THE JOURNAL OF
PHYSICAL
CHEMISTRY A

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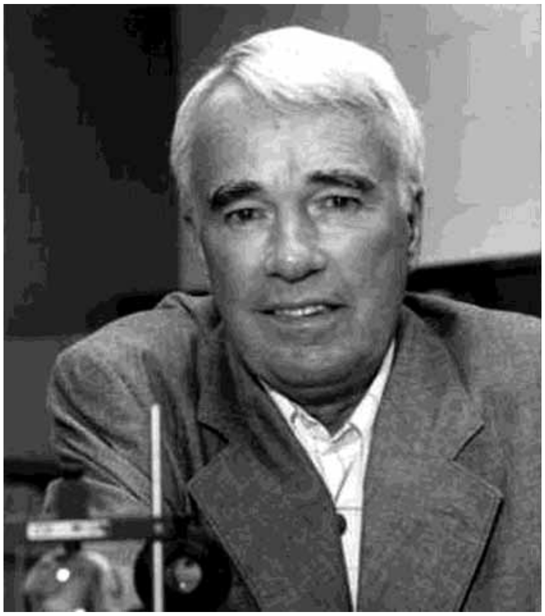
VOLUME 106, NUMBER 33, AUGUST 22, 2002

Biography of G. Wilse Robinson



Over a period of 40 years, Wilse Robinson led, inspired, and provoked generations of physical chemists. Throughout his career, Wilse combined experimental work with theoretical methods to study a staggeringly wide array of topics, often many years before they became popular subjects for investigation. Indeed, another innovative physical chemist, Kent Wilson, once commented that when he was wondering what topics to work on next, he would look to see what Wilse had been working on 10 years earlier!

Wilse Robinson was born in Kansas City, Missouri on July 27, 1924. He attended schools in Kansas City and Clearwater, Florida. Wilse served in the U.S. Navy during WW II in the Pacific theater, requiring at one point, memorization of the color-blindness test because he was quite red−green color blind! Wilse then enrolled at the Georgia Institute of Technology, where he earned both B.S. (1947) and M.S. (1949) degrees in Chemistry. His master's thesis, under the direction of Professor W. H. Eberhardt, concerned intensity perturbations in weak electronic transitions in molecular systems. He obtained his Ph.D. in Physical Chemistry at the University of Iowa (without a research advisor!) in 1952 for work on microwave spectroscopy and the theory of quadruple interactions.

In 1954, after two years as a research fellow at the University of Rochester, Wilse was appointed assistant professor of chemistry at the Johns Hopkins University. There, Wilse developed techniques for the study of isolated molecules and free radicals trapped in crystalline rare gases at liquid helium temperatures. He also carried out (with his students Velta E. DiGiorgio and William T. Raynes) a combined theoretical and experimental study of rotational fine structure in singlet−triplet transitions. The theory was applied to the singlet−triplet transition of formaldehyde—the first such analysis for a nonlinear polyatomic molecule. Wilse's spectroscopy work at Hopkins attracted considerable attention and in 1959, he was offered a position as an associate professor at Cal Tech. Within two years, Wilse was promoted to professor, and a stream of landmark publications followed. Wilse's contributions to the theory of radiationless transitions in 1960, 1962, and 1963 provided the cornerstone of modern understanding of electronic relaxation in large molecules. Pivotal in the development of

10.1021/jp0209300 CCC: $22.00 © 2002 American Chemical Society
Published on Web 07/27/2002

Wilse's thinking was a Faraday Discussion meeting at which the work of George Porter convinced him that the dissipation of excess vibrational energy to the environment was not the rate limiting process. The two *J. Chem. Phys.* papers with Peter Frosch are models of clarity and have had enormous impact far beyond photochemistry and photobiology in areas such as solid-state physics and electron and energy transfer. In the early 1970s, Wilse returned to the radiationless transitions problem, including explicit account of the light–matter interaction, which allowed him (with students Charles Langhoff and Jacqueline Berg) to make important contributions to the theory of time-resolved light scattering, the intermediate case of radiationless decay, and the untangling of strongly vibronically coupled spectra such as the S_o-S_2 spectrum of naphthalene. This latter spectrum had remained unanalyzed since it was recorded by Don McClure in 1954 and studied in detail in the thesis of John Wessel in 1971.

During the mid 1960s to early 1970s the understanding of the molecular crystal exciton structure and dynamics was significantly advanced. There was wide international interest in this topic with major efforts in Russia, England, Israel, and the USA. Wilse built a strong group of postdocs and students including Steve Colson, Elliot Bernstein, David Hanson, Mostafa El-Sayed, Raoul Kopelman, George Nieman, and Dino Tinti. The approach was typical of Wilse's science: creative experiments combined with fundamental theory and vigorous discussion enabling the group to create new experimental paradigms without "leaving the theory to the theorists." In essence, Wilse's philosophy foreshadowed and anticipated the current multidisciplinary approach to science. Using it, Wilse's group assumed leadership in the field and prepared group members for successful careers at universities and in industry.

Wilse's ability to consider a new field and rapidly make an important contribution is epitomized by his paper for the Brookhaven Symposium on Biology in 1966. Here, building on work with his postdoctoral fellow Mostafa El-Sayed, Wilse developed theories of contemporary validity for the molecular interactions that lead to energy migration in organic crystals and in photosynthetic pigment–protein complexes. The work developed to include exciton splittings and exction-exciton annihilation.

With student Mark Allen, Wilse initiated a theoretical effort to describe how hydrogen atoms are trapped and eventually react on very small, cold interstellar dust particles. The model shows that, through the released heat of formation of small molecules, H_2 and other weakly bound molecules can escape into interstellar medium. This work was the first to suggest a mechanism for the formation of gas-phase molecules in the interstellar dark environment and has become an important model for molecule formation in interstellar space.

In the early 1970s, Wilse had become fascinated with the new field of picosecond spectroscopy, sensing that the new laser methods would bring many of the fundamental processes in condensed phase dynamics within reach. He carried out early studies of vibrational relaxation with Paul Monson, S. Patumtevapibal, and Ken Kaufmann. However, Wilse was having difficulty raising sufficient funds for his ultrafast spectroscopy, and this combined with some uncomfortable interactions at Caltech made an offer to take up the Chair of the Physical Chemistry Department at the University of Melbourne in Australia very attractive. In December 1974, Wilse, Ellen, and a single post doc, Graham Fleming, moved to Melbourne to establish a new laboratory. Joined very soon by John Morris, the new laboratories were soon functioning and defining the state-of-the art in picosecond emission spectroscopy. Wilse worked side-by-side with his post docs in the lab and was very proud of his optical interface of the new Electrophotonics streak camera with an optical multichannel analyzer via a camera lens! Some of the early work concerned the rotational diffusion of medium-sized molecules in solutions. The experiments were perhaps the first to have sufficient time resolution to observe the correct limiting fluorescence anisotropy of 0.4, and showed that various dianions were sufficiently "sticky" that they rotated with attached solvent molecules, thus increasing their molecular volume substantially over that of the "bare" molecule. The work continued with student Ray Robbins and the various hydrodynamic boundary conditions—slip, stick, and "super" stick were all observed with different solute/solvent combinations. Many other investigations were initiated in Melbourne, ranging from exciton fission in molecular crystals, through stimulated emission in dye solutions to solvent-dependent excited-state dynamics and a world center for ultrafast spectroscopy was created in a very short period.

Unfortunately, personal and family matters made it very difficult for Wilse and Ellen to remain in Australia and in 1976 Wilse and Ellen left Melbourne for Texas Tech University, where Wilse was appointed Robert A. Welch Professor of Chemistry and Professor of Physics, positions he held until his death. At Texas Tech, Wilse established the Picosecond Spectroscopy and Quantum Radiation Laboratory to continue his investigations into condensed phase, and especially aqueous, dynamics. As a result of experimental studies in the 1980s of the solvent-dependent photophysics of naphthols and anilironaphthalene sulfonates, Wilse began to focus on the structure and dynamics of the hydrated electron and proton, and eventually on the structure of liquid water itself. A long-time contributor to this effort was Jamine Lee. Often the ideas generated in this work were quite different from the conventional models—for example, Wilse proposed a model for the hydrated electron of $(OH_3....OH^-)_{aq}$, which differs strongly from the conventional picture of the electron residing in a solvent cavity.

Although by the 1990s, Wilse had begun to focus very strongly on the properties of liquid water, in the 1980s and 90s, he also made a series of contributions to the barrier crossing processes that lie at the heart of Kramers' reaction rate theory. In particular, Wilse, with physicist S. Singh and student R. Krishnan, connected the intermediate friction regime of Kramers theory to critical phenomena, showing the presence of scaling and universality in the system behavior.

For nearly two decades, Wilse endeavored to understand liquid water with his focus being primarily on the fundamental problem of solvation, and the underlying issue of liquid water structure. His work in this area culminated in the publication of a book "Water in Biology, Chemistry and Physics: Experiment Overviews and Computational Methodologies" (World Scientific: River Edge, New Jersey, 1996) coauthored S–B. Zhu, S. Singh, and M. W. Evans. His work on water was nearly entirely theoretical in character, including aspects of theory, modeling, and simulation, and included several publications on the general theory of condensed phase reaction dynamics. His contributions in the area of solvation and liquid structure were distinctive in his consideration of a wide range of thermodynamic conditions and physical environments. These environments included bulk water, the solvation spheres of ions and solvated electrons, and interfacial water in films and at biomolecular surfaces.

Wilse concentrated most on developing and implementing a model of water that would faithfully describe the solvent density as a function of temperature and pressure, a feature that he felt was critical to any model that could accurately describe solvation in diverse contexts. The water model that emerged was based on a two-state mixture description of the components of the liquid, and emphasized the interaction of nonnearest neighbors in addition to the traditional focus on near-neighbor tetrahedral coordination. In the context of the model, the density maximum arises from outer-neighbor structural transformations. In 1996, Wilse developed a simple one-dimensional analytical model that is able to reproduce the density and other properties of water over a wide range of temperatures and pressures. Typically, the new ideas and approaches were applied to biological systems and, in 1999, he described a model for cold and heat denaturation of proteins in solution based on the temperature-dependent proportions of ice-Ih-type and ice-II-type bonding in the liquid.

Many of Wilse' views on liquids and solvation were controversial. But his unconventional thinking and strong defense of his own ideas reflected the imagination and determination that contributed heavily to his considerable impact on our current understanding of molecular systems. As before, his approach was outside the mainstream but introduced revolutionary ideas emanating from the desire to understand the physics governing the formation and stability of the various phases of ice as a prerequisite for understanding the liquid. Time will have to settle the question of the lasting contribution Wilse made to liquid water, but to all who worked with him, Harry Gray's prediction that, "When the dust settles, and someday it surely will, Wilse Robinson will be recognized as the scientist whose work led to a fundamental understanding of the properties of this amazing substance" strikes a strongly resonant chord.

Wilse and Ellen were married on June 5, 1950 in Cedar Rapids, Iowa. She was the light of his life and confidant of many students and postdocs. Warm and lasting friendships were many between Wilse and his group members and his unremarked and selfless boosting of their subsequent aspirations, aided the launch of many wonderful careers. Wilse could appear gruff and forbidding, but was truly a soft-hearted push-over whose friendships withstood the tests of time and distance. Above all, he was an original thinker, who constantly thought "outside the box" and used his passion for science and his stubborn streak to persevere against the mainstream. The world of chemistry is the poorer for his passing.

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Guest Editors