# Ultrafast Photoinduced Energy and Charge Transfer: Concluding Remarks

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## Abstract

The ability to characterize and control the energy and charge transfer events triggered by the photoexcitation of molecules and materials is of fundamental importance to many fields, including the sustainable capture and conversion of solar energy. This article summarizes the papers that were presented and discussed at the recent Faraday Discussion meeting on Ultrafast Photoinduced Energy and Charge Transfer. Ultrafast laser spectroscopy and theory were at the center of discussions on photoinduced phenomena in biological and nanoscale systems of interacting absorbers. Many of the questions that motivate this field of science have occupied scientists for many decades as a look back to a Faraday discussion meeting that took place 60 years earlier reveals.

## 1. Introduction

The meeting on Ultrafast Photoinduced Energy and Charge Transfer, which is recorded in Faraday Discussions volume 217, took place April 8 – 10, 2019 in Ventura. It was the first time that a Faraday discussion meeting was held in California, and the abundant sunshine of the region was a fitting accompaniment to a meeting focused on photoinduced phenomena. Although "It never rains in Southern California", at least according to an old song, it had clearly rained a great deal leading up to the meeting, and participants were rewarded with views of verdant, flower-dotted hillsides on the drive to the conference hotel—a further treat for the many fans of photosynthesis in attendance.

As the title indicates, the meeting was focused on the dynamical phenomena of energy and charge (i.e., electron and/or proton) transfer initiated by the photoexcitation of molecules and materials. The word "ultrafast" is an indication of the rapid time scales involved, and most of the authors of the experimental papers discussed at the meeting reported results obtained using a variety of ultrafast laser spectroscopies. The theoretical frameworks that are crucial for interpreting the experimental observations were also at the core of this meeting that attracted the participation of many theorists. The organizing committee encouraged investigators to attend, who use spectroscopic and computational approaches to learn about fundamental events that play out in molecules and in their nanoscale assemblies.

Although biology is not mentioned in the meeting title, biomolecules and their assemblies were discussed in nearly half of the papers presented, and most of the remaining papers were inspired to a lesser or greater degree by the photodynamics of natural systems. The natural photosynthesis that powers life on Earth makes extensive use of excitation energy transfer and this constituted another theme of the meeting as will be discussed below. While the ability to probe events on ultrafast time scales continues to improve, nature remains the master of results, meaning that human engineered systems for efficiently and sustainably generating electricity or chemical fuels from sunlight still leave much to be desired. Possible strategies for achieving advances in manmade systems were discussed frequently.

With only a few exceptions, the systems presented in the many excellent papers and posters involved two or more interacting light absorbers. Only a handful of papers were concerned with solids with their long-range translational symmetry and delocalized states. Most studies addressed systems in the fascinating middle ground between small molecules and extended solids. It is an area of special interest and opportunity for physical chemists, who bring their familiarity with localized states of molecular units to complex systems in which interactions among multiple chromophores over nanoscale distances give rise to rich new phenomena in energy and charge transfer.

## 2. Excited States Through the Lens of Time

The meeting attracted many excellent contributions that spanned an impressively broad range of topics, as even cursory inspection of this volume indicates. Distilling these diverse contributions into a coherent summary is a nearly impossible task. The scientific heterogeneity on display at the meeting is both a hallmark and strength of a field that seeks to characterize and exploit the multiple paths that lead from excited electronic states back to the ground state or to photoproducts.

Many of the themes and questions addressed at the meeting have old roots that are worth reflecting on. As the introduction to Prof. Fleming's paper in this volume (DOI: 10.1039/c8fd00190a) indicates, efforts to understand energy transfer in photosynthetic organisms began in earnest more than 70 years ago. Given the focus on fundamental light-matter interactions, a theme with great longevity in physical chemistry circles, it is hardly a surprise that a substantial number of preceding Faraday Discussion meetings have had at least some topical overlap with the 2019 meeting. There have been, for example, multiple Faraday discussions on electron and proton transfer and ones on photochemistry topics date back to at least 1925.

There is, however, one Faraday discussion meeting from the past that is a particularly interesting precursor to the April 2019 meeting. This discussion, which was titled "Energy Transfer with special reference to Biological Systems", took place almost exactly 60 years earlier at Nottingham University from April 14 – 16, 1959. Sixty is of course an appropriately round number, but as the number of seconds in a minute, and the number of minutes in an hour, it is an irresistible anniversary for celebrating a field that revolves around time-domain observations.

The 1959 meeting featured many notable scientists working in spectroscopy and photoinduced energy transfer. Participants included a past (Albert Szent-Györgyi) and a future (George Porter) Nobel laureate. Szent-Györgyi received the 1937 Nobel Prize in Physiology or Medicine, while George Porter would receive a Nobel Prize in 1967. Other distinguished scientists present in Nottingham whose names would be recognizable to many of the 2019 participants included: John B. Birks, Edmund J. Bowen, Henry Erying, Theodor Förster, H. Christopher Longuet-Higgins, John P. Simons, Gregorio Weber, Eugene

Rabinowitch, Joseph Weiss, and Albert Weller. Most of these individuals and many of the other scientists in attendance were younger than 50 in 1959, and the paper presenters were on average younger than their counterparts in 2019. To underscore this youthful dynamism, there was even an Olympic champion among the attendees (American Britton Chance, inventor of the stopped flow technique, and a sailing gold medalist at the 1952 Games in Helsinki).

That energy and charge transfer usually play out on ultrafast time scales was already well known sixty years ago. With a simple and direct elegance, Nobel laureate Albert Szent-Györgyi succinctly described this challenge in the opening sentences of his written contribution,[1]

> If a photon, ejected by the sun, interacts with an electron of a molecule on our globe, then the electron is raised to a higher energy level to drop back, as a rule within $10^{-8}$-$10^{-9}$ sec, to its ground state… Life has shoved itself between the two processes, catches the electron in its high-energy state and lets it drop back to the ground level within its machinery, using the energy thus released for its maintenance…

The business of understanding this "machinery" and how it functions has occupied physical chemists and other scientists for many years now. The lack of techniques for directly observing energy transfer over the fastest time scales on which it takes place was an obvious barrier to progress six decades ago. Because lasers and the ultrashort light pulses they produce had not yet been invented, observing excited state dynamics, particularly of short-lived singlet excited states, required an extra measure of ingenuity and effort in the late 1950s.

Two of the 25 papers from the 1959 meeting include figures that depict transient measurements of excited electronic states. Fittingly, one of the papers is by George Porter, who would go on to receive the 1967 Nobel Prize in Chemistry together with Manfred Eigen and George Norrish for pioneering studies of fast reactions. At the 1959 meeting, Porter and Wright described flash photolysis measurements with microsecond time resolution, which they used to determine the lifetime of the lowest triplet state of naphthalene in various solvents.[2]

The second paper by Burton and Dreeskamp reported measurements of luminescence decay times from scintillators excited by 11 ns X-ray pulses.[3] Their apparatus permitted measurements of lifetimes as short as a few nanoseconds, a remarkable, state-of-the-art achievement in 1959. Although the time delays in their experiments were laboriously generated by manually swapping out coaxial cables cut to just the right length to delay an electrical gate pulse by the desired amount of time, the sampling approach of performing many repeated measurements at discrete values of the time after photoexcitation is in essence the same one used in the many pump-probe experiments discussed in the 2019 meeting.

The ability to directly observe excited state dynamics using ultrafast lasers has been revolutionary. Lasers are mentioned explicitly in all but a few of the experimental papers at the meeting. Ultrafast laser sources and related technology have matured greatly since the first lasers that directly generated femtosecond laser pulses became widely available in the early 1980s, and it is now possible to generate subpicosecond laser pulses across a broad swath of the electromagnetic spectrum from Thz radiation to X-rays. The remarkable range of observations that are now possible using ultrafast laser techniques was well documented in the introductory lecture by Prof. Majed Chergui (DOI: 10.1039/c9fd00036d).

The papers discussed at the 2019 meeting explored many themes in energy and charge transfer studies at a level of microscopic detail that would have been hardly imaginable in 1959. The organizing committee organized the meeting into four sessions each with a distinct theme. These are briefly presented in the following followed by some concluding remarks that look back as well as ahead.

## 3. Energy Transfer and Charge Transfer in Natural Photosynthesis

A special feature of Faraday Discussion meetings has always been the exchanges among participants that are preserved for posterity. Even though both questions and answers acquire some additional luster through editing by questioner and questionee after the meeting, they nevertheless serve up freshly baked (and occasionally half-baked) science at the frontiers of a field, as it unfolded in real time. One of the more interesting comments from the 1959 meeting came from Prof. Rufus Lumry from the University of Minnesota (italics added):

> The comments of several contributors to this Discussion *indicate a yearning for the appearance in biological systems of exotic processes depending upon the quantum mechanics of highly ordered* systems and the like. While one should not at present dismiss these in any confident manner, it seems desirable not to

> neglect unusual mechanisms for which we already have evidence and which might be reasonably expected to exist in biological systems.

This comment captures the longstanding interest in (and occasional uneasiness about) quantum effects in biology that continues to the present day.[4] The papers in this first session of the meeting dealt with experimental and theoretical advances in understanding transient processes relevant to natural photosynthesis and the "exotic processes" mentioned by Lumry. While most of the presentations investigated events that occur in natural systems, Prof. Leggett described how light harvesting complexes isolated from spinach can be deposited on arrays of gold nanostructures and used to observe and control plasmon-exciton couplings (DOI: 10.1039/c8fd00241j).

The other presentations in this session sought insight into how the electronic and vibrational coherences observed in natural systems influence energy and charge transfer dynamics. Since the report that quantum coherences can be detected in experiments that monitor the transport of excitation energy in photosynthetic complexes,[5] there has been great interest in the physics underlying this phenomenon,[6-8] and how it might be used to design improved synthetic systems for solar energy harvesting.[9]

Prof. Olaya-Castro reported on fundamental quantum effects that appear when two coupled oscillators become synchronized (DOI: 10.1039/c9fd00006b). Theoretical treatments like this one are important because they can ask questions about the functioning of isolated or altered subsystems that may be difficult or impossible to probe experimentally. The paper presented by Dr. Fingerhut explored the effects of intramolecular vibrations on the coherent dynamics in a model system based on a bacterial reaction center (DOI: 10.1039/c8fd00189h). The calculations suggest that charge transfer proceeds nonadiabatically at room temperature, following the equilibration of excitonic coherences.

In a further theoretical study, Prof. Cheng investigated the photosystem II supercomplex using large-scale molecular dynamics simulations and quantum chemical calculations that modeled excitonic couplings among all 74 pigments (DOI: 10.1039/c8fd00205c). A coarse-grained version of the model reproduces key excitation energy transfer pathways and shows promise for simulating dynamics in large networks. In his contribution, Prof. Fleming (DOI: 10.1039/c8fd00190a) described advantages of two-dimensional electronic-vibrational spectroscopy for studying photosynthetic energy transfer. This recently developed technique is advantageous for studying correlations between electronic and vibrational degrees of freedom.

## 4. Photovoltaics and Bioinspired Light Harvesting

The papers in this session are notable for their diversity of topics. Prof. Persson reported on his latest efforts to understand the photophysics of iron carbene complexes, which have remarkably long $^3$MLCT state lifetimes (DOI: 10.1039/c8fd00232k). Prof. Weiss discussed in her presentation the dynamics of singlet fission in aggregates of pentacene derivatives that form spontaneously on the surface of PbS quantum dots (DOI: 10.1039/c8fd00157j). The rate of singlet fission was observed to increase by a factor of five, suggesting a possible strategy for increasing the efficiency of photovoltaic devices.

An artificial light harvesting system in which porphyrin chromophores are arranged on the 'struts' of a metal organic framework was discussed by Prof. Morris together with her team's observations of exciton migration by time-resolved spectroscopy (DOI: 10.1039/c8fd00194d). Prof. Marcus discussed how interchromophoric couplings among a dimer of dye molecules can be used to reveal dynamically fluctuating conformations at junctions between single- and double-stranded DNA (DOI: 10.1039/c8fd00245b). This work illustrates how spectroscopy and theory can yield powerful insights into fluctuating structures on time scales that are not accessible by other techniques.

The debate about what allows a photogenerated electron and hole to form free charge carriers in an organic photovoltaic device despite their strong mutual Coulombic attraction of ~0.5 eV was addressed by Prof. Bittner (DOI: 10.1039/c8fd00182k). Entropy has been shown to play an important role in reducing the free energy barrier to charge separation even in the face of a significant potential energy barrier.[10, 11] The formalism presented by Prof. Bittner was used to calculate the degree of quantum entanglement and the Shannon entropy of excitonic and charge transfer states in a model heterojunction. Finally, the light-driven movement of protons and the factors that influence the photobasicity of organic molecules were the focus of Prof. Dawlaty's presentation (DOI: 10.1039/c8fd00215k).

## 5. Photoinduced Electron Transfer

When two or more pathways connect initial and final states, quantum interference can enhance and suppress rates. This fundamental aspect of quantum systems has recently motivated attempts to control rate processes. Quantum interference among pathways that couple two molecules that undergo Dexter energy transfer was the subject of the presentation by Prof. Beratan (DOI: 10.1039/c9fd00007k). Prof. Wasielewski presented results of spectroscopic experiments showing a non-statistical rate enhancement for intramolecular electron transfer in a compound containing one vs. two electron acceptors at cryogenic temperatures (DOI: 10.1039/c8fd00218e). However, bath fluctuations at room temperature spoil the coherent coupling between the two acceptors, resulting in a statistical rate.

Three papers discussed further issues of importance in the field of organic photovoltaic devices. Prof. Schwartz discussed a new spectroscopic approach for distinguishing free polarons from trapped polarons in doped organic polymers (DOI: 10.1039/c8fd00210j). The role played by the solvent in influencing charge separation was studied at the fundamental level of two identical chromophores in a paper presented by Prof. Thompson (DOI: 10.1039/c8fd00201k). The contribution from Prof. Penfold examined factors affecting triplet-triplet energy transfer (DOI: 10.1039/c8fd00174j). Triplet states can be low energy traps, but their long lifetimes can potentially allow them to diffuse over great distances.

Biology often couples proton and electron transfers to efficiently separate charge using light. Marcus[12] first predicted theoretically the so-called inverted region behavior in which electron transfer rates decrease even as the reaction exergonicity increases—an effect that was subsequently observed experimentally in the 1980s.[13] Prof. Hammes-Schiffer described in her presentation the conditions necessary for observing inverted region behavior in photoinduced proton-coupled electron transfer (PCET) (DOI: 10.1039/c8fd00240a), which has now been seen in very recent experiments by Parada et al.[14]

A final paper in this session presented an analysis of thermal effects in high repetition rate ultrafast X-ray studies. Prof. Gessner and his team studied the lattice heating that results from electron-phonon coupling in the transition metal oxide semiconductor CuO (DOI: 10.1039/c8fd00236c). While time-resolved X-ray experiments are still performed overwhelmingly on inorganic systems, the thermal effects described by Gessner will also be important in systems of organic chromophores, like the ones that dominated the presentations in the meeting.

## 6. Photoprotection/Photodamage in Natural Systems

The final session addressed the downside to using energy-rich excited electronic states. Even minute quantum yields of photoproduct formation or other off-pathway events pose a significant challenge to the long-term viability of photoactive systems, both natural and man-made. The generation of triplet excited states poses a particularly grave threat due to their long lifetimes and their ability to form reactive oxygen species like singlet oxygen. The specific pathways that give rise to photodamage can be as varied as the chromophores involved, and papers in the final session covered a range of biomolecular absorbers that included carotenoids, melanin model compounds, mycosporine-like amino acids, and nucleobases. These chemically diverse chromophores absorb from the visible to the deep UV and are all thought to contribute in one way or another to enhancing the photostability of the structures they occur in.

Carotenoids play a key role in the nonphotochemical quenching mechanism that protects the photosynthetic machinery from high light levels,[15, 16] but they also act as accessory absorbers capable of transferring energy to chlorophyll. Prof. Polívka described how energy transfer from fucoxanthin keto-carotenoids to chlorophyll is slowed when chemical modifications eliminate the intramolecular charge transfer state of fucoxanthin (DOI: 10.1039/c8fd00193f). In spite of this change, overall energy transfer efficiency is not compromised because slower energy transfer is compensated by a longer $S_1$ lifetime.

The linear polyenes that are the chromophores of carotenoids have long fascinated spectroscopists because the lowest singlet excited state is a dark state.[17] Although one-photon excitation to the $S_1$ state is forbidden, this state can be readily reached via an allowed two-photon transition. The paper presented by Dr. Lokstein (DOI: 10.1039/c8fd00198g) addressed an important issue in studies of light harvesting complexes that contain two or more chromophores that can be excited by two-photon absorption. Polarization-dependent emission spectra revealed that the two-photon excitation of chlorophyll using wavelengths between 1000 and 1500 nm is two orders of magnitude more probable than the two-photon excitation of a xanthophyll carotenoid when two-photon excitation is detected by bacteriochlorophyll fluorescence.

Prof. Matsika explored in her paper how base sequence and the methylation state of a nucleobase affect the energies of charge transfer states in DNA strands (DOI: 10.1039/c8fd00184g). Charge transfer states are of great importance in DNA strands because the short distances between stacked nucleobases promote their coupling. Depending on spin multiplicity, these states can quench or enhance the formation of the cyclobutane pyrimidine dimer photoproduct formed in DNA by UV radiation.

Mycosporine-like amino acids (MAAs) are UVB sunscreens found in algae. Prof. Habershon used MAA analogs to test "on-the-fly" wavefunction propagation methods (DOI: 10.1039/c8fd00228b). Quantum dynamical simulations like these can directly simulate ultrafast excited state dynamics and help to bridge the gap between experiments that are generally focused on kinetics and theoretical treatments that are most often focused on energy landscapes.

Melanin is a ubiquitous biopolymer found in organisms throughout the tree of life, but the lack of a molecular structure has severely hampered structure-function studies. Dr. Grieco (DOI: 10.1039/c8fd00231b) discussed photoinduced hydrogen atom transfer in catechol:quinone dimers that are thought to model some of the molecular motifs present in this polymer.

## 7. Outlook

It is easy to imagine that the 1959 participants would have greatly enjoyed the 2019 meeting due, on the one hand, to themes that have obvious connections to the science that they discussed 60 years earlier, and, on the other hand, to the delight they would certainly feel at the stunning technological advances that have transformed how experiments (lasers) and theoretical studies (vastly more powerful computers) are performed today. It is also worth noting that several of the participants at the 1959 meeting coined terms like excimer (B. Stevens in 1960[18]) and exciplex (R. Lumry in 1966[19]) that are now part of the vocabulary of the field and that were invoked in Ventura on multiple occasions.

The fact that many of the questions discussed in 2019 have roots that can be easily recognized in the program from a meeting from sixty years earlier (a near eternity given the pace of modern science) might give the impression that there is "nothing new under the sun". However, it would be a mistake to confuse this thematic continuity with the steady and dramatic progress that has taken place in a field focused on complex phenomena.

There are plenty of reasons to believe that fundamental studies of excited states will continue to be important for years to come, but what ideas imported from other fields will fuel new advances? What new technology will be as indispensable and transformative to the field as the laser was beginning in the early 1960s?

Answering these questions seems just as foolhardy today as predicting the state of the field in 2019 would have been in 1959, but a new direction poised to occupy scientists in the field, at least in the short term, was discussed in Ventura. Several speakers commented on the new frontier in quantum information science and the contributions that workers in the field of ultrafast energy and charge transfer are expected to make in this emerging area. Prof. Fleming was frank in his assessment of the difficulties faced by experimentalists who will need to work with quantum light sources. However, he offered ultimately an optimistic view of the future when he reminded the audience of the difficulties, which previous generations of scientists overcame to break into the regime of picosecond and femtosecond optical studies. This journey, which has largely been completed in the sixty years since the 1959 meeting, clearly illustrates the folly of predicting the trajectory or limits of scientific discovery.

The diversity of the science presented in Ventura in 2019 is also a platform for future success. Science that advances incrementally along a predictable trajectory established by small numbers of insiders is often science in a rut. Newcomers and researchers from other fields bring unorthodox approaches and occasionally 'heretical' perspectives that have driven advances in unexpected directions time and time again. These scientist immigrants have the special mixture of courage and naïveté needed to break out from the well-worn paths laid down in a field. It seems certain that new impulses from unexpected corners will move the field forward into the future.

The strength of the field today is measured not just by the diversity of the themes, but also by the diversity of the participants. The use of first name initials in the discussion proceedings makes it difficult to tell with certainty whether there were any female participants at the 1959 meeting, but the striking imbalance in gender pronouns in the published general discussions tells its own story: There are plenty of instances of 'he', 'his', and 'Mr.', zero mentions of 'she' or 'her', and only a solitary 'Miss' in a comment by a Dr. Redfern about work conducted with a Miss A. M. Pumphrey, who may or may not have been at the meeting. In 2019, women scientists were present in large numbers that will hopefully increase further in the future.

The papers and posters presented in Ventura document the exquisitely fine probing of excited electronic states that is now possible. Yet, for all of the splendid advances in theory and ultrafast laser spectroscopy, the ability to synthesize chemicals at will using solar photons—the ability to do what plants do with efficiency and using earth-abundant materials—remains elusive. Many decades of effort testify to the magnitude of the difficulty, but it nevertheless seems reasonable to predict that there will be a breakthrough in artificial photosynthesis that will end the currently unsustainable and climate-damaging energy economy of fossil fuels.

The fact that life was able to shove itself into the niche in time between photon absorption and excited-state deactivation as Szent-Györgyi wrote in 1959 indicates that the problem of how to store solar energy in chemical bonds for later retrieval is not an intractable one. Although the desirability of accomplishing this has been discussed for many years,[20] the urgency of finding a solution has never felt greater. A rapidly degrading climate, mass extinction of species, deforestation and damage to Earth's ocean ecosystems are all reasons to move swiftly toward a solution with all of the optimism that science can muster. When push comes to shove, it is a grand challenge too important to cede to the future.

## Acknowledgements

The author thanks Professors Michael Ashfold and Stephen Bradforth and the members of the Organizing Committee for the invitation to present the Concluding Remarks lecture and this written contribution.

## References

1. A. Szent-Győrgyi, *Discuss. Faraday Soc.*, 1959, **27**, 111-114.
2. G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18-27.
3. M. Burton and H. Dreeskamp, *Discuss. Faraday Soc.*, 1959, **27**, 64-73.
4. N. Lambert, Y. N. Chen, Y. C. Cheng, C. M. Li, G. Y. Chen and F. Nori, *Nat. Phys.*, 2013, **9**, 10-18.
5. G. S. Engel, T. R. Calhoun, E. L. Read, T. K. Ahn, T. Mancal, Y. C. Cheng, R. E. Blankenship and G. R. Fleming, *Nature*, 2007, **446**, 782-786.
6. N. Christensson, H. F. Kauffmann, T. Pullerits and T. Mancal, *J. Phys. Chem. B*, 2012, **116**, 7449-7454.

7. V. Tiwari, W. K. Peters and D. M. Jonas, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 1203-1208.

8. A. Chenu and G. D. Scholes, *Annu. Rev. Phys. Chem.*, 2015, **66**, 69-96.

9. G. D. Scholes, G. R. Fleming, A. Olaya-Castro and R. van Grondelle, *Nature Chem.*, 2011, **3**, 763-774.

10. N. R. Monahan, K. W. Williams, B. Kumar, C. Nuckolls and X. Y. Zhu, *Phys. Rev. Lett.*, 2015, **114**, 5.

11. S. N. Hood and I. Kassal, *J. Phys. Chem. Lett.*, 2016, **7**, 4495-4500.

12. R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 966-978.

13. J. R. Miller, L. T. Calcaterra and G. L. Closs, *J. Am. Chem. Soc.*, 1984, **106**, 3047-3049.

14. G. A. Parada, Z. K. Goldsmith, S. Kolmar, B. Pettersson Rimgard, B. Q. Mercado, L. Hammarström, S. Hammes-Schiffer and J. M. Mayer, *Science*, 2019, **364**, 471.

15. A. V. Ruban, M. P. Johnson and C. D. P. Duffy, *Biochim. Biophys. Acta-Bioenerg.*, 2012, **1817**, 167-181.

16. P. Jahns and A. R. Holzwarth, *Biochim. Biophys. Acta-Bioenerg.*, 2012, **1817**, 182-193.

17. B. S. Hudson and B. E. Kohler, *J. Chem. Phys.*, 1973, **59**, 4984-5002.

18. B. Stevens and E. Hutton, *Nature*, 1960, **186**, 1045-1046.

19. M. S. Walker, T. W. Bednar and R. Lumry, *J. Chem. Phys.*, 1966, **45**, 3455-3456.

20. G. Ciamician, *Science*, 1912, **36**, 385-394.