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Biography of Kenneth B. Eisenthal

Ken Eisenthal was born and grew up in New York City. Although he planned to be a premed student when he entered Brooklyn College, the excitement of science, stimulated in large part by two of his chemistry professors, Nicholas Cheronis and Homer Jacobson, convinced him to opt for science. This led to his graduate work at Harvard University where he obtained an MA in Physics and a Ph.D. in Chemical Physics. His graduate advisor was Marshall Fixman, and the thesis research topic was protein−protein interactions. After Harvard, he went to UCLA, where he used his NIH postdoctoral fellowship to carry out research with Bill McMillan, using a collective coordinate treatment to calculate the activity coefficients of strong electrolytes, which went well beyond Debye−Huckel results in yielding agreement with experiment up to 1.0 molarities. To advance his knowledge of molecular spectroscopy, he joined the group of Mostafa El-Sayed (UCLA), which was at the forefront in breaking new ground in the spectroscopy of organic molecules. Ken then went for a short period of time to the Aerospace Corporation, where he worked on intermolecular singlet and triplet energy transfer in collaboration with Seymour Siegel, who was a classmate at both Brooklyn College and Harvard. Ken then moved from southern California to northern California, joining the chemical physics group at the IBM Almaden (then in San Jose) Research Division Laboratory. The laser know-how at the IBM lab led to his first laser experiments in collaboration with Warner Peticolas, Klaus Rieckoff, and Mark Dowley, which included the first two-photon spectrum of molecules, a theoretical treatment of two-photon excitation of polycyclic aromatic molecules, application of the theory to their experimental data, and an induced birefringent method to measure the polarizabilities of molecules in excited electronic states.

With the development of picosecond lasers in the late 1960s, it became possible to directly measure molecular relaxation dynamics in a new time domain. In his initial picosecond experiments, Ken measured orientational relaxation of molecules in liquids and the effects of hydrogen bonding on rotational dynamics; obtained for the first time the exact expressions for the time-dependent molecular fluorescence depolarization starting with an analytical solution of anisotropic rotational diffusion, which finally resolved the controversy about the correct expression; and also tested the applicability of the Förster model of intermolecular singlet−singlet energy transfer, into the picosecond time domain.

One of Ken's earliest landmark ultrafast experiments focused on a problem that had intrigued chemists for half a century, photodissociation in liquids and the solvent cage effect. From experiments on I_2, Ken obtained the first estimate of the rate of collision-induced predissociation in liquids, and from measurements of the ground state recovery dynamics, he obtained the

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fraction of iodine atoms that escaped recombination in real time. This was the first time-dependent observation of the cage effect in liquids. His results showed that the then-current theories had to be revised. Subsequently, Casey Hynes theoretically predicted and Charles Harris experimentally showed that the dynamics in the recovery of the I_2 molecule was dominated by vibrational relaxation of the hot I_2 molecule generated by the caged iodine atoms recombination. Ken went on to carry out the first characterization of the dynamics of an atom—molecule reaction in the liquid state, iodine atom plus benzene and iodine atom plus mesitylene, work that stimulated many further experimental studies and entirely new theoretical investigations of the dynamics of liquid-phase chemical reactions. Ken carried out the first ultrafast studies of photoinitiated intermolecular electron transfer in liquids, which yielded the electron-transfer rate constant, and showed and explained the strong orientational dependence of the reaction in nonpolar liquids but not in polar liquids. His later investigation of double-proton transfer and intramolecular proton transfer opened the gates to time-resolved studies of proton transfer. These latter studies were carried out at Columbia University. Ken left the ivory tower of the IBM Physical Sciences Department in 1975 to go to Columbia University, thereby entering the "real world," that is, academia, where one must be self-supporting.

At Columbia, Ken's group carried out extensive and ground-breaking studies of the generation and reaction dynamics of carbenes, a very reactive and mechanistically important class of short-lived intermediates. These experiments, many of which were carried out in collaboration with Nick Turro, paved the way for the photochemistry community to utilize ultrafast methods to probe transient species and, thereby, the mechanisms of chemical reactions. Turning his attention to photoisomerization reactions, Ken showed that it was a polarity-dependent barrier, rather than viscosity, as was generally thought, that controlled the dynamics of twisted intramolecular charge-transfer reactions. In his photoisomerization studies of frictional effects on barrier crossing in liquids, he found one of the few molecules, 1,1′-binaphthyl, for which the Kramers theory was in good agreement with experiment. The power of ultrafast methods in chemistry was further demonstrated in his studies with Nick Turro on the photodissociation of aromatic endoperoxides, a class of molecules of great interest because they generated a critical chemical reagent, singlet $^1O_2$. From the dynamics, it was established that the singlet $^1\Delta_g\ O_2$ was not generated by the simultaneous rupture of the two C—O—O—C bonds, that is, a concerted reaction as was generally thought, but rather, that the two C—O bonds broke sequentially.

In the late 1980s, Ken initiated a series of femtosecond experiments on a topic of great importance in chemistry; namely, electrons in liquids. With the high time resolution possible with femtosecond laser techniques, he was able to definitively test and validate the much-debated Onsager model of the geminate recombination of an electron—cation pair in neat liquid alkanes. He then turned his studies to the electron dynamics following the photoionization of neat water. Measurements of the spectrum and decay of the presolvated electron led him to propose that the short-lived presolvated electron is an excited state of the solvated electron. He suggested that the dynamics of formation of the solvated electron should, therefore, be viewed as an internal conversion from the excited state (presolvated electron) to the ground state (solvated electron). His interpretation of the experimental findings was in agreement with a theoretical model that was developed independently by Peter Rossky and Rich Friesner. Continuing his research on electrons in liquids led him to look at solvated electrons generated by UV photoexcitation of simple anions—halides and hydroxide—in water. Before Ken's work, there was no dynamical information on the relaxation processes of these photoexcited charge-transfer-to-solvent states, CTTS, which arise from the stabilization of a photoexcited electron by a solvent polarization well. His dynamical measurements showed that the decay from the CTTS excited state to a free electron was a minor relaxation pathway, a finding that could not be obtained from the many quantum yield measurements of electron generation.

Ken's research took an interesting turn following a meeting in Alexandria, Egypt, which was organized by Ahmed Zewail. Parenthetically, in addition to arranging an outstanding conference, Zewail made a difficult and courageous decision in inviting Israeli scientists to this conference in Egypt, which added a significant dimension to the international character of the conference. It was at this meeting that Ken learned of the interface specificity of second harmonic generation, SHG, from a talk given by Ron Shen on the use of SHG to measure the orientation of molecules adsorbed on an amorphous solid. As Ken wrote in an *Accounts of Chemical Research* article on SHG, the idea that raised his temperature was the possibility to actually "look at" the surface of a liquid, for example, a solution or neat liquid/gas interface, something that had not been done before by an optical spectroscopy because of the overwhelming optical signal generated by the molecules in the bulk liquid. Using a femtosecond pump—SHG probe method, Ken opened the study of ultrafast molecular processes at liquid interfaces. He used the surface-selective process of SHG to isolate the dynamics of relaxation at air/liquid, liquid/liquid, and liquid/solid interfaces. With his measurements of the cis—trans isomerizaton of a cyanine dye at the air/water interface and subsequent isomerization dynamics studies of other molecules at organic liquid/water interfaces, he showed that isomerization has very different dynamical properties at the interface as compared to the bulk liquid, and even opposite behaviors for different interfacial molecules.

Because there is no clear way to determine the friction at liquid interfaces, Ken's measurements of orientational relaxation are particularly valuable as a measure of interfacial rotational friction. He showed that for some molecules, the isomerization times scaled with the orientational relaxation times. However, interfacial rotations differ in a fundamental way from bulk rotations because the asymmetry of the interface results in distinguishable out-of-plane and in-plane rotational motions. In a series of imaginative experiments, he was able to isolate the out-of-plane from the in-plane orientational relaxations. He subsequently determined the effects of charged surfactants at an aqueous interface on these rotational motions, a topic of direct relevance to the negatively charged biomembrane/aqueous interface. Ken recognized that as solvent molecules reorganize about a photoexcited molecule, the change in the excited-state energy will change the hyperpolarizability of the excited molecule. This could be used to unravel the dynamics of interfacial solvation dynamics, since the change in hyperpolarizability would be expressed in a change in the SHG signal. Solvation measurements at air/water, neutral and charged surfactant/water, and silica/organic liquid interfaces yield very different results. For example, the dynamics of water was faster at a neutral surfactant/water interface than in bulk water, whereas for the charged form of the surfactant, the interface dynamics was slower than in bulk water. In experiments on intermolecular energy transfer between donor and acceptor molecules at an air/water interface, he investigated the theoretical prediction that dipole−dipole energy transfer has a different time profile in the two-dimensional environment of the interface than in the three dimensions of the bulk. Indeed, Ken found that the interfacial energy transfer dynamics has the $\exp(-at^{1/3})$ two-dimensional time dependence and not the three-dimensional $\exp(-bt^{1/2})$ dependence.

In collaboration with Tony Heinz, the first measurements of the orientation of molecules at liquid interfaces were performed. Although the orientational measurements yield the tilt angle of a molecular axis with respect to the interface normal, it does not yield the “up” vs “down” alignment of the interfacial molecules. Using a method developed by Niko Bloembergen to measure the phase of the SHG light, the experiments at Columbia showed that the phase of the SHG light provides information on the “up” vs “down” alignment of the interfacial molecules. Among their findings was the determination that the dipole moment of water at the air/water interface preferentially aligns with its dipole moment pointing toward the bulk water, and they were able to determine which end of phenol, *para*-bromo- and *para*-chlorophenol, $X-C_6H_4-OH$, was up vs down at the air/water interface. There are many other equilibrium properties at liquid interfaces that were shown to be accessible to the SHG methodology. Among them were measurements of molecular adsorption free energies and interfacial population; chemical equilibria, in particular, interfacial acid−base pK_a values and interface polarity obtained from measured spectral shifts of solvatochromic molecules; unexpected structural phase transitions; and the development of an optical method (SHG) to measure the electrostatic potential of charged interfaces.

It is commonly assumed that SHG and SFG (sum frequency generation) are electric dipole-forbidden in centrosymmetric systems, but not at the intrinsically noncentrosymmetric interface that separates bulk media. A consequence of this viewpoint is that most SHG and SFG studies have been carried out on planar interfaces that separate isotropic or centrosymmetric bulk media, that is, bulk liquids, gases, and isotropic or centrosymmetric solids. It was roughly 10 years ago that Ken made a major breakthrough in recognizing that SHG and SFG are interface-selective for centrosymmetric systems if the interface is not locally centrosymmetric; to, for example, aligned adsorbates. The SHG and SFG signal generated at the particle interface was shown to depend on the size of the centrosymmetric particle and the coherence length of the process. This new method to investigate the surfaces of centrosymmetric systems extending in size from micrometers to tens of nanometers, without any significant contribution to the SHG and SFG signals from the molecules present in the bulk media, has the potential to significantly advance knowledge of the surface properties of colloidal particles. The applicability of this method to colloidal science has been demonstrated in Ken’s lab at Columbia for adsorbates on polymer beads, emulsions, charged polymer beads, charged emulsions, liposomes, clay particles, and semiconductor colloids; for example, TiO_2 and CdO. All of the interfacial equilibrium properties that were previously investigated at planar liquid interfaces have been carried out at particle/solution interfaces. This ranges from adsorbate populations, adsorbate spectra (for example, charge transfer in the TiO_2 colloid−catechol complex), surface electrostatic potential of charged particles (which differ from electrophoresis measurements, the reason being that SHG yields the potential at the charged surface and electrophoresis is at the shear plane), and pK_a at the particle/water interface, and extends to many other properties. Among these are the observations in real time of the kinetics of transfer of an organic cation across a liposome phospholipid bilayer and the effects of cholesterol on the transport dynamics, as well as the effects on the crossing dynamics of surface charge and antibiotics that transport alkali ions across the bilayer or provide an ion channel for small ions to move across the bilayer.

A new area of Ken’s research (past 2 years), is in the use of SHG imaging to investigate electrical signaling properties of neurons in live brain tissue of mice. This work is carried out in collaboration with Rafa Yuste, a distinguished neuroscience professor at Columbia University. They have used SHG to image and selectively probe the electrostatic potential drop across the neuronal membrane. In particular, they have studied the very abundant, $\sim 10^4$ per neuron; small, $\sim 1\ \mu$m, neuronal structures called spines, which are the predominant sites of excitatory inputs into a neuron. The traditional method of inserting a microelectrode into the body or dendritic shaft of the neuron is a powerful technique in the investigation of the electrical properties of these neuronal structures. However, it cannot be used for spines, because they are far too small to accommodate the insertion of a microelectrode. An optical method such as SHG appears to be a very promising approach. In their first experiments, they settled the long-standing controversy as to whether spines were electrically passive or served chiefly as a biochemical compartment. Their studies resolved this question and with SHG established that the spines were, indeed, electrically active. In another experiment, they investigated the “mathematics” by which neurons integrate input excitation signals. They showed that the voltage signals generated at different spines are added linearly by the body of the cell, which is where the final computation by the neuron is performed. A further noteworthy result was their discovery that spines having long necks do not send a voltage signal to the cell body, even though they were shown to be excited by photoreleased neurotransmitters adjacent to the spine. It is known that there are far more long-neck spines in the human brain than that of other mammals, which might be relevant to learning and memory.

This neuroscience direction is typical of Ken’s scientific career in the evolution of his research activities. He started his studies of molecular processes in bulk media using mercury and xenon excitation sources, advancing to multiphoton molecular excitation processes with the development of the ruby and neodymium nanosecond lasers. The major jump in time resolution achieved with the advent of picosecond lasers led Ken into the initial development of picosecond chemistry, together with the groundbreaking experiments on azulene relaxation by Peter Rentzepis, and then into the field of femtochemistry. The increased power afforded by lasers made feasible not only the study of multiphoton spectroscopy, photoionization and dynamic properties of molecules, but also the investigation of nonlinear optical phenomena. Ken moved into this latter research area using the second-order spectroscopies, SHG and SFG, to selectively probe equilibrium and dynamic properties of liquid interfaces. From this point, it was not too surprising that he extend his research into neuroscience using SHG to selectively probe the static and dynamic electrical properties of the plasma/membrane interfaces of neurons in live brain nerve tissue.

Despite the markedly different research that Ken is now engaged in, that is, liquid interfaces and neuroscience, we can see a continuous line that led from his earliest work to the present. Clearly, Ken was fortunate, and he gratefully recognizes the talented collaborators and students who made it possible to carry out research in these diverse areas of science.

Beyond his research, Ken’s service to the community involved serving on various government panels and advisory boards, as chairperson of the Division of Chemical Physics of the American Physical Society, as chairperson of many U.S.A. and international conferences, and on the editorial boards of many journals. One area that continues to give him great satisfaction is his participation for many years in the NSF Research Experience for Undergraduates. This program has made it possible for students from colleges that do not have cutting edge equipment and facilities to participate in forefront research using state-of-the-art equipment and, most importantly, to work with the graduate students and postdoctoral scientists in Ken's group and in the Chemistry Department as a whole. One very positive aspect of the program is that it brought minority and female students to his laboratory with the hopeful expectation that the scientific excitement at Columbia would point them to careers in science. Ken's scientific activities over the years have been recognized in various ways, among which are the ACS Hildebrand Award in Theoretical and Experimental Chemistry of Liquids, the ACS Adamson award for Distinguished Service to Chemistry, election to the National Academy of Sciences, the Bryce Crawford Award in Molecular Spectroscopy, the Hinshelwood Professor and Lectures at Oxford University, the Troisieme Cycle Distinguished Lecturer in Switzerland, various other named lectureships, Fellow of the American Physical Society, Guggenheim Fellow, and visiting professor at universities at home and abroad.

The Eisenthal Group