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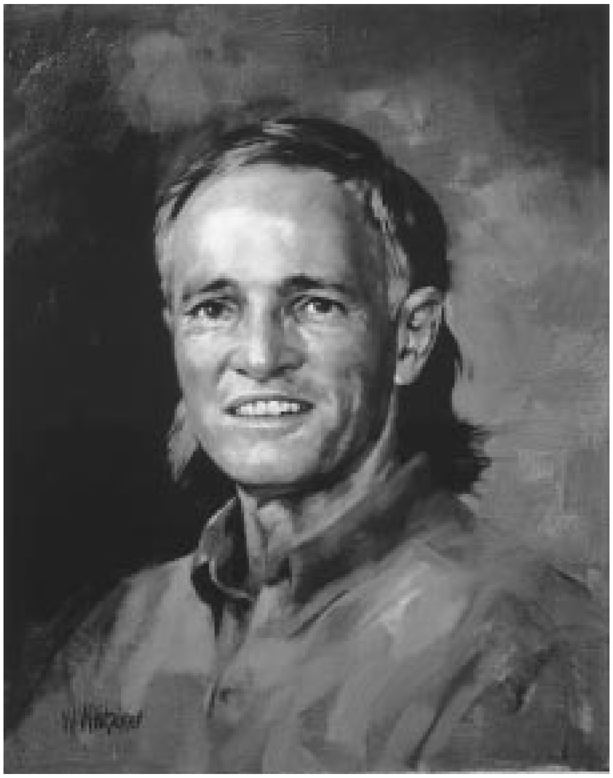

Painting by William Whitaker

Bryan Earl Kohler, 1940−1997

Biographical Sketch

Bryan Kohler was born in Heber City, UT, in 1940. He entered the University of Utah in 1958 originally intending to major in engineering but, fortunately for us, he changed his major to chemistry. He did undergraduate research with F. William (Bill) Cagle. His research project involved an extensive study of the literature on the use of polyaromatic compounds as materials in the nuclear industry. He received his B.A. degree in 1962 and entered graduate school at the University of Chicago. After a long trip by car from Utah he was greated in Chicago by a sign that said “Welcome to the West!”

At Chicago he became a student with Clyde A. Hutchison, Jr. His first scientific publication in 1965 in *The Journal of Chemical Physics*, with I. Y. Chan, David C. Doetschman, and Clyde Hutchison was on the paramagnetic resonance spectrum of divalent vanadium as a mixed crystal in cadmium chloride. The spectroscopy of mixed crystal systems remained one of his life-long interests. Inorganic systems were short-lived in his evolving list of interests.

Bryan’s second paper, also in 1965 and also in *J. Chem. Phys.*, concerned the main subject of his thesis, the magnetic resonance of the ground triplet state of diphenylmethylene in mixed crystals. This paper was coauthored with Richard W. Brandon, Gerhard R. Closs, Clark Davorst, Clyde Hutchison, and Robert Silbey. Alphabetical order was used in the Hutchison group, a

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pattern that persisted through Bryan's publications. Subsequent studies of diphenylmethylene included the optical spectroscopy of such mixed crystal systems and the use of a variety of mixed crystal systems for the isolation of diphenylmethylene. A consultation with David Beveridge in Pittsburgh involved the then state of the art in calculations of spin densities for such triplet state carbenes. He was an Enrico Fermi Research Fellow in 1967. Bryan received his Ph.D. degree from the University of Chicago in 1967. After a brief continuation as a postdoc at Chicago, he took up an NSF Fellowship funded postdoctoral position with G. Wilse Robinson at the California Institute of Technology.

Bryan's work with Wilse was to do with photosynthesis in algae "but the chlorella died". His attention turned initially to high-resolution studies of the Wolff bands of ozone (Oliver Wolff was a well-known personage in the halls of Gates and Crellin at Caltech) before returning to studies of photosynthesis. He also worked on the development of an optical modulation method. This technique was devised to detect sharp optical spectral features in the presence of excessive amounts of broad band contributions. It consisted of drilling a hole through the middle of a quartz plate at an angle of 45° and mounting the plate on a synchronous motor. This was then placed inside a monochromator just before the exit slit. When spun ("at 137 Hz") the result was to periodically shift the spectrum back and forth and thus to modulate the signal at the detector. This is, of course, an analogue of a conventional field modulation magnetic resonance technique. I was told that the Caltech patent office wrote an initial version of a patent application "that would have essentially covered the Fourier Transform." The patent, presumably in modified form, was awarded.

Bryan then took up a position (and took a salary cut) to become a junior faculty member at Harvard University in the Fall of 1969. The course of his subsequent research at Harvard, continuing later at Wesleyan University and at The University of California at Riverside, can be traced from the series of resulting publications. Dick Anderson continued the magnetic resonance studies of single crystals containing diphenylmethylene. Peter Esherick developed the apparatus for low-temperature magnetic optical rotation spectroscopy and applied this to single crystals of tetraphenyltin and also initiated a study of the spectroscopy of benzil ($C_6H_5{-}CO{-}CO{-}C_6H_5$), later continued by Rich Loda at Wesleyan.

The major new project that started at Harvard concerned the electronic spectroscopy of linear conjugated polyenes. This project was part of a more broad based collaborative project involving Brian Sykes and Martin Karplus. This project was funded by the National Eye Institute [EY00062]. Bryan's part of this project involved the optical spectroscopy of the visual pigment chromophore retinal. In the visual pigment this aldehyde reacts with a lysine residue to produce a Schiff's base, which becomes protonated. Retinal itself is expected to have a low-lying $n\pi^*$ excitation. To simplify matters as much as possible, we started to investigate retinoic acid. The objective was to obtain high-resolution vibronically resolved spectra from which the excited state potential surface involved in the visual photochemistry could, in principle, be determined. To reduce inhomogeneous line widths of vibronic spectra to values less than the vibronic intervals, it is necessary that all molecules in the sample have the same local environment. This is, of course, possible with single crystals but in that case the very strong absorption of these chromophores would prevent penetration of light in the absorption region into the crystal and there would be very strong exciton effects. Emission would be expected to be for defect or impurity sites. The trick, we believed, was to find the appropriate mixed crystal system so that only one or a few types of sites would be occupied, each giving rise to a set of sharp lines. Since these sites would not interconvert at low temperature, it should be possible to selectively excite each of these in turn and thus obtain the vibronic spectrum of each site. This is a special case of laser site selective excitation pioneered by Personov. Our lead in this approach was the work of Don McClure on studies on naphthalene in durene (1,2,4,5-tetramethylbenzene), the same system with which Hutchison had established the triplet nature of the species from which phosphorescence originates. We knew, however, from the work of Shpolsikii, that, in contrast with the naphthalene/durene case, it was not necessary that the host crystal have exactly the same shape as the guest molecule. Polycyclic aromatic hydrocarbons in some *n*-alkanes resulted in sharp lines. I spent several months (and many dollars) plunging solutions of retinoic acid into liquid helium and looking for vibronically resolved fluorescence. (I even tried the wobbling plate FM method!) No success was forthcoming. Bryan never lost his enthusiasm. He just came up with more ideas.

One of the highlights of being a graduate student with Bryan was the irregular monthly (averaging probably every other month) spectroscopy meetings that were attended by the research groups of his then East Coast Caltech associates, Steve Colson (Yale), Elliot Bernstein (Princeton), and Dave Hanson (SUNY Stony Brook). The meetings were usually held at Yale due to its relatively central location but were held once a year at the other sites. Bryan put his ever present charm to good use when we were stranded on Long Island without cash due to a miscalculation of the time it would take to get to the ferry in time for the last trip to Connecticut. He was able to charge a motel room for us on his credit card. His gasoline credit card. The only rule that I recall about these extended group meetings was that only graduate students could speak. One of the difficulties with this arrangement, in terms of practice at speaking, was that one had the same audience for each talk. This meant that a new talk had to be developed every four months or so. There was no point in giving the same talk in a more polished fashion if the results were the same!

We had group meetings too, of course, Very lively ones. "Saturday morning group meetings" were held on Thursday nights. We usually read a long article or a book and gave presentations on this reading in turn. Robinson and Frosch on radiationless transitions. Craig and Walmsley on Molecular Excitons. There were also several other books that were very often handed to us to read when questions arose. Birks' "Photophysics of Aromatic Molecules" and Murrell's "The Theory of the Electronic Spectra of Organic Molecules", for example. Murrell's book has a reference to the 1935 work of R. Kuhn, Hausser, Smakula, and others, a series of six papers on the spectroscopy of organic chromophores in organic glass-forming solvents at 77 K. One of these six papers describes such specta of diphenylpolyenes and also absorption and fluorescence spectra for a variety of solvents at room temperature. This paper shows well-resolved absorption and fluorescence spectra of the diphenylpolyenes, which exhibit a smooth Franck−Condon progression in two modes. The first peak in absorption and in fluorescence is strong and is easily assigned as the vibrationless origin. There is one peculiarity. These two features do not have the same frequency. For diphenyloctatetraene the separation between these vibrationless origins is 3200

cm^{-1} in the low-temperature glass spectra. Another peculiarity shown in this paper for these compounds is that when the solvent is changed, the absorption spectrum moves (to lower energy in solvents of higher polarizability) but the fluorescence hardly moves at all. No explanation was given for this behavior (or anything else) in these papers.

From the book from Bryan by Birks I found reference to the work of Birks and Dyson on the anomalous fluorescence behavior of the diphenylpolyenes. Division of the observed fluorescence decay rate by the quantum yield results in a radiative lifetime that is longer than that expected on the basis of the integrated absorption by a factor of as much as 10. An explanation was given which will not be discussed here. I recognized that a single hypothesis would explain the peculiar results of both Birks and Dyson concerning the radiative lifetime and also the peculiar spectral and spectral shift results of R. Kuhn, Hausser, and co-workers. That hypothesis was that linear polyenes had a low-lying excited electronic state that resulted in a very weak transition and was $\pi\pi^*$ in nature (because it moved to lower energy with increasing chain length). To be forbidden by symmetry and of $\pi\pi^*$ origin, such an excited state would have to have A_g symmetry. This hypothesis contradicted theoretical expectations in a major way. This was no problem for Bryan. (He had seen how well theory—of an earlier day—did with spin densities.) I presented this hypothesis in a group meeting that now had a different format in that the Karplus Group, which included Klaus Schulten and Barry Honig, was now involved. The rest of this story is elaborated in the long series of papers that started in 1972 in *Chemical Physics Letters* and which continued up until at least 1998.

Bryan was an internationally known and connected scientist. He was a Guest Professor at the University of Leiden in 1972 where he worked with J. H. van der Waals at the Kamerlingh Onnes Laboratory. He made so many visits to the University of Bayreuth beginning in 1979 that he and Susan were well-known to the local community. (It certainly helped that one of them learned to speak German.) He was an Alexander von Humboldt Fellow in 1979 and a Guggenheim Fellow in 1983–84. He attended many international scientific conferences, especially those in molecular crystals, photochemistry, and hole-burning spectroscopy. His long-term interest in condensed phase high-resolution spectral methods resulted in his having Roman Person from the Russian Academy Institute of Spectroscopy in Troitsk come for an extended stay at Riverside. He continued this international connection through 1996. I visited him and Susan in Bayreuth in August of that year. We had front row seats at a very fancy musical event. He was an A. P. Sloan Foundation Fellow in 1974. Bryan was also a JILA Fellow in 1978. At JILA he worked with Carl Lineberger on “a very complicated molecule”, $C2^-$. “Diatomics are complicated!”

Bryan moved from Harvard to Wesleyan University in 1975 where he stayed until moving to the University of California at Riverside in 1985. While at Wesleyan he wrote a description of his research specialty:

“Physical Chemistry. 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.” and of his recent accomplishments:

“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 4K. 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.”

This same CV notes “health: excellent (2:59 for 1981 New York City Marathon)”.

The key technique used in the establishment of the $1A_g$ nature of the lowest lying excited electronic state of linear conjugated polyenes was two-photon excitation of fluorescence of these compounds where 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. For a strictly centrosymmetric polyene it is then expected—and observed—that the vibrationless electronic origin transition will be observed in the two-photon spectrum as a feature that falls 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 is observed for octatetraene in *n*-octane. *n*-Octane apparently provides a centrosymmetric environment for octatetraene, as might be expected. Octatetraene in *n*-nonane or *n*-undecane has a very different spectral pattern, with vibronic structure characteristic of an “allowed” transition with an overlapping origin transition. This is due to the induction of mixing between the low-lying allowed and forbidden excited states due to the “crystal field” of the asymmetric *n*-alkane environment. This strong effect of lowered symmetry even in *n*-alkane crystals was a theme that Bryan continued to investigate and is the subject of several of his last papers.

At Riverside Bryan’s research activities broadened to include a quantitative experimental investigation of this effect of environmental effect on vibronic spectra. By application of an external electric field, he was able to establish the magnitude of this internal field. Much of this work involved ultrahigh resolution hole-burning experiments. He has been quoted as thinking that this was the best and most generally applicable work he had done. He also broadened his choice of molecules to include, for example, terthiophene, a model for a class of conducting or semiconducting polymers (as are polyenes for polyacetylene).

Bryan was always quite active in University affairs at Wesleyan and at Riverside. He was engaged in what has turned out to be some very successful faculty recruitment efforts at Wesleyan. At Riverside he was a well-known “activist” in the University promotion and tenure committee.

He was a member of Sigma Xi, the American Physical Society, the New York Academy of Sciences, the Biophysical Society, the American Chemical Society, the American Society for Photobiology, the Connecticut Academy of Arts and Sciences. He was the founder of the Society for, and chief proponent of, Gonzo Spectroscopy, an “organization” inspired by “Fear and Loathing in Las Vegas” by Hunter S. Thompson.

The infectious enthusiasm, sense of humor and dedication to rigor -all at once! − that Bryan Kohler exhibited in all of his life is the main aspect of his personality that is remembered by his many friends.

Bruce S. Hudson

Syracuse University