

Nobel Centennial Essays

A Century of Chemical Dynamics Traced through the Nobel Prizes

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1986: Dudley Herschbach, Yuan Lee, and John Polanyi

by J. Van Houten

Nobel Prize in Chemistry 1986

Dudley Herschbach (1932–)

Yuan Lee (1936–)

John Polanyi (1929–)

for their contributions concerning the dynamics of chemical elementary processes

This is the ninth in a series of essays commemorating the centennial of the Nobel Prize and examining the history of chemical dynamics in the 20th century (1).^W The thirteen Nobel Prizes in chemical dynamics have been divided into four groups. Three prizes awarded during the century's first decade recognized Jacobus van't Hoff, Svante Arrhenius, and Wilhelm Ostwald, who laid the foundation for all of physical chemistry, including chemical dynamics. Three prizes were awarded during the middle decades for advancing the study of chemical reaction mechanisms to the molecular level through isotope tracer techniques (George de Hevesy), elucidation of free-radical reaction mechanisms (Cyril Hinshelwood and Nicolay Semenov), and development of techniques to study rapid reactions (Manfred Eigen, Ronald Norrish, and George Porter). In the 1980s three prizes recognized work that extended chemical dynamics to the level of individual atoms and molecules (this essay), of electrons (Henry Taube) and of the orbital symmetry of the reacting molecules (Kenichi Fukui and Roald Hoffmann).

Nature of the 1986 Prize

The 1986 Nobel Laureates extended the study of reaction dynamics to the level of individual reacting particles using molecular beam and infrared chemiluminescence experiments. These techniques are complementary: each provides a different type of information about reaction dynamics. The same reactions were often studied in different laboratories with one or the other of the two methods. The techniques require highly specialized apparatus, and so most students of chemistry have little exposure to them. This is unfortunate because the information provided by those techniques is fundamental to understanding the intimate details of chemical reaction mechanisms. Although chemists typically represent reactions with equations showing individual molecules, atoms, or ions (such as $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$), those reactions are studied in the laboratory with macroscopic samples containing on the order of 10^{18} to 10^{23} reacting particles, all in random motion. Under those circumstances, the only measurements that can be made are those representing an average behavior of the reacting system.

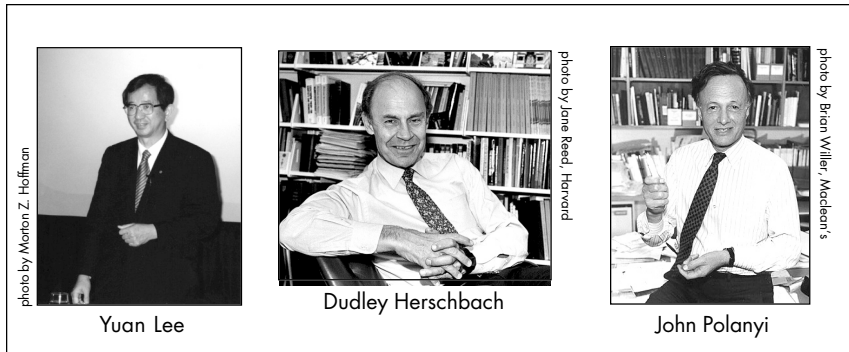
Molecular beam and infrared chemiluminescence experiments allow us to discover details of the dynamics of individual, reactive molecular collisions.

Although the recipients of the 1986 Nobel Prize (2) worked at separate geographic locations, their careers have been interconnected. Sometimes shared Nobel Prizes (for example, those awarded in 1956, 1967, and 1981) have recognized work performed "simultaneously and independently", but the 1986 prize recognized work that, although independently performed, was strongly interdependent. Each recipient began his Nobel award address by stressing that interdependence while describing his contributions in a historical context.

Herschbach (3) observed that the field of chemical kinetics can be viewed on three levels. The simplest is a qualitative description of a reaction system: what products are formed from what reactants under a particular set of conditions. The next level involves describing a reaction mechanism in terms of elementary steps, transition states, and intermediates. Reaction rates are determined as a function of concentration, pressure, temperature, and other conditions and summarized by a rate law and the Arrhenius (1*b*) equation, $k = A \exp(-E_a/RT)$. At the ultimate level, the intimate molecular dynamics of individual reactive collisions is studied. That level is attainable using the techniques for which the 1986 Nobel Prize was awarded.

Lee (4) began his award address in a similar fashion and then observed that "detailed information on the nascent quantum state distributions of [reaction products]" could be obtained from Polanyi's infrared chemiluminescence technique, from "an analysis of the threshold operating conditions of a chemical laser" (another reference to Polanyi's work (5)), or from linear or nonlinear laser spectra. Lee went on to state that crossed molecular beams are best suited to "(1) control[ing] the energies of the reagents, (2) understand[ing] the dependence of chemical reactivity on molecular orientation, (3) explor[ing] the nature of reaction intermediates and their subsequent decay dynamics, and (4) identify[ing] complex reaction mechanisms involving polyatomic radical products."

Polanyi (6) also provided a historical survey and then discussed how infrared chemiluminescence contributed to our understanding of chemical dynamics and to the development of the chemical laser. He spoke of the influence of previous Nobel Laureates including Ronald Norrish (1*f*) and Gerhard Herzberg (Nobel 1971 and a mentor of Henry Taube (1*h*)). As a postdoctoral fellow at the National Research Council of Canada in Ottawa, Polanyi worked in



Herzberg's laboratory, assembling spectroscopic equipment and observing vibrational and rotational excitation in molecules (7).

The Science behind the 1986 Prize

Herschbach played a significant role in developing modern molecular beam techniques. While he was an undergraduate at Stanford University, he learned of Otto Stern's work in Frankfurt in 1920 measuring the Maxwell-Boltzmann velocity distribution of silver atoms using an early molecular beam device (3, 8). Herschbach credited Stern with developing the early molecular beam techniques in the 1920s, shortly after the invention of the high-speed vacuum pump made it possible to form directed "rays" of neutral molecules without having them collide with the background gas. From Stern, Herschbach also learned about the importance of serendipity in science. In the Stern-Gerlach experiment of 1920 a beam of silver atoms was split into two upon passing through a magnetic field, thereby demonstrating the existence of electron spin quantization. However, the silver atoms on the detector plate were invisible until sulfur from Stern's cheap cigars reacted with the silver to form two black streaks of silver sulfide.

Serendipity also aided Herschbach's molecular beam experiments. His first attempt to study molecular-scale chemical dynamics involved the reaction between potassium atoms and bromine molecules that had been studied in flame diffusion experiments by John Polanyi's father, Michael,

about 30 years earlier. However the hot-wire tungsten and platinum filament detectors (originally developed by Stern) in Herschbach's molecular beam apparatus behaved unreliably. He then turned to the reaction $K + CH_3I \rightarrow KI + CH_3$ with a much better outcome. Reliable detection required pre-treatment of the filaments with hydrocarbons and, as Herschbach put it, "it turned out that CH_3I played the role of Stern's cigar." (3)

Yuan Lee joined Herschbach's group as a postdoctoral fellow in 1967. By that time the "alkali age" of molecular beam reaction dynamics had matured, and researchers were anxious to study reactions of other types of covalent molecules (3). In just ten months working with two of Herschbach's graduate students, Lee built an apparatus (termed a "universal machine" and nicknamed "Hope") capable of monitoring reaction systems such as $Cl + Br_2$, $Cl + HI$, and $H + Cl_2$. The last of those reactions had also been the prototype for John Polanyi's earlier IR chemiluminescence work in 1958. Herschbach said: "Hope [was constructed by] a group of extraordinary skill and zeal, inspired by Yuan's genius and fervent sense of mission. Blissfully as each of the myriad design questions was settled, we all relished his verdict: 'Should be all right.'" (3) Unlike their predecessors, the newer "supermachines" employed two well-defined crossed molecular beams, a movable mass spectrometric detector with electron-impact ionization, and several stages of differential pumping to achieve vacuum partial pressures as low

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as 10^{-14} torr, thereby approaching the vacuum in interstellar space (2, 3).¹

Lee established himself as an independent leader in the field of molecular beam reaction dynamics. His laboratories continued to build ever-more-sophisticated molecular beam devices capable of studying ever-more-complicated reaction systems and came to be considered “the North American capital of molecular beam studies of collision processes” (9). By the time he received the Nobel Prize, Lee had extended his work into what became known as the “organic age” to study reactions involving polyatomic molecules such as aldehydes, alcohols, benzene, and chlorotoluene. He observed: “The fact that one can control kinetic energy precisely and carry out a synthetic study of delicate new radicals through endothermic reactions is certainly among the most dramatic features of crossed molecular beams.” (4)

Lee extended molecular beam studies into the realm of photochemical processes by studying reactions such as (a) $\text{Na} + \text{O}_2 \rightarrow \text{NaO} + \text{O}$, (b) $\text{Na} + \text{NO}_2 \rightarrow \text{NaO} + \text{NO}$, and (c) $\text{Na} + \text{HCl} \rightarrow \text{NaCl} + \text{H}$ utilizing both ground-state and photoexcited sodium atoms (4). He used linearly polarized dye lasers to sequentially and selectively excite sodium atoms in the beam into electron configurations resulting from promotion of the $3s^1$ valence electron into p and d orbitals. Furthermore he was able to control the orientation of the orbital containing the excited electron relative to the collision axis, demonstrating that reaction (a) above is favored when the $\text{Na } 4d_{z^2}$ orbital is oriented perpendicular to the collision axis, whereas the most favorable approach for reaction (b) has the $\text{Na } d_{z^2}$ orbital oriented perpendicular to the O–N axis of NO_2 and lying in the plane of the molecule.

John Polanyi’s work on infrared chemiluminescence was performed independently from Herschbach and Lee, although Polanyi studied similar chemical systems and the work is closely connected. In his Nobel lecture Polanyi pointed out that “a degree of overlap existed between the approaches. It was not, however, until the incorporation of universal detectors by Lee and Herschbach, following what we have come to know as the ‘alkali age’ of beam chemistry, that the same systems could be studied by infrared chemiluminescence and molecular-beam scattering.” (6)

Infrared chemiluminescence involves measuring and analyzing the extremely weak infrared emission from vibrationally excited product molecules following a gas-phase chemical reaction. At the beginning of his lecture Polanyi noted that in 1928 Michael Polanyi had provided indirect evidence for vibrationally excited reaction products in his study of alkali metal atoms reacting with halogen molecules (6). (Those same studies had provided early guidance and inspiration to Herschbach (3).) John Polanyi exploited infrared emissions to investigate the energy distribution among the reaction products and determine directly the quantum mechanical vibrational states of the products immediately following the reactive encounter. The theoretical foundation for this work had been laid in the 1920s and 1930s by London, Debye, Eyring, Hirschfelder, Michael Polanyi, and others.²

Polanyi employed two approaches to obtain infrared chemiluminescence spectra. In the *measured relaxation* (MR) method, separate streams of reactant atoms and molecules were introduced and mixed in a flow cell that had reflective coatings and sapphire windows positioned along its length. The resulting infrared chemiluminescence was observed as a function of distance (and hence time, given a known flow rate) down the length of the cell. In the *arrested relaxation* (AR) method, the gaseous reaction products were rapidly deactivated at the cold (typically 20–77 K) inner surface of the vessel. In this way, the observed infrared chemiluminescence comes only from the small fraction of the product molecules that emitted early in their lifetimes.

Polanyi used the data from his infrared chemiluminescence experiments to obtain detailed rate constants and translational and rotational, as well as vibrational, energy distributions for a variety of reactions of the type $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, where A, B, and C represent H, D, F, Cl, Br, and I in virtually all their possible combinations. He visualized his data in the form of “triangle plots” on which contours of the detailed rate constant, $k(V', R', T')$, were plotted as a function of the reaction-product vibrational (V') and rotational (R') energies. Polanyi admitted (6) that triangle plot presentations

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were based in classical mechanics and thus “rode roughshod over the quantized nature” of the vibrational and rotational energy levels, but nevertheless they provided a useful way of viewing the experimental results in graphical form. He surmised: “Since classical mechanics is widely used in order to interpret energy distributions, these classical ‘fingerprints’ of differing chemical reactions help us to picture constraining types of behavior.” The plots showed, for example, that the reactions $\text{H} + \text{Cl}_2$ and $\text{H} + \text{F}_2$ exhibited efficient translational excitation in the products, whereas $\text{F} + \text{H}_2$ exhibited efficient vibrational excitation and $\text{Cl} + \text{HI}$ exhibited both vibrational and rotational excitation. Polanyi also viewed his results in terms of the potential energy surfaces first developed by London, Eyring, Michael Polanyi, and Sato. Such surfaces represent the energy contours of a reacting system, $\text{A} + \text{BC} \rightarrow \text{AB} + \text{C}$, plotted on a graph where one axis represents the interatomic distance, r_{AB} and the second axis is the distance r_{BC} . Those plots show “valleys” for stable reactants and products, and a “saddle” for the transition state.

Although Polanyi’s Nobel Prize was for chemical dynamics, his infrared chemiluminescence research was also intimately connected with the development of the chemical laser and the infrared laser. When he began his research career in the mid 1950s, the optical laser had not yet been developed. The first example was a maser, an acronym for “microwave amplification by stimulated emission of radiation”. Because the rotational energy levels responsible for microwave emission are more closely spaced than vibrational or electronic levels, the necessary population inversion was more readily attained for the maser than for an infrared or visible laser. In his 1959 paper “Energy Distribution among Reagents and Products of Atomic Reactions” (10), Polanyi showed that a population inversion was possible for vibrational states. At the time, this vibrational population inversion was considered to represent a “negative temperature” (6) in the Boltzmann sense. Two years later, in “Proposal for an Infrared Maser Dependent on Vibrational Excitation” (11), he showed that a *positive* temperature—vibration “hotter” than rotation—could result in vibrational lasing. Polanyi realized that a vibrational population inversion can readily occur in the products of a gas phase chemical reaction, and suggested $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ as a likely chemical laser.³ The first vibrational laser was reported by Patel and coworkers in 1964 (12). The next year George Pimentel⁴ built an operating chemical laser based on the $\text{H} + \text{Cl}_2$ reaction (13). Polanyi has remarked that granting agencies, often overly concerned with practical applications, might not have realized that powerful chemical lasers would evolve from studying the feeble chemiluminescence of this simple reaction (7).

Backgrounds of the Laureates

Although there was considerable overlap in their scientific careers, the three 1986 Laureates’ personal backgrounds could not have been more different. Herschbach was born into a working-class family in what was then a rural area outside San Jose, California and grew up doing farm

work. Lee was born in Hinchu, Taiwan, the son of an accomplished artist and a schoolteacher. Polanyi’s parents were Hungarian; his father was a leading researcher in physical chemistry at the Kaiser Wilhelm Institute in Berlin at the time of John’s birth.

Dudley Herschbach was the first in his family to receive a college degree. His interest in science was kindled at age nine by an article on astronomy in *National Geographic* (2), and he was inspired to go into chemistry by his high school teacher. He gives much credit to his mentors from high school through graduate school for providing the necessary guidance and encouragement. His first exposure to collision processes came as a star player on his high school football team, and he had the option of attending Stanford University as an undergraduate on either an academic scholarship or a football scholarship (8). He ultimately chose the former because the football coach told him he should not take any lab courses. He began research in chemical kinetics with Harold Johnston in the summer following his sophomore year, became interested in the detailed study of chemical kinetics, and completed a master’s thesis at Stanford on careful calculations of Arrhenius *A*-factors for gas-phase reactions (employing the transition state theory of Henry Eyring and Michael Polanyi).

As a Ph.D. student with E. Bright Wilson at Harvard, Herschbach utilized microwave spectroscopy to pursue answers to internal rotation problems stemming from his earlier work with Johnston. He had learned of Stern’s work with molecular beams while still at Stanford and he said that he realized “that this was *the way* to study elementary chemical reactions.” (8) After receiving his Ph.D. he spent an additional year at Harvard as a Junior Fellow where he formulated his plans for molecular beam research. In his first search for a faculty position in 1958 Herschbach was a victim of “the cultural chasm between the eras” (3)—when the established scientific community fails to recognize the significance of radical new developments.⁵ Herschbach took his first faculty position at the University of California at Berkeley in 1959, where he built “Big Bertha”, a rudimentary molecular beam apparatus, in a small (4 m × 6 m) corner of a lab. He was promoted to associate professor in 1961, but in 1963 returned to Harvard, where he has spent the balance of his career and is known as an outstanding and dedicated teacher. He has taught courses at all levels of chemistry and reports that his very popular general chemistry course was his “most challenging assignment.” In a contribution from the Task Force on the General Chemistry Curriculum reported in this *Journal* (14), Herschbach briefly described his own teaching philosophy in “Paradigms in Research and Parables in Teaching” in which he discussed the synergy between the two.

Yuan Lee’s early education was interrupted when his family fled to the mountains of Taiwan to escape the Allied bombing of the Japanese-occupied island during World War II. His interest in science was kindled by reading the biography of Marie Curie written by her daughter, Eve. Like Herschbach’s, Lee’s early experience with collisions involved sports in which he excelled—collisions between balls

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and baseball bats, tennis racquets, or ping-pong paddles. Both Lee and Herschbach used baseball analogies when discussing their Nobel-Prize-winning research with the press in October 1986.

Lee entered National Taiwan University in 1955 without having to take an entrance examination (2). He had chosen chemistry as his field by the end of his freshman year and he did a B.S. thesis on the separation of Sr and Ba by paper chromatography with Hus-sheng Cheng. He received his M. S. for studies on natural radioisotopes in mineral hot-spring sediments under the direction of H. Hamaguchi at National Tsinghua University. He stayed an additional year at Tsinghua University, carrying out the X-ray structure determination of tricylopentadienyl samarium as a research assistant of C. H. Wong. He entered Berkeley in 1962, completed his Ph.D. degree in 1965 working with Bruce Mahan on chemiionization of electronically excited alkali atoms, and stayed an additional year learning to use ion-beam techniques in Ron Gentry's lab.

When Lee arrived in Berkeley in 1962, Herschbach was a new faculty member there, but the two did not collaborate until 1967 when Lee went to Harvard as a postdoctoral fellow. There he worked with Herschbach building "Hope", and with Robert Gordon on the reactions of hydrogen atoms and diatomic alkali molecules. In 1968 he was appointed as an assistant professor at the University of Chicago, where he rose quickly through the ranks to professor in 1973. The following year he became a naturalized U.S. citizen and returned to Berkeley as professor of chemistry and principal investigator at Lawrence Berkeley Lab. He remained at Berkeley until 1994 when he "retired" to return to his native Taiwan. He is now President of the Academia Sinica and continues to improve on molecular beam apparatus designs.

Polanyi received his B. Sc. and Ph. D. degrees in 1949 and 1952 at Manchester University. His research director, Ernest Warhurst, had been Michael Polanyi's student. John Polanyi worked as a postdoctoral fellow on transition-state theory with E. W. R. Stacie at the Canadian National Research Council in Ottawa and for a few months with Gerhard Herzberg (see above). When he moved to a position in Princeton as a research assistant in 1954, he took with him some large mercury lamps he had employed in Herzberg's lab. He moved to the University of Toronto in 1956 where he has remained.

In 1970 Polanyi produced a film, "Concepts in Reaction Dynamics", that provides a lucid treatment of that topic. In addition to his scientific prowess, Polanyi has been a strong advocate for science policy issues and has worked for world peace as a critic of the nuclear arms race, publishing more than a hundred articles on those topics. He wrote eloquently on both those topics in "On Being a Scientist: A Personal View" (15). He has served on Canada's National Advisory Board on Science and Technology, chaired by the Prime Minister; he was the founding chairman of the Canadian Pugwash Group in 1960; and in 1979 he co-edited a book entitled "The Dangers of Nuclear War" (2, 7).

Interrelationships

In addition to his influence on the 1986 Laureates, John Polanyi's father, Michael, also had important connections to earlier Nobelists. When Michael Polanyi was at the Kaiser Wilhelm Institute in Berlin, its director was Fritz Haber (Nobel 1918) (16). Haber, who was Jewish, and Polanyi, who was Hungarian, resigned from the institute in 1933 when the Nazi Party came to power in Germany. In 1920 the elder Polanyi proposed a chain mechanism for the $H_2 + Br_2$ reaction (17); investigating chain mechanisms led to the 1956 Nobel Prize awarded to Cyril Hinshelwood and Nicolay Semenov (18). After leaving Berlin, Polanyi moved with his family, including four-year-old John, to Manchester, England where Melvin Calvin (Nobel 1961) was one of his postdoctoral fellows (18).

The 1986 Laureates' work also is intimately connected to the four Nobel Prizes in chemical dynamics of the 1990s. Herschbach related his discussion (3) of reaction-product energy distributions in bimolecular reactions to the statistical treatment of the transition state in Rice-Ramsperger-Kassel-Marcus (RRKM) treatment of unimolecular rates. Rudy Marcus won the 1992 Nobel Prize for his work on electron transfer kinetics, although his name is associated with a wide range of topics in chemical dynamics. Early in his Nobel lecture Herschbach said: "*Ab initio* electronic structure calculations have also begun to contribute significantly to the exploration of reaction dynamics, although (except for $H + H_2$) satisfying overall accuracy has yet to be achieved for potential energy surfaces." (3) In his concluding remarks Lee said: "because of recent improvements in the accuracy of theoretical predictions based on large-scale *ab initio* quantum-mechanical calculations, meaningful comparisons between theoretical and experimental findings have become possible." (4) Walter Kohn and John Pople received the 1998 Nobel Prize for making those large-scale calculations possible, and some of the earliest large-scale theoretical calculations were done on the reaction systems studied experimentally by the 1986 Laureates. Near the end of his Nobel lecture Polanyi spoke of his lab's early experiments on "transition state spectroscopy (TSS)" saying that "attempts are being made to observe the molecular partners while they are, so to speak, on the stage, rather than immediately prior to and following the reactive dance...it is a young but burgeoning field." (6) Polanyi had proposed in 1979 (19) that we were "standing on the threshold of...the last frontier of chemical dynamics...the spectroscopy of the [transition state]." The following year he reported on his lab's early experimental TSS results—the visible chemiluminescence spectrum observed in the "wings" (570–630 nm) of the sodium D-line arising from the transition state, $FNaNa^{\ddagger}$ (estimated to have a picosecond effective lifetime), for the reaction of F with Na_2 in a crossed-beam apparatus (20). A year after that, he outlined the theory of TSS to model his experimental results for $FNaNa^{\ddagger}$ (21). That TSS work clearly foreshadowed the "femtochemistry" research leading to Ahmed Zewail's 1999 Nobel Prize. Lee concluded by say-

ing: “In the remaining years of the 20th century, there is no doubt that the experimental investigation of dynamics and mechanisms of elementary chemical reactions will play a very important role in bridging the gap between the basic laws of mechanism and the real world of chemistry.” (4) Nothing could be more “real world” than the investigations of the chemical mechanisms of the destruction of the stratospheric ozone layer for which Paul Crutzen, Sherwood Rowland, and Mario Molina received the 1995 Nobel Prize.

The concluding sentence of Polanyi’s Nobel lecture is a reflection of his view of the chemical world and of the global political situation (6). In both those senses his words remain true today, more than 15 years later. He said, “Even in the world of molecules the civilizing influence of modest restraints is a cause for rejoicing.”

Supplemental Material

A list of all recipients of the Nobel Prize in Chemistry, their affiliations, and the work for which the award was made, is available in this issue of *JCE Online*.

Notes

1. In his Nobel autobiography, Herschbach provides a list of some of his important early papers: *Adv. Chem. Phys.* **1966**, *10*, 319–393; *Disc. Faraday Soc.* **1967**, *44*, 108–122; *J. Chem. Phys.* **1972**, *56*, 769–788; *Faraday Disc. Chem. Soc.* **1973**, *55*, 233–251; *Pure and Applied Chem.* **1976**, *47*, 61–73; *Mol. Phys.* **1978**, *35*, 541–573; *J. Phys. Chem.* **1983**, *87*, 2781–2786. In addition, he recommended two books as background reading for those who wish to learn more about the fundamentals of chemical dynamics and molecular beams: Bernstein, R. B.; *Chemical Dynamics via Molecular Beam and Laser Techniques*; Clarendon: Oxford, 1982; Levine, R. D.; Bernstein, R. B.; *Molecular Reaction Dynamics*, 2nd ed.; Oxford University Press: New York, 1987.

2. Polanyi cites specific references to original papers by all these early workers in his Nobel lecture (ref. 6 below).

3. Laidler reported (ref. 7) that Polanyi’s 1961 paper (ref. 11) had been rejected the previous year to *Physical Review Letters*. The same thing happened for Theodore Maiman’s paper announcing the first operating laser.

4. George Pimentel’s name is familiar within the chemical education community because of both the American Chemical Society award in chemical education that is named in his honor and the eponymous “Pimentel Report”, *Opportunities in Chemistry*, National Academy Press, Washington, DC, 1985.

5. When Hirschbach was leaving Harvard, George Kistiakowski—whom he revered as a “sage” but who had a few years earlier destroyed a molecular beam apparatus with an ax when it did not perform as expected—told him “So you have been bitten by the molecular beam bug. Too bad! The trouble is that there are no collisions in one beam and no collisions in the other beam, so when you cross them there are still no collisions!”

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