Herschbach, Lee and Polanyi receive 1986 Chemistry Nobel

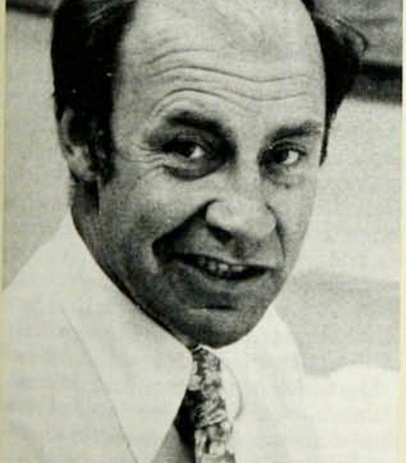
For "contributions concerning the dynamics of chemical elementary processes" the Royal Swedish Academy of Sciences has awarded the 1986 Nobel Prize in Chemistry to Dudley R. Herschbach (Harvard), Yuan T. Lee (Berkeley) and John C. Polanyi (University of Toronto). Their research in chemical physics—specifically reaction dynamics—is basic to a detailed understanding of chemical reactions. The award honors the development of two important techniques for probing what happens when molecules collide and atoms rearrange themselves to form new molecules. These techniques, crossed molecular beams and infrared chemiluminescence, provide a basis for the determination of the potential energy surfaces of specific reactions.

Whether or not a molecular collision results in a chemical reaction depends on the collision energy, vibrotational energy and orientation of the molecules. Because molecular velocities in a fluid (whether gas or liquid) are random, it is difficult to obtain details about the molecular collision dynamics. "Under a microscope, the structures of stationary molecules are revealed," says Lee, "but it is impossible to study them in motion." Earlier chemists could study only the behavior of large groups of molecules—not individual pairs. As Polanyi puts it, "It was as if the chemists were sociologists, dealing with the behavior of societies, and the physicists were psychologists, recognizing only the rules of behavior for individuals." The three Nobel laureates developed techniques borrowed from physics to observe molecular collisions and to detect their products.

Herschbach, a pioneer of the molecular beam method, told us how his interest in using beam methods in chemistry started. As a master's degree candidate at Stanford he heard Walter Meyerhof discuss Otto Stern's atomic beam experiments to verify the Maxwell–Boltzmann distribution, and while pursuing his doctorate at Harvard he attended a lecture about I. I. Rabi's technique in Norman Ramsey's course on molecular beams and resonated when Ramsey remarked, "This is the way to do chemistry." As a young faculty member at Berkeley he did experiments in which he collided alkali atomic beams with methyl halide molecular beams. This work interested Lee, who took a class in quantum mechanics from Herschbach and afterward did high-energy ion scattering experiments with Bruce Mahan. After Herschbach moved to Harvard, Lee joined him as a postdoctoral fellow and they improved the technique by using mass spectrometer detectors to examine reaction products. (See the article by Lee and Ron Shen in PHYSICS TODAY, November 1980, page 52.) By controlling both the internal energy and the velocity of colliding molecular beams, researchers can "view" chemical reactions on a microscopic scale by mapping out the angular distribution of reaction products and measuring their released energy. Physical chemists consider the crossed-molecular-beam technique to be one of the most important advances within the field of reaction dynamics.

Independently Polanyi developed the method of infrared chemiluminescence to study newly born reaction products. The term "chemiluminescence" refers to photon emission from vibrationally excited molecules formed in an exothermic reaction. By measuring and spectroscopically analyzing the extremely weak infrared radiation emitted by newly formed molecules, one can

HERSCHBACH



LEE

POLANYI

0031-9228 / 87 / 0300 17- 06 / $01.00 © 1987 American Institute of Physics

monitor the energy flow at the molecular level during a chemical reaction. Polanyi's research produced the first quantitative data about vibrational and rotational excitation in chemical reaction products. Combined with molecular beam scattering experiments, these data led to insights about the specific forces operating when chemical bonds break apart and form anew. Polanyi's method can be considered a first step toward more sophisticated laser-based methods for the study of chemical reaction dynamics.

Chemiluminescence and lasers. Polanyi first tried to see infrared emission from newly born reaction products in 1956, shortly after he came to the University of Toronto. He and Ken Cashion, his first graduate student, chose the room-temperature reaction of atomic hydrogen with molecular chlorine to form hydrogen chloride—HCl being the classic molecule for study by infrared absorption. They hoped that this fast exothermic reaction would give birth to molecules with substantial vibrational excitation. The necessary condition for success was that the molecules emit before being collisionally deactivated; hence Polanyi and Cashion used a low-pressure flow system to minimize collisions. Detection of photons from either vibrational or rotational states could have been used as a measure of the motion in the newborn products. However, a rotational energy state is very easily dissipated by collisions and emits feebly. Also, rotational transitions occur in the far infrared, where detectors are inefficient. The direct measurement of molecular speed, or translational energy, had to wait for the development a few years later of the crossed-molecular-beam method, where one knows that the molecules started at the crossing point of two beams and how long they took to get to the detector. "So speed measurement wasn't available to us; it was available to the beam people," Polanyi says. "By elimination, vibration was the best bet, and there had been indications in the literature for 30 years that vibrational excitation was present in reaction products."

Even though the reaction vessel was at room temperature, the reaction product, HCl, was at a vibrational temperature of 3000 K, as deduced from its infrared chemiluminescent spectrum. The high vibrational excitation could only come from oscillatory motion present in the HCl molecule at the moment of its formation. As the recorder traced out this spectrum of HCl, the mild-mannered Cashion pounded his fists on the top of the spectrometer, shouting "Holy crowbar!" The experiment had succeeded.

The paper describing this research, published in the *Journal of Chemical Physics* in 1958, concludes, "The method promises to provide for the first time information concerning the distribution of vibrational and possibly rotational energy among the products of a three-center reaction." Recalls Polanyi, "we allowed our imagination to roam a bit," and in the last sentence of the paper "we actually said not only that one could hope to see the initial vibrational distributions but also perhaps the initial rotational distributions." That in fact eventually turned out to be possible.

As early as 1916 Einstein introduced the concept of stimulated emission in his elegant derivation of the Planck function for blackbody radiation. The theoretical and experimental research into maser action was carried out in the 1950s mainly in the US by Charles Townes, but also by Nicolai Basov and Aleksandr Prochorov in the USSR. In 1958 Arthur Schawlow and Townes proposed amplifying visible radiation by passing it through a medium excited to population inversion with respect to electronic energy states. Theodore Maiman built the first operating laser in 1960. In the same year Polanyi suggested an alternative: an infrared laser dependent on vibrational excitation. Following his own line of research, Kumar Patel invented the first vibrational laser in 1964.

Polanyi noted that one could produce a molecular laser in its simplest form merely by partial cooling of a hot gas, making use of the phenomenon of "partial population inversion" where the vibrational temperature is sufficiently in excess of the rotational. A chemical reaction, such as the hydrogen–chlorine reaction then under study in Polanyi's laboratory, could also produce molecules in a state of complete (or partial) population inversion.

Meanwhile George Pimentel (Berkeley) realized the potential of the concept by developing several chemical lasers about 1965, with some operating on the HCl reaction. His group used them subsequently to study reaction dynamics. "George and I talked about it," recalls Polanyi, "but I didn't then realize how important it was. The paper that I wrote was turned down in 1960 by *Phys. Rev. Letters* and so I stuck it away and thought, 'Well, it must be a bit boring.'" The *Journal of Physical Chemistry* published that paper in 1961. Although Polanyi did not attempt to build a chemical laser at that time, "We actually saw lasing action once in a while from our infrared luminescence reaction products—it was a nuisance, so we took steps to try to avoid it." In 1982 Polanyi shared the Wolf Prize with Pimentel.

Pioneers of the 'alkali age.' The crossed-molecular-beam method allows collisions to occur among isolated molecules at the intersection point of collimated beams in a high-vacuum environment. Although the desirability of studying reactions this way had long been recognized, the low intensities available deterred chemists from trying such experiments. Other chemists thought neutron activation from a reactor was necessary to study chemical reaction dynamics. However, in the early 1950s Ellison Taylor and Sheldon Datz (Oak Ridge National Laboratory) showed that they could obtain detectable product signals from crossed beams of alkali atoms reacting with halogen-containing molecules. For easy detection, they chose to study the reaction of potassium with hydrogen bromide because the light recoiling hydrogen atom would not spread the product beam. Such systems have very large reaction cross sections, as was shown in the 1920s by Michael Polanyi, a physical chemist and father of the Nobel laureate. And Irving Langmuir had shown in the 1930s that for alkali species, surface ionization on hot tungsten filaments provided a sensitive and specific detector.

Datz and Taylor discovered that a platinum surface under certain conditions would detect only alkali atoms, not alkali halides. Hence, Datz told us, "detection was possible with just two hot wires—one of tungsten and one of platinum—using differential surface ionization, so anybody could do it." As a result, much of this research moved to universities. "This work had a lot to do with making everyone bold about what could be done with molecular beams," says Richard Zare (Stanford), who did his thesis with Herschbach. Other groups working with crossed molecular beams about this time were led by Richard Bernstein (now at UCLA), then at the University of Wisconsin, and John Ross and Ned Green at Brown University.

In 1960 Herschbach's team at Lawrence Berkeley Laboratory crossed beams of potassium atoms and methyl iodide molecules and measured the angular distribution of potassium iodide products, formed with a yield estimated by Herschbach at "a monolayer a month." The product was ionized on tungsten or platinum filaments and detected with an electrometer. A vacuum as poor as 10^{-7} torr was adequate, thanks to the specificity of detection of alkali species.

Herschbach told us that Michael Polanyi once visited his lab and witnessed an experiment rendered unsuccessful by "poisoning" of detection filaments. Polanyi, who had himself contributed extensively to the experimental and theoretical study of alkali metal reactions, in a casual conversation originated the term "harpooning," subsequently used by Herschbach to describe many reaction processes involving long-range electron transfer.

In his seminal work, Herschbach in 1961–62 demonstrated anisotropy in the angular distribution by discovering product rebound in the center-of-mass system, that is, that the reaction is characterized by backscattering. "This did not show orientation dependence directly, but was significant in suggesting the importance of orientation," says Bernstein. In 1966 groups led by Bernstein and Philip Brooks (Rice) independently demonstrated orientation dependence, using oriented beams.

In the early 1960s Datz started using mass spectrometers for detection of products from crossed-molecular-beam chemical reactions. There was not enough signal and too much noise for definitive results. The problem was getting a vacuum good enough that the background was under control.

Virtuoso chemical physics. Lee and Herschbach in 1967 replaced wire detectors with extremely sensitive mass spectrometers, providing a more universal detector for the study of reactions more varied than those of the alkali age. They also exploited supersonic expansion techniques to enhance the beam intensity and narrow the velocity spread. These beamed sources enable use of aerodynamic acceleration—whereby a mixture of light and heavy particles, previously heated in an oven, expands from high pressure—with velocity selectors before and after a reaction, to allow the experimenter to vary speeds, and hence energies. By beam chopping, one can use the time-of-flight method to calculate the speed. Ideally one wants to study single collisions from the intersection of the beams; the background, however, is a complication.

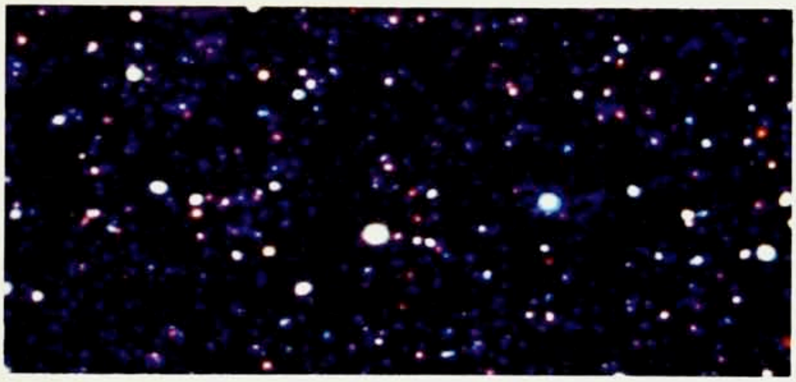
One can gain some control over background by doing the experiment in a nitrogen-cooled environment—but still more can be done. A combination of many stages of differential pumping could yield an equivalent partial pressure of about 10^{-14} torr in the detector for many species of interest, although in 1965 an ion pump could produce a pressure only as low as about 10^{-10} torr. According to Herschbach, the virtuoso experimental skills of Lee—"the Mozart of chemical physics"—and several stages of differential pumping were key factors in their success with the crossed-molecular-beam method.

Crossed beams provide the best method at present for the simultaneous measurement of energy and angles. The experimenter records reaction product intensity at various scattering angles to obtain a contour map for the reaction. Scattering diagrams (termed "Newton diagrams" by Herschbach) are helpful in keeping track of vector transformations, describing reactant and product motion, between the laboratory and center-of-mass reference frames. What is essential is to analyze the product angular distribution immediately after the reaction. If the reaction complex is long lived, its tumbling will yield a symmetric angular distribution, but for impulsive reactions information about the initial approach is retained by the product angular distribution. An anisotropic distribution in the contour plot shows that the time scale for the reaction is less than one molecular rotation. Measurement of the speeds of the products determines how the available energy is partitioned between translation and vibration after a reaction. When these data are combined with the scattering plot, the chemist can deduce much about the forces governing the making and breaking of bonds.

Recently, in high-resolution studies on the $F + H_2 \rightarrow HF + H$ reaction, Lee and his coworkers have observed a strong dependence of product vibrational state on angular distribution—a consequence of the dynamic resonance phenomenon, a quantum mechanical effect in chemical reactions. The formation and decay of the quasibound states in a chemical reaction were predicted in previous theoretical studies. "The experimental observation of dynamic resonance—almost equivalent to vibrational spectroscopy of reaction intermediates—provides a more direct and sensitive probing of the potential energy surface near the critical region of the transition state," Lee told us.

Sophisticated techniques. The infrared chemiluminescence method has yielded the first information about the channeling of reagent excitation into product excitation of the vibrational, rotational and translational states. One can explain these effects in terms

Galaxies near the confusion limit



In producing this composite photo of three two-hour exposures, Tony Tyson (AT&T Bell Labs) and Patrick Seitzer (National Optical Astronomy Observatories) used novel observing and image-processing techniques to remove sky background to a precision better than 0.05%, thereby pushing state-of-the-art charge-coupled devices to record extremely distant galaxies. They observed with the 4-meter telescope at Cerro Tololo, Chile, to obtain separate images at three wavelengths (0.4, 0.6 and 0.9 micron) from many 500-sec charge-coupled device exposures in a 2.3×4.2-arcminute region near the south Galactic pole. Sky background prevents direct observation of extended sources (such as galaxies) fainter than about magnitude 22, about 100 times brighter than the faintest galaxies shown here as fuzzy resolved objects with redshifts as high as 3 and brightnesses as faint as magnitude 27 in the blue spectral region (that is, 2×10^{-8} photons/sec cm^2 Å). The anomalous brightness in the blue (0.4 micron) image may represent ultraviolet light from star formation that has been redshifted into the visible. The brightest objects, near the center of the field, are a star and a galaxy at about magnitude 19, but only ten stars are brighter than magnitude 24. Many of the 1500 galaxies in the photo are near the distance, or look-back time, beyond which galaxies do not appear as distinct objects. Cosmologists require data about the faintest, most distant—and hence most nearly primordial—galaxies. David Hartwick and Chris Pritchet (University of Victoria) have been using similar techniques in an attempt (so far unsuccessful) to detect emission lines from primordial galaxies as faint as equivalent magnitude 27.5 in a 100-Å band in the infrared. Tyson, Carol Christian (Canada–France–Hawaii Telescope), Pritchet and others are trying to detect structure in galaxies by relying on these techniques and the excellent seeing in Hawaii. —PHA of the distortion of the reaction intermediate, that is, the introduction of new patterns of molecular motion in the presence of additional reagent energy. Enhanced vibration permits reaction through a stretched intermediate, whereas enhanced translation gives rise to reaction through more compressed and bent intermediates.

An observation that reactions consuming a substantial amount of energy can be most efficiently accelerated if the reagents are vibrationally rather than translationally excited was linked in Polanyi's study to the existence of a "late barrier crest" for such reactions. In simple terms one would say the energy is optimally employed in stretching the bond under attack, through vibrational excitation, rather than in compressing the reaction intermediate through reagent translation, that is, collision energy.

Infrared chemiluminescence has also revealed families of reactions that give rise to a single reaction product with bimodal distributions over the vibrational, rotational and translational states. In these cases the reaction dynamics exhibits "microscopic branching"—two different, identifiable patterns of molecular motion lead to the formation of the same chemical species. The existence of alternative routes to reaction, dependent on reaction energy, is a phenomenon of general interest in reaction dynamics.

The methods developed by Polanyi, Herschbach and Lee are complementary in describing the details of a chemical reaction. In the laser-induced fluorescence method developed by Zare (see the article by Zare and Bernstein in PHYSICS TODAY, November 1980, page 43), one combines crossed molecular beams and lasers to study reaction dynamics.

The study of intermediate products in a reaction is still in its infancy. "Instead of looking at the newborn products or looking at the effect of reagent motions you try to interact with the few actors who, at any given time, are actually on the stage," says Polanyi. His group has done this by looking at chemiluminescence originating from the colliding species, that is, the transition state. Brooks and Robert Curl (Rice) have evidence of laser absorption by reaction intermediates. Only in the last few years have chemists seen indications that these transient intermediates can actually be observed.

In reaction dynamics the interest is not in the overall rate at which reagents form products. That was the earlier focus of research by physical chemists. What engrosses people who work on reaction dynamics is the detailed rate constants for the formation of products with specified vibration, rotation and translation states and—if possible—from specified states of vibration, rotation and translation in the reagents. This state-to-state chemistry is in fact synonymous with reaction dynamics. The intention nowadays of trying to open up the field of transition state spectroscopy is to provide still another tool for the study of molecular motion in chemical reactions.

The three Nobel Prize winners are currently engaged in a variety of theoretical and experimental research. Herschbach is doing theoretical calculations of electron configurations as well as experiments using coincidence measurements of velocity and rotational angular momentum vectors to undo averaging over initial impact parameters and molecular orientations. In recent years, Lee and his group, using seven molecular beam machines in the laboratory, have been leaders in studying the chemical reactions of large organic molecules such as those significant for combustion chemistry and atmospheric chemistry. Polanyi says of his group that "our current major interest these days is to induce reactions at sub-monolayer coverages on surfaces—single crystal surfaces. We are trying to move our reaction dynamics from the three-dimensional world of gas to the two-dimensional world of the adsorbed state. We have to go back to the classroom to learn about surfaces from the people who have been making great strides in studying them—among whom are the winners of the 1986 Nobel Prize in Physics" (see PHYSICS TODAY, January, page 17).

Vital statistics. Herschbach received his BS in mathematics in 1954 and his MS in chemistry in 1955, both from Stanford. He received a second master's degree in physics in 1956 and his PhD in chemical physics in 1958, both from Harvard. Since then Herschbach has held positions at Harvard, except for the period 1959–63, when he was an assistant and an associate professor at Berkeley. He has been Baird Professor of Science at Harvard since 1976.

Lee received his BS in 1959 from National Taiwan University and his MS in 1961 from National Tsing Hua University (also in Taiwan). He received his PhD in chemistry from Berkeley in 1965. He carried out postdoctoral research beginning in 1965 at both Lawrence Berkeley Laboratory and Harvard prior to his joining the chemistry faculty at the University of Chicago. Since 1974 he has been a professor of chemistry at Berkeley and a principal investigator with the Materials and Molecular Research Division at Lawrence Berkeley.

Polanyi received his BSc (1949), MSc (1950) and PhD (1952) in chemistry from the University of Manchester. After positions at the National Research Council (Ottawa) and at Princeton, Polanyi moved in 1956 to the University of Toronto, where since 1974 he has held the position of University Professor of Chemistry.

—PER H. ANDERSEN

Still more squeezing of optical noise

Quantum optics experimenters have been pushing hard to generate greater "squeezing." This drive was encouraged by last year's milestone demonstration at AT&T Bell Labs that the noise from an optical cavity had been measurably squeezed, that is, that the noise in one phase of the signal had been reduced below the level normally associated with quantum mechanical fluctuations in the vacuum field. Until then, that vacuum noise level had represented the fundamental quantum limit to precision in optical experiments. The Bell Labs experiment reduced the noise by 7–10% below this normal quantum limit (see PHYSICS TODAY, March 1986, page 17), and several experiments since then have achieved noise reductions of at least 20%. The most spectacular results to date have been obtained by a team at the University of Texas at Austin consisting of Ling-An Wu, Min Xiao, H. Jeffrey Kimble, John L. Hall (of the Joint Institute for Laboratory Astrophysics) and Huifa Wu, who have observed noise reductions to more than 60% below the normal level.[1]

Furthermore, the Texas team demonstrated the squeezing of light into a minimum-uncertainty state, and they inferred that the state had actually been squeezed by more than a factor of ten. By eliminating some experimental sources of noise that now degrade this large degree of squeezing, they hope to translate it into comparable reductions in the noise levels actually observed. Thus not only did the Texas experiment dispel any doubts that a usable amount of squeezing is available, but it also indicated a viable path to achieve that squeezing.

Squeezed states of light are a macroscopic manifestation of quantum behavior. They are best understood if one writes the electric field vector as the sum of two terms whose time variations are given by sine and cosine functions,