William A. Klemperer

1927–2017

BIOGRAPHICAL *Memoirs*

A Biographical Memoir by
Joseph S. Francisco
and Jeffrey I. Steinfeld

NATIONAL ACADEMY OF SCIENCES

WILLIAM A. **KLEMPERER**

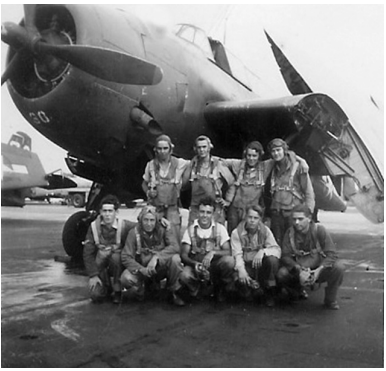
October 6, 1927–November 5, 2017

Elected to the NAS, 1969

By Joseph S. Francisco and Jeffrey I. Steinfeld

William A. (Bill) Klemperer was a world-renowned and highly regarded practitioner of chemical physics and molecular spectroscopy. During his career at Harvard University, he made important and often foundational contributions to high-temperature spectroscopy, molecular beam techniques, molecular energy transfer, spectroscopy of weakly bound complexes at low temperatures, and chemistry of the interstellar medium. His versatility, creativity, and integrity, coupled with irresistible enthusiasm, lively humor, and a warm, engaging personality, attracted many co-workers to his research group, including undergraduates, Ph.D. students, and postdoctoral fellows and associates. Through this community of "Klemperians," Bill's legacy continues to influence the style and content of the scientific enterprise today.

Bill Klemperer was born in New York City on October 6, 1927, one of two sons of Paul and Margit Klemperer (the renowned symphony conductor Otto Klemperer was a distant relation). Bill graduated from New Rochelle (New York) High School in 1944; he is commemorated there by a plaque on the New Rochelle High School "Wall of Fame." He served in the U.S. Navy Air Corps from 1944 to 1946 and was trained as a tail gunner. Following his demobilization in 1946, he enrolled at Harvard University and received his bachelor's degree in 1950. He was married to Elizabeth Lillian (Beth) Cole in January 1948. Beth earned a Ph.D. in chemistry at Tufts University and later worked at the U.S. Army Research Laboratories in Natick, Massachusetts. Their three children, however, did not follow scientific careers: Paul (b. 1957) plays in a jazz band, Wendy (b. 1958) creates intriguing metal sculptures, and Joyce (b. 1953) is a social worker for the City of New York, providing assistance to underprivileged communities.



Bill Klemperer with his US Navy Air Corps crew, ca. 1945. Bill is the one taking a knee in the front row at the left.

Following his graduation from Harvard, Bill began graduate studies at the University of California, Berkeley, where he joined George Pimentel's research group, completing his Ph.D. in 1954. In the spring of that year, he made a return visit to Harvard for an informal get-together with one of his undergraduate professors and was offered a position as Instructor in Analytical (!) Chemistry on the spot. Despite Harvard's reputation at the time for not promoting or tenuring faculty from within, Bill rose steadily through the academic ranks, becoming Full Professor in 1965. He spent 1968 to 1969 on sabbatical with astronomers at Cambridge University in the United Kingdom, and 1979 to 1981 as Assistant Director for Mathematical and Physical Sciences at the U.S. National Science Foundation (NSF) in Washington, D.C. He was a visiting scientist at Bell Laboratories in New Jersey during a time when it was the premier industrial laboratory. Klemperer was promoted to Emeritus Professor at Harvard in 2002 but remained active in both research and teaching beyond his appointment.

Research Interests and Achievements

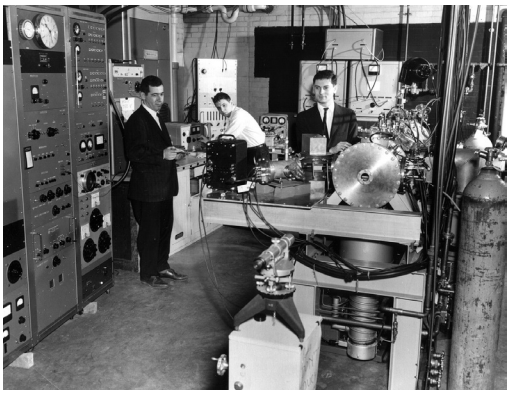
Bill's first few publications (between 1952 and 1955) involved condensed-phase systems: hydrolysis of 2-methoxy ethyl iodide, the infrared spectrum of deuterated solid n-octane. But from 1955 onwards, all of his 279 publications dealt with isolated molecules, in the gas phase, molecular beams, or interstellar space. Bill once remarked that "any experiment that requires statistics for its interpretation is a poorly designed experiment".[1] This principle guided Bill's research throughout his career.

Infrared Spectroscopy of High-Temperature Species in the Gas Phase.

Bill's earliest experimental work in this area concerned lithium hydride, LiH. The measurements enabled determination of binding energy, force constant, and dipole moment derivative. At the time, this four-electron system just about represented the limit of quantum-chemical calculations, so these results served as a valuable benchmark for such calculations. These experiments were subsequently extended to metal halide molecules across the periodic table. But more was needed to achieve the insights into molecular structure and bonding that Bill was after.

Molecular Beam Electric Resonance Spectroscopy

In the late 1950s and early 1960s, Bill launched a major ambitious new undertaking: the construction of a molecular beam apparatus for molecular spectroscopy. In this he received material assistance and encouragement from Norman Ramsey of the Harvard Physics Department, which is located across Oxford Street from the Mallinckrodt Chemical Laboratories. The skill and talents of Lennard Wharton, an engineering undergraduate of the Massachusetts Institute of Technology who received his Ph.D. (1963) from Harvard, helped make the project a success, and copious results began to appear in 1962-63.



The "Big Beam Machine" in the basement of Mallinckrodt. Left to right: Bill Klemperer, L. Peter Gold, Lennard Wharton. Note the absence of digital instrumentation in the electronics racks.

The apparatus consists of a large high-vacuum chamber, a high-temperature effusive source, electric dipole and/or quadrupole fields to Stark-shift energy levels and focus the polar molecules as desired, an intervening microwave or radiofrequency "C" field to induce transitions among rotational and hyperfine levels, and mass-spectrometric detection. With this apparatus, Bill and his students were able to determine electric dipole and quadrupole moments for a wide variety of metal oxides and halides. Microwave spectroscopy afforded rotational constants and thus the geometry and structure of many gas-phase species. Measurements could also be carried out on metastable molecules with a lifetime sufficient to travel from source to detector, such as CO $a^3\prod$ and, later, acetylene.

Low-Temperature Molecular Complexes and Intermolecular Interactions

At about this time, several research groups discovered that, by expanding a high-pressure gas through a suitably configured nozzle, it was possible to produce a high-intensity molecular beam having high forward velocity and concomitant low transverse velocity components. If a monatomic inert gas is seeded with some molecular species, the molecules are cooled to a low effective vibrational and rotational temperature (ca. 10 K), since the energy for the forward acceleration is drawn from both the transverse velocity

components and the internal degrees of freedom. Bill saw right away that these supersonically cooled beams would simplify the rotational spectrum of complicated molecules and, importantly, promote the formation of weakly bound molecular complexes, since the low effective temperature allows hydrogen bonding or van der Waals (vdW) forces to produce stable complexes while retaining their isolation from medium effects. Using this innovative method, the geometry, structure, electric dipole moment, and other properties of these non-covalently bonded complexes could be determined by means of high-resolution spectroscopy.

The first such system studied using this technique was the hydrogen-bonded HF dimer, which turned out to be a nonlinear semirigid complex undergoing hydrogen atom tunneling. Between 1972 and 2015, Bill's group synthesized and studied one hundred more complexes, including vdW complexes with monatomic inert gases. For many of these, the resulting structures and low-frequency motions turned out to not follow the simplified rules of chemical bonding, providing challenges for quantum chemical calculations.

Molecular Energy Transfer

Some of the first important studies of state-to-state molecular energy transfer were carried out during the 1960s using iodine vapor B→X fluorescence as a model system. The actual measurements were performed using a venerable Raman spectrometer fitted with a high-intensity mercury vapor lamp located in the sub-basement of Mallinckrodt. Fluorescence data were saved on a strip-chart recorder and the areas under resolved spectroscopic features were measured on the chart paper with the aid of an Ott planimeter. These experiments, further developed by Klemperer group alumni, led to among other things the first observations of laser-induced molecular fluorescence and provided a set of benchmark data for testing theoretical models of molecular inelastic collisions, including quasiclassical trajectory calculations, scaling laws, and information-theoretic analysis. These studies also helped to motivate the startup of the Gordon Research Conference on Molecular Energy Transfer (GR-COMET), which continued in both Gordon and non-Gordon formats in ensuing years.

Bill and some graduate students examine (exult over) I_2* fluorescence data on chart recorder paper, ca. 1963.

Chemistry of Interstellar Space ("Astrochemistry")

In 1968-69, Bill took a sabbatical year with the astronomy group at Cambridge University, where he attempted to understand the formation of molecular species observed in interstellar space by radio astronomy. Following his return, Bill presented these ideas in a physical chemistry seminar at Harvard, during the course of which he discussed "logarithmic order-of-magnitude" estimates for reaction rates and species' half-lives. As usual, George Kistiakowsky sat in the front row and pretended to be asleep. At the end of the seminar, Kisty raised his head and in a loud, clear voice uttered a highly uncomplimentary one-word exclamation.

Kisty's negative opinion was unwarranted, however. Radio astronomers had been observing a strong emission at 89.190 GHz but were unable to identify the carrier. Bill's kinetic model provided the solution to the puzzle, as described by Dudley Herschbach in the obituary published in *Nature Astronomy* in January 2018:

> *The huge dark clouds where most interstellar molecules have been seen are 99% composed of hydrogen and helium. After H_2, carbon monoxide is the most abundant molecule…Ionization by the pervasive flux of 100 MeV cosmic rays creates some H_2^+ and He^+, from which emerge many reaction sequences. The H_2^+ rapidly reacts with H_2 to form H_3^+ which, as known from laboratory studies, readily transfers a proton to many other molecular species. Hence Bill predicted that most of the H_3^+should be converted to HCO^+, a very stable species. This prediction was a seminal triumph for Bill's model. Soon after, interstellar emission from a species dubbed 'Xogen', that had not yet been seen on Earth, was shown to come from the HCO^+ ion. It turned out to be the most abundant ion in dark clouds and has even been observed in distant galaxies [as well as in subsequent laboratory studies].*[2]

Bill continued to make contributions to the chemistry of interstellar space throughout the rest of his career.

Recognizing his wide range of scientific interests, and the enthusiasm and integrity with which he pursued them, the NSF named Bill its Assistant Director for Mathematical and Physical Sciences during 1979-81. Even during this period, Bill maintained a large, active, and productive research program.

Bill and Gerhard Herzberg, ca. 1970.

Reminiscences from a Colleague by Dudley R. Herschbach

I met Bill Klemperer in 1955 at Harvard, when he was a 28-year-old Instructor. I was a 23-year-old graduate student, starting microwave spectroscopy in the lab of E. Bright Wilson, Jr. Bill and I became immediate friends; he was innovative, versatile and ebullient! Also, both of us found Bright a joy, a wonder. Ten years later, Bill and I were tenured full professors, with nearby offices. Each had very active labs, together in a long basement, both with several molecular beams. Bill was pursuing spectroscopy, and I pursuing dynamics of reactive collisions. Both of us had many graduate students and postdocs. We often discussed together our research and teaching activities, along with issues in the chemistry department. As a pair, for more a decade we consulted to assess other groups to be funded for experiments related to stratospheric ozone depletion. On occasion, we borrowed a truck to shovel manure from a horse stable to feed Bill's bountiful rose garden. Bill delivered "*Some Spectroscopic Reminiscences*," in *Ann. Rev. Phys. Chem*. 45:1-26 (1995). That "made a particular impact," focusing on topics and special colleagues.

For Bill, "Bright Wilson remains the model scientist—always totally rational, with a sharp critical judgment; totally unselfish; and the least egotistical." Bill's 65th Birthday Symposium was held 3 October 1992, but sadly Bright died 12 July 1992. Bill and I along with three colleagues gave talks about Bright in Harvard Memorial Church at 16 October 1992; the talks are available together in a booklet. In retrospect, Bill told me to be in charge of his Memorial Symposium, not held in a Church but a big party. Twenty-six years later the party came, 24 March 2018, a full day with six sessions, followed by music and dinner. Each session had five or so panelists plus tributes from brief videos from friends away. The sixth session dealt with Astrochemistry included videos from Bill and from Pat Thaddeus. The Harvard Media Production Group filmed the entire program and collected many other videos that I found involving Bill, his science and his family. All those memoirs were launched into a "Klemperer Cloud."[3] The K-Cloud conveys the inspiring legacy of the Klemperer era and Bill's ebullient spirit.

Honors and Awards

Bill was elected to the American Academy of Arts and Sciences in 1963 and to the National Academy of Sciences (USA) in 1969. His many professional awards included the Langmuir, Peter Debye, and E. B. Wilson Awards from the American Chemical Society (ACS), the Remsen Award from the ACS Maryland Section, and the Earle Plyler Award from the American Physical Society. In 1995, Bill was awarded the Faraday Medal by the Royal Society of Chemistry (U.K.) and gave an especially memorable lecture on that occasion.

Teaching and Mentoring

Bill possessed a uniquely enthusiastic teaching style, which included guiding and mentoring 63 Ph.D. students, 32 research fellows and associates, and numerous Harvard undergraduates. This community of "Klemperians" has gone on to influence the style and content of the scientific enterprise in academic departments, industry, and government laboratories all over the world. Bill's approach to educating young scientists was beautifully described by Steve Wofsy and Stew Novick at the Klemperer Memorial Symposium in 2018 as follows:

> *It was amazing how much he trusted us, and how much that trust was rewarded with great science. But, his scientific rigor and his personality shaped the personality of the group. This was in sharp contrast to other groups I have observed. It just seemed to come naturally to Bill.*

An instance of Bill's unique approach to teaching was the "Chemistry 160" course at Harvard. During the 1960s, all chemistry graduate students were required to pass courses in organic, inorganic, and physical chemistry. Chem 160 satisfied the inorganic chemistry requirement, but the way Bill taught the course, it was essentially a survey of diatomic molecule spectroscopy. Naturally, Chem 160 was taken by all of the physical chemistry graduate students to satisfy the inorganic requirement which, somehow, it did.

Bill's group seminars were also collaborative teaching and learning experiences, unlike the highly competitive endurance sessions of some research groups. One semester we worked through Mitchell and Zemansky's *Resonance Radiation and Excited Atoms*, where we all learned a great deal—including Bill.

Life among the Klemperians

The atmosphere in Bill's group was supportive and exhilarating. Some examples will serve to illustrate this:

- The Columbus Symposium on Molecular Spectroscopy (which at that time actually was held in Columbus, Ohio) was a formative experience for graduate students to network, learn about research in other laboratories, and practice organizing and presenting their own results. Bill would load a collection of students into his blue Cadillac and make the drive from Cambridge, Mass., to Columbus, typically in a single day. It was a big car, so a good number of students could come along.
- Bill displayed forbearance with disaster-prone students. One in particular was studying acetylene-oxygen flames in a flow tube equipped with a large pump that exhausted into the building's ventilation system. One day he came into the laboratory and started up the flow but the flame refused to light. After a number of tries he concluded that the flow mixture was too fuel-rich so he turned down the acetylene flow and tried again. This time the flame lit, propagated down the tube, through the pump and thence through the HVAC ducts, depositing black soot on every surface throughout Mallinckrodt. Nevertheless, the student in question completed his Ph.D. in due course.
- During his public servitude at NSF in 1979-81, Bill kept in close touch with his research group. In those days there was no such thing as Skype or Zoom, so Bill commuted regularly between Washington and Cambridge to confer with his students.
- A highlight of the year was Bill's annual "Wine and Rose" party, which took place in the back garden of the Watertown house in which there was a profusion of roses lovingly tended by Bill. Guests included current and former students, Harvard colleagues, friends, neighbors, and people who just liked Bill (of which there were many). These continued until the mid-2010s, when Bill's failing health made it no longer possible.

Milestones

Bill's 65th Birthday Symposium took place on October 3, 1992. The scientific program, chaired by Stew Novick and featuring a chronological selection of former and current group members, demonstrated the wide range of interests and accomplishments possessed by this group. The celebratory dinner that followed at the Thai restaurant in

Cambridge was memorable for its banquet menu, which reflected Bill's broad range of research, as reproduced below.

> A van der Waals cluster of appetizers
>
> Iodine adventure (seafood)
>
> Cosmological chicken
>
> Duck à la 1800 G Street NW (at the time, NSF Headquarters was located at this address in Washington, D.C.)
>
> Beef with hot bands in a highly excited state
>
> Pad Thai with beam curd, peamuts, beam sprouts, and scallioms
>
> Rice Mallinckrodt

Bill's Retiral (sic) Symposium was held on May 11, 2002, marking his promotion to Emeritus Professor. This time, the program, chaired by Steve Berry and Stuart Rice, featured Klemperer Group alumni in random order from 1960 to 1998.

Group picture of people attending Bill Klemperer's retirement symposium, May 2002.

The 80th Birthday Symposium took place in October 2007. Bob Field (Ph.D. 1971) and Kelly Higgins (Ph.D. 1998) chaired the scientific sessions. Professor of Physics Norman Ramsey—who had helped Bill get his molecular beam experiments going some fifty years earlier—welcomed the guests. The program included Raoul Kopelman, Bill's first postdoc, and Zhenhong Yu, then a postdoc in his research group.

On the occasion of his 90th birthday in October 2017, Bill's health did not allow for a group event. So Stew Novick organized an "inundation of birthday cards," of which at least fifty found their way to him and were much enjoyed. One month later, on November 5, 2017, Bill succumbed quickly to a heart attack. Beth passed away soon thereafter, on December 21. A Memorial Symposium for William and Elizabeth Klem-

perer was held at Harvard on March 24, 2018. Joyce, Paul, and Wendy presented a session on "Bill and Beth Family Life." This was followed by sessions highlighting Bill's research career presented by "clusters" of former associates. The entire program has been archived in a "Klemperer Cloud."[3]

Epilogue

An eminent physical chemist is supposed (probably apocryphally) to have remarked "Love molecules and use people." Bill loved both molecules and people, and was loved by both molecules and people in return.

ACKNOWLEDGMENTS

We thank Stew Novick and Bob Field for their suggestions and reminiscences. Stew provided copies of the slides he presented in his talks on "The Science and Humanity of William Klemperer" presented at the 2019 International (formerly Columbus) Symposium on Molecular Spectroscopy. Most of the figures have been taken from these slides. We also thank Steve Berry for encouraging us to prepare this memoir, and Laura Francisco for technical assistance. And we especially thank Bill Klemperer for his guidance and inspiration over the years.

NOTES

1. Novick, S., private communication by telephone, May 19 2020.
2. Herschbach, D. 2018. William Klemperer obituary. *Nature Astronomy* 2:24-25.
3. "Klemperer Cloud" available at https://spaces.hightail.com/space/Y9hAfan0Xm

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