New Mexico. The report predicted a nuclear arms race that would follow the introduction of this new weapon into warfare and a concomitant threat to the security of all nations, including the United States. The report called for the first use of this weapon as a pre-announced demonstration release in an uninhabited area. Although the chief recommendation of the report was not accepted, this episode reflects on the seriousness of purpose and of concern for human welfare shown by Franck and the other authors of this historical document (Rabinowitch 1964).

Photosynthesis research

Franck's experimental work in photosynthesis dealt mainly with chlorophyll fluorescence (Franck et al. 1941; Shiao and Franck 1947); flashing light experiments (Weller and Franck 1941); and 'afterglow' (Brugger and Franck 1958). He spent most of his time and energy, however, in attempting to construct an overall theory of photosynthesis consistent with the major observations, largely made by others. From his first major paper with Herzfeld (Franck and Herzfeld 1937) to his final one, with the author (Franck and Rosenberg 1964), his theories had some explanatory validity at the time they were advanced but often turned out to be inconsistent with experiments which he did not consider or with later empirical results. For example, Franck (1958) had written a physical explanation of the Emerson enhancement effect (Emerson et al. 1957) that included an excitation from one triplet state to another using two photons of light. Had he used his earlier model (Franck and Herzfeld 1941; see below), he would have been prescient with what later became known as the Z-scheme of photosynthesis (Hill and Bendall 1960). He did not hesitate to reject his earlier formulations in favor of later successive proposals.

His earlier versions defined in formal terms the minimum number of light and dark reactions needed for the full photosynthetic cycle, and the time requirements for each step. His second paper with Herzfeld (Franck and Herzfeld 1941) had an elaborate set of simultaneous differential equations defining successive steps, with solutions based on certain assumptions. On the basis of measurements of overall gas production (O_2) or consumption (CO_2) and of chlorophyll fluorescence as a function of light intensity, concentrations of CO_2 and inhibitors, time from the onset of oxygen evolution, and regimens of intervening dark times, he proposed a scheme in which chlorophyll pre-complexed with a primary oxidant undergoes direct photochemical oxidation with a reaction time in the picosecond range. A scheme was mapped out in which three rate-limiting enzymatic steps were involved: one, a reaction inhibited by cyanide, the regeneration of the primary photo-oxidant; one, the oxidation of a class of intermediates S_n by the photo-oxidized chlorophyll to S_{n+1}; and one, the ultimate evolution of O_2. Although we might now consider this an oversimplified description of a complex sequence of events, the outline was remarkable even in terms of present understandings, except for the fact that the paper departed from its otherwise generalized proposals in identifying CO_2 as the primary photo-oxidant (an idea that must have been a vestige from Willstätter and Stoll 1918). In today's perspective, one might wonder why he considered the primary photo-oxidation of chlorophyll only in terms of a transfer of a hydrogen atom without considering charge separation. It should be noted, however, that this paper was written prior to all the technical discoveries and improvements of the past six decades, including the detailed exploitation of ^{14}C as a tracer in the carbon pathway, the technology of very short light flashes, the improvement in 'monochromaticizing' incident and emitted light, and the isolation and analysis of reaction centers. The existence of two photosystems was, of course, not known at that time. Rabinowitch (1945) presented the hypothesis of Franck and Herzfeld (1941) in a manner that resembles very much the current schemes of photosynthesis, but without the names of the intermediates.

On the purpose of theories

Franck wrote of the fate of his theories in this same paper (Franck and Herzfeld 1941):

> The change in the situation (new methods of observation and new results) is indeed so far-reaching that practically all theories published hitherto are now obsolete. ...These theories have served the purposes for which they were developed; they have clarified the situation, they have stimulated new experiments, and most of them contained parts which have been used in each subsequent attempt... A theory... by its very nature can contain only a partial truth.

In this light we might take just a few examples of where Franck's proposals have turned out to be incorrect. (1) One reason for invoking the chlorophyll triplet state as the vehicle for sensitizing Photoreaction I (Franck and Rosenberg 1964) is that fluorescence of the far-red forms of chlorophyll had not been established. At about the same time as the Franck paper was submitted Butler and Norris (1963) published a determination from low temperature experiments that Chl705 has a fluorescence at 730 nm with a good yield, from which they determined its lifetime, adequate to allow Photoreaction I to occur directly from the lowest excited singlet state. (2) The calculations of Franck and Teller (1938) for exciton transfer in a unidimensional linear array of chlorophyll molecules led the authors to conclude that this type of energy transfer was not fast enough to bring excitation energy to a reaction center. Bay and Pearlstein (1963) later extended the model to two and three dimensions and found that in the higher dimensions the migration of exciton energy is indeed fast enough (also see a discussion by Robinson 1967). Gaffron and Wohl (1936) had earlier alluded to some cooperative process, without offering a mechanism for energy migration, to explain the pioneering research of Emerson and Arnold (1932a, b) where it was shown that 2500 chlorophyll molecules cooperated to evolve one oxygen molecule. (3) Franck tried to explain how a natural system that had two independent types of functioning photosynthetic units could manage to proportion the excitation energy from illumination below the saturation point equally into two types of reaction center, so that Photoreactions I and II would occur at equal rates. He, together with the author, postulated that if there were only one type of photochemically functioning reaction center, the temporary chemical modification of a substrate for one of the photochemical reactions by its recent participation in that reaction would force the next quantum of excitation to be used for the other photochemical reaction (Franck and Rosenberg 1964). At the time this proposal was made, the major advances in membrane fractionation that led to the isolation and characterization of separate reaction centers I and II had not yet been made. Although we now know that there are separate loci for Photoreactions I and II, the mechanism for balancing the two photoreactions at a steady state of photosynthesis over a broad spectral range of excitation is still a subject of differing opinions.

My personal experiences: a tribute

My personal experiences of working with Franck were very rewarding. He spent day and night thinking about how the numerous experimental observations he was aware of could be brought into one unified picture of photosynthesis. This may have been an impossible task during his lifetime, and he may have neglected some of the accumulating evidence obtained by methods or in sub-disciplines with which he was not too comfortable. Nevertheless, the daily personal encounters were always intellectually stimulating. He would put all ideas up for serious discussion, even those which to him seemed off the wall, and would apply the test of falsifiability, looking for flaws in every hypothesis.

I was not alone in respecting his deep intellectual power. During my several years in his laboratory, many scientists would visit, both to report on their latest findings or to discuss some recent observation of their own or of others, whether in photosynthesis or any branch of science. Among the visitors I can recall seeing during those years were William Arnold, Britton Chance, Rod Clayton, Robert Emerson, Albert Frenkel, Martin Kamen, Michael Kasha, Robert Livingston, Rufus Lumry, Eugene Rabinowitch and Bernard Strehler. Rabinowitch (1956) expressed his admiration of Franck and his scientific indebtedness to him :

> The author has had the privilege of studying or working with several great scientists of our time; but Dr James Franck is the one of whom he likes to consider himself a pupil – not only in the narrower field of common scientific specialization, but in the whole approach to the world of atoms and molecules. While the author has not been able to match the persistence, concentration, and clarity of thinking that have made James Franck one of the great pathfinders in this enchanted world (not to speak of acquiring his humility and deep understanding of the world of men), he can plead that these have been among the strongest influences he has experienced, and guiding lights he has tried to follow.

Because of his own scientific origins, Franck never became fluent in biochemical concepts, but he took some measures to be educated in those ideas foreign to him. One should remember that he chose to invite Hans Gaffron to his laboratory as his principal scientific colleague. Gaffron, known for his work in photoreduction, comparative photosynthesis, and bacterial biochemistry, made many of his important contributions to science in that laboratory. Gaffron attracted visiting fellows to spend short research periods in the laboratory, including Mary Belle Allen, Norman Bishop and Allen Mehler. Incidentally, the Mehler reaction (Mehler 1951) was discovered during this visit.

My remembered experiences with Franck went far beyond scientific interaction. He was a gentlemanly and gentle person, exuding kindliness and warmth on every encounter. The daily afternoon teatime brought everybody in the laboratory together, to talk not only about science but also about any topic that came up, whether it be family, music, or the day's news. It was on these occasions that I heard some of Franck's reminiscences of many famous personages, including Fritz Haber, Albert Einstein, Niels Bohr and Max Planck. He took great pride in his own family, the Liscos and von Hippels, and enjoyed telling about the changing introductions at MIT when he would be accompanied by scientists in his family, starting with references to Arthur von Hippel as Franck's son-in-law, moving to reference to himself as von Hippel's father-in-law, and ending later to references to himself as Peter von Hippel's grandfather. Another of his anecdotes expressed his pride in sharing the Nobel Prize with Bohr and Planck, because for safekeeping Bohr had dissolved all three of their gold Nobel medals in *aqua regia* and stored them as a solution in an unmarked bottle in his Copenhagen laboratory during World War II, to be reprecipitated and cast into three new medals after the war.

Almost 30 years elapsed between Franck's first (Franck 1935) and last (Franck and Rosenberg 1964) publications on plant photosynthesis. He did not live to see the solution to this problem, which he originally thought could be achieved very quickly. But will any of us engaged in science in 2003 live to see the final answer?

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