Electron Transfer and Other Gray Areas
An Interview with Harry Gray
The Spectrum

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On the cover
The cover depicts electron transfer processes induced by photoexcitation of a ruthenium-diimine sensitizers bound to a blue copper protein. Flash-quench experiments of this type have been employed to determine activationless electron tunneling times at widely varying donor-acceptor distances for many proteins. Courtesy of Harry Gray.
Physicists have declared 2005 as “The World Year of Physics.” This year has been chosen since it marks the 100th anniversary of Albert Einstein’s “miraculous year” in which he published three fundamental papers in Annalen der Physik within a few months. These publications redefined (or defined) at least three areas of science—photochemistry, nuclear physics and particle motion in liquids. Interestingly, Robert Gnehm, the originator of my beloved Rose Bengal, was President of ETH Zurich in 1912 when Einstein was originally appointed. (I found the original letter of appointment and Einstein’s letter of resignation in Gnehm’s papers in the ETH library over 20 years ago. See page 38. Special thanks to Werner Rutsch, from Ciba Specialty Chemicals in Basel, Switzerland, for helping us get copies of these documents from ETH.) However, we’ll lay no claim to the infamous Albert in this issue. This anniversary provided Brigitte Wex, a doctoral student in the Center for Photochemical Sciences, and me with an excuse to look into the historical development of Einstein’s work in the photosciences and the evolution of the quantum yield. What we found surprised us.

Einstein himself first wrote \( \Delta E = h\nu \) in 1912; Gilbert Newton Lewis first used the word photon in 1926; and Arnold Beckman made what we think are the most careful early experiments that reported quantum yield measurements working with Roscoe Gilpin at Caltech in the 1920s. Farrington Daniels was able to collect all the known quantum yields for chemical processes in Chemical Reviews in 1938.

We were surprised to find Beckman’s work. Beckman, to most, means pH meter, recording spectrometer, philanthropy, and highly profile corporate mergers, not photochemistry.

Delightfully and totally coincidentally, this issue of The Spectrum features an interview with Harry B. Gray, Arnold Beckman’s devoted mentee. In the 1960s, Beckman was serving as chairman of the board of Caltech, and Harry was a fledgling professor there. They became fast friends and respected colleagues. Gray went on to become the Arnold O. Beckman Professor of Chemistry and founding Director of the Beckman Institute at Caltech. Harry is internationally known for his work in electron transfer.

Reading Einstein in the original, as Brigitte and I did, gives one appreciation for his personality. In spite of later life images, Einstein was extraordinarily meticulous and wrote precisely and carefully. Arnold Beckman, on the other hand, clearly loved doing experiments. From his papers and dissertation it seems that if he needed to make a measurement, and no technique was available, he’d invent it. I don’t know how far it was from Pasadena to the Mount Wilson Observatory, but Beckman, in the 1920s, must have driven there to use their exotic photometer to measure the density of images so that the absorption coefficient of hydrazoic acid at various wavelengths might be measured. Clearly, Beckman invented the recording spectrometer to save the next generation of Caltech students from driving up the mountain to measure absorption spectra!

History can instruct. Einstein’s papers were published in 1905 when most of the world was still reading by candlelight. The incandescent bulb, though invented, was of little consequence in most of Europe. So the best minds, like Einstein’s were worrying about turning electricity into a glowing beam. On the way to discovering how to do that, they discovered much, much else. Not long before his death Einstein wrote, “One thing I have learned in a long life: that all our science, measured against reality, is primitive and childlike—and yet it is the most precious thing we have.” True in 1905, and true well into the next millennia.
The Royal Society of Chemistry (RSC), Europe’s biggest organization for advancing the chemical sciences, was preparing an article on the 2004 winner of the prestigious Wolf Foundation Prize in Chemistry. It found just the right sound bite to capture the career and personality of the winner, and picked the headline: “Colorful Shades of Gray.”

At age 11, a fascination with colored compounds got Harry Gray interested in chemistry. It led him into research on metalloproteins, and that landmark 1982 demonstration of electron tunneling. “Colorful” also fits the personality of this scientist, who is so well known and widely admired that if you’re talking about photochemistry, metalloprotein chemistry, or a few other fields, and mention “Harry,” everybody just seems to know.

They know him as the Arnold O. Beckman Professor of Chemistry at the California Institute of Technology, founding director of Caltech’s Beckman Institute, and recipient of awards and honors galore: Six national awards from the American Chemical Society, including its highest honor, the Priestley Medal; the National Medal of Science; and the National Academy of Sciences Award in Chemical Sciences.

Gray won the $100,000 Wolf Prize for his best-known research, which the Wolf Foundation described as “pioneering work in bio-inorganic chemistry, unraveling novel principles of structure and long-range electron transfer in proteins. His ingenious chemistry, meticulously executed, has given us a real understanding, for the first time, of a biological process of great significance to life.”

There’s a wonderful technical description of the eight years of hard work that led to the discovery of electron tunneling, or electron transfer, which Gray and Jay R. Winkler published in *Quarterly Reviews of Biophysics* (2003, 36 (3), 341–372). Electron transfer is so critical for life—for the generation of energy in cells, breaking down food, fixing nitrogen, carrying out photosynthesis, and other biological processes—that we can’t help waxing a bit poetic on the process.

Scientists had long known that bits of iron, copper, and other inorganic material inside proteins transfer electrons. Conventional wisdom, however, held that the molecules had to be physically close together to interact. So here’s the dilemma: There are only a handful of metal atoms in proteins, and they are surrounded by thousands of other atoms. Further, the timing has to be precise for processes like energy production and photosynthesis to work. How could the metal atoms maneuver close enough together to interact?

Gray and his colleagues found that the metal atoms don’t move. The electrons do. They established that electrons could tunnel through a protein’s three-dimensional structure, leaping over at least 30 other atoms from one metal atom to another in less than a millionth of a second.

Electron-transfer reactions are so ubiquitous that the discovery promises practical applications in fields ranging from new drug design to energy storage and artificial photosynthesis to computer miniaturization. Numerous winners of the Wolf Prize have gone on to win the Nobel Prize.

Gray and his Caltech associates are now working to apply the techniques developed for studying electron transfer to one of the biggest mysteries about proteins: How do proteins fold into the three-dimensional structures so essential for carrying out their functions? Alzheimer’s disease, Parkinson’s disease, and type-2 diabetes are among the major diseases linked to abnormal protein folding.

He and his group are trying to create a new kind of photosynthesis using metals like ruthenium and rhenium in specially engineered structures that would split water into oxygen and hydrogen fuel instead of reducing carbon dioxide to food and producing oxygen.

Born in Woodburn, Kentucky, Harry B. Gray received a Bachelor of Science degree from Western Kentucky University in 1957 and then held Dow and National Science Foundation (NSF) Fellowships at Northwestern University where he began inorganic chemistry research, which led to his Ph.D. degree in 1960. After an NSF...
postdoctoral fellowship to study electronic structures of metal complexes at the University of Copenhagen in 1960-61, Gray joined Columbia University’s chemistry department and in 1966 moved to Caltech.

He has served on the Council of the National Academy of Sciences (NAS), the governing board of the National Research Council, chair of the NAS Section of Chemistry, and chair of the NSF Advisory Committee for Chemistry. We are proud to add that Harry serves on the scientific advisory board of the Bowling Green State University Center for Photochemical Sciences, which publishes The Spectrum.

Harry and his wife, Shirley, have three children, Vicki, Andrew, and Mike.

The Spectrum: At the George Hammond symposium, you remarked: “I was a decent inorganic chemist, and then I met George.” Could you expand a little on how George influenced you? Did he convert you to photochemistry? Did he lure you away from Columbia?

Gray: George was an enormous influence on me. I was very taken with his ideas for changes in the chemistry curriculum and I also wanted to learn more about photochemistry. I liked his style and approach both to research and teaching. He played a key role in my decision to move to Caltech in 1966. But he did not convert me to photochemistry. Mark Wrighton can be blamed for that!

The Spectrum: You and George co-directed the dissertations of at least two university presidents—Mark Wrighton at Washington University and Greg Geoffrey at Iowa State. Any idea that you were in the midst of future presidents?

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Gray: Both Mark and Greg were incredibly impressive young scientists. I knew they would go far, but I never in my wildest dreams expected them to defect to the dark side!

The Spectrum: What traits in a student get your attention and earn your admiration?

Gray: Love of science, ability to see the humor in an otherwise difficult situation, and hard work! Enthusiasm is the most important trait. If you don’t love it and show it, do something else!

The Spectrum: Is it true that a student put you on track for the electron tunneling work by suggesting that you try to understand how electrons move through proteins? Tell us how it happened.

Gray: Where did you hear that one!!! There were many discussions of electron transfer through proteins in the 1960s and 1970s. No one person “put me on any track!” But it is true that a graduate student, Bob Holwerda, got us started on experiments. I had been doing lots of spectroscopic studies of metalloproteins, including some with Bob, and we had been discussing how electrons might transfer through proteins. One day I think he was sick and tired of hearing me talk about it, so he said, let's get going with kinetics experiments. We picked chromous ion as reductant and several blue copper proteins as oxidants for the first experiments. Our first paper on metalloprotein electron transfer kinetics was published in the Proceedings of the National Academy of Sciences in 1972. So, credit should go to Bob for getting us started in the right direction.

The Spectrum: Please take us back to the point in 1982 when you discovered electron tunneling. What was the experiment, for instance? Did you at first doubt the findings? What steps did you take to verify the results? What was the reaction among members of the group?

Gray: I need to go back to 1974 on this one. We were following up on Bob Holwerda’s kinetics work with chromous as reductant by employing many inorganic oxidants and reductants in combination with heme and copper proteins as redox partners. But these were all bimolecular reactions in solution, and we could never figure out exactly how close the redox partners were when electrons were transferred. I knew that we needed a fixed distance experiment, which would involve attaching one of our metal complexes to the protein redox partner, and then figuring out how to trigger electron
transfer from the attached metal complex to the redox center of the protein. In this intramolecular electron transfer experiment, we could determine just how far an electron could travel through a protein in biologically relevant times. We started to prepare metal-modified proteins after a visit by Henry Taube to Caltech in 1974. We discussed the problem with Taube, and he encouraged us to go for it. We did. Starting with a graduate student, Kathy Yocom, and a visitor from Italy, Milo Bordignon, we attempted to attach ruthenium complexes to a surface methionine on cytochrome c.

The Spectrum: And the reaction didn’t work?

Gray: It did not. So we switched to labeling with Pt(II) complexes, to which we attached Co(III) units that would serve as oxidants in reactions with ferrocytochrome c. We made the labeled cytochrome all right, but we couldn’t get an electron from Fe(II) to Co(III) in any reasonable time.

Of course I’m not sure why we expected this experiment to work because we knew inner sphere barriers for electron transfer to Co(III) are very high, so even at short range the reaction would be slow. At long range, roughly 15 to 20 angstroms, electron transfer would take forever. (I guess it did!) So, we went back to Ru(III) labeling, and Kathy made several derivatives of cytochrome c, and with the help of Roger and Joan Shelton in Walt Schroeder’s lab, characterized a Ru(III)(histidine-33)cytochrome c. With this Ru(III)-cyt c, Jay Winkler and Dan Nocera worked out a flash/quench method to rapidly inject an electron in the Ru(III) site, making it a reductant, Ru(II), thereby triggering electron transfer from Ru(II) to the Fe(III) cytochrome c center some 18 angstroms away. Could this long-range electron transfer be real? We were very excited, of course, with this stunning finding, and we repeated the experiment many times to make sure it was not some artifact. It wasn’t! We had observed long-range electron transfer through a protein on a biologically relevant timescale (milliseconds). In the JACS communication reporting the results, we suggested that the transfer must occur by electron tunneling.

The Spectrum: Who was it that first used the term, “electron tunneling?”

Gray: I’m not sure who first used the term. I do know that Britton Chance suggested that electron tunneling occurred between redox centers in photosynthetic reaction centers in his papers in the 1960s. Our contribution was to demonstrate that electron tunneling can occur over distances in the 15-20 angstrom range in millisecond to microsecond times.

The Spectrum: What, exactly, was the problem in transferring an electron between metal ions over long distances?

Gray: We were faced with the problem that all inorganic chemists know, and I will now share with you that metal ions in water solution don’t transfer electrons very rapidly. There are enormous barriers; we call them reorganization barriers, reorganizing water around highly-charged metal ions. And so it’s actually difficult for Fe$^{2+}$ and Fe$^{3+}$ to transfer an electron in water even when in contact with each other. I did a quick calculation for you just to dramatize this problem. The barrier in water is so high it would take 10^{16} years to get an electron to travel 20 angstroms between metal ions. We don’t have that much time! However, we believed we could reduce 10^{16} years to 1 millisecond by embedding iron ions in a protein, effectively making them the same size, reducing the reorganization barrier. And that’s when I got the team together again and said we’ve got to figure out whether it takes a zillion years or 1 millisecond with...
iron embedded in a protein. And my group said, “Harry, we certainly hope it’s a millisecond, because if it isn’t it’s going to take a long time to get our degrees!”

The Spectrum: Have students—graduate and undergraduate—changed in any significant ways over the years that would allow you to contrast and compare the current generation with past generations?

Gray: The good students haven’t changed in their approach to science. They are excited about science and willing to work hard to achieve their goals. But I would venture that in my time students have become more conservative in many ways. I’m not sure why. Maybe they are worried about getting jobs.

The Spectrum: Arnold Beckman already had been a great financial friend of Caltech when you approached him about funding the institute. Were you reluctant to approach him again? How did you make the approach? What was your relationship with him?

Gray: Arnold Beckman was a good friend. I didn’t approach him about a gift. We had lots of discussions about the future of science and Caltech. Both the Beckman Laboratory of Chemical Synthesis and the Beckman Institute emerged from these discussions. Arnold Beckman did not respond to anyone who just asked him for money. He was a hands on scientist who loved to discuss promising projects. He pointed the way.

The Spectrum: You’ve been quite successful at fund raising. The Beckman gift, for instance, hinged on your raising $10 million—$20 million independently. What advice do you have for chemists who are trying to raise money in terms of identifying potential donors, making the presentation, and following up?

Gray: My advice is to not do it in that order. Make sure you really believe in a project first. Are you passionate? If you are, then discuss your ideas with many people, including potential donors. See who is interested in the project. Then make presentations to a selected group of interested parties. Don’t take no for an answer. Keep at it, even if it takes years. I didn’t raise the money for the Beckman Institute overnight. It was a five-year adventure involving many friends and donors, of course with the lead gift coming from Dr. Beckman. A Caltech trustee and very good friend, Jim Glanville, played a leading role in raising the matching funds. I worked with him very closely for several years. And many other colleagues made important contributions.

The Spectrum: The institute certainly is big chemistry at its biggest. Do you have any concerns that small chemistry—chemistry in small departments without a strong funding base—may have difficulty surviving in the future?

Gray: You have hit upon one of my biggest concerns. I worry that small departments may not be able to keep up. Instrumentation is so expensive. I don’t have an answer.

The Spectrum: A number of chemistry departments in the U.K. are merging and consolidating for that reason. Is that an option that should get more attention in the U.S.?

Gray: We are in better shape than the U.K. We have many great small colleges where chemistry is done well. There may be some mergers, but I suspect chemistry departments will exist for some time to come. Chemistry is the central science. Most of the most pressing problems facing us today will require chemistry research to find solutions. Energy is one. Health is another. And on and on. Chemistry is not going to go away! We may change names from time to time (nano is now very popular!), but the science is the same.

The Spectrum: A wonderful talk that you’ve presented in the past—Clean Fuel from Solar Photochemistry, argues, in effect, that photochemists can save the Earth during the 21st Century. What’s the challenge?

Gray: We’ve got to stop burning hydrocarbons. I’ve been saying this for 20 years, and I’ve talked myself into really believing it. We’ve got to stop burning hydrocarbons for energy and producing carbon dioxide in the process. This is a very poor use of hydrocarbons; we need them for materials. Most people have been talking about global warming as the reason that we’ve got to stop burning them, but that’s only part of the story. As Mendeleev said right after he invented the Periodic Table, it’s crazy—burning hydrocarbons is just like burning $100 bills. There’s no doubt that in the next 20 or 30 years the production of oil is going to start dropping and we’re going to be faced with an immense energy crisis. Some of you will be around to see that crisis if we don’t do something about it. We really have to get smarter and use clean fuels. We have to replace dirty fuels with clean fuels that don’t contribute to global warming; the clean fuels are
electrons, or electricity if you like, and hydrogen. There’s no doubt that we’ve got to convert this planet to electricity and hydrogen, and we only have two real choices. You can talk about windmills all you want, you can talk about geothermal until you’re blue in the face, but I could care less because we’ve only got two real choices: one is nuclear and the other one is solar. And, speaking tongue-in-cheek, since we’re all chemists—most of us are chemists—the one thing we have in common is that we enjoy beating physicists. I’m the captain of the team, and I’m telling you right now that we’ve got to win the game this time. They’ve got nuclear—we’ve got solar.

The Spectrum: Have we reached a kind of break point in scientific knowledge about solar energy conversion, where big infusions of research money would break through the barriers, and quickly yield an efficient, durable, water-splitting device? Suppose DOE provided $2 billion or $5 billion annually for five years for solar photochemistry?

Gray: Certainly more funds for fundamental research in photochemistry would help. The field is under funded at the present time, especially if you consider the promise of solar energy conversion. At Caltech my colleagues Nate Lewis, Harry Atwater, and Sossina Haile are leading an effort that we call “Powering the Planet”. You can get lots of information about this initiative by sending an email to Nate Lewis.

The Spectrum: What can chemists be doing to speed things up?

Gray: In my talks I tell them to go back to their classrooms and recruit the very best students to go into photochemistry. We need them to solve these problems. We’ve got to keep talking it up, we’ve got to keep working on it. If we are successful, in 20 years, we will be driving cars that don’t pollute; what is more, we also may have big power stations that don’t pollute. We’ll be running this planet with chemistry that’s almost as good as the chemistry nature developed so many years ago.

The Spectrum: At ACS national meetings, and other conferences, one is struck by the graying of the chemistry population. A sizable proportion of chemists and photochemists are approaching retirement age. Do we have the right people in the pipeline to replace them?

Gray: There are lots of truly outstanding young investigators. My advice is to go to the undergraduate chemistry poster session at ACS national meetings. No gray hair there!

Harry with Sina Yeganeh, an undergraduate student (and recent Caltech grad) who worked in Gray’s group on photo-sensitized nanocrystalline TiO$_2$. Courtesy of Caltech

The Spectrum: Controversies are a central part of science, and the fallout often is beneficial. Some, however, involve personalities that clash. Woodward-Hoffmann is an obvious example. What’s your view on personality clashes like that?

Gray: Science is a very human undertaking. There will be many differences of opinions. Makes for fun discussions. If we didn’t have them, science would be boring.

The Spectrum: The collaboration between your group and George Hammond’s group was very fruitful. Are there any “dos” and “don’ts” for a successful collaboration that you could share with us?

Gray: It was a natural collaboration. We really liked working together. It won’t work if you don’t get along.

The Spectrum: The Royal Society of Chemistry once termed Harry Gray “one of the most colorful characters in chemistry,” and that leads to several questions. Tell us how your interest in colors as a kid got you hooked on chemistry as a career.

Gray: I was fascinated with colorful compounds at an early age. I wanted to know what the colors were due to.
finally found out when I studied with Fred Basolo and Ralph Pearson at Northwestern.

**The Spectrum:** Are those stories about your childhood experiments with fuming sulfuric acid true?

**Gray:** I liked big bottles of sulfuric and nitric acid, which I managed to order from a supply company in Chicago. Of course, they never knew I was only 11 years old. Now I look back and realize that it was pretty dangerous. I liked to run reactions, and I poured the acid on colored cloth and all kinds of different things.

**The Spectrum:** Who were your most memorable chemistry teachers?

**Gray:** Ward Sumpter and Glenn Dooley at Western Kentucky University; Fred Basolo and Ralph Pearson at Northwestern. All four inspired me. I owe a great debt to each of them.

**The Spectrum:** Everybody seems to enjoy being with you. We understand that being a live wire date to your undergrad years at WKU, where you liked to stir up a little excitement now and then with a group called the 13’ers.

**Gray:** We were just a fun bunch. Lots of dances and parties. Helped me get through lots of boring classes in school. I learned that social life is important. I have spent lots of time with my research group over the years. We have fun together. And we work hard at science together. It is not everyone’s cup of tea. But it is mine!

**The Spectrum:** How do you keep all the honors and prizes in perspective, so they don’t go to your head?

**Gray:** I have been very lucky with prizes. I have enjoyed all of them. But I love science more than prizes. There are many questions I would like to answer. The most fun I have is in planning new experiments with my group. Prizes don’t solve problems. People do.

**The Spectrum:** Mention “photochemistry” or “photochemical sciences” to non-scientists, and you can see the eyes glaze over. The mindset is, “I will never understand this.” Maybe photochemistry needs a new name?

**Gray:** I don’t agree. I have found that people are fascinated by the word “photochemistry”. I have had many discussions with people about photochemistry. I expect to have many more.

**The Spectrum:** What's the answer to the most important question you wished we had asked?

**Gray:** I have been married to a wonderful woman—Dr. Shirley Gray, a mathematics professor at the California State University in Los Angeles—for almost 48 years. We have three wonderful children (Vicki, Andy, and Mike) and three grandchildren. Our grandchildren, Sarah, Alex, and Anna, think I’m much too cool to be “grandpa”. They call me “grandoods!!”

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*Some of Professor Gray’s teaching methods have been unorthodox, but very successful. Here, assisted by graduate student George Rossman—now a faculty member at Caltech, Professor Gray makes a point in Chem 1.*

*Courtesy of Brian Leigh, Caltech*
The 19th century, when Grotthuss still saw light as a line of elements of Aether with undetectable separation\cite{1} and Draper\cite{2} explained that photochemical reactions depended on compounds sensitive to incident radiation, came to a close with a paradigm shift.\cite{3} This accompanied, or was driven, by the tremendous changes occurring throughout society at the turn of the 20th century. Even rural areas of America were being electrified and the light bulb was soon to replace the kerosene lantern in houses across the country. Telephones appeared, the auto arrived and little towns were made safer by community water supplies. The last years of the 19th century also saw enormous intellectual resources expended in German research institutes\cite{4} that were funded collaboratively by industry and the government and directed to develop, among other things, new ways to produce electric lighting. The emission of light from heated so-called “black bodies” represented one possibility for converting electricity into light that was studied in detail by physicists and engineers at the PTR\cite{5} in Berlin of which Werner von Siemens was a member of the Board of Directors. Wien’s\cite{6} equation, and experiments on emissions from black bodies by Fringsheim, Lummer and especially Rubens triggered Planck’s law which appeared in December 1900.\cite{7} Planck defined the natural constant $h$ ($h = 6.55 \times 10^{-27}$ erg sec) and used equation 1 to successfully model the recorded spectra of light emitted from black bodies. The energy $E$ is composed of a specific number of finite, equal parts the number of which can be calculated by multiplying the frequency, $ν$, by the constant $h$ which yields the energy element $e$ (erg) of the oscillator. Planck termed these parts *quant* (meaning “how much” in Latin).

$$E = \frac{8πhν^3}{c^3}$$

(1)

A little later Einstein, secluded in Bern, worked on physics in the evening following a day at the patent office. Perhaps beneficially he was not tied to any of the Berlin groups, and was, therefore, unaware of certain salient papers in the field. The first four of four papers in 1905 on the *photoelectric effect* was just one that established his legacy and the work for which he was awarded the Nobel Prize. Though Einstein did not use the word *photon* (that insight goes to Gilbert Newton Lewis),\cite{8} he did postulate that light was discontinuous and suggested that light is comprised of indivisible moving energy quanta that can only be absorbed or created in discrete units. Einstein based this on several specific examples other than black body emissions such as the creation of cathode rays by UV light.\cite{9} He argues that a view in which light was continuous had to be incorrect because it contradicts the observation of the photoelectric effect\cite{10} and he goes on to theorize that the photoelectric effect is triggered by light quanta impinging on a material surface where the energy of said light quanta are at least partially transformed into electrons with a kinetic energy $E_{kin}$ (equation 2). If the energy of each *quant* of incident radiation is independently transferred to an electron, then the velocity of the electrons emitted is independent of the intensity of the incident radiation. On the other hand, the number of ejected electrons is proportional to the intensity of the incident light.

$$E_{kin} = \frac{R}{N} βν - P$$

(2)

By 1908 Johannes Stark, whose work was overlooked for a while, had reported the first application of the quantum hypothesis to photochemistry.\cite{11} He defined that a direct photochemical reaction consists of first a chemical absorption (light-triggered ionization) reaction and second a light independent reaction. Stark proposed that the valence electrons of unsaturated and carbonyl groups in organic compounds are responsible for UV absorption. In his third law of photochemical reactions, Stark reports proportionality between the intensity of the effective light and the conversion of the photochemically transformed compound in a unit time—an obvious recognition of what became quantum yield.

Einstein legitimately surfaced in the cult that better enabled scientific communication of the day at the first Solvay Conference in 1911.\cite{12} Walther Nernst had fueled Ernest Solvay’s interest in the *light debate* and the latter, a Belgian industrialist whose process produced 90% of the world’s supply of soda by then, paid the travel/subsistence/honoraria that brought 23 leading physicists to Brussels for a scientific conference concerned with “Radiation theory and the quanta”.\cite{13} This conference gave birth to the most important experiments on the nature of light and its interactions with matter that lasted over the next decade and eventually confirmed Einstein’s postulates. The concept of the quantum yield developed as a result.

In a 1912 paper from the Karl-Ferdinand University in Prague that followed the October Solvay Conference, Einstein\cite{14} clarified the equivalence law with the further assumptions that “the decomposition of a molecule occurs as if the other molecules were not present” and that the

**Brigitte Wex & D. C. Neckers**

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absorbed light. The Planck’s energy elements contained in the absorbed radia
cess predicted an estimation of the upper yield of the primary 
chemistry” [sic] was told by Einstein that he (the latter) thought that the number of primary photochemical processes is equivalent to the number of wavelength-specific Planck’s energy elements contained in the absorbed radiation. Using equations of the “Einsteinchen Satz” and the “Wien-Planckschen Strahlungsgesetz”, Warburg thus calculated that the theoretical yield of the primary photochemical process of the ozonolysis of oxygen (3 O → 2 O₂) at 209 nm to be 50% and in later experiments measured a yield of 46% based on the number of “photons” absorbed. This was the first literature example in which the quantum hypothesis predicted an estimation of the upper yield of the primary photochemical process.

Warburg’s observations on the photochemical formation of ozone lead to the question “is it the frequency of the incident radiation or the frequency of the absorbing molecule (‘Eigenfrequenz’) that is responsible for the amount of energy absorbed per molecule decomposed?”. Einstein had postulated that it is the frequency of the incident radiation and it is he who first explains this, in his answer to Warburg’s questions. On the last page of his 1912 paper, he indicated, for the first time, that the energy carried by each light quantum is e = hv. Specifically, he also deduced that the absorbed energy per molecular decomposition is only dependent on the frequency of incident radiation.

The Bohr model of the atom (1913), familiar to every high school student, caused Einstein to deduce a rationalization for the energy changes resulting from the emission of an electron from an atom. This further clarified what he meant by a photochemical event and suggested a way to at least partially explain the resulting atomic spectra.

An early theory of photochemical kinetics, that of Bodenstein, viewed the absorption process as a photoelectric process in which the first step is the scission of the absorbing molecule into the “positiven Rest” and electrons. The immediate reactions of the “positiven Rest” were termed “primary light reactions”, while the reactions of the atom-like electrons, which are dependent on other reagents and reaction conditions, were termed “light reactions” (equation 3).

\[ R \xrightarrow{hv} R^* + e^- \]

\[ \text{R} \xleftarrow{} \text{primary photochemical reactions} \]

\[ e^- \xrightarrow{} \text{light reactions} \]

Bodenstein calculated the energy (cal) of the absorbed radiation and the energy (cal) released from the decompositions of the photoproducts as two completely independent processes dismissing Warburg’s attempt of 1912. Post scriptum Bodenstein admits to have missed the work of Lenard and Ramsauer, which contradicts the ionization event in chlorine and ozone, though he continued to insist on the integrity of his theory.

G. N. Lewis (“The Atom and The Molecule”, 1916) elaborated on the classification of polar and non-polar compounds and on the valence bonding of compounds. In a separate paragraph on the color, Lewis describes that if a molecule is exposed to light of a frequency close to that of the molecule, the energy of the light is absorbed by setting the molecule in vibration. Compounds appear colorless if they do not absorb in the visible range and if their electrons are tightly bound. The molecular compound, the more loosely held their electrons, the more shifted the absorption to the violet/blue and yellow appearance of the compound. If the absorption of the compounds is shifted to the visible range, then the compounds exhibit different colors, such as in the case of dyes. The extreme case is that of an alkali metal that is dissolved in liquid ammonia, which has a maximum absorption in the ultra-red and appears blue.

Otto Stern was an Einstein assistant first in Prague and later in Zurich. In 1919 he and Volmer analyzed the lifetime of fluorescence of iodine vapors mixed with nitrogen and postulated that fluorescence results from the same molecular process as light emission after thermal and electrical excitation. They calculated the lifetime of iodine fluorescence to be \(\tau = 2 \times 10^{-8} \text{ s}\). Since Stokes’ law applied, fluorescence was classified as a quantum effect. In a molecule capable of fluorescence, an electron is moving in a path of an enlarged radius compared to the ground state molecule. The quantum theory falls short on predicting the mean lifetime of excited species, therefore, Stern and Volmer turned back to classical theory to determine the lifetime of the molecules.

Warburg was credited with defining an effective photochemical equivalent as the number of moles decomposed or converted by or through the absorption of 1 g-cal of
radiation, defining the unit \( \varphi \) as an experimental number that expresses a combination of all the primary and secondary processes leading to overall production of a product. \( \varphi \) is the indicated photochemical equivalent as expressed in the number of excited molecules in moles per absorption of 1 g-cal. The qualitative ratio (Güteverhältnis) \( \gamma \), is \( \gamma = \varphi / \rho \). Warburg insists that the law of photochemical equivalence has limited validity, especially in cases where the excited molecules do not undergo photochemical reactions.

Stern and Volmer\(^{35} \) analyzed the equivalent law using the Bohr-Einstein model of light absorption. Citing the work of Warburg, Nernst and Wolf, they rejected the hypothesis that the scission of the irradiated molecule is the primary photoreaction using iodine as an example. In fact, Bohr’s proposal that the molecules undergo a change in the quantum state upon absorption of a quant [sic] with energy \( h\nu \), is the primary photochemical process. The reactions of these primary photochemical products lead to the known products. Stern and Volmer verified that the published experiments do not contradict Bohr’s model.

By this time, Einstein’s work on the nature of light had been sufficiently confirmed so that in 1921 he was awarded the Nobel prize in physics. His presentation of the Nobel lecture, however, was delayed until August 1922 because controversy remained about his theories. He was employed in a German research institute and the vestiges of World War I still hung heavily. However, the nature of light was now recognized,\(^{36} \) and it was accepted sufficiently to have commanded the world’s most important prize in physics.\(^{32} \)

Winter\(^{33} \) published a convenient method to determine absorption spectra of compounds in the UV region in 1923 while Bowen verified the equivalence law using solutions of chlorine oxides (\( \text{ClO}_2, \text{Cl}_2\text{O} \)) in carbon tetrachloride and discussed possible values of quantum yields.\(^{34} \) In his second paper on photochemical decomposition of gaseous dichlorine monoxide, he reported a quantum yield of \( \geq 2 \),\(^{35} \) though the purity of these gaseous reactants tainted his results. Bodenstein and Kistiakowski,\(^{36} \) who developed a method to purify chlorine monoxide, measured reaction kinetics as well as quantum yields for its decomposition in the gas phase. The quantum yield of chlorine monoxide decomposition was again measured as 2 and found independent of whether the reaction is stimulated through direct irradiation or sensitized with chlorine. These were nearly the first examples of which we are aware that overall chemical processes were included in the resulting quantum yields of product production.

Warburg exemplified and declared the quantum hypothesis a complete victory for the cases in which the equivalent law is applicable. If the quantum hypothesis is not applicable, the law delivers an upper limit for such reactions that is based on the primary photo processes. For those cases in which the quantum hypothesis is not applicable, Warburg closed by saying that the properties of “beanspruchten”, that is, excited molecules under application of Bohr’s model, such as lifetime, should be studied to find solutions.\(^{37} \) Warburg suggested further investigation of the interaction of light with molecules, especially with respect to the nature (in eine höhere Quantenbahn befördert) and lifetime (Verweilzeit) of the excited states.

Gas phase experiments where manometry could be used to follow chemical change with molecules (compounds) of high energy content which might be thought to dissociate in a single step, were an early target of study. A significant advantage that developed as a result was that photochemical events were more easily controlled than runaway thermal reactions. Hydrazoic acid is, as most know, highly explosive. Arnold Beckman found no evidence that its photochemical reactivity generated an uncontrolled chain reaction even at pressures as high as 130 mm Hg and even though the irradiating wavelengths were in the deep UV.\(^{38} \) There is no evidence that, if Beckman knew the word photon, he used it regularly because it does not appear in his Ph.D. thesis.\(^{39} \)

Ramsperger\(^{40} \) investigated the photochemical decomposition of azomethane using the mercury lines at 366 nm. Independent on temperature and pressure, he also observed a quantum yield of 2 for all the reactions. He postulated that “the energy transfer of the product (high in energy) of the first decomposition to a second molecule of azomethane causes the decomposition of the second molecule”.

In a succinct paper in 1929, Bodenstein and Wagner\(^{31} \) attempted to simplify the kinetic equations of photochemical reactions by defining \( 6.06 \times 10^{23} \) quanta as one light equivalent. This is the first appearance of the term Einstein as the defined unit of a mole of photons.

The measurement of quantum yields for photochemical reactions of various kinds was an extraordinarily arduous process. In the first place there were no UV spectrometers, so spectra, had to be measured point by point. Secondly, there were no commercial light sources. Xenon bulbs and mercury resonance lamps were still experimental. The commercial photomultiplier tube also had not appeared. In the third place, there were few ways to follow quantitatively chemical processes. One of the best ways was to follow pressure change, so many of the early measurements were made in the gas phase using manometry. Beckman, working as a Ph.D. student with Roscoe Dickenson at Caltech,\(^{39} \) studied the photochemical decomposition of hydrogen azide...
(hydrazoic acid) to hydrazine\(^4\) and ammonia.\(^3\) Two other products were nitrogen and hydrogen. He followed total pressure and certain products individually only with gas phase techniques.

Beckman must have been an extraordinary experimentalist.\(^4\) Some of the lengths to which he went to make the measurements are indicated below. His first vacuum line (Figure 1) included a quartz fiber manometer, H, he had modified himself in order to measure the absolute concentrations of hydrogen and nitrogen. Hydrazoic acid\(^3\) was introduced from A and purified by freezing it out with liquid air at P. Once non-condensed contaminants (hydrogen and nitrogen) had been pumped off, it was admitted to the quartz cylinder marked N, 2.5 cm in diameter and 4.8 cm long that had flat windows on each end. The pressure of HN\(_3\) in N was measured by a gauge, M. Following irradiation, liquid air was again applied at P and the pressure of the non-condensed gases measured with the McLeod gauge. The mole fraction of hydrogen in these gases was measured with the quartz fiber gauge H.\(^3\)

Beckman used an aluminum electrode light source because its emissions could be controlled by passing the light through a monochromator, and the lines were approximately where hydrazoic acid absorbed. The light source was a spark produced between aluminum electrodes placed close to a monochromator. The flux of radiation was measured by vacuum thermocouple, Q, also constructed by the experimenter and described in detail in the paper.

Hydrazoic acid is transparent until about 220 nm and then shows strong lines at 199, 194, 186 and 185 nms. The absorption spectrum of HN\(_3\) was measured by hand. This consisted of photographing a series of exposures of the radiation from the aluminum spark on the same photographic plate. A second photographic plate was imaged as a standard. In one-half of the cases the radiation was passed through the reaction cell empty. In the remaining cases the emission from the spark was passed through the cell with varying and increasing measured pressures of HN\(_3\). The plates were calibrated for response with wire screens, and then the experimental plate photometered using the microphotometer of the Mount Wilson Observatory. The spark emission at 199 nm was isolated and used for the irradiation experiments, so the equivalent of the molar extinction coefficient at that wavelength was measured in a number of successive experiments. To measure the absorption coefficients at other wavelengths, an absorption at that wavelength was measured and this was bracketed by the absorptions of two of the wire screens. From the known absorption values of the screens, and known concentrations, the molar extinction coefficient could be calculated. The spectrum of hydrazoic acid measured this way is shown in Figure 2.

Is it any wonder that in 1940 Beckman invented an absorption spectrometer and made particularly sure that it was useful in the UV?\(^6\)

Quantum yields of HN\(_3\) disappearance measured this way averaged about 3.0 with approximately 10% of the non-condensable product being hydrogen and the remainder being nitrogen. Yields were constant up to about 50 mm at which point they began to increase significantly presumably because hydrazoic acid decomposition began to follow chain reaction kinetics.

Beckman wrote a possible mechanism for the initial decomposition in which the primary step is conversion to HN\(_3\) and molecular nitrogen. He pointed out that even at 1950 Å the energy of the light absorbed is insufficient to produce individual atoms of N and H.
Beckman and Dickenson stated, “we regard the ad hoc invention of intermediate compounds as a pastime usually indulged in more for entertainment than for profit.” So much for a lot of the work that has occupied Beckman spectrometers over the last 70+ years!

The first chemical actinometers of consequence were those using uranyl oxalate and developed practically and theoretically by Leighton and Forbes. In the experiment, a 0.01 M solution of uranyl sulfate in 0.05 M oxalic acid was used as the standard. The quantum yield of the reduction of \( \text{UO}_2^2+ \) to \( \text{UO}_2^- \) (or \( \text{H}_2\text{C}_2\text{O}_4^- \)) varies from 0.6 at 254 nm to 0.58 at 435 nm dipping to a minimum of 0.49 at 366 nm. Because of this variation it was later deemed inconvenient to use and eventually completely replaced by actinometers that used potassium ferrioxalate. The latter was more versatile over a wide range of wavelengths, easy to use and both sensitive and precise. IUPAC published a report on the various methods of chemical actinometry quite recently.

By 1938, Farrington Daniels was able to assemble a vast table of experimental data on quantum yields and explained that the deactivation of excited states by competing processes lead to a decrease in quantum yield below unity, while continuing reactions can result in a quantum yield of higher than unity. “In the early development of quantitative photochemistry, it was believed by some that the Einstein relation would apply in many cases not only to the primary process of photoexcitation but also to the overall reaction as well. Quantum yields were summarized with the purpose of testing this hypothesis. Any hope of simplicity in chemical kinetics disappeared long ago.”

The consequence of Beckman’s work, and the work of many others that led to Farrington Daniels’ extensive review in 1938 and the extraordinary compendium in English written in 1941, which Francis Heyroth said to be a second edition of “The Chemistry of Ultraviolet Rays”, essentially brought the boom initial period of photochemistry to a leveling off point that lasted until new experimental methods like spectrometers and chromatographs became commercial in the mid-1950s. By that time Beckman was well on his way to building the fortune that became his legacy, and the world of photoscience was able to use the fruits of his student labors in creative activity around the world.

Suffice it to say, chemical and physical measurements of quantum yields developed from these simple beginnings.

It is appropriate, in this the 100th year anniversary of Einstein’s publication on the photoelectric effect, to look at the history and reflect on it. Careful measurements over many, many years have brought quantitative photoscience to the stage it is today. And in spite of Beckman’s exhortation that mechanism studies are more for entertainment than for anything else, have kept quite a few chemists and physicists occupied for many years. We propose they continue to do so well into the 21st century.

References
10. In 1905, Phillip Lenard earned the Nobel Prize for his research work on Cathode Rays. Lenard proved that electrons were ejected when ultraviolet light impinged

11. Nobel Prize in 1921+.

12. \( \beta \) from Planck's equation; \( \beta = 4.866 \times 10^{-11} \); \( R = \) gas constant; \( N = \) number of real molecules; \( v = \) frequency of oscillator; \( P = \) work required for the release of an electron from the material.


14. He made a strong impression at the conference and three in attendance, Madame Curie, Henry Poincare and Max Planck, wrote letters to the ETH faculty in Zurich in 1911/12 that caused a job offer and eventual Professorship in higher mathematics and theoretical physics. This appointment was in response to a job offer from Utrecht (Lorentz/Omnes) which Einstein subsequently declined. Arnold Sommerfeld, who was also at the conference, wrote a strong letter of support later. ETH-Zurich Bibliotech archiv und Nachlässe (http://www.ethbib.ethz.ch/dachs-online/einstein/SR_Missiven_1912_1_S26bis32.pdf).

15. Dardo, M. In Nobel Laureates and Twentieth-Century Physics. Cambridge University Press: Cambridge, 2004; pp 83-84 and references therein. Einstein, whose first professorial position was in Prague, only completed negotiations to return to Zurich to take up the position in theoretical physics at the university in August 1912.


19. There are many biographies of Einstein and in this year many more can be expected. Occasionally, we have used Clark, R. W. Einstein, The Life and Times. World Publishing: New York, 1971.


22. Einstein actually used the Greek epsilon (\( \epsilon \)) not the current E or \( \Delta E \).

23. Einstein moved from Prague to Zurich in August 1912. The official appointment letter from Rudolph Gnehm, President of ETH, to Einstein is in Gnehm’s archives at the ETH library. Though physicists like Madame Curie and others were ecstatic in supporting the appointment, there seemed some contention about it at the ETH as noted in letters from physiologist Herman Zangger, also in the archives.


25. Pauling says “Bohr developed the simple theory of the hydrogen atom and expanded it over the next 12 years (from 1913 to 1925) and refined it into our present theory of atomic structure”... “Knowledge of electronic structure is important to the student of chemistry, and the mathematical theory of quantum mechanics is not suited to the study of a beginning student.” Pauling, L. College Chemistry, 2nd ed.; W. H. Freeman: New York, 1955.


31. Even Planck remained skeptical until experiments completed around 1915 convinced him.

32. The story is that Einstein’s first wife, Mileva, requested Einstein’s Nobel winnings as part of their divorce settlement. That was part of the settlement when the divorce became official in February 1919.


37. Warburg, E. Naturwiss. 1924, 47, 1058.


44. A picture of Beckman’s photochemistry vacuum line can be found at http://www.chemheritage.org/explore/Beckman/beckman.htm.


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rotaxane molecular shuttles: light-driven motor molecules

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The concept of a molecular machine has a strong appeal to the imagination of scientists and engineers. It is a translation into chemical terms of the bold suggestions of Feynman in his famous 1959 lecture. Several elements of machine-like operation have in the meantime been realized, and this article will focus on one of them. However, the construction of artificial molecular systems capable of moving individual objects of a nanometer size within a fixed frame of reference is still beyond the capabilities of synthetic chemistry. In this arena, chemists have been (temporarily?) overtaken by biologists, physicists and engineers who exploited the capabilities of existing motor proteins, combined with surface chemistry, photochemistry (for controlled delivery of ATP as an energy source), and chemistry and spectroscopy of fluorescent dyes as labels for visualization. Our own motivation to work in the field of synthetic motor molecules is fueled by a number of challenges: to design molecular systems achieving photoinduced motor-like activity at a length scale of nanometers (one or two orders of magnitude smaller than that of motor proteins) and to fundamentally understand their working mechanism at a chemical, molecular level. An important target is to find useful applications of such systems. Progress has been made in applications in the field of molecular electronics, but there should also be interesting possibilities within a chemical context, for example, in switching catalytic activity by moving groups together or apart, or in controlled delivery.

Rotaxane Molecular Shuttles

Mechanically interlocked architectures such as catenanes and rotaxanes have a feature which makes them a particularly attractive playground for studying and manipulating intermolecular interactions. The local interactions which determine the orientation of the components with respect to each other do not need to be very strong because the components are forced to stay together by the mechanical bond. Typical intercomponent interaction energies of the order of 10-20 kcal/mol are used to assemble the systems. These are small enough to allow reasonably rapid dynamics, but would not prevent dissociation at the low concentrations, which we like to use for optical spectroscopic studies. We will focus on a type of molecular shuttle built up by a condensation reaction forming macrocycle 1 around a template typically containing a diamide with two bulky stopper groups as exemplified in “thread” 2 (Figure 1). In the assembly 3, the preferred co-conformation is the one with the macrocyclic ring hydrogen bonded to the succinamide station. One of the stoppers is an aromatic imide, which is a much poorer hydrogen bond acceptor than the diamide.

Figure 1. Molecular structures of macrocycle 1, thread 2, and rotaxane 3.

A reversible change of the co-conformational state of 3 can be achieved by reducing the naphthalimide to its radical anion and oxidizing it back to the neutral form (Figure 2). The macrocycle will move from the succinamide to the naphthalimide station upon reduction and back upon re-oxidation. This reversible translational motion, often denoted “shuttling”, is an elementary motion of a mechanical machine.

Reduction of the naphthalimide can be accomplished electrochemically but also by means of photochemistry. The latter has the advantage that time-resolved spectroscopic studies can be applied. In principle, electrochemical experiments using ultra-microelectrodes can reach nanoseconds time resolution, but in our opinion the use of time-resolved optical spectroscopy is more straightforward for deriving kinetic information on the shuttling process.

Formation of the naphthalimide radical anion is accomplished by a reaction of the excited naphthalimide chromophore with an electron donor. The singlet excited state is relatively short-lived (1.6 ns in acetonitrile) and singlet radical ion pairs undergo rapid charge recombination to form the ground state in competition with ion pair separation. We therefore considered it advantageous to use a strong electron donor (1,4-diazabicyclooctane (DABCO)) in a millimolar concentration at which it does not intercept much of the excited singlet state, but reacts efficiently with the chromophore in its long-lived triplet state. An overall quantum efficiency of formation of the radical anion of 20-30% is achieved in this way. By using an electron donor that gives a kinetically stable radical cation, we ensure that the ions decay almost exclusively by bimolecular charge recombination. In this way a time window of several hundred microseconds is created for spectroscopic
observation of the radical ions after which the solution can be excited again.

The naphthalimide radical anion is characterized by a strong and narrow absorption band near 420 nm, in addition to weaker and broader bands at long wavelengths. The DABCO radical cation has a weak absorption band near 480 nm. Interestingly, in the rotaxane 3 the absorption band of the radical anion is shifted about 5 nm to shorter wavelengths, apparently because the ground state of the anion is stabilized by hydrogen bonding more than the resonant excited state. In flash photolysis experiments on rotaxane 3, the radical anion absorption band is seen to shift in time from an initial position similar to that in thread 2 to a wavelength similar to that observed in spectroelectrochemical measurements of the rotaxane (Figures 3 and 4).

Interestingly, it can be shown that under the assumption that the band is composed of two shifted bands with the same shape and intensity, the position of the band maximum is a direct measure of the relative populations of the two species present. Thus we can quantitatively monitor the shuttling process without having to know the absolute concentration of the radical ions. Because the shuttling is complete within 10–20 μs, as discussed below, its efficiency is nearly 100%.
Solvent and Temperature Effects on the Rate of Shuttling

The rate of the shuttling process was measured in acetonitrile, propionitrile and in butyronitrile over a range of temperatures. It was found to decrease with solvent polarity, from $1.35 \times 10^6$ s$^{-1}$ at room temperature in acetonitrile to $0.45 \times 10^6$ s$^{-1}$ in propionitrile and $0.21 \times 10^6$ s$^{-1}$ in butyronitrile, and with temperature. An Arrhenius activation energy of 8.3 kcal/mol was derived in the latter solvent. The shuttling rates in this system are the fastest that have been determined in rotaxane architectures to date.

These results are consistent with a mechanism in which the breaking of hydrogen bonds is the rate-determining step. Because of the important contribution of electrostatic interaction to the strengths of hydrogen bonds, they are weaker in the more polar acetonitrile than in propionitrile and butyronitrile. The activation energy is somewhat lower than that determined for hydrogen bond breaking processes such as the degenerate shuttling in a system with two similar stations or the activation energy for the pirouetting motion in 3, both measured in less polar solvents.

For the application of molecular machines, it is important to evaluate their ability to move under a variety of conditions. The liquid state, in which such systems are primarily studied, is not likely to be suitable for device applications. Stoddart, Heath and their coworkers have used rotaxanes in tunnel junctions in which an electrically induced mechanical movement is used to generate a metastable readable state. They recently measured the activation energies for the decay of this metastable co-conformation in acetonitrile, in an LB-film and in a polymer electrolyte gel. We have initiated a systematic evaluation of the effect of viscosity on the rates of shuttling in 3 by studying the shuttling rates in solutions of poly(methacrylonitrile) in acetonitrile. Using optical probes it could be shown that the polarity of such solutions does not differ much from that of the neat solvent, while the viscosity increases by more than 6 orders of magnitude in going from acetonitrile to a solution containing 33% of polymer. Under these conditions the spectral shift of the radical anion absorption band could no longer be observed, indicating that the bimolecular electron transfer process used to generate the transient radical ions still works but shuttling is frozen out. Remarkably, in a 23% polymer solution, which is 33,000 times more viscous, the rate is only four times smaller than in acetonitrile. Stoddart’s rotaxane, which is a much slower molecular switch than 3 in liquid solution, is slowed down by a factor of about 40 in a polymer matrix compared to liquid solution which is estimated to be $10^4$ times less viscous.

Immobilization on a Surface

As a first step from solution towards a more ordered environment we, like other groups, have turned to immobilization of rotaxanes on surfaces. A flexible approach is one in which alkanethiol carboxylic acids are used to form a self-assembled monolayer (SAM) on gold, to which rotaxanes are attached via hydrogen bonding. For that purpose, the macrocycle in 3 was replaced by one containing two pyridine rings, yielding rotaxane 4 (Figure 5).

Rotaxane 4 in this way forms rather densely packed monolayers on top of the carboxylic acid-terminated alkanethiol monolayer. Because the transient absorption technique used to monitor the shuttling cannot be applied to the small quantity of material in a monolayer, we only studied the fluorescence of 4 on the SAM. The fluorescence emission and excitation spectra were found to be substantially red-shifted compared to the acetonitrile solution. In trifluoroethanol, however, the naphthalimide chromophore is hydrogen-bonded to the solvent, which also causes a red shift. Therefore, we supposed that on the SAM not only the pyridine but also the imide is hydrogen bonded.

The effect of hydrogen bonding on the fluorescence spectra of aromatic imides can potentially be exploited to monitor the presence or absence of a macrocycle near the chromophore. This should allow us to study rotaxane shuttling using fluorescence methods.

Mechanism of the Shuttling Process

A machine is a device that can exert a force. Can a molecule really do that? In principle, the answer is yes. An example is a molecule such as Z-stilbene, which from its relaxed ground state structure is excited to a point on the
The excitation state potential energy surface where a large energy gradient exists which puts the atoms into motion. For our rotaxane 3 the situation is quite different. In the initial state the macrocyclic ring is hydrogen bonded to the succinamide station. The activation process involves a reduction of the naphthalimide station, quite far away from the succinamide station. We have no prior reason, nor experimental evidence, to assume that the reduced naphthalimide plays an active role in pulling the macrocycle off its original binding site. In spite of this, the macrocycle moves over to the naphthalimide radical anion with a rate of about $10^6 \text{s}^{-1}$.

Note that the time scale of shuttling has nothing to do with the speed at which the macrocycle moves from one station to the other. Our experiments give no information about that. Molecular dynamics simulations suggest that the macrocycle can move down the $C_12$-chain in a few hundred picoseconds. After this journey, the macrocycle makes hydrogen bonds with the naphthalimide radical anion, and several kcal/mol of energy are gained, as estimated from electrochemical experiments. Thus, there is a free energy driving force for the movement, which could in principle be coupled to an external load to actually move some object.

The energy that causes the macrocycle to migrate is in fact obtained from the environment. It is the thermal activation energy that is needed to break the hydrogen bonds between the macrocycle and the succinamide station. In this respect, the mechanism of motion in molecular shuttle 3 is similar to that in motor proteins. To emphasize this similarity, and to avoid the association with classical engines, we like to use the term “motor molecule” instead of “molecular machine” for molecular shuttles such as 3.

**Development of Rotaxane Molecular Shuttles**

Among mechanical molecular switches, rotaxane 3 is a fast one. Yet, the microsecond time scale leaves considerable room for improvement. The distance moved by the macrocyclic ring in 3 is only about 1.5 nm. There is a challenge in increasing this distance, and also in controlling the conformation of the thread. Coupling the movement of the shuttle to picking up and releasing a cargo will yield a mimic of a motor protein, but the development of such a system will require the addition of considerable chemical complexity. Many other options are open. More and more research groups are using mechanically interlocked architectures to design motor molecules. Although in my opinion most of us are still at the stage where Feynman’s words apply: “What are the possibilities of small but movable machines? They may or may not be useful, but they surely would be fun to make.”, there is enough reason to expect that the spectacular increase in possibilities to synthesize and study molecular machines will lead to useful applications within the next decade.

**Acknowledgment**

Our work has been made possible due to a fruitful collaboration with Professor David Leigh (Edinburgh, UK), whose synthetic ingenuity has been the human motor for a series of European networks (EU contracts: DRUM PMRX-CT97-0097, EMMA HPRN-CT-2002-00168, MechMol IST-2001-35504). In this context, I wish to thank, in particular, Professors Francesco Paolucci and Petra Rudolf and their coworkers whose work has been discussed here. In our own laboratory, my colleague Professor Wybren Jan Buma has played a key role, and Céline Frochot, Sjors Wurpel, Natalia Haraszkiewicz, Sandro Fazio, Dhiredj Jagesar and Jacob Baggerman have done all the experimental work and a lot of good thinking. The work was supported in part by The Netherlands Organization for the Advancement of Research (NWO) and the Netherlands Research School Combination Catalysis. Finally, I thank Professor Jan W. Verhoeven for many stimulating discussions.

**References**


Continued on page 27
polymers with self-assessing capabilities

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Introduction

Due to the pronounced \(\pi-\pi\) interactions encountered in the crystalline lattice of cyano-substituted oligo(p-phenylene vinylene)s (cyano-OPVs) (Figure 1), these photoluminescent (PL) dyes exhibit strong tendencies toward excimer formation.\(^1\) As a result cyano-OPVs display remarkably large differences (in some cases \(>140\) nm) when comparing the emission maxima of dilute solutions with those of the crystalline dyes (Table 1).\(^2,3\) We have recently embarked to utilize cyano-OPVs for the design of self-assessing polymer materials by blending minute quantities of these sensory molecules with conventional host polymers.\(^4,5,6\) Our approach exploits that the (non-equilibrium) phase behavior of these materials can be significantly influenced by the choice of the polymer, the specific chemistry of the dye as well as the processing protocol. Most importantly the exposure of such materials to external stimuli can lead to a pronounced variation of the relative contributions of monomer and excimer emission. For example, phase-separated systems with nanoscale dye aggregates can be produced by quenching melt-processed blends of conventional semicrystalline polymers such as linear low density polyethylene (LLDPE) or polypropylene (PP) and cyano-OPVs. Mechanical deformation of these materials leads to shear-induced mixing,\(^7\) which transforms the nanophase-separated systems into molecular mixtures, concomitant with a pronounced shift from excimer- to monomer-dominated emission.\(^4,5,8\) The inverse mechanism, that is, the phase separation of initially molecularly mixed blends of cyano-OPVs and glassy amorphous host materials represents another versatile sensing mechanism, which, for example, may be useful for the fabrication of time-temperature indicators (TTIs).\(^6\) Here, the general scheme relies on kinetically trapping molecular mixtures of cyano-OPVs and amorphous host materials in a thermodynamically unstable glassy state. Subjecting these blends to temperatures above their glass transition temperature leads to permanent and pronounced changes of their PL emission spectra, as a result of phase separation and excimer formation.

Results and Discussion

A number of research groups have previously reported on the electronic characteristics of cyano-OPVs.\(^9,10,11,12\) Intrigued by the possibility to control the emission color and physical properties of this family of PL dyes over a wide range by tuning the chemical structure, we have synthesized a series of cyano-OPVs\(^2,3\) for use as molecular sensors. All members of this series were prepared in good yield by the Knoevenagel reaction of appropriately substituted phenylacetonitriles with 2,5-di-substituted terephthalic aldehydes according to a previously published reaction protocol (Figure 1, Table 1).\(^2,3\)

![Figure 1. Chemical structure of cyano-OPVs.](image)

<table>
<thead>
<tr>
<th>Dye</th>
<th>PL (\lambda_{\text{max}}) Solution(^1) [nm]</th>
<th>PL (\lambda_{\text{max}}) Solid(^2) [nm]</th>
<th>Melting Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>427, 449</td>
<td>527</td>
<td>n.a.</td>
</tr>
<tr>
<td>1b</td>
<td>461, 486</td>
<td>550</td>
<td>245</td>
</tr>
<tr>
<td>1c</td>
<td>506, 538</td>
<td>644</td>
<td>248</td>
</tr>
<tr>
<td>1d</td>
<td>508, 541</td>
<td>619</td>
<td>131</td>
</tr>
<tr>
<td>1e</td>
<td>471, 495</td>
<td>545</td>
<td>n.a.</td>
</tr>
<tr>
<td>1f</td>
<td>480</td>
<td>538</td>
<td>n.a.</td>
</tr>
<tr>
<td>1g</td>
<td>536, 560</td>
<td>665</td>
<td>183</td>
</tr>
</tbody>
</table>

\(^1\) Measured in CHCl\(_3\) at a dye concentration of \(2-2.5\times10^{-3}\) mol L\(^{-1}\).
\(^2\) Semicrystalline powder as synthesized.

1) Measured in CHCl$_3$ at a dye concentration of $2-2.5 \times 10^{-3}$ mol L$^{-1}$.
2) Semicrystalline powder as synthesized.
All cyano-OPVs 1a-g are highly photoluminescent. In dilute solutions these dyes display emission spectra that feature well-resolved vibronic structures, characteristic of monomer emission.\textsuperscript{2,3} As might be expected, the maximum of the PL emission band ($\lambda_{\text{max}}$) shifts to lower energies upon extending the conjugation length (1g) and introduction of polar substituents (1b-1f). The PL emission characteristics of these cyano-OPVs strongly depend on their state of matter. Some of these dyes exhibit bathochromic shifts of up to 140 nm when comparing the PL emission of the crystalline solid with that of a dilute solution. (Table 1) This effect originates from the pronounced $\pi-\pi$ interactions encountered in the crystalline lattice of these planar conjugated molecules, which causes them to arrange under co-facial $\pi-\pi$ stacking into “sandwich structures”. This architecture leads to the formation of excimers, which characteristically exhibit red-shifted fluorescence bands and long fluorescence lifetimes. Figure 2 exemplarily shows the PL emission spectra of 1g in dilute chloroform solution (535, 562 nm) and in the crystalline solid state (665 nm).

As the concentration of the dye is increased, the solubility limit is exceeded and the system slowly phase separates forming small aggregates of dye molecules embedded in the polymer host. Phase separation is possible due to the mobility experienced by the dye molecules above the glass transition temperature ($T_g$) of LLDPE and is accompanied by the development of a broad, unstructured excimer emission band, the intensity of which increases with increasing dye concentration. This phenomenon is shown exemplarily in Figure 3 for blends of 1c in LLDPE at concentrations between 0.01 and 0.4% w/w.\textsuperscript{5}

Upon blending these dyes with semicrystalline polyolefin host polymers, such as linear low-density polyethylene or polypropylene, literally any combination of monomer and excimer emission can be achieved by tuning the phase behavior of the blends via composition, processing conditions, or temperature.\textsuperscript{5} Films containing low concentrations of cyano-OPVs display emission spectra that feature well-resolved vibronic structures, suggesting that at low concentration the cyano-OPV molecules are incorporated in the amorphous fraction of the host polymers in an apparently molecularly dispersed or dissolved fashion.

In order to develop a better understanding of the phase behavior of the systems at hand, we have investigated the solubility of three cyano-OPVs (1b-d) in LLDPE in the temperature regime between 20 and 180 °C using polarized optical microscopy and PL spectroscopy (Figure 4).\textsuperscript{5} The phase behavior of blends with a dye content of >0.20% w/w was usually characterized by optical microscopy. The temperature of the blends was increased in increments of 10°, and the temperature at which the dye crystals (which had previously phase-separated from the LLDPE matrix) had completely dissolved was taken as the solubility limit. The phase behavior of blends of lower concentration was difficult to study by optical microscopy, since the crystals were either too small, or they dissolved below the melting temperature of LLDPE and light scattering from the LLDPE matrix impeded the microscopy. Thus, in this case PL spectroscopy was employed, and the solubility limit was defined as the temperature at which the characteristic
signal of the excimer band had fully disappeared. Gratifyingly, these complementary methods provided consistent data (cf. Figure 4) and logarithmic plots of the solubility of the various dyes (in % w/w) against 1/T display a linear relation, which is consistent with standard solution theory. As can be seen from Figure 4, the absolute solubility of the dyes significantly varies with their molecular structure (cf. Figure 1) and sharply increases with the number and length of aliphatic substituents, which allow for favorable van der Waals interactions with the LLDPE matrix. The comparison of 1b-d indicates further that the temperature dependence of the solubility becomes less pronounced as the molar heat of fusion of the dye decreases (109, 101 and 54 J/g). This finding appears to be consistent with a comparably weak temperature dependence of the Flory-Huggins parameter $\chi$. Thus, these results seem to suggest that the phase behavior of OPV/polyolefin blends can readily be controlled via (minor) chemical modifications of the molecular structure of the dye.

Phase-separated blends with apparently very small aggregates can be produced by rapidly quenching the samples after melt-processing. Small dye aggregates are important, if the dye molecules are to be used as integral strain sensors (vide infra) since large-scale phase separation prevents an efficient break-up of the aggregates. However, we observed that in quenched blends the relative intensity of the excimer emission band is initially small, and only slowly increases upon storage under ambient conditions. This effect is attributed to slow de-mixing and aggregation of the dye molecules after being kinetically trapped upon rapidly cooling the blends to room temperature. Briefly swells blend films in hexanes, which is a poor solvent for the cyano-OPVs but swells LLDPE reasonably well, increases the speed of the de-mixing process. Due to the plasticizing effect of the hexanes, the dye molecules aggregate rapidly and the PL spectra of the films change quickly upon immersion in hexanes. No significant change in PL spectra is observed after treatment for 15 minutes, and a comparison of the PL spectra of 1c (0.18% w/w) / LLDPE blend films stored at ambient for three months and plasticized with hexanes show similar results.

Figure 5 clearly demonstrates that solid-state tensile deformation has a pronounced effect on the emission characteristics of blends of LLDPE and 1b or 1c. Upon stretching the films to a draw ratio $\lambda = 500\%$, films of both materials (at dye concentration of ca. 0.2% w/w) display good visual contrast (Figure 5). Concomitantly, PL emission spectra show a large reduction in the relative intensity of the excimer band (Figure 6). These findings are consistent with our previous experiments, which have shown that tensile deformation can indeed cause the transformation of a phase-separated polymer blend into an apparent molecular dispersion or solution.

The inverse process, that is, the phase separation of initially molecularly mixed blends of cyano-OPVs (or other suitable excimer-forming dyes) and appropriate host polymers represents another sensing scheme which, for example, may be useful for the fabrication of time-temperature indicators. Interestingly, most literature studies that have dealt with the incorporation of excimer-forming dyes into glassy amorphous polymers have relied on solution-casting. This approach typically leads to phase-separated systems, if the dye concentration is above the solubility limit. To explore the possibility to create molecularly mixed blends which phase separate above a given temperature, we blended either PMMA and between 0.01 and 5% w/w 1b or PC and between 0.05 and 10% w/w of the dye by melt-mixing.
the respective components at 200-230 °C in a co-rotating twin-screw mini-extruder. These blends were subsequently compression molded at the temperature at which they were extruded and rapidly quenched to below their T_g in order to prevent phase separation between the polymer host and the dye (vide infra) and “freeze” a glassy polymer solution instead.

DSC traces performed on 1.6 and 5% w/w PMMA/1b blends and 5 and 10% w/w PC/1b blends, as well as on the neat polymers reveal a weak endothermic transition that is associated with the glass transition of the material. As shown in Figure 7 for the investigated PC/1b blends, the addition of the dye caused a depression of T_g, which scaled inversely with the concentration of dye. Interestingly, the DSC traces of samples with high dye concentration (5% w/w in case of PMMA and 10% w/w in case of PC) further display exothermic signals around 160 °C (PC) and 145 °C (PMMA), and broad endothermic transitions around 200 °C (PC) and 195 °C (PMMA). We assign the exothermic transitions to phase separation and crystallization of 1b and explain the endothermic processes around 200 °C (PC) and 195 °C (PMMA) with dissolution of the dye. These assignments have been verified via optical microscopy. The absence of any thermal transitions above 210 °C suggest that at the processing temperatures the dye is, at least at the concentrations of the systems investigated here, indeed completely dissolved in the polymer host. Gratifyingly, quenched blends comprising either 5% w/w 1b in PMMA or 10% w/w of the dye in PC that had been stored at ambient for four weeks display DSC traces that are identical to those of freshly prepared samples, indicating good long-term stability of the kinetically trapped systems.

The photophysical characteristics of the new blends were investigated by PL spectroscopy. Upon excitation with UV light, 0.01% w/w PMMA/1b blend films fluoresce blue and their emission spectra display a well-resolved vibronic structure with an emission maximum (λ_max) at 473 nm and a shoulder at 450 nm (Figure 8a). The spectrum displays a modest (~10 nm) hypsochromic shift and a redistribution of the two phonon bands if compared to the spectrum of a dilute chloroform solution of the dye, but otherwise matches the latter well. Interestingly, upon increasing the concentration of dye in the blends, the emission spectra display a modest bathochromic shift, increasing λ_max to 493 nm at a concentration of 5% w/w 1b. A similar trend can be observed for PC/1b blends comprising between 0.05 and 10% w/w of the dye (Figure 8b), although the concentration-dependent color shift is less pronounced. This effect can be attributed to a combination of internal
re-absorption, caused by the overlap of the dye’s absorption band with the high-energy portion of its emission spectrum, and the formation of (small amounts of) excimers at higher dye concentrations.

To allow for the optical temperature sensing scheme discussed above, the transition from molecular mixtures to phase separated systems when heating high-concentration blends above their $T_g$, should also be accompanied by a significant change of the material’s PL emission characteristics. Spectra were collected for freshly quenched films as well as for samples that were annealed for 20 h at 130 °C (PMMA) and 42 h at 150 °C (PC). Longer annealing at these temperatures had virtually no effect on the emission spectra. As can be seen from the emission spectra shown in Figure 9 for a PC/1b blend, annealing above $T_g$ leads to a 46 nm bathochromic shift of the PL emission maximum (22 nm for PMMA). This is consistent with an increased contribution of the longer wavelength excimer emission in the samples after annealing. Especially in case of the 10% w/w PC/1b blend, this change can readily be detected by the unassisted eye (Figure 10).

In order to probe the usefulness of the new blends as time-temperature indicators, we have finally investigated the kinetics of the temperature-induced phase separation by means of in-situ PL spectroscopy. For this study, 5% w/w PMMA/1b and 10% w/w PC/1b blend films were annealed on a hot stage at temperatures between the $T_g$ of the blend and the onset of the crystallization exotherm established by DSC experiments. In addition, a 10% w/w PC/1b blend film was annealed at 100 °C, that is, just below its $T_g$. Figures 11a and 11b show plots of $\lambda_{max}$ as a function of annealing time and temperature. Kinetic data acquired at 130 °C or below fit well to a single exponential function, and the process appears to be well described by Avrami transformation kinetics. In case of the 10% w/w PC/1b blend annealed at 140

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**Figure 8.** PL emission spectra of melt-processed, quenched blend films of PMMA/1b (a) and PC/1b (b) as a function of dye concentration.

**Figure 9.** PL emission spectra of 10% w/w PC/1b blend films before (solid) and after (dashed) annealing the sample for 42 h at 150 °C.

**Figure 10.** Picture of 10% PC/1b blend films (shown under excitation with a 365 nm UV lamp) before (left) and after (right) annealing for 42 h at 150 °C.
and 150 °C, a double exponential function was required to fit the data accurately. A comparison of the data sets measured at different temperatures reveals an increase in the rate at which \( \lambda_{\text{max}} \) changes consistent with Arrhenius type behavior, as is evident from logarithmic plots of the time constant against \( 1/T \) (Figures 11c and 11d). Not surprisingly, the time constant obtained by fitting the data for the sub-\( T_g \) annealing process of the 10% 1b/PC sample deviates from the trend set by the data acquired above \( T_g \), consistent with different relaxation processes in these temperature regimes.

Conclusions

The general concept of introducing excimer forming cyano-OPVs into polymeric blends provides a broad opportunity for the creation of a wide variety of “polymer chameleons” with self-assessing capabilities. A key advantage of the general approach described here is that the transduction scheme is a significant, readily detectable color (not intensity/PL lifetime) change. Cyano-OPVs are an excellent candidate for use in these materials due to the large differences observed when comparing the emission maxima of dilute solutions with those of the crystalline dyes and the ease with which they can be tailored to adjust their physical and PL properties. The sensing schemes described here exploit that the phase behavior of certain polymer/cyano-OPV compositions is significantly influenced by exposure to external stimuli, which leads to a pronounced variation of the relative contributions of monomer and excimer emission. Examples presented here are the deformation of ductile polyolefins in which pre-formed excimer nanoaggregates are dispersed by shear-induced mixing, concomitant with a shift from excimer- to monomer-dominated emission and the thermally induced phase separation of kinetically trapped, glassy molecular mixtures, which display an inverse change.

Figure 11. a,b) PL emission maxima as a function of annealing time. Symbols represent experimental data while lines represent exponential fits. a) Blend films of PMMA and 5% w/w 1b annealed at 110 (○), 120 (●), and 130 °C (∆). b) Blend films of PC and 10% w/w 1b annealed at 100 (●), 130 (○), 140 (∆) and 150 °C (□). c,d) Logarithmic plots of the first order rate constants for blends of PMMA and 5% w/w 1b (c) and PC and 10% w/w 1b (d) against the inverse annealing temperature.
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8. In line with the common terminology, the term “monomer” is used here to describe emission from single-molecule excited states, as opposed to excimers.

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Neckers Continued from Page 15

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“green photochemistry” with moderately concentrated sunlight

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Introduction
During his general lecture before the International Congress of Applied Chemistry in New York in 1912, Giacomo Ciamician, one of the pioneers of modern organic photochemistry, presented his spectacular vision on “The Photochemistry of the Future”:1

“On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is.”

During that time, photochemical experiments mostly took place on the roof tops of chemical institutes or in southern countries (Figure 1), and the reaction mixtures were exposed to direct sunlight over long periods of time—often several months.2 With the development of powerful artificial light-sources, photochemistry finally moved into the laboratories and became an important and successful research field. However, despite obvious advantages in terms of selectivity and sustainability, photochemical applications for the production of chemicals on large industrial scales remained rare and Ciamician’s dream seemed unfulfilled.3

Over the last decades, the call for environmentally friendly technologies has led to an increasing interest in Green Chemistry.4 Among the known green chemical approaches, solar photochemistry can serve as a valuable application since sunlight is used as energy and as light source.5 This concept leads back to the beginnings of organic photochemistry in the late 19th century and consequently “back to the roofs”. In contrast to the often improvised early equipment, today’s solar photochemical reactions are performed with modern solar reactors and moderately to highly concentrated sunlight which allows high time-space yields. Following this approach, Scharf and co-workers have summarized the first promising examples for the solarchemical production of selected fine chemicals.6 During the last decade, we have added a number of experiments from our laboratory and representative examples will be highlighted in this article.

Results and Discussions
Close to Cologne, Germany, the German Aerospace Center (DLR) operates a solarchemical facility (Figure 2). The research plant comprises a high-flux solar furnace and several other sunlight collecting systems.7 Per year, the research site of the DLR (latitude 50°51’ N, 7°07’ E, 70 m above sea level) receives about 1500 hours of direct sunshine (with a peak in July/August) and about 850 kWh/m² of direct insolation, which makes it suitable for solarchemical operations.

With the exception of the photooxygenation of 1,5-dihydroxynaphthalene (vide infra), the PROPHIS plant was used as a sunlight-collecting system. The loop (Figure 3) is based on a line-focusing parabolic trough collector and comprises a MAN-Helioman module (4 troughs) and feeding equipment (storage vessel, pump, heat exchanger, gas fitting, etc.).8,9 The collector enables a geometric concentration factor (CF) corresponding to about 32 suns, but it can only concentrate the direct normal part of the global radiation. In practice, the concentration factor is reduced significantly by optical losses. The mirror elements (each 1 m²; 8 elements per trough) are made of silver-coated glass and follow the sun by a three-dimensional tracking system.
on two axes. The given storage vessel and feeding equipment allows experiments on 35 to 120 l scales.

The quality of the direct sunlight that reaches the earth’s surface is strongly dependent upon the geographic location. For Cologne, Germany, Figure 4 shows the calculated molar spectral direct solar irradiance ($E_{\text{p}\lambda}$) on October 10, 1995, (12:00 a.m.) together with the extraterrestrial irradiance. Not all photoreactions known from the laboratory are suitable for solarchemical applications. For example, no solar photons in the photochemically important region below 300 nm are detectable on the earth’s surface. Furthermore, only the region up to the threshold wavelength ($\lambda_s$) of 700 nm is energetically suitable to induce structural changes.

For our studies, we have chosen two model reactions: (1) photoacylations involving quinones and (2) photooxygenations with rose bengal as a sensitizer.

**Photoacylation of Quinones**

Due to their absorption at wavelengths above 350 nm (Figure 4), quinones are excellent substrates for solarchemical applications. Therefore, we have selected the photochemical reaction between a quinone and an aldehyde as a mild and efficient alternative to thermal Friedel-Crafts acylations or Fries-rearrangements. This photoacylation was discovered in 1891 by Heinrich Klinger who exposed the starting materials to natural sunlight over long periods of time. To find optimal reaction conditions for our modern “outdoor” approach, the photoreaction between 1,4-naphthoquinone (1) and butyraldehyde (2) has been chosen as a model system for a detailed laboratory study with artificial light. A major disadvantage of the laboratory protocol was the usage of the toxic solvents benzene or acetonitrile, respectively, but non-toxic tertiary butanol was found as a suitable alternative and the photoproduct (3) was obtained in an isolated yield of 84%.

![Scheme 1](image)

With these optimized reaction conditions, the photoacylation of the 1/2-pair (Scheme 1) was performed on a 500 g (3.2 mol, 1) scale using the PROPHIS plant (three troughs = 24 m$^2$). Due to the difficult handling of pure tertiary butanol (relatively high freezing range), a 3:1 mixture with acetone was used. The illumination took place during August 20 and 22, 1996, for a total illumination time of 24 h (CEST: 09:00-17:00 each day), and experimental details and results are summarized in Table 1. As not untypical for the location and time of the year, the weather conditions were varying, and only the first day was optimal for reaching a high conversion. This becomes especially obvious when comparing the direct normal irradiance for the three-day period (Figure 5) and the amounts of photons collected. At the end of the experiment, complete conversion was achieved and a yield of 90% of 3 was determined via GC-analysis (vs. eicosane). During the experimental phase, the three troughs of the PROPHIS plant collected almost 300 mol photons in the important absorption region of 1,4-quinones between 300-500 nm. Of these more than 240 mol were received during the first day.
The photosensitized oxygenation (or Scheck-ene-reaction) of citronellol was studied as a second example of the solarchemical synthesis concept (Scheme 2). This reaction is currently performed industrially on a >100 t/a scale using artificial light sources. Further reduction and acid mediated cyclization of the regioisomer 5b gives the important fragrance rose oxide, which makes this photo-reaction a prototype for solar photochemical comparison studies. For the solar reactions in the PROPHIS loop, the sensitizer rose bengal was selected since it shows favorable absorption (Figure 4) up to 600 nm with a maximum at 555 nm (data in ethanol). Additionally, the solvent methanol from the industrial process was replaced by the less hazardous isopropanol.

The first experiment was performed on August 11, 1997, with only one trough (8 m²) and the reactor was loaded with a solution of 5.8 l (31.8 mol) of citronellol (4) and 20 g of rose bengal in 40 l of isopropanol. Upon illumination, the amount of citronellol was rapidly consumed and after about 3 h, an almost quantitative conversion of 4 was achieved. GC-analysis (vs. tetradecane), performed after reduction of the corresponding sample with Na₂SO₃, furthermore proved the high purity of the regioisomeric photoproducts, which were formed in a ratio of about 45:55 in favor of 5b. The latter finding is in good agreement with the reported isolated yield ratio of 35:60 from the laboratory experiments with artificial light. During the experimental period, the reactor collected 47.1 mol of photons between 500-600 nm. In the second run on September 12, 2002, all four troughs were used, giving a total aperture of 32 m² (Figure 6). In addition, the experiment was scaled-up to 8.0 l (43.9 mol) of citronellol and 36 g of rose bengal in 72 l of isopropanol. The weather conditions were again optimal and consequently, total conversion was readily observed after less than 2 ½ h (Figure 7). During this time, the PROPHIS plant received...
133.4 mol of photons in the range of 500-600 nm, almost three times as much as during the experiment in 1997.

For the solarchemical experiments, we have selected a small parabolic trough collector designed for laboratory-scale (<500 ml) applications (Figure 8). Its one-axis design allows automatically tracking of the sun only for the elevation, whereas tracking of the azimuth is performed manually every 15 minutes. The reactor offers a geometric concentration factor of about 15 suns. The trough itself is equipped with holographic mirrors, which are designed to reduce warm-up effects (and thus the costs for process cooling) caused by infrared radiation. The given holographic concentrators (2 elements; 20 × 100 cm total) are made of dichromated gelatin (Holotec GmbH/Germany) and show a reflectivity range of 550±140 nm—optimal for the usage of rose bengal.

Photooxygenation of 1,5-Dihydroxynapthalene

An additionally interesting application was the synthesis of the important intermediate Juglone (5-hydroxy-1,4-naphthoquinone; 7) from 1,5-dihydroxynaphthalene (Scheme 3). Most of the thermal pathways suffer from severe disadvantages concerning yield, selectivity, sustainability or reproducibility, respectively. In contrast, the photosensitized oxygenation of 6 with artificial light sources furnishes Juglone in yields of 70-75%, even on multigram scales.

Two experiments were conducted in August 2003 using rose bengal as the sensitizer and isopropanol as the solvent. In contrast, the laboratory procedure commonly uses methylene blue and acetonitrile or a mixture of methanol/dichloromethane, respectively. The experimental details are summarized in Table 2.

Table 2. Experimental data for the photooxygenation reactions of citronellol.

<table>
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<tr>
<th>date</th>
<th>rose bengal</th>
<th>i-PrOH</th>
<th>O₂-flow</th>
<th>aperture</th>
<th>fluid-flow</th>
<th>time</th>
<th>photons 500-600 nm</th>
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<td>5.81</td>
<td>20 g</td>
<td>40 l</td>
<td>600 1/ₘᵢₙ</td>
<td>8 m²</td>
<td>ca. 3 h</td>
<td>47.1</td>
<td>&gt;95%</td>
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<tr>
<td>12.09.2000</td>
<td>8.01</td>
<td>36 g</td>
<td>72 l</td>
<td>200 1/ₘᵢₙ</td>
<td>32 m²</td>
<td>ca. 2 1/2 h</td>
<td>133.4</td>
<td>&gt;95%</td>
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</table>

Scheme 3

Figure 7. Direct normal irradiance and conversion versus illumination time for the photooxygenation of citronellol.

Figure 8. Parabolic trough reactor equipped with holographic mirrors during the rose bengal sensitized photooxygenation of 1,5-dihydroxynaphthalene.
and results from the solarchemical studies are summarized in Table 3. In both cases, the progress of the reaction was followed via GC-analysis versus tetradecane as internal standard. The first test run was performed between August 4 and 5 with 2.0 g (12.5 mmol) of diol (6) and 0.1 g of rose bengal in 200 ml of solvent. The starting material was readily consumed and after less than 8 h, the conversion reached a constant value of 83%. During that period the reactor collected 7.4 mol of photons between 500-600 nm. After work-up, the desired product (7) was obtained in 54% yield (65% based on conversion). For the second experiment on August 12, the amount of diol (6) was reduced to 1.0 g (6.2 mmol) in order to achieve complete conversion. After less than 3 h (Figure 9), GC-analysis revealed that most of the starting diol had been consumed. At this stage the collector has received 2.3 mol of photons. After a total illumination period of about 9 1/2 h, Juglone was isolated in a compared to the laboratory experiments improved yield of 79%.

![Figure 9. Direct normal irradiance and product composition versus illumination time for the photooxygenation of 1,5-dihydroxynaphthalene.](image)

Although the photooxygenations of 6 required relatively long illumination times in comparison to the large scale experiments involving citronellol (4), it must be taken into account that solarchemical experiments with non-concentrated sunlight often require several days or weeks to reach high conversion rates. Furthermore, the oxygen feeding mechanism of the given reactor was not optimal.

### Conclusion

In conclusion, the results obtained from the solar photochemical experiments described above clearly show that the solarchemical bulk production of specific fine chemicals can serve as a useful and environmentally friendly alternative to existing technical processes. Cost estimates for specific fine chemicals (e.g., rose oxide17 or ε-caprolactam22) furthermore proved that an industrial solarchemical production could operate economically. Consequently, a realization of Giacomo Cianciomian’s vision of the “Photochemistry of the Future” seems within range.

### Acknowledgments

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### References


### Table 3. Experimental data for the photooxygenation reactions of 1,5-dihydroxynaphthalene.

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<tr>
<th>date</th>
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<th>rose bengal</th>
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<th>aperture</th>
<th>fluid-flow</th>
<th>time</th>
<th>photons 500-600 nm</th>
<th>conversion</th>
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<td>4.-5.8.2003</td>
<td>2 g</td>
<td>0.1 g</td>
<td>200 ml</td>
<td>0.188 m²</td>
<td>60 ml/min</td>
<td>ca. 8 h</td>
<td>7.4</td>
<td>83%</td>
<td>54 (65)</td>
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<tr>
<td>12.8.2003</td>
<td>1 g</td>
<td>0.1 g</td>
<td>200 ml</td>
<td>0.188 m²</td>
<td>60 ml/min</td>
<td>ca. 3 h</td>
<td>2.3</td>
<td>&gt;95%</td>
<td>79</td>
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</table>


22. (a) Funken, K.-H.; Müller, F.-J.; Ortner, J.; Riffelmann, K.-J.; Sattler, C. Energy 1999, 24, 681; (b) Sattler, C.; Müller, F.-J.; Riffelmann, K.-J.; Ortner, J.; Funken, K.-H. J. Phys. IV (France) 1999, 9, Pr3-723.

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Elmar Zimmermann is currently working on his Ph.D. thesis in the group of Prof. A. G. Griesbeck.
Enhancing Digital Images

The vagaries of natural lighting limit the sharpness of images taken with devices ranging from $100 point-and-shoot cameras to the $10-million optics on interplanetary space probes.

Despite tricks like averaging the total illumination that falls on an object, existing imaging sensors often leave brightly illuminated areas of a scene looking washed out. Dimly illuminated areas can be lost in shadow. If the system averages total illumination falling on an object, the image loses the sharpness and contrast critical for revealing fine detail.

The problem hinders performance of optics in mass market digital cameras; biometric identification and other security and surveillance systems; X-ray diagnostics; space probes; and unmanned combat vehicles.

Researchers at Intrigue Technologies, Inc. have reported a first step toward solving the problem with technology that mimics performance of the retina, the photosensitive tissue at the back of the eye. The spin-off firm is commercializing technology developed by Vladimir Brajovic and his associates at Carnegie-Mellon University in Pittsburgh.

“Most of the problems in robotic imaging can be traced back to having too much light in some parts of the image and too little in others,” said Brajovic. “The washed out and underexposed images captured by today’s digital cameras are simply too confusing for machines to interpret, ultimately leading to failure of their vision systems in critical applications.”

The human eye, he explained, has a built-in mechanism for adapting to local illumination conditions, with retina cells processing information to adapt to lighting conditions before sending image data to the brain.

Brajovic and colleagues have developed software for a new image sensor that will work more like the retina. Its pixels will communicate with each other about lighting conditions, and modify their behavior in response to lighting conditions, gathering sharper images even under adverse natural lighting conditions.

The researchers have demonstrated the power of the software, which they call “Shadow Illuminator”, by using it to process more than 80,000 images including the lungs (above). By balancing exposure, it improves contrast, revealing missing detail. In some instances, the software has uncovered concealed individuals in images from security cameras and obscured detail in medical X-ray images.

Photovoltaic Fabric

Mention high-tech fabrics, and people usually think of cloth that resists tearing, penetration, heat, stains, or wrinkles. Konarka Technologies, Inc. in Lowell, Massachusetts, has revealed an R&D effort to develop and commercialize a photovoltaic fabric that converts sunlight into electricity.

Konarka already has produced a working photovoltaic fiber. Now the firm, which specializes in power plastics that convert light into energy, is collaborating with Ecole Polytechnique Fédérale de Lausanne (EPFL) in Switzerland on what it terms the Photovoltaic Fibers and Textiles Based on Nanotechnology Program. The goal is the first fully integrated woven photovoltaic material.

Such material would allow for tighter integration of power generation capabilities into devices, systems and structures beyond what is possible with photovoltaic plastic film.

“Photovoltaic textiles could positively increase the number of applications available to solar technology by extending integration to objects made from fabrics, such as garments, tents or coverings,” said Daniel Patrick McGahn, executive vice president and chief marketing officer, Konarka. “We’ll be able to offer to the marketplace practical new products, such as wearable power generation for mobile electronics made from the solar fabric.”

To weave a fabric, Konarka and EPFL will optimize the strength, thickness and electrical performance of the photovoltaic fiber. The team will work to interweave fibers to maximize the performance of the textile without compromising the fibers’ integrity. The goal is to produce a fabric sample with a four percent efficiency rating.
“This unique solar fabric represents a leap forward for photovoltaic technology,” said Dr. Russell Gaudiana, Konarka’s vice president of research and development. “It will enable power generation capabilities to be woven in rather than applied. For example, we’re able to incorporate our light-activated power plastic onto tenting materials, such as canvas or nylon. Using the fiber, the tent’s base material becomes photovoltaic.”

Dr. Jan-Anders Manson, the director of the Laboratory of Composite and Polymer Technology, will lead the EPFL team. Manson was scientific coordinator for the EPFL-Alinghi Project, which designed the yacht that won the 2003 Americas Cup. The project, expected to take one year, is funded by the Swiss Commission for Technology and Innovation (CTI). CTI promotes the rapid conversion of state-of-the-art laboratory findings to marketable products through cooperation between educational institutions and industry.

The new collaboration deepens Konarka’s close relationship with EPFL. In 2002, Konarka became the first company in the United States to license Dr. Michael Grätzel’s dye-sensitized solar cell technology, which augmented its own intellectual property. Since then, Dr. Grätzel has served as a senior scientific advisor to the company, helping it to commercialize its light-activated plastic power.

Alan J. Heeger, University of California-Santa Barbara, who shared the 2000 Nobel Prize in Chemistry, is Konarka’s chief scientist.

**Nanovision for Optical Microscopes**

In the 1870s, Ernst Abbe explained why the resolution of an optical microscope is limited. Since the microscope uses visible light, it can’t image an object smaller than the wavelength of light. That limits the resolution of the best optical microscopes to about 200 nanometers (nm) or 2,000 angstroms.

New research at the National Institute of Standards and Technology (NIST), however, suggests that a hybrid version of the optical microscope might be able to image and measure features smaller than 10 nm—a fraction of the wavelength of visible light.

If successfully developed, the imaging technology could be readily incorporated into chip-making and other commercial-scale processes for making parts and products with nanometer-scale dimensions, NIST said.

The five-year research effort at NIST, just underway, suggests that a novel combination of illumination, detection and computing technologies can circumvent the limitations of optical microscopy. Success would extend the technology’s 400-year-long record as an indispensable imaging and measurement tool well into the expanding realm of nanotechnology. The nanoworld begins, by most definitions, at sizes of about 100 nm.

Called phase-sensitive, scatter-field optical imaging, the computer-intensive technique under development at NIST uses a set of dynamically engineered light waves optimized for particular properties (such as angular orientation and polarization). How
focus on

this structured illumination field—engineered differently to highlight the particular geometry of each type of specimen—scatters after striking the target can reveal the tiniest of details.

“The scattering patterns are extremely sensitive to small changes in the shape and size of the scattering feature,” said Rick Silver, of NIST’s Precision Engineering Division.

Open Access Journal Database

Spiraling subscription charges for scientific journals triggered a “serials crisis” in the 1990s. With subscriptions costing hundreds or thousands of dollars annually, university libraries were forced to cancel some scientific journals. The average price of a subscription to a scholarly journal tripled between 1986 and 2000, according to a report from Mark McCabe, Georgia Institute of Technology, at the 2005 annual meeting of the American Association for the Advancement of Science.

The crisis spawned a movement toward “Open Access” journals. Authors pay a fee to submit or publish a paper, which is available with the rest of the journal at no cost on the Internet.

Open Access journals are proliferating so fast that two European universities are developing one of the first directories to keep track of the publications. The University of Nottingham in the United Kingdom and Sweden’s University of Lund call the new service DOAR—the Directory of Open Access Repositories. It will categorize and list the wide variety of Open Access research archives that have grown up around the world.

Lund operates the Directory of Open Access Journals (www.doaj.org), which is known throughout the world. Nottingham leads SHERPA (www.sherpa.ac.uk), an institutional repository project that has helped establish Open Access archives in 20 top UK research universities. Nottingham also runs the SHERPA/RoMEO database (www.sherpa.ac.uk/romeo.php), which is used worldwide as a reference for publisher’s copyright policies.

DOAR will provide a comprehensive and authoritative list of institutional and subject-based repositories, as well as archives set up by funding agencies, such as the National Institutes for Health and the Wellcome Trust. Users of the service will be able to analyze repositories by location, type, the material they hold and other measures. This will be of use both to users wishing to find original research papers and for third-party “service providers,” such as search engines or alert services, which need easy-to-use tools for developing tailored search services to suit specific user communities.

For more information, see the project’s website, www.opendoar.org.

Optically Efficient Displays

Electronic displays for everything from wall-sized TV monitors to mobile phones produce more light than the user sees, due to internal losses. The wasted energy becomes especially important in battery-operated mobile devices like personal digital assistants, PocketPCs, and mobile phones because it reduces operating times.

Cambridge Display Technology (CDT) in the United Kingdom and ILFORD Imaging Switzerland have launched a joint project to use nanoparticulate layer technology to improve the display efficiency.

The goal is to increase the proportion of observed light, (the “optical efficiency”) of display devices. In doing so, the display can be made brighter for any given energy input, or energy consumption can be reduced for any given brightness.

Researchers at ILFORD, a leading manufacturer of precision-coated ink jet printing consumables, have discovered that certain nanoporous structures have potentially valuable properties when applied to polymer light emitting diode (PLED) displays. PLEDs are part of the family of organic light emitting diodes, or OLEDs, which are thin, lightweight and power efficient devices that emit light when an electric current flows. PLEDs offer an enhanced visual experience and superior performance characteristics compared with other flat panel display technologies such as liquid crystal displays.

When integrated into a display device, the new nanoporous materials have optical properties, which help to transmit light that would otherwise be trapped and lost.

The firms expect to move well beyond the proof-of-principle phase before summer. Work is underway at CDT’s Technology Development Centre near Cambridge, UK, where much of the work is carried out in developing and preparing PLED technology for commercialization.

Visa Delays for Foreign Scholars

The average wait for security clearances for visas for foreign scholars studying sensitive subjects dropped from 75 days in 2003 to 15 days by November 2004, the U.S. General Accountability Office (GAO) reported. GAO is a congressional investigative and auditing agency that studies
The Spectrum

Ties of agencies involved in the Mantis tem, clarifying roles and responsibili
developing an electronic tracking sys
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process Mantis cases, providing ad
The actions included adding staff to
facilitate travel to the United States.

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of the major reasons for visa delays
among foreign students and scientists
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The Visas Mantis process is de
The clearances have been one
The programs and expenditures of the
federal government.
The number of Mantis cases pend-
ing more than 60 days has also dropped
significantly, the agency said.
U.S. Rep. Sherwood L. Boehlert, a
Republican from New York who chairs
the House Science Committee (which
requested the study), suggested that
the wait period for such clearances
might not get significantly shorter.

While GAO agreed that important
changes have been made, it said more
changes are needed to further stream-
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The clearances have been one
of the major reasons for visa delays
among foreign students and scientists
trying to enter the United States. In
some instances, the delays have run
into months, causing such frustration
that foreign scientists were forced to
abandon plans for study or work in the
United States.

GAO cited a number of steps by the
State Department and other agencies
to speed Mantis processing times and
facilitate travel to the United States.
The actions included adding staff to
process Mantis cases, providing ad-
tional guidance to consular officers,
developing an electronic tracking sys-
tem, clarifying roles and responsibili-
ties of agencies involved in the Mantis
program, reiterating State’s policy of
giving students and scholars priority
interviews, and extending the validity
of Mantis clearances.

“Nonetheless, some issues remain
unresolved,” GAO said. “Consular
officers at posts we visited continue to
need guidance on the Mantis program,
particularly through direct interaction
with State officials knowledgeable
about the program. Several agencies
that receive Mantis cases are not fully
connected to State’s electronic track-
ing system. This can lead to unneces-
sary delays in the process.”

GAO also noted that students and
scholars from China are limited to six-
month, two-entry visas. The Chinese
government has rejected a proposal
by the United States to extend visa
validities, on a reciprocal basis, for
students and scholars.

**Toward an X-Ray Laser**

Ever since the discovery of lasers,
scientists have dreamed of a compact
laboratory source emitting X-rays in
one direction in a laser-like beam.
The device would have a range of ap-
lications in chemistry, biology, and
materials science. Medical diagnostic
X-rays, for instance, could be taken
with far higher resolution at smaller
doses and microscopes could visualize
nanometer-sized biomolecules.

Researchers at Vienna University
of Technology, the University of
Würzburg, the University of Munich
and Max Planck Institute of Quantum
Optics have demonstrated the first
source of laser-like X-rays at a 1 nano-
meter (nm) wavelength with a comp-
act laboratory apparatus.

The Austrian-German team focused
a sequence of intense ultrashort flashes
of red light at a gas of helium atoms to
convert 700-nm laser light into a 1-nm
wave of X-ray light emitted by the
excited atoms. The intense laser field
makes the negatively charged elec-
tron cloud perform giant oscillations
around the positively charged atomic
core, thereby turning the atoms into
antennas.

Because the oscillations have such
a large amplitude, the atoms radiate
waves not only at the wavelength of
the driving laser (700 nm) but also at
shorter wavelengths. Since the anten-
as are in phase over in time, they also
keep time when emitting their waves.
Although these tiny “atomic” waves
are extraordinarily faint, because they
all oscillate in time they add to build
up an X-ray wave of significant intensi-
ity delivered in a highly-directed beam
parallel to the incident laser.

Researchers previously used the
same technique to produce laser-like
extreme ultraviolet radiation at wave-
lengths down to the 10 nm. That,
however, became a barrier. Pushing
the technology to shorter wavelengths
meant exposing atoms to more intense
laser light, which tends to disintegrate
the atoms. Even worse, free electrons
ripped off the atoms by the strong
laser field impeding the buildup of an
intense wave from the faint “atomic”
waves.

The team from Vienna-Würzburg-
Munich overcame those problems by
irradiating the atoms with shorter
high-intensity laser pulses, lasting
five femtoseconds. The pulses are so
brief that the atoms don’t have time
to disintegrate before emitting the
X-ray burst. With the extremely short
interaction time, the researchers broke
the nanometer barrier and also created
a source of X-ray bursts that may, for
the first time, be briefer than 0.1 fem-
tosecond.

Researchers emphasized that X-ray
beam from the new source is too weak
for any practical use, but they believe
its power can be boosted by several
orders of magnitude.
An Historic Anniversary

March 17, 2005 marked the 100th anniversary of Einstein’s submission to Annalen der Physik of his publication on the photoelectric effect, “Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtpunkt”. This paper was the first of three published by him in 1905, a year that is now described as his “Annus Mirabilis”. The other papers were published in May 1905 and June 1905. At the time Einstein was working as a patent examiner in Bern. The photoelectric effect paper, as well as Max Planck’s 1900 paper on the quantum nature of light, is reprinted in Selected Papers on Photochemistry, D. C. Neckers, editor (SPIE milestone series; v. MS 65).

Einstein’s first academic position at the German university in Prague led to, among other things, his ΔE = hν paper and an association with Otto Stern that resulted in early experimental confirmation of his quantum yield postulates. The Eidgenössische Technische Hochschule (ETH) finally agreed to provide him a position in 1911 based, in part, on strong letters of recommendation from Planck, Poincare, Sommerfeld and Madame Curie. The reprinted letter from Gnehm made the appointment final in early 1912.

Einstein remained in Zurich only for a short time resigning his position in 1913 (in fact he was heavily recruited by Planck) to accept one at the University of Berlin in 1914. He was also offered the directorship of the Kaiser Wilhelm Institute of Physics in Berlin which was about to be established. Though his family remained in Zurich, perhaps because of World War I, his reputation grew and productivity continued and in 1915 he published the definitive theory of general relativity.

Einstein received the Nobel Prize in 1921, not for relativity rather for his 1905 work on the photoelectric effect.
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