Nobel Laureate F. Sherwood Rowland
Environmental Photochemistry
The Spectrum

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On the cover
NASA's EarthProbe spacecraft used the Total Ozone Mapping Spectrometer (TOMS) for this image of the Antarctic ozone hole late in September 2002. TOMS instruments are monochromators with 1 nm bandpass channels at six ultraviolet wavelengths. Spatial resolution is 50 x 50 km at nadir. TOMS measures total column amounts of ozone by observing backscattered ultraviolet sunlight and direct irradiance. The coldest temperatures over the South Pole typically occur in August and September. Thin clouds form in these cold conditions, and chemical reactions on the cloud particles help chlorine and bromine gases to rapidly destroy ozone. By early October, temperatures usually begin to warm, and the ozone layer starts to recover. The 2002 hole not only was smaller than it was in 2001 and 2000, but it split into two separate areas of depleted ozone. Researchers stressed that the smaller hole was due to peculiar stratospheric weather patterns, rather than a long-term trend indicating recovery of the ozone layer. Photo courtesy NASA Goddard Space Flight Center Scientific Visualization Studio.
This issue of *The Spectrum* is the first with a substantially expanded technical news coverage. In addition to the short reviews we have always published, we have now added a feature interview and several sections of the photosciences in the news. Much of what we’ve added comes from the pen of Michael Woods. Mike is an award winning science writer, the current editor of the ACS newspaper *Chemistry* and a syndicated science columnist.

When I moved to Bowling Green in the early 1970s I was surprised by the quality of science reporting in the *Toledo Blade*, the largest newspaper in our area. Traditionally, the public press paid no attention to science. I remember reading an article about the Diels Alder reaction in one issue, and was dumbfounded to see it there. I was amazed by the quality of writing and noted the byline of Michael Woods, Science Editor. Paul Block, the publisher of the *Toledo Blade* and a president of the Toledo Section of the American Chemical Society in 1975, first introduced me to Mike.

Over the years Mike has become a friend and collaborator. I was delighted when he agreed to join in our efforts to move *The Spectrum* to its next level. Our new look incorporates excellent technical articles and features on technology in the news. We will also publish a feature interview in each issue of *The Spectrum*. This spring, we’re featuring an interview with Nobel Laureate F. Sherwood Rowland.

Sherry Rowland, Mike Woods and I go back a long way too. Sherry was beginning his research career when I started graduate school at Kansas, and we shared a number of common interests. Mike, for his part, reported on Sherry’s article with Mario Molina in *Nature* that began the freon controversy. Thus, we read about chlorofluorocarbons in the *Toledo Blade* before any other news organization had recognized the significance of the work.

The interview format in this issue is deliberate. Mike observed that extremely busy scientists might not have the time to write an article, but could answer a few questions by email. So we approached Professor Rowland with this idea. He agreed to the format, and his interview is published in this issue. We think you’ll find some of the revelations most interesting.

The news sections will change from issue to issue, but this issue focuses on news from a number of fronts: The American Association for the Advancement of Science meeting in Denver, the publication of the most cited papers in JACS during the last 125 years, the IUPAC draft of Guidelines for Photochemistry and others. We hope you’ll also find these useful and interesting.

Sixteen years ago we started publishing *The Spectrum* as an experiment. The results have been better than we ever imagined. *The Spectrum* has become a highly regarded publication worldwide. This new format is also an experiment. We hope you’ll like it and we’re anxious to hear from you. Please let us know what you think.
“By explaining the chemical mechanisms that affect the thickness of the ozone layer, the three researchers have contributed to our salvation from a global environmental problem that could have catastrophic consequences.”

The Royal Swedish Academy of Sciences

F. Sherwood Rowland was one of the famous trio sharing the 1995 Nobel Prize for Chemistry with Mario J. Molina and Paul J. Crutzen for pioneering research on how ozone is formed and decomposes through photochemical processes in the upper atmosphere. The implications of the research, done in the 1970s, were utterly unlikely.

“Underarm Deodorants Threaten End of the World!” newspaper headlines declared. And the controversy that ensued almost unimaginable.

Rowland and Molina proposed the seemingly inconceivable idea that chlorofluorocarbon (CFC) propellants (“freons”) used in household aerosol sprays, refrigeration systems, and certain industrial processes were destroying stratospheric ozone. Ozone in the upper atmosphere shields the surface from dangerous levels of UV radiation. The idea was so unbelievable because CFCs had been known for decades as inert, chemically stable, unreactive, and harmless. How could these compounds set off a chain reaction that destroys ozone?

Millions of Americans needed no further answer than the Rowland-Molina data. They tossed out household aerosol spray cans, and refused to buy more CFC products.

The CFC industry, with $2 billion in annual sales at stake in the 1970s, launched an attack on the theory, and on Rowland, who pressed home the implications of ozone destruction in public and scientific appearances. Eventually, the theory was proven correct, and basic research in atmospheric photochemistry became global policy. In 1987, the United Nations convened a meeting of 56 nations in Montreal. Delegates hammered out an unprecedented agreement, the Montreal Protocol, to phase out CFCs.

Much popular mythology has surrounded Sherry Rowland, including the notion the he became involved in atmospheric chemistry by making a 360-degree career turnaround at age 46.

In this exclusive interview with The Spectrum, Rowland explains that atmospheric chemistry had been a research interest long before the CFC research. He also reveals that his early research detected evidence of the then-super secret United States hydrogen bomb project years before the first bomb test. He offers advice to younger scientists on how to sense when a career shift is due, and describes some of the big challenges facing environmental photochemistry in the 21st Century. Rowland is still active in tackling these challenges as the Donald Bren Research Professor of Chemistry and Earth System Science at the University of California-Irvine.

The Spectrum: You made a mid-career shift in research focus, which obviously was successful. It sometimes is cited as an example of how pulling up your roots and venturing into a fresh field can be beneficial. People say, “Well, Sherry Rowland changed fields at age 46, and look what happened.” Exactly how big a career shift did it represent for you?

Rowland: My “innocence” towards atmospheric chemistry in 1973 can easily be exaggerated. At that time, I was not doing any active research in the field, but I had been at least peripherally involved ever since my graduate student days. My graduate research was carried out at the University of Chicago under the direction of Professor Willard Libby, who had invented the concept of Carbon-14 Dating shortly before I joined his research group. He himself was carrying out experiments in a regular, near-daily routine which produced the carbon-14 data providing information about how long ago trees and other biological artifacts had grown through measurement of the fraction of the original radioactive $^{14}$C was still left. The $^{14}$C atoms are produced in the lower stratosphere by incoming cosmic radiation, quickly react to form $^{14}$CO and then oxidize to $^{14}$CO$_2$ which undergoes photosynthesis to include the $^{14}$C in green plants.

This starting sequence is all atmospheric chemistry starting with an unusual initial ingredient, a bare carbon atom. While my thesis work did not involve atmospheric chemistry, another graduate student in the Libby group, Sheldon Kaufman, was working on the behavior of atmospheric tritium, the mass 3 isotope of hydrogen—also produced by cosmic ray bombardment of the atmosphere. The atmospheric chemistry of tritium leads it into the form of water, HTO, and eventually reaching earth in rainfall. Libby
The Spectrum: That had to be one of the first measurements of radioactive atmospheric hydrogen.

Rowland: During my eight years there, a number of my radiochemical projects ventured into the geophysical arena—using neutron activation analysis to measure the uranium content of limestone, investigating the distribution of energetic tritium atoms between HT and HTO after reaction with $\text{H}_2\text{O}$; the chemical state of radioactive chlorine atoms produced in chlorinated minerals. And I attended the conference on Radioactivity in the Atmosphere held in Utrecht in 1962. For the next three years, I was on the Board of Editors of the *Journal of Geophysical Research*.

What did happen, however, between 1960 and 1970 was that cessation of atmospheric testing of nuclear weapons by international agreement made obsolete the extensive U.S. aircraft system for monitoring radioactive fallout, and lead to its termination over that decade. This also meant that by the 1970s, with the advent of concern about the possible effects on stratospheric ozone from a fleet of supersonic aircraft, most of the atmospheric scientists were no longer experts in radiochemistry, but in other areas of physics, chemistry and engineering.

I attended a Symposium on the Environmental Applications of Radioisotopes in Salzburg, Austria. By chance at the conclusion of that symposium, I shared a compartment for several hours on the train from Salzburg to Vienna with Dr. William Marlowe of the U.S. Atomic Energy Commission (AEC). Our conversation about radioisotopes drifted into the subject of Carbon-14 dating, and he found out that I was quite interested in the current developments but was not doing any work specifically related to it. He also found that my research had been supported by the AEC for fourteen years. And I found out that one of Dr. Marlowe’s AEC tasks concerned organizing the first joint Chemistry/Meteorology Workshop for early in 1971.

Basically, the AEC felt that more interaction between chemists and meteorologists needed to be strongly encouraged, and the workshop was the intended vehicle for improving the mutual understanding. In due course the next summer, I received an invitation to attend the Second Workshop, held in Fort Lauderdale. One of the first speakers, Dr. Lester Machta, a scientist with much prior experience in studying radioactive fallout in the atmosphere, presented a talk on a possible non-radioactive tracer for atmospheric motions, the inert molecule, trichlorofluoromethane, $\text{CCl}_3\text{F}$.

The Spectrum: How can chemists tell when it’s time to consider a change in their own careers?

Rowland: How often should a scientist change fields? Consider this scenario: The scientist has a new idea that he thinks might lead to a good experiment. He (or she) manages to scrape together some equipment that is not quite right, but can be made to work, and tries it with propane. And it works! So, the next step is to do it with n-butane. However,
after publishing a paper on the propane work, he has also applied for federal funding, and has been able to purchase the right equipment. And the n-butane experiment works like a charm. And the isobutane experiment, and the n-pentane experiment. When the time came for the isopentane experiment, he wrote down his prediction in advance, and nailed the result almost perfectly. Which, of course, meant that it was no longer really an experiment—the system was well enough understood that the actual experiment wasn’t really necessary. So, how long do you continue? N-decane? You have the correct equipment now, it is working very well, and there is a slight feeling of triumph when the result comes out “right.” And do you walk away from this string of successes to start again with a different idea, not very well understood, slightly the wrong arrangement of equipment—and no applicable contract because you haven’t yet had a successful result? Well, yes, somewhere along the line.

**The Spectrum: Did that kind of progression occur in your research?**

**Rowland:** In my group, there was a progression from energetic tritium reactions, to energetic chlorine atoms, to energetic fluorine atoms, to creating methylene fragments labeled with tritium or with carbon-14, to thermalizing the chlorine atoms in multiple collisions prior to reaction, and so forth. On one occasion, we created a methylene labeled with two tritium atoms, CHT, and found that when it reacted with O₂, one of the products was T₂. This meant that the other product should be CO₂. So we tried ¹⁴CH₂ with O₂, and did find ¹⁴CO₂—but we also found ¹³CO in about an equal yield. This implied, of course, that the other product from this reaction route was H₂O. But the reaction is so exothermic that H₂O could break up to give an energetic H atom. The final two experiments in this sequence used CHT, and observed the reaction of T with CH₃CH=CHCH₃ to give CH₃CH=CHT. The latter reaction required an energetic tritium atom, and the inclusion of helium in the system eliminated that reaction by deactivating the tritium atom before it found the butene molecule.

**The Spectrum: What made you question the conventional wisdom that CFCs were inert and environmentally benign?**

**Rowland:** The study of the atmospheric fate of the CFCs began with a short proposal to the U.S. Atomic Energy Commission submitted as an addendum to my regular yearly request for renewal of funding for our studies of the reactions of radioactive molecules, then entering its 17th year. Our studies of hot atom chemistry had long since shown that essentially all molecules could decompose if excited by enough energy, and specifically that some of the CFCs were not inert when attacked by highly energetic chlorine or fluorine atoms. In these cases, the attacking atoms were radioactive, and carried excess kinetic energy from their birth in nuclear reactions, and could be traced later through their radioactivity. Energetic ³⁶Cl atoms could react with CCl₃F to form CCl₃CF₂ or CCl₂³⁶ClF and leave sufficient energy on the product molecule that it would undergo secondary decomposition. Likewise, energetic ³⁷F atoms could even react with CF₃ to produce CF₃³⁷F which in turn could decompose by loss of two fluorine atoms to give radioactive difluoromethylene, which in turn could be trapped by gaseous hydrogen iodide to form CHF³⁷FI. The latter sequence required that the CF₃³⁷F molecule must have contained more than nine electron volts of excitation energy.

Similarly, we knew that all polyatomic molecules have ultraviolet spectra, which in most cases represent absorption with dissociation, and that the sun gives off high energy ultraviolet radiation. So the “inertness” of the CFCs was clearly a generalization to which there were some possible exceptions. At some altitude in the atmosphere at some time, the CFCs (and all other polyatomic molecules) would encounter very short wavelength solar ultraviolet light that they could absorb and would cause them to decompose. This was a qualitative background fact that was known separately both to Mario Molina and to me, but at what altitude and after how long was not known.

The “environmentally benign” aspect of your question did not come into play until later for the obvious reason that the CFCs were present in the atmosphere in very small quantities.

**The Spectrum: What made you look to the stratosphere to understand CFCs fate?**

**Rowland:** The question of the fate of such molecules in the atmosphere can in retrospect simply be a study of the cradle-to-the-grave history of these particular molecules. For many compounds, this “life” path can be relatively short. Molecular chlorine, Cl₂, photolyzes in direct sunlight in an hour or so, breaking down into two chlorine atoms. Hydrogen chloride dissolves in raindrops, making very dilute hydrochloric acid, which falls to earth as rain within a few months. Methyl chloride, CH₃Cl, is oxidized by hydroxyl abstraction of one of the hydrogen atoms, leaving the CH₂Cl radical that then immediately reacts with molecular oxygen. But the CFCs are inert toward these chemical mechanisms and last much longer in the atmosphere. Beyond these three process types, none of the increasingly unlikely tropospheric reactions investigated by Mario Molina disclosed any which would materially affect the CFCs.

**The Spectrum: That left the stratosphere and solar ultraviolet.**
Rowland: The absorption of ultraviolet radiation by ozone in the stratosphere removes all UV radiation with wavelengths shorter than 290 nanometers, and the CFCs only begin to absorb in wavelengths around 220 nm which leads to chemical decomposition by breaking the C-Cl bond (weaker than C-F bond) to form an atom of chlorine and leaving a CCl$_2$F radical from CCl$_3$F or a CClF$_2$ residue from CClF$_3$. Consequently, solar photolysis of CFCs can only begin when the molecules have risen high enough in the atmosphere to encounter 220 nm ultraviolet radiation, which means above most of the ozone in the atmosphere (and most of the O$_3$ as well). This requires a long time—an estimated 40-60 years for CCl$_3$F and 100 years or more for CCl$_2$F$_2$. Because during the 1960s and 1970s the CFCs were entering into the atmosphere at a rate doubling every seven years, the potential atmospheric concentrations were lagging far behind the actual observed concentrations. The calculations with a simple atmospheric model gave future concentrations 10 to 30 times larger than the presently observed ones.

The Spectrum: What if you had stopped or detoured right there, without asking about the fate of the chlorine atom produced in the photolysis?

Rowland: With that step, the outlook quickly changed from an interesting scientific problem about a “nearly inert” molecule—after all, something that lasts unchanged in the atmosphere for a century is inert enough for most purposes except release to the atmosphere—into an important global environmental problem. This transformation came about because of the existence of a chain reaction by which atoms of Cl can be present either in the atomic form or tied up as ClO radicals in a very long alternating sequence which ends up destroying 100,000 molecules of ozone or its precursor, O atoms. When this great reactivity was put into the future equation with its much larger CFC concentrations, it became clear that in that future time frame, the CFCs were competing very effectively with the natural processes that control ozone formation and destruction. The interesting scientific study now had a major global atmospheric problem associated with it.

The Spectrum: Your research led with relative speed to international agreement on a CFC ban. What’s needed—scientifically, politically, socially—to bring the global warming issue to a policy conclusion?

Rowland: The initial steps—the banning of CFCs as aerosol propellants in the United States, Canada and some Scandinavian countries—took place within a few years after the problem first surfaced. Our initial publication came out in *Nature* in June 1974, and both their presence in the stratosphere and their decomposition by ultraviolet radiation were quickly confirmed.

In the United States, for instance, the ban on non-essential uses as aerosol propellants was announced in October 1976, to take effect 18 months later. The initial attitude of the Environmental Protection Agency changed in 1981 to a do-nothing approach to CFCs, nor was there any real regulatory activity in Europe or Japan until after the discovery of the Antarctic Ozone Hole. This changed the public view of the CFC problem from a possible future loss of perhaps 10% of the ozone 25 or 50 years in the future to a 50% loss in Antarctica last year. The appearance of massive ozone loss galvanized action both in exploring the causes of Antarctic ozone loss, ascertaining that ozone loss was occurring in the north temperate zone as well, and quickly resulted in the Montreal Protocol, and then toward strengthening it into a total ban.

The global warming problem is of course much larger because the uses of energy play a much more inclusive role in all societies than the uses of CFCs. The evidence that carbon dioxide has been increasing in the atmosphere has now been known for more than 30 years, and that of the other greenhouse gases for two decades, while the global temperature increase in the past 20-25 years is quite striking. What is missing so far is the greenhouse analog of the Antarctic Ozone Hole—some spectacularly dangerous development never seen before.

The Spectrum: What do you regard as one of the biggest challenges for atmospheric chemistry and environmental photochemistry in the 21st Century?

Rowland: The “official” discovery that methane is a pervasive component of the atmosphere is credited to Migeotte in 1948. The discovery that its atmospheric concentration was increasing came in 1979. Now, the emphasis is on the sources and sinks, and the amounts not only of CH$_4$ but also CH$_4$D, CH$_3$T, $^{13}$CH$_4$ and $^{14}$CH$_4$ in literally hundreds of different locations, all measured with very high precision. And similar experiments for hundreds of other molecules.
highly energetic radical ion pair. In this context, charge-separation and, thereby, recovering most of the excited state energy, should, if conceivable, take place at small free energy changes, $-\Delta G^{\circ}_{CS}$. The energy gap characterizing the charge-recombination ($-\Delta G^{\circ}_{CR}$), on the other hand, should be kept as large as feasible. Ideally, large energy gaps should ensure dynamics that are deeply shifted into the *inverted* region and, consequently, to slow down the limiting and energy wasting charge recombination.

Variation of the reorganization energy ($\lambda$) is an effective way to modulate the electron transfer rates. In particular, modifying $\lambda$ influences the maximum of the parabolic log-$k_{ET}$ versus $-\Delta G^{\circ}_{CS}$ dependence on the abscissa. An even more dramatic impact is seen on the activation energies for the charge separation ($-\Delta G^{\circ}_{CS}$) and the reverse charge recombination ($-\Delta G^{\circ}_{CR}$) are much reduced and increased, respectively. Figure 1 illustrates this explanatory for a spherical C$_{60}$ and a planar naphthalenediimide. Thus, under optimal conditions, small reorganization energies lead to optimal charge-separation kinetics, which are located near the top of the Marcus curve—even if the driving forces are small—and a deceleration of the charge-recombination rates, which are buried far into the *inverted* region.

The ultimate goal is to power a thermodynamically driven charge-separation event and yield a highly energetic radical ion pair. In this context, charge-separation and, thereby, recovering most of the excited state energy, should, if conceivable, take place at small free energy changes, $-\Delta G^{\circ}_{CS}$. The energy gap characterizing the charge-recombination ($-\Delta G^{\circ}_{CR}$), on the other hand, should be kept as large as feasible. Ideally, large energy gaps should ensure dynamics that are deeply shifted into the *inverted* region and, consequently, to slow down the limiting and energy wasting charge recombination.

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As the major conclusion of our considerations stands the fact that both, donor and acceptor moieties, should support the stabilization of charges—electrons or holes—within their chemical structures. Delocalization of charges, over a large and extended π-system is unquestionably a very valuable approach to ensure small reorganization energies (λ).

This raises the crucial question what would determine a small λ-value and especially what would render fullerenes and, more precisely, fullerene-based donor-acceptor ensembles particularly promising acceptor candidates. It should be noted that the reorganization energy (λ) consists of two constituents. A purely structural component (λs), which include mainly vibrations of the molecules, etc., and contributions stemming from the polarization changes in the solvent environment (λq).4

The energy required to reorganize any given system to an optimum configuration for electron transfer defines λ. Thus, the characteristic λ-value for individual donor-acceptor systems emerges as one of the most significant parameters to understand the solute-solvent interaction in the electron transfer process. In the context of the fullerene’s structure several criteria are worthwhile to refer to.

Firstly, the high degree of delocalization within the extended π-system should be considered and its immediate impact on λs. In particular, a set of 60 molecular orbitals split into 30 bonding/30 antibonding π-molecular orbitals. The resulting electronic configuration discloses for C60 a five-fold degenerate HOMO (t1) and a three-fold degenerate LUMO (t1u), which are separated by an energy gap of 1.8 eV.5 The three isoenergetic LUMOs have consequences that in electrochemical experiments, six equally-spaced reduction waves were registered for C60.6 The separation between any two successive reduction steps is ca. 450 ± 50 mV. This is regarded as a clear manifestation for conditions that guarantee the optimal delocalization of charges, namely, electrons. In other words, even in a highly reduced fullerene state, electrons, as they are being subsequently added to the fullerene’s π-system, experience little, if any, repulsive forces. An expedient bond-order-based method to calculate bond reorganization energies (λq) strengthens the electrochemical observation.7 The bond reorganization energies, which relate explicitly to structural changes, such as bond length variations etc., upon adding electrons, are for C60, C60+, C60–, C602–, C603–, C604–, C605– all nearly identical. Another interesting point is that λs in fullerenes is smaller than those estimated for linear polyenes, including that of benzene, naphthalene, anthracene etc.

Secondly, the structural rigidity of the fullerene core is another crucial matter in regard to λs. For example, from small Stokes-shifts, as they were determined for C60 derivatives from the energetic difference between the 0-0-0 absorption and the 0-0-0 emission transitions, one can infer the fact that the force constants, controlling the vibrational levels in the first singlet excited state, resemble those in the singlet ground state.8 The minor Stokes-shift, expressing a Franck-Condon instability energy of only ~20 cm–1, is very compatible with the highly symmetric and rigid structure found in fullerenes and their functionalized derivatives.

Similarly, the difference between ground and one-electron reduced state, as expressed by Raman shifts of the totally symmetric “pentagonal pinch” mode is negligible.9 The exact experimental number is 6 cm–1 for C60. In addition, for the insulating K2C60 composition, reflecting the complete filling of the three-fold degenerate LUMO (t1u), the vibrational frequency shifts from 1467 cm–1 to 1430 cm–1, which corresponds to a frequency shift of 6–7 cm–1 per added electron.10

Thirdly, the symmetrical shape and large size of the fullerene framework evokes that the solvent-dependent term (λq) is small.11 This term expresses the required energy for the adjustment of a generated state, which is either an excited or reduced state, to the new solvent environment, relative to the ground state. A simple picture depicts this rationalization: It is conceivable that solvent molecules in a solvation sphere are little perturbed by a small charge density. The charge density is highly delocalized in each carbon atom of C60 and contributes less or marginally to λs.

To accommodate all these observations we must conclude that in C60 the structure of the electron acceptor in its ground, reduced and also excited state is similar. Therefore, changes in the equilibrium nuclear configurations, that is, the vertical displacement on the reaction coordinate, which are associated with the transformation of a molecule in a photoinduced charge transfer reaction from an initial (i.e., photoexcited state) to a final (i.e., charge-separated state) are in the case of C60 notably small.

For second-order intermolecular electron transfer processes of electron donors and electron acceptors at diffusional encounter, however, definitive evidence for the inverted region is almost nonexistent, although the inverted effect has been well-established for the first-order back electron transfer process in the radical ion pair produced by intermolecular electron transfer reactions.12 One of the central obstacles to overcome is the fact that the rate constants for intermolecular reactions consist not only of an activation component (kact), but also include a diffusion related term (kdiff), with the latter defining the upper limit of the observable rate. Thus, generally the rate constant first
increases with increasing the overall driving force as far as the following relationship holds: \( k_{\text{diff}} > k_{\text{act}} \). Once \( k_{\text{act}} \) starts to equal \( k_{\text{diff}} \), the rate constants enter the diffusional limit. Notwithstanding the rate constant fails, in most cases, to display a decrease at higher \( -\Delta G^\circ \). Instead it remains at this purely diffusion-controlled level and only the normal and top—assuming that \( k_{\text{diff}} \) is not too slow—region is observed.

The difficulty to realize the inverted region may have various reasons such as a low \( k_{\text{diff}} \) obscuring the decline of the overall rate and/or the distribution of intermolecular donor-acceptor distance on the energy gap. As for the latter reasoning, enlargement of the driving force, especially into the highly exergonic region (\( -\Delta G^\circ > 0 \)), results in an increase in \( \lambda \). Notably strong is the impact on the term that alludes to the solvation dynamics (\( \lambda \)). To illustrate this, for a reaction between particular donor and acceptor—controlled by a diffusional encounter—a larger solvent reorganization energy holds the rate constant large for greater energy gaps (\( -\Delta G^\circ \)). For a given donor-acceptor pair, a large \( \lambda \) means, however, a bigger encounter distance. This distance distribution effect makes it plausible that the observation of the Marcus inverted region in intermolecular electron transfer systems is an extremely difficult task.

Pulse-radiolytic studies were performed to determine the rate constants of intermolecular charge-shift (\( k_{\text{CSH}} \)) from fullerenes (\( \text{C}_{60} \), \( \text{C}_{78} \), and \( \text{C}_{84} \)) to a series of arene \( \pi \)-radical cations in dichloromethane.\(^{13}\) The one-electron oxidation potentials of the employed arenas—corresponding to the one-electron reduction potentials of arene \( \pi \)-radical cations—were complementary determined in dichloromethane to evaluate the driving forces (\( -\Delta G_{\text{CSH}}^\circ \)) of electron transfer oxidation of fullerenes with arene \( \pi \)-radical cations. In particular, varying the oxidation strength of the arene \( \pi \)-radical cation, that was generated in a radical-induced oxidation evolving from the solvent radical cation [dichloromethane]\(^{•+} \), helped to vary the free energy changes, \( -\Delta G_{\text{CSH}}^\circ \). In such charge-shift type electron transfer reactions, the solvation before and after the electron transfer may be largely canceled out when the free energy change of electron transfer is expected to be rather independent of the solvent polarity. On the other hand, the solvent reorganization energy for the electron transfer reaction is expected to decrease with decreasing the solvent polarity. Thus, this is an ideal system to examine whether fullerenes have a small intrinsic reorganization energy (\( \lambda \)) or not in a less polar solvent such as dichloromethane. The driving force dependence of \( k_{\text{CSH}} \) shows a pronounced decrease towards the highly exothermic region—see Figure 2, representing the first definitive confirmation of the existence of the Marcus inverted region in a truly intermolecular electron transfer. The log \( k_{\text{CSH}} \) value increases with increasing the driving force to reach a diffusion-limited value and then decreases with further increase in the driving force. Please note that the \( k_{\text{CSH}} \) value (2.3 x 10\(^{9} \) M\(^{-1}\) s\(^{-1}\)) for a highly exergonic electron transfer from \( \text{C}_{78} \) to mesitylene radical cation (\( -\Delta G_{\text{CSH}}^\circ = 0.73 \) eV) is about 20 times smaller than the value (4.5 x 10\(^{10} \) M\(^{-1}\) s\(^{-1}\)) for a much less exergonic electron transfer from \( \text{C}_{78} \) to, for example, chrysene radical cation (\( -\Delta G_{\text{CSH}}^\circ = 0.32 \) eV). From these experiments an experimental value of about 0.36 ± 0.04 eV was deduced for the total reorganization energy of \( \text{C}_{78} \) and \( \text{C}_{84} \) in oxidative charge-shift processes in dichloromethane.

As far as intramolecular electron transfer reactions is concerned, marked effects were seen in a study, in which we probed a fullerene-porphyrin conjugate with van der Waals contacts (edge-to-edge separation (\( R_e \))

\[ \text{Figure 2. Plot of } \log k_{\text{CSH}} \text{ vs } -\Delta G_{\text{CSH}}^\circ \text{ for electron transfer from } \text{C}_{60} \text{ (circle with interior point), } \text{C}_{78} \text{ (solid circles) and } \text{C}_{84} \text{ (hollow circles) to arene radical cations in dichloromethane. The solid line is drawn based on the Marcus theory of electron transfer.} \]
\( \lambda \approx 3.0 \text{ Å} \) such as trans-2-ZnP-C_{\infty} \cite{14} reminiscent of the trans-1-ZnP-C_{\infty} ensemble reported by Diederich et al.\cite{15} The short separation guaranteed that an intramolecular charge-separation succeeds in virtually any solvent and dominates over the competing energy transfer. The rapid formation and decay of ZnP\(^{2+}\) between 670–680 nm and C_{\infty}\(^{-}\) around 900 nm in toluene testifies to the charge-separation and charge-recombination processes, respectively. Now, the systematic change in solvent polarity, for example, from non-polar toluene to polar benzonitrile provided the powerful means to alter the free energy changes over a wide range—no change in the chemical structure deemed necessary. Indeed, a marked acceleration of the charge-recombination rates was seen at smaller \(-\Delta G_{cr}^\circ\), namely, at higher dielectric constants, which corroborated our working hypothesis. To illustrate this, the lifetimes varied over a wide range: 619 ps (toluene) to 38 ps (benzonitrile). Most importantly, correlating \( \log k_{cr} \) with \(-\Delta G_{ET}^\circ\) (i.e., charge-separation and charge-recombination) and fitting of the resulting parabolic dependence yielded an experimental \( \lambda \)-value of 0.86 eV. The delocalization of electrons in C_{\infty} provided by its large three-dimensional \( \pi \)-system, leads to the conclusion that the reorganization energy in the ZnP-C_{\infty} systems is not receptive towards large changes in the solvent polarity in going, for example, from toluene and THF to benzonitrile. Accordingly, the reorganization energies of the dyad are reasonably assumed to be comparable in the different solvents.

Recently, we reported the first comprehensive assay of \( \lambda \)-values for intramolecular electron transfer involving a three-dimensional acceptor—spherical C_{\infty}—and a two-dimensional acceptor—planar naphthalenediimide (NIm).\cite{16} In this context we probed a series of porphyrin-linked C_{\infty} and NIm ensembles, endowed with similar rigid spacers. Importantly, in all ZnP-C_{\infty} dyads, the value of charge separation is much larger than the value of charge recombination. Conversely, the charge recombination rate in the corresponding NIm-based dyad, ZnP-NIm, is much larger than the value of charge separation as determined by the picosecond transient absorption spectrum and the decay of the porphyrin’s fluorescence. The \( \lambda \)- and \( V \)-values are obtained from the intercept and the slope as \( \lambda = 0.59 \pm 0.15 \text{ eV} \) and \( V = 7.9 \pm 1.7 \text{ cm}^{-1} \), respectively, ZnP-C_{\infty}. A linear correlation was also obtained for ZnP-NIm, which afforded a much larger \( \lambda \)-value (1.41 \pm 0.33 eV) together with a similar \( V \)-value (7.8 \pm 3.2 cm\(^{-1}\)). Such an extraordinary large difference in \( \lambda \) between the C_{\infty} and NIm dyads is the reason why the ratio of \( k_{cs} \) to \( k_{cr} \) is reversed in the two donor-acceptor systems and why the difference in charge recombination is as large as four orders of magnitude.

In summary, the delocalization of charges—electrons or holes—within the giant, spherical carbon framework of fullerenes (diameter > 7.5 Å) offers unique opportunities for stabilizing charged entities. Important incentives evolved from the small reorganization energy (\( \lambda \)). The reorganization energy (\( \lambda \)) in C_{\infty}-based donor-acceptor structures is smaller than those reported previously for porphyrin-quinone\cite{17} and zincporphyrin-freebase porphyrin\cite{18} linked systems, which typically are in the range between 0.8 eV and 1.2 eV. Unquestionably, the most striking observation is that charge-recombination in zinc porphyrin/fullerene dyads and triads is located deep in the inverted region of the Marcus parabola, with lifetimes ranging from as short as tens of picoseconds to nearly hundred microseconds. This phenomenon led to a conceptual breakthrough in our work. Recent results regarding a 24\% efficient charge-separation within a molecular tetrad. The lifetime of the spatially-separated (\( \sim 49 \) Å) radical pair, product of a sequence of energy and electron transfer reactions, reaches well beyond milliseconds (0.38 s), into a time domain which has never been accomplished so far in an artificial photosynthetic reaction center.\cite{19} Our results open the way to use C_{\infty}-based donor-acceptor constructs\cite{20} as integrative components in solar energy conversion and photovoltaic applications.

Acknowledgment

This work was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is document NDRL-4441 from the Notre Dame Radiation Laboratory. I appreciate the fruitful and stimulating collaborations with Professors Klaus-Dieter Asmus, Shunichi Fukuzumi, Andreas Hirsch, Hiroshi Imahori, Nazario Martin, Maurizio Prato, and David Schuster.

References

Introduction and Overview

The Stark effect (electroabsorption) measures the perturbation of the states of a molecule due to the application of an external electric field that is typically $10^5$-$10^6$ V/cm in magnitude. Stark spectroscopy is somewhat analogous to solvatochromism with the important distinction that the magnitude of the externally applied electric field is used as a variable rather than the solvent polarity. Using Stark spectroscopy, one may obtain the magnitude of the change in dipole moment ($\Delta \mu$) and the trace of the change in polarizability ($\text{Tr} \Delta \alpha$) between two rotational, vibrational, or, most commonly, two electronic states of a molecule. We refer to these quantities as the dipolar properties of the molecule and they represent some of the most fundamental parameters that characterize the electronic structure of the system. In general, the change in molecular polarizability is not obtained from a solvatochromic analysis, particularly if the molecules of interest are polar. Another attribute that makes Stark spectroscopy powerful is the ability to study optical chromophores in a wide range of environments including glasses, proteins, membranes, and polymers (Figure 1).

In our labs, we have used Stark spectroscopy to probe the electronic properties of polymers such as MEH-PPV, and polyaniline in its emeraldine base (EB) form and in its conductive form as well as oligomers of these species (Figures 2 and 3). This review focuses on the use of this technique as a probe for disorder in these polymers embedded in glasses and in films. Understanding and ultimately controlling the presence of disorder in such samples is critical to developing and manufacturing efficient devices based on organic electronics.

Before describing our results, we first introduce the technique of Stark spectroscopy and the computational methods that our collaborators have used to model the experimental findings. In the discussion of the computational results, the term “we” should be taken to refer primarily to our collaborators, Prof. David Yaron (CMU) and his graduate student, Angela Liu.

Experimental Methods

Apparatus: The instrument that we have constructed to perform the measurements reported here is described in detail in reference 4. A diagram, labeling the most important elements is shown in Figure 1. The methods for analyzing Stark spectroscopy have not been included in this article due to space constraints. Please refer to references 5-7 for details.

Computational Methods: One of our primary interests is in establishing whether or not good correspondence exists between the results of electronic structure calculations, which are usually gas phase, and the measured properties of molecular systems in the condensed phase. In this area, we have greatly benefited from collaboration with Prof. David Yaron of our Department. His group has developed a direct CI method applied to INDO/s that greatly speeds up the calculation of excited state properties.
It is therefore possible, in a short period of time, to calculate the values of $\Delta \mu$ and $\text{Tr} \, \Delta \alpha$ for a large distribution of molecular conformers that have been generated by varying dihedral bond angles in a systematic fashion. This allows for a realistic comparison between theory and experiment as it is to be expected that a distribution of molecular structures exist within our samples.

In our earlier studies on smaller molecules, we typically used a modified Onsager reaction field formalism to correct the calculated values for $\Delta \mu$ and $\text{Tr} \, \Delta \alpha$ for the effect of the dielectric environment of our matrices.$^9$ A critical aspect of implementing these corrections is accurately accounting for the true volume of the cavity occupied by the molecule in the dielectric medium. For large molecules, such as those described here, accurate cavity corrections are extremely difficult to implement. Nonetheless, it is still important to account for the effect of the dielectric environment on $\Delta \mu$ and $\text{Tr} \, \Delta \alpha$, particularly if the system is highly polarizable as are MEH-PPV and its oligomers. In order to do this we are again fortunate to have collaborated with Prof. David Yaron. His group has developed a method to solvate the electronic states of conjugated molecules embedded in a dielectric, detailed in reference 10, that gives very good agreement with our experimental results with a minimum of adjustable parameters. This method is used to model the electronic properties of the MEH-PPV oligomer described here.

**Results and Discussion**

The structures of MEH-PPV and their associated oligomers are shown in Figure 3. An important thing to notice is that, as drawn, all of these molecules possess a center of symmetry. Therefore, we would expect to measure a $\Delta \mu$ of $\sim 0$ for these systems in the absence of any disorder, either in the structure or in the environment. Either effect reduces the molecular symmetry, potentially making net charge transfer an energetically favorable process. Instead, a large $\Delta \mu$ (6-12 D) is measured for each molecule shown, implying the presence of substantial disorder.

In order to understand these results, there are a number of potential sources of disorder to consider:

1. **Chemical defects:** In the case of MEH-PPV, these can be carbonyls formed as photo-oxidation products over time with illumination.$^{11}$ Alternatively, they may be structural defects introduced in the polymerization process. One example is the presence of saturated links in MEH-PPV, which Barbara et al. have postulated to explain the polarization properties of this emission of this polymer measured using near field spectroscopy.$^{12}$ Similarly, defects can be observed in EB as a result of the synthetic process.$^{13}$ Because the values of $\Delta \mu$ of both EB and MEH-PPV are very similar to those of their corresponding oligomers, we do not expect chemical defects to make a substantial contribution. That is to say,
the oligomers are synthesized essentially free from defects though the polymers may not be. Moreover, the value of $\Delta \mu$ does not change with illumination time, suggesting that photo-oxidation does not play a role either.

(2) Aggregates: A tremendous amount of recent attention has been paid to the role of aggregation in altering the bulk conductivity of polymers that may be doped, such as EB and polythiophene. Likewise, aggregation has been argued to affect the efficiency of devices made from MEH-PPV by decreasing the charge mobility in the polymer though increase their photo-stability by restricting the diffusional entry of oxygen. Though aggregation may not necessarily lower the symmetry of the constituent molecules, there are numerous examples in which it nonetheless substantially affects $\Delta \mu$ and/or $\text{Tr } \Delta \alpha$. To the extent possible, we have minimized aggregation in our samples by examining the effect on the Stark spectrum of serially diluting the concentration of oligomer or polymer in the glass. We continue diluting until we reach a regime where the Stark spectrum does not change shape with decreasing concentration and the magnitude of the signal is linear in concentration. We then work at the lowest concentration that will yield spectra with reasonably high signal to noise.

(3) Torsional defects: The molecules shown in Figures 2 and 3 are necessarily symmetric only when planar; torsions about the single bonds connecting the rings may lessen the symmetry, leading to a non-zero $\Delta \mu$. The extent to which this effect accounts for the measured $\Delta \mu$ is estimated using computational techniques, as detailed for each molecule below.

(4) Asymmetric local fields due to the environment: Even a perfectly symmetrical molecule can exhibit a substantial $\Delta \mu$ due to disorder in its environment. Some of the most extensive studies of this effect are due to Bryan Kohler and his lab. These workers found that a $\Delta \mu$ of ~0.1 D could be induced in the symmetric polyene octatetraene embedded in a polycrystalline hydrocarbon matrix. Via extensive modeling, they showed that the local fields due to the C-H dipoles of the matrix, which can be on the order of $10^6$ V/cm, induce dipoles centered on the polyene. These can add up to a net macroscopic dipole moment, measured by the Stark effect, if the local fields are asymmetrically distributed. Because the magnitude of the induced dipole scales as the molecular polarizability (the induced dipole is given by the product of the dipole moment and the vectorial local field), conjugated molecules and other highly polarizable systems are most likely to show this effect. Moreover, the induced dipole is generally larger in the excited state, giving a large $\Delta \mu$, because the excited state is typically much more polarizable than the ground state. Here, we model this effect by calculating the predicted $\Delta \mu$ for an oligomer embedded in a surrounding matrix of random dipoles, as described below. We find that matrix disorder accounts for roughly half the measured $\Delta \mu$ of MEH-PPV and its oligomer, due, no doubt, to the large polarizability of the excited states of these molecules.

Below, the experimental and computational results for MEH-PPV, EB and their associated oligomers are elaborated. It is shown that torsional distortion accounts for nearly all of the charge-transfer character observed for EB and its oligomer, while both torsional and matrix-induced disorder contribute approximately equally to that observed for MEH-PPV and related molecules. This difference between EB and MEH-PPV is a consequence of the localized versus delocalized character of their respective excited states.
Torsional Disorder in Emeraldine Base (EB): Analysis of the Stark spectrum of EB dispersed in a film of polymethylmethacrylate (PMMA) yields a value for $\Delta \mu$ of 6.1 D and a Tr $\Delta \alpha$ of 200 Å$^3$. This value of Tr $\Delta \alpha$ is relatively small for extended conjugated systems. The properties of its oligomer (oEB) are quite similar, as is the position of its absorption maximum. This comparison indicates that, by modeling a short chain segment that is symmetrically terminated with phenyl rings (Figure 2a), we can capture the essential optical and electronic properties that characterize the more complex polymeric system.

Recent INDO/s calculations have shown that the optically excited state of this molecule is, in the planar geometry, one in which a symmetric charge transfer of ~0.25 e into the central quinoid from each of the two benzenes lying on either side occurs (Figure 2a). This model would predict a $\Delta \mu$ of ~0 because the polymer is then nominally symmetric in the long-chain limit. However, breaking the symmetry ever so slightly by rotating one of the phenyl rings about the single bond ~30° away from its value in the minimized structure (in computer), generates a degree of charge transfer asymmetry in the excited state consistent with the experimentally measured $\Delta \mu$ of 6 D. The ground-state dipole moment, on the other hand, remains close to 0. Naturally, to realistically simulate experiment, a distribution of $\Delta \mu$ values are obtained by systematically varying the torsional angles of the two benzene rings; these range from 1.3-8.6 D. The conformers that give substantial calculated $\Delta \mu$'s are predicted to be at most ~1000 cm$^{-1}$ higher in energy than the optimized structure. Therefore, it is reasonable to expect that they would be present in our sample, given the 1-2 kcal/mol expected error in the energy calculations. Because there are calculated to be numerous low energy conformers of EB, all having different values of $\Delta \mu$, it is expected that the Stark experiment returns the most probable value but that a distribution is present within the sample.

In the case of EB, it proved unnecessary to invoke matrix disorder in order to get good agreement between calculation and experiment. In fact, because the Tr $\Delta \alpha$ of EB is relatively small, it would be necessary to invoke un-physically large asymmetric local fields to rationalize an induced dipole of 6 D for a symmetric molecular geometry.

These findings demonstrate that electroabsorption is a highly effective method for demonstrating the presence of disorder in a polymeric system arising from geometric distortions of the polymer backbone. Such information is very useful because a much higher degree of conductivity upon doping EB is expected if the sample is initially in a more ordered state.

Torsional and Matrix-induced Disorder in MEH-PPV: For samples of MEH-PPV in frozen organic glasses such as toluene and methyl-tetrahydrofuran, electroabsorption returns a value in the range of 11 ± 2 D for $\Delta \mu$ and a relatively large value of Tr $\Delta \alpha$ of 2000 Å$^3$. The model 9-ring oligomer (Figure 3b) yields similar values ($\Delta \mu$ of 7 D, Tr $\Delta \alpha$ of 2000 Å$^3$), suggesting that these two properties saturate at roughly the same chain length as does the optical gap of this material. As for EB, we probed the effects of geometric disorder on a 8-ring model oligomer (in which the side chains were removed for simplicity) which we denote as PPV-8 (Figure 3c), by varying the torsional angles between all of the rings in small increments to create a distribution of structures which were then energy minimized constraining the specific bonds that were varied. Here we find some differences in behavior from EB. First, none of the rotamers generated in this fashion had a calculated gas-phase $\Delta \mu$ greater than 1 D. Though asymmetric charge transfer is clearly not favored in the gas phase, solvating the electronic states of the distorted molecule using the dielectric screening method developed by Yaron and co-workers yields a distribution of $\Delta \mu$ values peaked at ~8 D. This is a particularly striking illustration of the importance of even a uniform (continuum) matrix dielectric environment in stabilizing charge-transfer states. Moreover, we find that, when the matrix dielectric is accounted for, torsional distortions can account for roughly 50% of the experimentally observed $\Delta \mu$. We next explicitly included the effect of matrix disorder to determine its effect on $\Delta \mu$ of this system.

To focus entirely on the effect of the matrix electric fields in generating an induced $\Delta \mu$ in OPPV-9, as proposed in the model of Kohler et al., we modeled the system as a planar symmetric unsubstituted PPV-8 (Figure 3c) surrounded by one of two types of matrices. The first consists of ~200 explicit methyl tetrahydrofuran molecules, whose configuration has been generated using molecular mechanics. The second is a random dipole lattice in which the magnitude of the dipoles and their density have both been chosen to roughly match that of the solvents used and whose orientation is random. In the case of the explicit solvents, only a few configurations could be generated, for the random dipole model, 500 configurations were examined.

An important point is that the electronic states of the planar PPV-8 were solvated, as described above, so that the value of Tr $\Delta \alpha$ would be close to that measured experimentally. Without solvation, Tr $\Delta \alpha$ is calculated to be roughly 10% of this value and the induced dipoles would be similarly underestimated.

For each matrix studied, the electric fields at the position of the OPPV-9 molecule were calculated as were the induced
dipoles due to the interaction of these local fields with the molecular polarizability. The sum of these induced dipoles yields the macroscopic $\Delta \mu$, the distribution of which is shown in Figure 4 along with the distribution in the value of $\text{Tr} \Delta \alpha$. For both properties, the ground state values are much smaller than the associated excited state values.

Clearly, disordered matrix fields can account for a substantial portion of the experimentally measured $\Delta \mu$ for molecules having highly polarizable excited states such as MEH-PPV. This observation is in line with the findings of others for highly conjugated molecules such as polydiacetylene.
Summary and Future Directions
The work summarized in this review gives several examples of how electroabsorption can be used to easily and rapidly classify polymer films as to the extent of disorder present. We assert that the interpretation of the results are more straightforward than, for example, monitoring the absorption and/or emission spectrum for signs of aggregation, exiplex formation, or short chain segments, as is commonly done. Of course, electroabsorption performed as described here only informs about the bulk properties of the film. Another limitation is that the cause of the disorder observed must be inferred through molecular modeling. Both of these limitations can be overcome by the combination of microscopy with electric field methods which is a current goal of our laboratory.

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About the Author
Linda Peteanu received her Ph.D. in 1989 under the direction of Dr. Donald Levy, University of Chicago, where she studied the electronic spectroscopy of jet-cooled biomolecules. She held a three year postdoctoral position in the lab of Dr. Richard Mathies, University of California, Berkeley. There she studied the ultrafast dynamics of excited state proton transfer using resonance Raman spectroscopy and collaborated with the group of Dr. Charles Shank, Lawrence Berkeley Labs, to examine the time-resolved kinetics of retinal isomerization in the visual pigment rhodopsin. After a brief stay in the lab of Dr. Bryan Kohler, University of Riverside, Peteanu joined the faculty of the Department of Chemistry, Carnegie Mellon, where she has been since 1993 and is now an Associate Professor. Peteanu’s group has been involved in the application of Stark spectroscopy to problems in chemistry, biology, and materials science and is now examining similar systems using optical microscopy. Her address is Department of Chemistry, Carnegie Mellon, Pittsburgh, PA 15213; e-mail: peteanu@andrew.cmu.edu.

References
focus on

Lingua Photochemica

That draft manuscript mentions a sample’s isobestic point. Or should that be *isostilbic*? Ever confuse absorbance and absorptivity? The Franck-Condon state and the Franck-Condon principle—one in the same or different, and how do they relate to vertical transition?

When it is a question of the right terms, chemists often turn to the science’s ultimate authority, the International Union for Pure & Applied Chemistry (IUPAC). For photochemists, this is *Glossary of Terms Used in Photochemistry*. The Glossary now is being updated and Silvia E. Braslavsky, the IUPAC Task Group Chairman for the project, is soliciting input from photochemists who want additions to other changes to the science’s official vocabulary.

“The previous versions have had an important impact in the photochemical community,” Braslavsky told *The Spectrum*. Braslavsky, who is with the Max Planck Institute for Radiation Chemistry in Mülheim, Germany, noted that the glossary sees wide use—usually behind the scenes without citation—by researchers and students. Journals like *Photochemistry* and *Photobiology* and *Photochemical and Photobiological Sciences* recommend consulting the Glossary for terms and definitions (see, for example, [http://www.aspjournal.com/auth_instruct.html](http://www.aspjournal.com/auth_instruct.html)). The Glossary also has been included as a chapter in the *Handbook of Organic Photochemistry* and books like *Photochromism: Molecules and Systems*.

“We anticipate an expanded impact of the new version,” Braslavsky said. It should include terms used in the analysis of photoinduced reactions with polarized light, among other new terms, in addition to correcting mistakes and mismatches with other IUPAC glossaries.

“The use of the Glossary should improve the quality of presentation of publications on photochemistry and procedures utilizing photoinduced reactions, including those of industrial, environmental, and health-treatment relevance. It should also help in the standardization of procedures and in the teaching of photochemistry. Hopefully, it will be adopted by the photochemical societies and by journals.”

A provisional version of the Glossary was first published during 1983-1984 in the newsletters of the European Photochemical Association, the Inter-American Photochemical Society, and the Japanese Photochemical Association. Braslavsky and Kendall N. Houk, Harvard University, prepared the first edition, which IUPAC published in 1988 (*Pure Appl. Chem. 1988, 60, 1055–1106*). Braslavsky said the current 1966 edition needs updating because errors have been detected with respect to definitions in the “Green Book”—*Quantities, Units and Symbols in Physical Chemistry*—published by IUPAC’s Physical Chemistry Division. In addition, terms related to the use of polarized light in photoinduced reactions need to be included. Advances in photochemistry knowledge and technology also have produced new terminology that must be included to keep the Glossary current.

“Members of the working party for the update will propose changes to me,” Braslavsky said. “All photochemists are welcome to submit ideas directly to me (braslavskys@mpi-muelheim.mpg.de) or to any of the members of the working party, with deadline April 30, 2003.”

The working party consists of U. Acuña (Spain); J. Bolton (Canada); R. Bonneau (France); A. Braun (Germany); Alexander Chibisov (Russia); Ken Ghiggino (Australia); Hiroshi Miyasaka (Japan); Richard Weiss (USA); Massimo Olivucci (Italy); K. Razi Naqvi (Norway); and Shikang Wu (China).

“After collecting all suggestions and comments I will produce a revised version which will be sent to all members of the Sub-Committee on Photochemistry and will be published in the newsletters of the photochemical societies asking again for comments,” Braslavsky added.

After receiving further comments, a final revised version will be submitted to IUPAC for external refereeing and reconciling with other glossaries by the Interdivisional Commission on Nomenclature of IUPAC.

PDT Terminology

IUPAC also is nearing completion of a glossary of terms and basic protocols used in photodynamic therapy (PDT) studies, David Phillips told *The Spectrum*. Phillips, professor of chemistry at Imperial College London, chairs a Task Group that expects to complete a draft of the glossary by April. Plans then call for evaluation and comments from the photochemistry community, followed by publication. Task group members are Professor M. A. J. Rodgers, collaborator of long standing, Giulio Jori, University of Padova, and Antonio Tedesco, Sao Paulo University.

Who’s Who in Photochemistry?

Check the Inter-American Photochemical Society’s online directory. Then add or update entries for yourself and your research group in this definitive global directory. Who’s Who in Photochemistry includes photochemists’ web pages, email addresses, and bibliographies.

“It is a ‘self-serve’ operation, with entries added upon individual request,” says the IAP. Requests can be made by submitting the electronic form at [http://www.chemistry.mcmaster.ca/~iaps/joinwho.html](http://www.chemistry.mcmaster.ca/~iaps/joinwho.html). The form can also be used to correct an existing entry.

IAP’s criteria for a listing in the Who’s Who: You must be employed in a permanent position in academia, industry, or government. Students and postdoctoral fellows cannot be listed until permanently employed, but can use the directory as a resource.

Long-time users of the directory note that a growing number of names carry the “P,” which indicates online
availability of a selected publications list via hyperlinks. These publication lists reside either on the individual’s own server or at Columbia University, where they have been created by members of the Turro Group.

**Measuring Photomask Flatness**

Photomask and photomask manufacturers must meet increasingly tighter flatness specifications, while maintaining high levels of efficiency during production. Corning Tropel Corporation, a Corning Incorporated subsidiary, is moving ahead with new development plans for its UltraFlat™ 200 mask system, introduced late in 2002.

The system measures the flatness of polished photomasks, as well as film stress after coating, utilizing near-normal incidence interferometry and phase-shifting analysis software to deliver a 50 nanometer (nm) measurement uncertainty. It also can measure both sides of polished photomasks, coated or uncoated, in sizes up to six inches.

“Shrinking device features requires not only flatter wafers, but flatter photomasks,” said John Bruning, president, Corning Tropel. “The UltraFlat™ 200 mask system’s solid structural design and advanced optical fabrication techniques will help customers manufacture masks suitable for next-generation technologies.”

UltraFlat™ runs on Windows 2000 computers with intuitive menu-driven software that requires less than 30 seconds to display measurements. The 2003 development plans for UltraFlat™ 200 include integrated automated loading/unloading capabilities and even lower uncertainty specifications.

For additional information check out the website at www.corning.com/ SemiconductorMaterials.

**Walkin’ Down Memory Lane**

“You’re gonna drive yourself insane,” crooned country star Tim McGraw in that smash hit about a lost love, *Memory Lane*. “You’ll never find the sunshine,” he warned, “when you’re followin’ the rain.”

There’s plenty of sunshine awaiting chemists, however, who take a stroll down the memory lane that the *Journal of the American Chemical Society* built (http://pubs.acs.org/journals/jacsat/jacs125th/articles.html) as part of its 125th anniversary observation. It is a list of the 125 most frequently cited JACS articles, including blockbusters that have hooked individuals on career fields, fostered the emergence of whole new disciplines and industries, and won Nobels.

Papers by Dewar are there, and Merrifield, Corey, Pople, Lineweaver, Hammond, and Pauling. Some may find the list notable for who’s not on the most-frequently cited list. Where is Jack Roberts, for instance, Paul Bartlett, Arthur Cope, and ...?

**Lasing the Spectrum**

“In 10 years, laser light will span all the way to the x-ray region of the spectrum. The light will be used for the most precise microscopes that we can imagine, allowing real-time movies of the complex dance that atoms weave in chemical reactions and in pharmaceuticals yet to be visualized.”

Henry Kapteyn’s optimism came after the University of Colorado research team which he co-directs with Margaret M. Murnane developed an extreme-ultraviolet (EUV), laser-like beam. It produces highly focused light in a region of the electromagnetic spectrum not previously accessible. With wavelengths 10-100 times shorter than visible light, EUV lasers would have numerous applications—not only in microscopy but in lithography, nanotechnology, and other fields.

The EUV beam has peak powers approaching one megawatt, produces nanometer-scale light waves, and apparatus is smaller than any other EUV design. The entire apparatus fits on a moderately sized table. The beam’s peak power is higher than any other light source at the wavelengths it achieves, which range from the ultraviolet (UV) to around 6 nanometers in the EUV region.

It relies on a new “waveguide,” a hollow glass tube with internal ripples that coax light waves into traveling along at the same speed and help the waves reinforce each other. A femtosecond laser fired through the gas-filled waveguide in pulses of one quadrillionth—1/1,000,000,000,000,000—of a second creates the EUV beam.

Some of the EUV waves can be out of phase with the laser, canceling each other and weakening the beam’s coherence and strength. The ripples in the diameter of the waveguide, however, promote phase matching, coaxing light waves from the laser and EUV beams into traveling at the same speed.

“These waveguide structures are amazingly simple—just a modulated, hollow glass tube,” said Murnane. “It is as if the laser beam ‘surfs’ on the modulations and is slowed down—just as the speed bumps on the road slow a car down very simply and very effectively,” she added.

Slowing down the laser allows it to travel at the same speed as the EUV light and increases the efficiency of the process.

Murnane and Kapteyn hope to extend the beam’s range into the “water-window”—below 4-nanometers, which is ideal for imaging biological structures. Producing a beam in this region would allow construction of a small microscope for viewing objects at the nanoscale.
Popular Photomedicine: The Vampire Connection

"Stories of vampires date back thousands of years. Our modern concept stems from Bram Stoker’s quirky classic Dracula and Hollywood’s Bela Lugosi—the romantic, sexually charged, blood-sucking outcast with a fatal susceptibility to sunlight and an abhorrence of garlic and crosses. In searching for some underlying truth in vampire stories, researchers have speculated that the tales may have been inspired by real people who suffered from a rare blood disease, porphyria. And in seeking treatments for this disorder, scientists have stumbled on a new way to attack other, more common serious ills."

Check out the photomedicine profile that thousands of science enthusiasts are reading in the December 16, 2002, edition of Scientific American. It is a bloody good popular account, starting with the first use of psoralens thousands of years ago in Egypt and India for skin diseases to Tom Dougherty’s pioneering work at Roswell Park in Buffalo to tomorrow’s photomedicine research horizons.

Professional Photomedicine: The NCI Connection

"Photodynamic therapy (PDT) is hardly a mainstream cancer treatment, but new photosensitizers, new light sources and delivery devices, and a plethora of laboratory findings attempting to explain precisely how PDT kills tumor cells are expanding the understanding and use of the therapy."

And do not miss the review for clinicians and other health professionals published in the December 4, 2002, Journal of the National Cancer Institute. It updates PDT’s status in gastrointestinal cancers, brain tumors, head and neck cancer, bladder cancer, and inoperable and plural disease.

Cash for Compounds

Wanted by January 2004 by a long-established commercial firm in Europe with annual sales above $500 million annually: Dye, pigment or phosphor capable of shifting the wavelength of blue light (400 nm or 440 nm) to a 30-100 nm longer wavelength. The material should convert light of either 400 nm to light of 430-500 nm, or light of 430 nm to light of 460-500 nm. The dye, pigment or phosphor should absorb 90% of the incoming blue light when coated at a thickness of 10 to a few 100 microns. Conversion efficiency to the longer wavelength should be at least 90%. Resistance to intense red light irradiation (650-700 nm) would be a plus.

Like many of the solicitations for new technology that appear on yet2.com (www.yet2.com), the company seeking this compound is anonymous, the intended use not stated, and the bounty left to the imagination.

Yet2.com bills itself as “the first global forum for buying and selling technology on the Internet.” The technology marketplace offers companies and individuals opportunities to conveniently and privately purchase, sell, license and research new technology.

“Spanning all industries and areas of research and development, yet2.com is a community where technology officers, scientists and researchers can unearth cutting-edge discoveries as well as new applications for tried and true technologies. Yet2.com helps companies extract value from undervalued or unused technologies by streamlining the traditionally lengthy and ineffective process of technology transfer.”

Free registration at the site enables individuals and companies to find a technology that is needed, or list one they need.

Light Source On A Chip

An integrated light source on a semiconductor chip could be very useful in optical telecommunications, for lab-on-a-chip analytical work, or other applications. Phuong Le Minh, of the University of Twente in The Netherlands, claimed discovery of a principle that could be used for such a source, according to a February 21 announcement by the university.

Le Minh developed the nanoscale integrated light source by accident while doing semiconductor breakdown experiments, as part of his group’s research on transistor reliability. It was formed by controlled breakdown of the isolating oxide layer in a semiconductor device. Le Minh found that the area, termed an antifuse, emitted light and could be transformed into a working nano lamp. Researchers have integrated the light source and a photodetector with a micron-size fluid channel and is able to distinguish various fluids going through, as part of a laboratory-on-a-chip.

In addition, they are exploring optical telecommunications applications, focusing on an “all-optical” signal path, thus avoiding conversion losses, from optical to electronic and vice versa. Silicon has excellent properties for a broad range of applications, but it is a poor photon emitter, making it difficult to fabricate an efficient light source from silicon. Coupling an external lightsource to a chip is difficult.

The light source is placed above the microchannel in a chip, with a photo detector on the bottom. Information can be retrieved about the fluid going through the channel by detecting interference patterns.

Microfluidic Photomasks for Gray-Scale Photolithography

Traditional photomask technology limits the features that can be carved into microcircuits, micromechanical systems, and other devices with photolithography. It is based, of course, on illumination of a photosensitive layer (the photosist) with UV light through a glass or plastic layer containing opaque features in ink emulsion or metal (the photomask).

Limitation 1: Illumination is all-or-none in order to produce photosist features of uniform height. So fabrication of 3D microstructures requires multiple alignment and exposure steps which can be difficult and costly.

Limitation 2: Photomask features are permanent. Design changes involve the long and expensive process of
making a new photomask—a major hurdle in research settings that do microdevice prototyping and need quick turnovers.

“Gray-scale” photolithography with scanning lasers, micromirror projection displays, and other methods, do generate ranges of exposure and sidestep the all-or-none limitation. But existing gray-scale technology has its own drawbacks including high cost and limitations on the size and nature of patterns that can be produced.

Albert Folch and associates at the University of Washington have developed photomasks with light-absorbing features made of fluids. The opacity can be tailored to different gray-scale levels and the spatial pattern can be reconfigured in seconds.

The photomasks contain liquid channels, and opacity is controlled by varying the concentration of dye in the liquid. As different concentrations of dye impede the ultraviolet light, more or less of the material underneath can be shorn off, shaping a three-dimensional surface.

The liquid’s opacity can be altered continuously and within seconds to produce a variety of complex shapes.

Besides computer chips, this inexpensive new technique may be useful for fabricating miniature machines, optical elements, tissue-engineering scaffolds, and other biotechnology applications, Folch said.


**Photoscience at the AAAS**

Football has the Super Bowl. Soccer has the World Cup. For baseball it is the World Series, and professional hockey the Stanley Cup.

And science has the annual national meeting of the American Association for the Advancement of Science (AAAS). Best known as the publisher of *Science*, AAAS bills itself as the world’s biggest general scientific organization. It has 138,000 members, and is affiliated with organizations that represent 10 million scientists worldwide.

Every February, thousands gather for the AAAS national meeting for seminars and reports on topics ranging from astronomy to zoology. The 2003 gathering, held in Denver, did not ignore the photosciences.

Among the presentations:

**Margaret M. Murnane** (see “Lasing the Spectrum,” above), University of Colorado, described how photonics is opening up new regions of the spectrum for microscopy and nanoimaging. “Concepts from fiber optics and photonics can be used to create laser-like beams in the regions of the spectrum that were previously inaccessible—at very short wavelengths in the extreme ultraviolet.”

**Richard S. Givens**, University of Kansas, discussed research on photoremovable protecting groups that are being used to investigate biological reactions. The initial trigger for physiological and biological events is often a single molecular entity, and researchers have tried a variety of approaches for understanding and defining the triggering events. Givens described his group’s approach—constructing phototriggers or caged compounds by chemically converting active neurotransmitters into dormant, inactive forms by bonding a removable chromophore to the neurotransmitter, making it biologically inactive. Exposure to light breaks the bond and releases the neurotransmitter. He described the chemistry and photophysics involved in the development of a new class of phototriggers that permit scientists to study rates of even the fastest known biological processes.

**George P. Hess**, Cornell University, reported on potential uses of the laser-pulse photolysis technique developed in his lab. It allows study of an ensemble of molecules during the split-second reactions—often lasting less than 0.3 milliseconds—which relay electrical signals through the nervous system. It can characterize reactions during the microsecond time frames when they are active on the surface of nerve cells. Hess said it shows great promise, for instance, as a tool for understating the effects of disease-causing mutations on nerve cell receptors. The technique also promises to be a boon for mechanism-based drug design by showing investigators the exact role and timing of all the compounds active at the junctions between neurons or between and muscle cells.

“Attosecond science comes of age,” declared Ferenc Krausz, Vienna University of Technology, Austria. Krausz pointed out that ultrafast optical technologies have pushed the duration of laser pulses close to its natural limit—to the wave cycle itself, which lasts about one femtosecond, 10^{-15} second. However, sub-femtosecond pulses are essential to study electronic dynamics that evolve inside atoms, however, often evolve on an attosecond (10^{-18} second) timescale. Krausz described a collaboration with the University of Bielefeld and the National Research Council-Canada which makes feasible the generation of single, isolated sub-femtosecond soft x-ray pulses with precisely-reproduced wave form for attosecond diagnostics and spectroscopy.
the last few years. They range from clearer theoretical insights into the underlying chemistry, physics, and materials science to commercial applications such as the multi-billion dollar market in photoconductive films, light emitting diodes, and thin-film transistor displays.

What does the future hold for the burgeoning field, especially in terms of research needs?

A comprehensive new report will be available with answers this spring, Ananth Dodabalapur, University of Texas at Austin, told The Spectrum. Dodabalapur chaired a January National Science Foundation workshop in which two dozen authorities met to define the field’s future.

One, V. M. Kenkre, told The Spectrum that conferees identified a need for additional research in several areas. “General theoretical work is sorely needed for the interpretation of charge transport and injection,” said Kenkre, a professor at the University of New Mexico, Albuquerque. “That should be a top priority. Spintronics in organics should be another.”

Dodabalapur predicted that the report also will have an impact on graduate education.

“A large number of universities offer courses in the general area of organic semiconductors,” he said. “The workshop will help define directions in this area as well as in retraining high technology workers for careers in the organic semiconductor field.”

Watch for the report at: http://www.mrc.utexas.edu/NSFWorkshop. NSF also will make CD copies available to the photoscience community, he added.

Policy Spotlight: Environmental Photoscience

An expert panel organized by the National Academy of Sciences (NAS) will review a new draft of the Bush Administration’s global warming research plan later in 2003, after sharply criticizing the first draft in February.

Bush Administration officials had portrayed the plan as a roadmap for resolving questions about the seriousness of global warming and how to deal with it.

NAS’ review of the initial draft plan, however, concluded that it “lacks most of the elements of a strategic plan” and has goals that would be impossible to achieve without a bigger climate research budget than the Bush Administration has proposed.

Thomas E. Graedel, professor of industrial ecology at Yale University, chaired the 17-member panel.

NAS termed the draft “a good first step” toward better understanding and responding to climate change because it did propose new research initiatives. However, NAS added that the plan lacks a clear guiding vision and does not adequately meet the needs of decision-makers who must deal with the effects of climate change. The panel noted that Mr. Bush’s Fiscal 2004 budget request appears to provide no additional funding for the new initiatives described as so important in the plan.

“While past climate-change science has focused on how climate is changing and affecting other natural systems, future science must also focus on more applied research that can directly support decision-making,” Graedel said. “Research is especially needed to improve our understanding of the possible impacts of climate change on ecosystems and human society, as well as options for responding to—and reducing—these effects.”

The panel called for “substantial” revisions in the plan, including goals accompanied by ways to measure progress, clear timetables, and an assessment of whether current research efforts are capable of meeting them.

The Art of Science Competition

So that computer graphic, photo, illustration, animation, or other visual goes beyond the caliber of being just a research graphic and almost seems...well, like a work of art?

Then the National Science Foundation and the journal, Science, want to see it as an entry in their new international Science and Engineering Visualization Challenge. Open to individuals anywhere in the world, the competition will recognize outstanding achievement in the use of visual media to promote understanding of research results.

Entries must be postmarked by May 31, 2003. The material must have been produced in a research activity after January 1, 2000. Complete contest rules, entry submission instructions, and entry forms are at www.nsf.gov/od/lpa/events/sevs.

Winning selections will be featured in a special section of Science’s September 12 edition and winners will receive an expense-paid trip to NSF headquarters, located just outside Washington, DC, for the opening of its “Art of Science Project” exhibit and accompanying lecture.

“Visualization, especially in science and technology, has a special power to complement and enhance the written word in depicting phenomena,” NSF said in an announcement, “elucidating concepts, revealing new insights, provoking thought and appealing to the imagination—for both technical audiences and the general public.”

Judges will award first, second, and third place in photographs, illustrations, and active and/or multimedia.
Guldi continued


About the Author
Dirk M. Guldi graduated from the University of Cologne (Germany) in 1988, from where he received his Ph.D. in 1990. In 1992, after a postdoctoral appointment at the National Institute of Standards and Technology, he took a research position at the Hahn-Meitner-Institute Berlin. After a brief stay as a Feodor-Lynen Stipend (Alexander von Humboldt Foundation) at Syracuse University he joined in 1995 the faculty of the Notre Dame Radiation Laboratory where he was promoted to Associate Scientist in 1996. In 1999 he completed his Habilitation at the University of Leipzig (Germany). He was awarded with the “Heisenberg-Prize” (1999; Deutsche Forschungsgemeinschaft) and “Grammaticakis-Neumann-Prize” (2000; Swiss Society for Photochemistry and Photophysics). His primary research interests are in the areas of new multifunctional carbon-based nanostructures within the context of light-induced charge separation and solar-energy conversion. He can be reached at the University of Notre Dame, Radiation Laboratory, Notre Dame, IN 46556, USA. His e-mail is guldi.1@nd.edu.

The Spectrum is available on the WEB:
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