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Special Issue Honoring George S. Hammond and Michael Kasha

In April of 2001, friends and associates of two great scientists, George S. Hammond and Michael Kasha, gathered in California and Florida, respectively, to celebrate their 80th birthdays. From these events emerged the idea to recognize jointly with a special issue of this journal the crucial role of these two brilliant men in ushering in the field of modern molecular photochemistry by merging photophysics, spectroscopy, and physical organic chemistry. The common threads joining Kasha's and Hammond's research contributions lie in the triplet state and in the molecular orbital description of excited states. Kasha's assignment (with G. N. Lewis) of molecular phosphorescence to the triplet state and his lucid molecular orbital descriptions of excited states and their interconversion, coupled with Hammond's seminal application of electronic energy transfer to unlock the chemistry of the triplet state, gave excited states life in mechanistic photochemistry.

As the last doctoral student to complete his work with G. N. Lewis, who died in 1946, Kasha's monumental work on the phosphorescence of organic molecules was published in his first two scientific contributions (1944, 1945). Those papers advanced the then controversial idea that such delayed emissions are intrinsic molecular properties, originating from the lowest-energy spin-forbidden triplet states. As a young Ph.D. graduate, Michael Kasha found himself joined in battle with many prominent spectroscopists and theorists of that time (notably, Franck, Livingston, Rabinowitch, and Teller), all skeptical of the role of the triplet state. It was a decade and a half later, during which Kasha and his students explored *Z*-effects on spin−orbital coupling, and culminating in Hutchison's and van der Waals ESR spectra and Porter's triplet−triplet flash spectroscopic measurements that the triplet nature of those emitting states was universally accepted.

With his insights as a chemical kineticist, George S. Hammond was the first to establish unambiguously the role of the triplet state in solution photochemistry. In two definitive papers in 1959 and 1961, kinetics arguments, elegant in their simplicity, showed the lowest triplet state of benzophenone to be the key intermediate in its photoreduction. On the heels of that discovery emerged triplet−triplet energy transfer as an all-important mechanistic criterion used to sensitize or suppress triplet reactions. Through energy transfer one could quench, for instance, the photoreduction of benzophenone while populating reactive triplet states of molecules whose triplet states could not be accessed following direct light absorption. Triplet−triplet energy transfer, observed earlier by Terenin and Ermolaev in glassy solution and by Bäckstrom and Sandros and by Porter and his group in fluid solution, provided the procedure (triplet sensitization/quenching) for differentiating molecular reactivity of triplet and singlet excited states. The door to a dazzling array of novel triplet chemistry was thereby unlocked (photoisomerization, photocycloaddition, photoreduction, photooxygenation, and photofragmentation). In those early days that marked the emergence of mechanistic photochemistry, Kasha papers were required reading for the Hammond group. The rate and efficiency of triplet excitation transfer was shown to depend on the energetics of the process. A series of triplet donors/acceptors were needed, and the early Lewis and Kasha phosphorescence papers were invaluable guides in their development.

While the triplet state is an obvious link between these two scientists, their paths crossed in at least two other important areas. Kasha's description of n,π* and $\pi\pi$* electronic states from a spectroscopic viewpoint guided the photochemical studies in Hammond's group in deducing structural requirements for effective triplet sensitizers and for explaining the photochemical reactivity of electronically excited organic molecules. Hammond's revival of the Kautsky energy-transfer mechanism for formation of singlet oxygen to account for results of photosensitized oxygenation reactions followed and benefited from Kasha and Khan's detection of singlet oxygen chemiluminescence. Energy transfer replaced the then-favored addition−elimination photooxidation mechanism championed by the Schenck school, and Foote's beautiful studies on the chemistry of singlet oxygen were launched.

Michael Kasha's and George Hammond's contributions extend far beyond the discovery of a new electronic state with its own characteristic chemistry. The dynamic personalities, the breadth of their knowledge, and the remarkable creativity of these two scientists opened doors to new areas of research involving electronically excited molecules. By bringing together photochemistry and spectroscopy, they developed systematic ways for understanding excited-state processes. Kasha provided the picture of activation and deactivation of electronically excited molecules in terms of state diagrams with singlet and triplet state manifolds, correcting and extending the older Jablonski diagram. He played a pivotal role in studies of photomagnetism, radiative and radiationless transitions from electronically excited molecules (Kasha's Rules), mechanisms of spin−orbit coupling, orbital classification of electronic transitions (n,π*, etc.), molecular exciton effects, singlet mo-

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lecular oxygen, the solvent cage, and excited-state proton transfer spectroscopy, often introducing new theoretical concepts along the way. Hammond, with his exceptional insight into physical organic chemistry, exemplified by the Hammond Postulate on structure–reactivity relationship of molecules—now found in every introductory organic text—led the way to the systematic elucidation of the mechanisms of photochemical reactions. His pioneering studies on the use of triplet excitation transfer as a mechanistic criterion, the measurements of triplet quantum yields, the identification of new excited-state complexes and electron transfer processes, the use of bichromophoric systems as structurally defined donor–acceptor pairs, and the extension of this knowledge to inorganic systems advanced the sciences of photochemistry and spectroscopy immeasurably.

While the findings of Kasha and Hammond are now taken for granted by every modern spectroscopist and photochemist, pause for reflection points to the broad impact of their contributions in virtually every area of scientific activity involving photoexcitation, whether in basic research or in its applications. Thus, it is now possible to advance logical mechanistic concepts in the analysis of photochemical events in enormously complex systems exemplified by photosynthesis, visual transduction, DNA damage and recovery processes, photooxidations, and photomedicine or the design of practical systems as in photoimaging, photoinitiated polymerization, photoprotection, and solar energy storage—all requiring application of Kasha's and Hammond's fundamental discoveries and the methods they and their co-workers developed.

Teachers par excellence, Hammond's and Kasha's influence has been amplified manifold by the contributions of the many students and associates whose research careers began in their laboratories. Having experienced Hammond as a teacher and Kasha as a colleague, a few personal words are in order. How fortunate to have been in Hammond's laboratory in the early 1960s! Always approving of co-workers, Hammond embraced new observations, and his elegant interpretations were quick in coming. The generous free flow of ideas in that laboratory nurtured our science. No one that has experienced Kasha, a Renaissance man, string-instrument design, daylilies and all, can think of him as other than holding forth on the latest idea to capture his imagination. An endless stream that! At the beginning of the third millennium, as technology transfer and secrecy invade academia, it is good to reflect on the spirit of open inquiry symbolized by Hammond and Kasha.

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Guest Editors