



## IN MEMORIAM

Bryan Earl Kohler  
Professor of Chemistry  
UC Riverside  
1940 - 1997

Bryan Earl Kohler was born in Heber City, Utah in 1940. While in high school he worked as a motion picture projectionist at the Rio Theatre in Midway, Utah, a worthy beginning for a man who was to become one of the world's leading molecular spectroscopists. His tasks at the theatre included striking the arc prior to the evening show, and, on one occasion in 1954, courageously battling a projection room fire during a showing of *Gone with the Wind*. He entered the University of Utah in 1958 originally intending to major in engineering, but changed his major to chemistry. There he married his high school sweetheart and life companion, Susan Whitaker. Their family was later to include three amazing children — Bern, Dylan, and Brynja — of whom Bryan was extremely proud. He received his B.A. from Utah in 1962 and moved with Susan to attend graduate school at the University of Chicago.

At Chicago, he joined the research group of Clyde A. Hutchison Jr. His first scientific paper was on the electron paramagnetic resonance of divalent vanadium in a mixed crystal of cadmium chloride. The spectroscopy of mixed crystal systems remained one of his life-long interests. Bryan's second research paper, and also the subject of his PhD thesis, was on the magnetic resonance of ground state triplet diphenylmethylene in a mixed crystal. In that work, Bryan used magnetic resonance techniques to map out the electron spin density of the triplet. He received his PhD in 1967 at Chicago and was, briefly, an Enrico Fermi Research Fellow continuing as a postdoc at Chicago. He then moved to a postdoctoral position as an NSF Fellow with G. Wilse Robinson at the California Institute of Technology for about a year.

Bryan accepted a junior faculty position at Harvard University in the fall of 1968, knowing full well that Harvard did not generally promote their junior faculty at that time. Harvard's policy ultimately resulted in Bryan's subsequent move to Wesleyan University. His last faculty position was at the University of California, Riverside.

At Harvard, Bryan continued magnetic resonance studies of single crystals containing diphenylmethylene. There he developed techniques for low temperature magnetic optical rotation spectroscopy, applied to single crystals of tetraphenyl tin, and he initiated a spectroscopic study of benzil.

One of the new projects that Bryan began at Harvard was an investigation of the electronic spectroscopy of linear conjugated polyenes. This project involved collaboration with Professors Brian Sykes and Martin Karplus. In this project, Bryan and his research students, in particular, Bruce Hudson, set out to investigate the optical spectroscopy of the visual pigment chromophore retinal. In an effort to simplify matters, Bryan and Bruce began investigations of retinoic acid. Ultimately, this effort led them to investigate the absorption and fluorescence spectra of diphenylpolyenes, molecules for which the lowest energy peak in the electronic absorption and fluorescence spectra are both relatively strong and easily assigned to vibrationless origins. However, the excited electronic state involved in the fluorescence spectrum was not, as in the usual case for most molecules, the same excited state that they observed in absorption.

Bryan and Bruce developed a hypothesis that linear polyenes had a low-energy,  $\pi$ - $\pi^*$  excited electronic state that resulted in a very weak transition in absorption. Transitions from the ground state to this excited state were forbidden by the molecular symmetry, being  $A_g$ - $A_g$  in nature. Although this hypothesis contradicted theoretical expectations, Bryan was unconcerned. In the long run, they showed that this picture was correct. The initial paper of this "Eureka" discovery was published by Hudson and Kohler in 1972. This work at Harvard began his long-term interest in the details of the electronic structure of linear polyenes. In the succession of experimental and theoretical work on the subject, Bryan systematically showed that virtually all linear polyenes had a "symmetry forbidden" excited singlet state at lower energy than the one that is much more easily detected spectroscopically. His research in this area was highly influential and affected a variety of related fields.

Bryan moved from Harvard to Wesleyan University in 1975 as an Associate Professor. He became professor at Wesleyan in 1977 and beach professor in 1982. He also served as chair of the chemistry department at Wesleyan from 1980 to 1983. At Wesleyan, Bryan continued to study the unusual spectroscopic properties of linear polyenes, using ever more sophisticated techniques. In his own words, he described his research as: "... the spectroscopic determination of molecular electronic structure, especially in those cases where that structure is either novel or likely to determine photochemical behavior. High-resolution techniques which fully exploit laser technology are combined with very low temperatures as realized in liquid helium cryostats or supersonic molecular jets to obtain detailed information on electronic and nuclear motions and their couplings. Work currently in progress is centered around high resolution electronic spectroscopy of molecules related to the visual pigments and studies of the photochemical reactions of these species."

In his curriculum vitae of about the same time, Bryan described his accomplishments in the following way: "At Wesleyan high resolution studies of a number of polyenes have established the  $1A_g$  symmetry of the low lying polyene singlet and have mapped the dependence of excitation on chain length. High resolution one- and two-photon spectroscopic techniques have been developed to determine the potential energy surfaces for simple linear polyenes. We have recently established (somewhat surprisingly!) that polyene photoisomerization is an extremely rapid process even for molecules frozen in hydrocarbon matrices maintained at 4 K. The capability to determine high resolution electronic spectra under conditions where molecules are photochemically active is a new development and provides the key to determining the link between electronic excitation and chemical transformation. When these processes are understood, it will be possible to devise highly specific photochemical transformations using lasers and low temperatures. We have already used these techniques to synthesize di-cis octatetraene, a molecule which cannot be made using classical synthetic techniques."

The key technique that Bryan used in establishing the  $1A_g$  nature of the lowest lying excited electronic state of linear conjugated polyenes was two-photon excitation of fluorescence of these compounds, wherein the molecules in question were in a crystalline matrix that provided a centrosymmetric environment. The use of two-photon excitation makes the otherwise symmetry forbidden  $A_g$  (ground) to  $A_g$  (excited) state transition allowed by symmetry. Thus for a centrosymmetric polyene it was expected that the vibrationless electronic origin transition would be observed in the two-photon absorption spectrum. This origin transition would lie between the lowest energy feature of the vibronically induced one-photon absorption spectrum and the highest energy feature of the vibronically induced one-photon fluorescence spectrum. This is exactly what Bryan and his students observed for octatetraene in *n*-octane. They concluded that *n*-octane provides a centrosymmetric environment for octatetraene, as might be expected. Octatetraene in nonane or *n*-undecane gives a very different spectroscopic pattern, with vibronic structure characteristic of an "allowed" transition and overlapping absorption and emission origin transitions. This is due to the mixing of low lying allowed and forbidden excited states in the asymmetric alkane environment.

In 1985, Bryan joined the faculty of the chemistry department at the University of California, Riverside. At that time, there was still some controversy regarding whether the ordering of excited states that Bryan had discovered for longer polyenes applied to the shortest ones. Using new methods of multiphoton ionization of gaseous polyenes in supersonic jets, he was able to resolve the controversy for hexatriene and related shorter polyenes by observing very narrow, one-photon absorption spectra. Bryan described this accomplishment as follows: "The significance of this is hard to overstate: it forces a major paradigm shift affecting areas ranging from the quantum mechanical treatment of molecular electronic structure to modeling of the photochemistry of biologically active polyenes such as Vitamin D and the visual chromophore retinal." Bryan also studied longer, conjugated polymers such as polythiophenes, enabling the development of theoretical models (including his own "Hückel spectral simulator") for the electronic structure of polyenes as a function of chain length.

At UCR, Bryan developed photochemical hole burning experiments that improved spectroscopic resolution by as much as 100,000 times. These developments allowed Bryan and his research group and collaborators to directly determine the magnitude of internal electric fields at molecular sites in crystals with atomic resolution. Bryan felt that these experiments had profound implications for understanding the process of photo-induced charge separation. He showed how to use his favorite molecules-- linear polyenes-- as atomic resolution array detectors to map molecular and crystal electric fields. He believed that this discovery would prove to be an even more important scientific contribution than his reordering of the excited states of linear polyenes.

Bryan was a scientist of international renown. He was a guest professor at the University of Leiden in 1973, where he worked with Jan van der Waals at the Kamerlingh Onnes Laboratory. Bryan was also an A. P. Sloan Foundation Fellow in 1974. Beginning in 1979, he made the first of many visits to the department of physics at the University of Bayreuth in Germany. He was an Alexander von Humboldt Fellow in 1979 and a Guggenheim Fellow in 1983-84. He attended numerous international scientific conferences, especially those concerned with studies of molecular crystals, photochemistry, and hole burning spectroscopy. His long-term interest in condensed phase, high-resolution spectroscopy established his relationship with Roman Personov of the Russian Academy Institute of Spectroscopy in Troitsk, and Bryan arranged for Personov to come to Riverside for an extended stay in 1994-95. Bryan was a Fellow at the Joint Institute for Laboratory Astrophysics (JILA) in Boulder, CO in 1978. At JILA he worked with Carl Lineberger on diatomic carbon. Bryan concluded that, "Diatomics are complicated!" In 1991, he returned to JILA as a Visiting Fellow, working with Jan Hall.

Bryan was always active in University affairs, both at Wesleyan and at Riverside. At Wesleyan he led several very successful faculty recruitment efforts. At Riverside, he was well known as an "activist" member of the Committee on Academic Personnel.

Bryan was for many years an avid runner. Hence, in his CV during the Wesleyan years, he noted as a significant accomplishment: "2:59 for 1981 New York City Marathon." He remodeled old houses and built new ones, too. He loved hiking in the mountains and was able to do just that in Bavaria only a few months before his death.

Bryan was a member of Sigma Xi and a fellow of both the American Physical Society and the New York Academy of Sciences. He was also a member of the Biophysical Society, the American Chemical Society, the American Society for Photobiology, the Connecticut Academy of Arts and Sciences, Oroborus, and the American Academy of Arts and Sciences. He was the founder of the Institute for Gonzo Spectroscopy, a product of Bryan's keen sense of humor. His research group became Gonzo Spectroscopists, as they studied unusual molecules in unusual ways. This was Bryan's interpretation of Gonzo author Hunter Thompson's "sex and violence."

Bryan had an infectious enthusiasm for everything he did in life. He had a gentle and patient nature while maintaining a serious dedication to rigor! He was a wonderful colleague and a generous friend with a marvelous sense of humor. He was a first-class scientist whose work was always at the forefront of the field and will always be remembered as seminal and significant. In March 1999, the American Chemical Society held a symposium on linear polyenes in his memory at its 217th National Meeting. The Journal of Physical Chemistry A dedicated the 14th issue of volume 103, April 8, 1999, in his honor. In Riverside, a street has been named Kohler Court in his honor. By his friends and colleagues both here at UCR and throughout the world, he is sorely missed.

Gary W. Scott  
Eric L. Chronister  
David F. Bocian  
Thomas H. Morton