



Michael Kasha

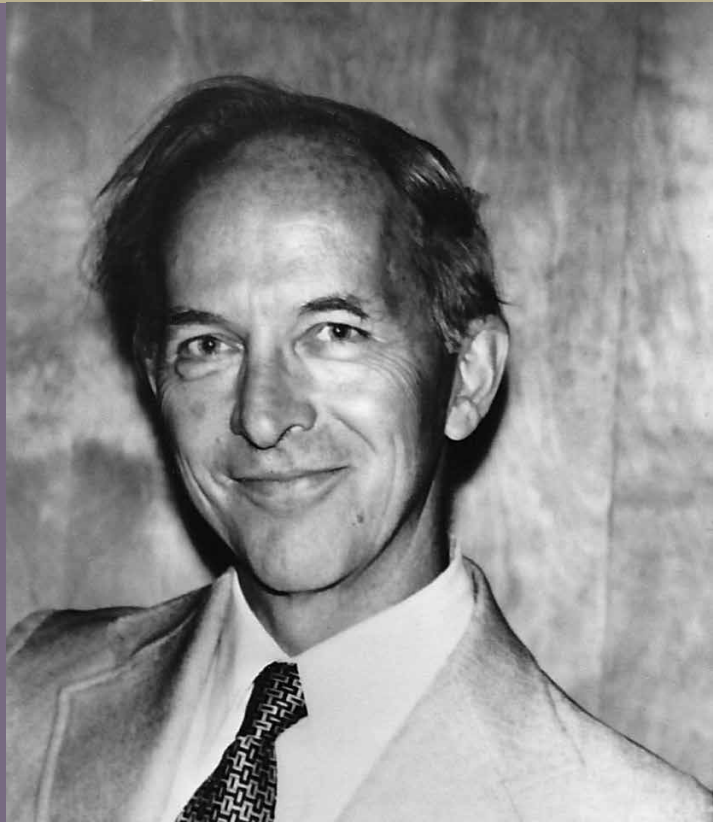
1920–2013

BIOGRAPHICAL

Memiors

*A Biographical Memoir by
Donald S. McClure
with a personal recollection
by Lionel Goodman*

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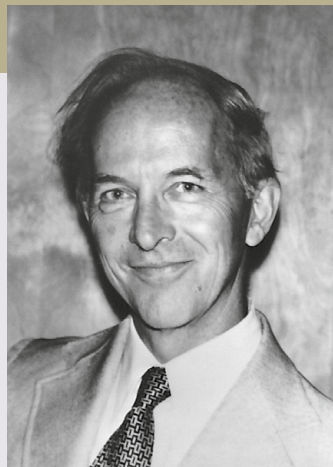
MICHAEL KASHA

December 6, 1920–June 12, 2013

Elected to the NAS, 1971

Michael Kasha significantly advanced the understanding of chemical bonding mechanisms and was a pioneer in recognizing the growing importance of interdisciplinary research among biochemists and physicists, culminating on his part in the Institute of Molecular Biophysics (IMB) at Florida State University.

Kasha, a first-generation Ukrainian-American chemist, began working for the Merck chemical company directly out of high school, then earned a B.S. in chemistry from the University of Michigan. Studying phosphorescence and molecular bonding under Gilbert Lewis at Berkeley, he got his Ph.D. in 1945, followed by a post-doctoral fellowship and several scientific sabbaticals abroad. Named a tenured full professor at the new Florida State in 1951, Kasha established the IMB in 1960 and was its director for 20 years.



Michael Kasha

By Donald S. McClure

Michael “Mike” Kasha was born on December 6, 1920, into a working-class family of Ukrainian immigrants in Elizabeth, New Jersey. His father and mother had not completed high school in the Ukraine before the Russian Revolution forced them to flee to the United States. Ukrainian was the only language spoken at home and in the Ukrainian Catholic elementary school where Mike was first enrolled. Fortunately for him, the local authorities required his parents to enroll him next in a public junior high school, where English was spoken. Mike completed junior high and high school with full English fluency.

Avid about chemistry from an early age, Mike built a small chem lab in the basement of his home and conducted experiments there while in high school. He was sure he wanted to be a chemist, but he had no idea of how to begin. The turning point came after he graduated from high school. He needed a job and found what looked like one made in heaven advertised in the local paper. The Merck chemical company needed a high

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school grad for a lab boy position in their research division! But when he called to inquire, he was told that the position had been filled. Mike thought, “I have to get that job!” He jumped on a train and took the 30-minute ride to meet the hiring manager in person. He was so convincing that he was hired on the spot, and he worked for Merck for two years. His academic brilliance brought him a scholarship first to the Cooper Union engineering school in New York City, which he attended at night while working for Merck during the day, and then to the University of Michigan, where he earned a bachelor’s degree in 1942.

The Michigan faculty advised him on the next step in his academic career, which was to go for a Ph.D. Mike, however, was appalled by their suggestion that he study under a young professor at a nearby college who was a former student of Mike’s professor at Michigan. Instead, Mike decided then and there that he would study with the famous chemist Gilbert Newton Lewis, probably the most brilliant member of the faculty of the University of California. Mike graduated with honors from Michigan and was quickly accepted for graduate school at Berkeley.

An entering graduate student was supposed to rotate through the different Berkeley chem labs before choosing a research advisor, but Mike had already made up his mind about working under Lewis. He went straight to the man and asked to be his student. Lewis was impressed and accepted him. Lewis had made major contributions to chemical thermodynamics and was using the new quantum theory to explain chemical bonding, and Mike was thrilled to work with him.

Lewis had discovered that many organic molecules, when excited by ultraviolet light, would emit fluorescence, but if a solution containing those molecules were cooled to the temperature of liquid nitrogen and then illuminated, a long-lived “phosphorescence” would appear in addition to the fluorescence. In a paper published by Lewis and Kasha in 1944, they identified phosphorescence as a triplet-to-singlet transition. This implied the existence of a hitherto unknown triplet state.

This interpretation was obvious for anyone conversant in the new subject of quantum mechanics. As the authors pointed out, the ground state of molecules had to have

bonding electron pairs consisting of two electrons with opposite spins. The excited states could be of two types: singlets that preserved the opposite-spin orientation and triplets with two electrons having the same spin orientation. There was a “selection rule,” which said that transitions between singlets and triplets are “forbidden.” But the transition happened anyway, though weakly, thus accounting for the long lifetime of phosphorescence.

The paper was read widely, and a number of chemists raised objections to the interpretation. Photochemists, for example, suggested that photoionization and recombination with light emission were involved. Settling a worldwide controversy was a wonderful way to start a Ph.D. dissertation, but there was a war going on, and Mike had to work full time on matters related to the war effort. This meant collaborating during the daytime with another Berkeley chemistry professor, Robert E. Connick, on the chemistry of plutonium and working for Lewis at night. The result for Mike, in 1945, was a doctorate in a year and a half and several papers on plutonium chemistry.

Mike became a post-doctoral fellow at Berkeley and was partly responsible for seeing to the graduate students in the Lewis group. These included Harrison Shull, Robert Naumann, and I. Tragically, the year after Mike received his Ph.D., Gilbert Lewis died in an apparent laboratory accident.

Latimer decided to keep the small group together and persuaded Professor Ernest Gibson to become the responsible supervisor. The four of us (Shull, Naumann, Mike, and I) were well along with research projects, and we benefited from the study of group theory with Gibson, using the distinguished Hungarian-American physicist Eugene P. Wigner’s original German-language volume on group theory. Sharing this experience with us were George Pimentel and Bill Simpson.

We were all in need of more understanding of quantum theory, so Mike made the acquaintance of David Bohm, in the Physics Department, who came to some of our



Gilbert N. Lewis.



From left: Michael Kasha, Donald S. McClure, George C. Pimentel and William T. Simpson. (Courtesy of the College of Chemistry, University of California, Berkeley.)

the mixing of singlet and triplet states and the resulting effect on the emission lifetimes: the greater the charge of the nuclei, the shorter the lifetime of the phosphorescence. The measured lifetimes strikingly confirmed this relationship. But even after much such evidence had been reported, it still took many years to convince everybody.

Mike spent another year at Berkeley and then took two consecutive postdoctoral years, one at the University of Chicago with future Nobel Laureate Robert S. Mulliken and another at Manchester with Evans. Mike was becoming well known nationally during these years, both as a scientist and as a leader. So it was not entirely surprising that in 1951 he received a fabulous offer: a full professorship with tenure in the Department of Chemistry at Florida State University. This university was just being formed, and it was up to Mike and other appointees to see that good people joined.

Mike could see that the traditional division of the sciences as taught in American universities was changing, as the biological part was becoming a more quantitative science. Then, in 1959, two extraordinary pieces of luck happened: First, Mike found himself invited to speak at a national conference in Atlanta. But the invitation was actually an error; another senior chemist with a last name almost identical to Kasha was to have been invited. Second, after the speeches were finished Mike happened to overhear a conversation in the hallway that changed everything. There was mention of a large federal

group meetings and told us about spin-orbit coupling. Now we could build a quantitative theory to explain the durations of the phosphores. A simple way to visualize spin-orbit coupling is to imagine the electron as a small bar magnet being acted on by the much larger magnetic field due to the orbital motion of the electron in the electric field of the nucleus. There are several spectroscopic effects of spin-orbit coupling. One is the splitting of spectral lines not usually observable in low-resolution molecular spectra. Another is

initiative to fund a new research enterprise at a university, and the officials in charge were looking for innovative proposals.

Mike raced back to Florida State to inform the president of the opportunity and write a proposal for a new Institute of Molecular Biophysics (IMB). The proposal was accepted, and the Florida legislature voted to match the federal funds. The new IMB building was completed in 1960. Mike was the institute's first director, a position he held for the next 20 years. His vision was to forge a new collaborative facility, where chemists, physicists, and biologists could pool their efforts to discover new phenomena at the level of biomolecular interactions.

Mike's influence at Berkeley—and vice-versa—did not end when he left in 1950. First, the entire research group found wives or girlfriends by 1949, including Mike, who married Lilli Cohn, a native of Gdansk, Poland, and a grad student at Berkeley. A key project suggested by Mike and finished in 1949 was my thesis on the measurement of the lifetimes of phosphorescences of organic molecules and the interpretation in terms of spin-orbit coupling. Still another vital project was to measure the quantum yield of the phosphorescence. If it did not turn out to be unity, then the measured lifetimes would have to be corrected in order to find the true radiative lifetime, a quantity that could be handled by quantum theory. The other influences on the lifetime would be environmental.

In the case of benzene, for instance, the measured lifetime of phosphorescences was 6 seconds, but the quantum yield correction requires 21 seconds. So most of the excitation went by a faster radiationless process. What was that process? The answer was worked out by many research labs, including Mike's, over the next decade. A tempting hint was that hexa-deutero benzene phosphorescence had a lifetime of 21 seconds.

The success of a laboratory like Mike's depends on finding interesting, previously unknown molecular behavior. One example was the discovery that oxygen in an excited state could be produced in a chemical reaction. The excited oxygen could then decay, leading to a red luminescence. This is an example of chemiluminescence. Related are the many examples of bioluminescence. Mike and Khan compared the chemically produced luminescence spectrum with that of oxygen under high pressure in order to assign the peaks of the luminescence spectra.

Khan and Mike worked together on many aspects of the chemistry of O_2 in solution. The molecule is in a singlet state while in solution, and the ground state is a triplet, thus



Kasha with a cello for which he redesigned the bracing. (Courtesy of the Kasha family.)

accounting for the metastability of O_2 . Yet another exciting subject discovered at the IMB was called proton-transfer spectroscopy, wherein a hydrogen atom jumps from one site to another on the framework of a complex molecule. Working out the details of the atomic and electronic motions while the luminescence is created is the fun part of doing science here.

It was evident that Mike had plenty of ideas for research. It turned out that he also had ideas to develop in other fields. He had bought a guitar for his son, Michael, and decided that the classical guitar needed a new design and proceeded to develop it. He showed that he meant business when he convinced the greatest performer in the field, Andres Segovia, to work with him on his ideas. The same unshakable self-confidence and intellectual brilliance that got him his first job at Merck as a boy were with him throughout his life. One of the best outcomes of working in Mike's lab was developing an appreciation of the excitement of doing scientific research.

Mike's son, Nicolas, said of his father:

He had a contagious enthusiasm for everything. He energized his surroundings. He could pinpoint subtleties or incongruities that other people had overlooked, then focus his attention and uncover something new under every unturned stone. He had the ability to dissect something that appeared complex and make it sound simple. We shared conversations about art, music, science...anything, really. My father was always

reading, always bringing up a new topic. He loved jokes, was a great storyteller, and was crazy about Calvin and Hobbes comics.

Summing up, Lilli and Nicolas said of Mike:

We were able to spend a great deal of time with him over the last two years, moments we will cherish forever. Like the many who came to know him through his work on guitars, violins, cellos, and basses; his academic career in the biophysics of excited states of molecules; his work on the biophysics of the effects of solar coronal mass ejections, (one of those was happening near to the time of his death); or his interests in wood-working, electronics, photography, and sailing, we will always remember him and feel lucky to have had him in our lives.



Mike in 1986.



Mike and Lilli. (Courtesy of the Kasha Family.)

A Wednesday in Mike's group (1955–early 60s)

by Lionel Goodman

Wednesday morning was the weekly group meeting. It was here that Mike revealed his superb ability as an educator and also as “poet of molecular spectroscopy”, throwing out complex ideas on competition between radiationless and radiative processes in clear language unencumbered by distracting details. Our task was that of marksmen: try to shoot down Mike's rationalizations, for example, of why molecular excited states involving promotion of nonbonding electrons do not fluoresce (but only phosphoresce), whereas excited states that involve promotion of bonding (for example, π) electrons frequently exhibit both fluorescence and phosphorescence.

Wednesday (warm weather) afternoons generally found the group augmented by spouses and boy/girl friends (sometimes including Lilli) at the local 200 foot-deep swimming hole, Wakulla Springs. The real work began after supper with much discussion of experiments that might best provide further insight into Mike's posits that morning. The 5-7 graduate students, Postdocs, and visiting scholars took turns on the Steinheil glass optics spectrograph and first-generation Beckman recording spectrometer. Mike had spent time in Robert Mulliken's (Chicago) group just before coming to FSU and, though an experimentalist himself, fully appreciated having a full-time theoretician in the group. The first theoretical member was Ian G. Ross, from Australia. I. G. subsequently gained a reputation through his articles on vibrational-electronic coupling.

A student in Mike's group would find sources of knowledge of all kinds, theoretical and experimental. One just had to find the right person and ask the right question. Often this person was Mike.

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