

Visualizing matter in transformation with ultrashort flashes of electromagnetic waves

A young inexperienced PhD student of Umeå University in Sweden enters the vast laboratories of Bell Labs in Murray Hill (NJ, USA). That is how my scientific life, and ultrafast science in Scandinavia, started in 1975 when Peter Rentzepis, one of the pioneers of the field, accepted me as a visiting student to his labs. For one and a half year I had the privilege to work with two more experienced scientists as my mentors, Danny Huppert and Ken Kaufmann. After learning the ins and outs of generating short, in these days, picosecond ($1 \text{ ps} = 10^{-12} \text{ s}$) pulses of light and to use them to measure very fast chemical events, I returned to Umeå, wrote my PhD thesis and started to build the first picosecond laboratory in Scandinavia. The very first experiments were performed in 1979 and fifteen years later, in 1994, the cradle of ultrafast science in Sweden was relocated to the south of Sweden and Lund University, where a brand new ultrafast lab was built.

Decades of research have shown that chemical transformations occur over a very broad time scale, from femtoseconds ($1 \text{ fs} = 10^{-15} \text{ s}$) to seconds, minutes... – fundamental processes like breaking and formation of chemical bonds, or redistribution of energy and charge within or between molecules, belong to the fastest processes, while compound chemical reactions can be very slow. Since long, scientists have therefore been developing experimental methods for the study of increasingly faster processes. A particularly powerful method is to initiate a reaction with a short flash of light and characterize the reaction progress

with a series of increasingly delayed flashes. This development started in the early 1950s with the work of Lord George Porter and colleagues and was rewarded with the Nobel Prize in chemistry in 1967. In the early days of this development the accessible time scale was milliseconds, but the invention of the laser in 1960 and following rapid technological progress gave us the microsecond, nanosecond, picosecond and finally femtosecond time scales. The opening of the femtosecond time window and ability to study the fastest and most elementary reactions was coined femtochemistry and rewarded with the Nobel Prize in chemistry to Ahmed Zewail in 1999. In the early days of fast spectroscopy there was a very limited choice of wavelengths of short light pulses, severely limiting which molecules and processes that could be studied. The part of the 2018 Nobel Prize in physics awarded to Gérard Mourou and Donna Strickland for “chirped pulse amplification” makes it possible to generate very intense ultrashort laser pulses of almost any wavelength. *Figure 1* illustrates this “magic”: an intense green femtosecond pulse is converted to white light when passing through a plate of calcium fluoride. This has opened up the possibility to study ultrafast dynamics in atoms, small molecules, large biomolecules, materials of practical importance, etc.

In my own research I have been driven by a curiosity and interest to understand Nature's processes. Photosynthesis, the ultimate process supplying all of the organic compounds and most of the energy necessary for life on Earth, appeared to be

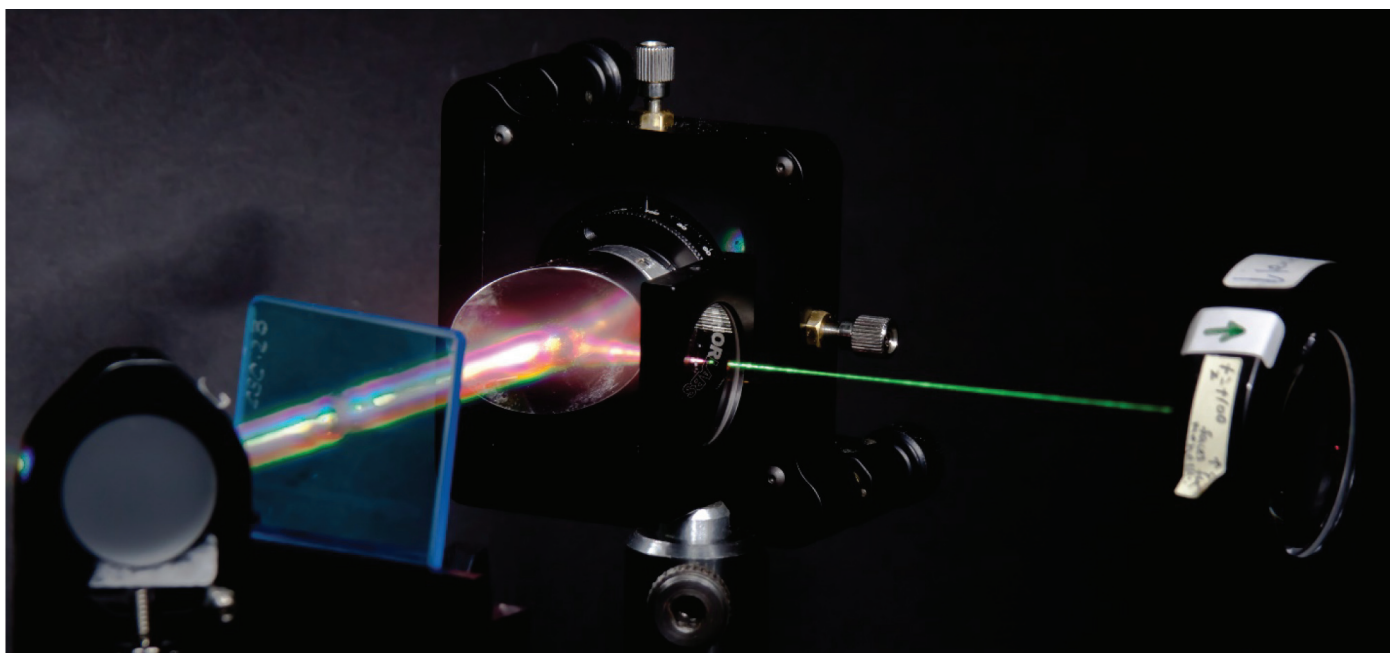


Figure 1 - White light generation by passing an intense femtosecond pulse through a plate of calcium fluoride. © Dr Jens Uhlig, Division of Chemical Physics, Lund University.

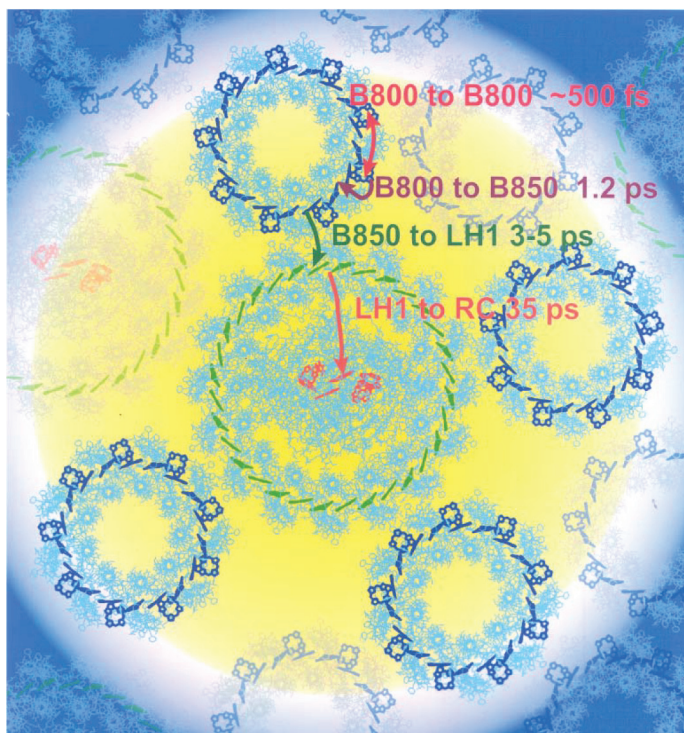


Figure 2 - Energy flow through the photosynthetic membrane of photosynthetic purple bacteria. The circles are antenna proteins – the smaller ones are the peripheral LH2 antenna, with dark blue bacteriochlorophylls (BChls), and the larger circle containing the reaction center in the middle (red pigment molecules) is the core antenna LH1 with green BChls. B800 and B850 denotes the wavelength of absorption, 800 and 850 nm, respectively, of the BChl molecules. © Prof. Tonu Pullerits, Division of Chemical Physics, Lund University.

a good choice and the light driven processes of photosynthesis was therefore an early target for my research. These processes include energy and electron transfer processes through pigment-protein complexes, so called antenna complexes, harvesting the light and reaction centers converting and storing the energy of light as electrochemical potential. Knowledge obtained from the study of photosynthetic systems could perhaps also be used in the development of solar cell materials or materials for artificial photosynthesis, i.e. production of fuels based on the photosynthetic principles.

Photosynthetic purple bacteria were chosen for these studies and a series of investigations, in collaboration with my colleague and friend Rienk van Grondelle of the Free University of Amsterdam, resulted in a detailed picture of the energy dynamics in these pigment systems. When the high resolution structure of the antenna proteins became available in 1995 through the work of Richard Cogdell and coworkers, dynamics and structure could be reconciled into a detailed picture of energy and charge flow through the whole photosynthetic unit [1]. This is illustrated in figure 2 with superfast, 0.5-1 ps, energy transfer between neighboring chlorophylls within an antenna complex. On a somewhat slower time scale, 3-5 ps, the energy is transferred from the peripheral LH2 to the LH1 core antenna, and finally in about 35 ps to the reaction center. The ~50 ps it takes from absorption of a photon to storing it as an electrochemical potential in the reaction center is almost hundred times faster than all loss processes, implying that the process is almost 100% efficient. Thus, Nature shows us how energy of light can be converted to charge with close to 100% quantum efficiency, a goal to aim for in devices for solar energy conversion.

The unique ability of photosynthetic pigment-proteins to convert light to charge with very high quantum efficiency has inspired design of materials for new types of solar cells, dye sensitized solar cells (DSC) and plastic solar cells are two examples. In a DSC a thin film of titanium dioxide (TiO_2) nanoparticles is coated on an electrode and covered by a monolayer of dye molecules. The dye molecules play the role of the photosynthetic antenna and absorb the light, followed by injection of an electron from the excited state of the dye molecule into the TiO_2 nanoparticle. The injected electrons from many absorbed photons are transported through the network of nanoparticles of the thin film and collected at the electrode to perform work in an external circuit [2]. Until recently the best DSC used metal-organic complexes containing rare and expensive metals like ruthenium as dyes. For large scale implementation of DSCs, metal-free dyes or dyes containing cheap and abundant metals can only be used. Scientists have tried hard to replace ruthenium with iron, the fourth most common element in the Earth's crust, but with very limited success. Solar cells based on iron-containing dyes have a disappointingly low efficiency, because the excited states of these dyes have very short lifetimes and therefore very inefficient electron injection into the TiO_2 nanoparticles. In other words, very few of the absorbed photons are converted to electrons and electrical current in the solar cell.

In an effort to solve this problem, we started a collaboration at the Chemistry Department of our university where organic chemists lead by Prof. Kenneth Wärnmark designed and synthesized new iron-based complexes (Fe N-heterocyclic carbenes, Fe-NHC), spectroscopists from my own group studied the photochemistry and photophysics of the new molecules, and quantum chemists under the guidance of Prof. Petter Persson calculated and predicted energetics and dynamics to be compared with the experimental results. The work has been very successful: one of the first Fe-NHCs that we made had hundred times longer excited state lifetime than any other Fe-based dye, a second generation Fe-NHC could inject electrons into a TiO_2 nanoparticle film with 92% efficiency [3], and the most recent development has produced Fe-NHCs with hundreds of ps and even ns excited state lifetimes [4]. Luminescent iron-based dyes have also been produced for the first time ever [4]. This shows that complexes of Earth-abundant iron are becoming fully viable alternatives to noble metal complexes for a wide range of light-harvesting, light-emitting and photocatalytic applications.

A long nourished dream of chemists is to not only see static structures of molecules, but also see how these structures change in the course of a chemical reaction, like a molecular movie. The ultrafast spectroscopy methods used in the studies discussed above do not give direct information about how the structures change. Since static structures of molecules are obtained with X-ray radiation, it should be possible to catch changes in structure by taking snapshots of a chemical event with the help of short X-ray pulses. Synchrotrons provide ~100 ps X-ray pulses and X-ray Free Electron Lasers (XFELs) even shorter ones down to a few femtoseconds. There are two different types of time resolved (TR) X-ray experiments providing structural dynamics information – TR-X-ray diffraction provides information about global structural changes, while TR-X-ray spectroscopy gives more local structure information. Combining the two types of

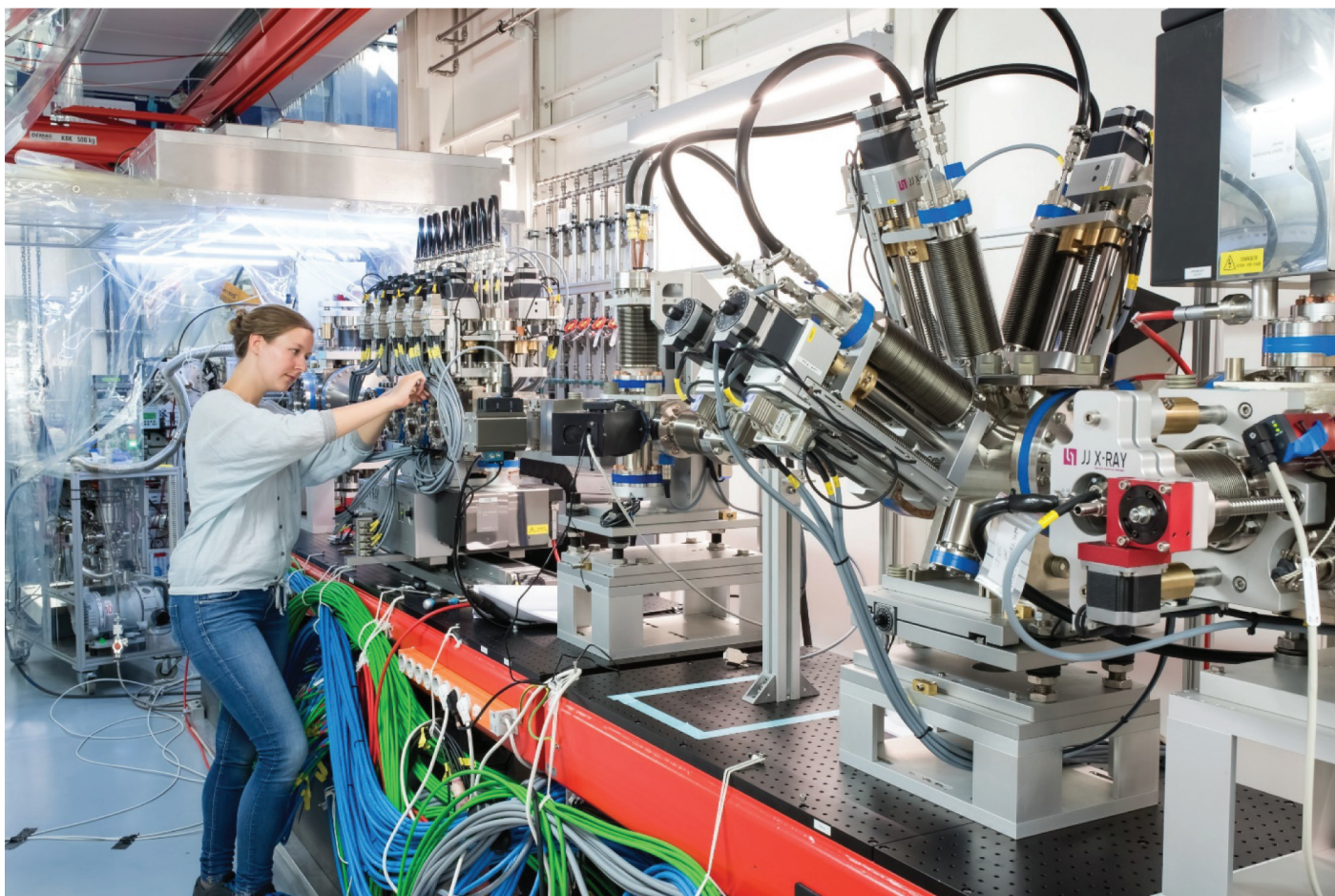


Figure 3 - Part of the FXE beamline of the European XFEL in Hamburg. © Dr Frank Poppe, European XFEL Hamburg.

experiments makes the chemist's dream come true; we can now visualize how atoms move during a chemical reaction, passing through short-lived intermediates, to the final configuration of the products. *Figure 3* shows the part of the FXE-beamline of the European XFEL in Hamburg where such experiments can be performed.

In our own work, we have used these methods to explore the coupled ultrafast structural and electronic dynamics of supramolecular complexes for solar energy conversion. The X-ray experiments provided a uniquely detailed picture of the processes storing energy of light in chemical bond energy [5]. A handful of X-ray free electron lasers are presently in operation worldwide and several more are being built. This implies that powerful X-ray methods are becoming available to an increasing number of scientist and I believe that these machines have great potential to give us a wealth of new fundamental knowledge in chemistry, biology and physics, as well as help solving problems of more applied nature.

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