

# The 1986 Nobel Prize In Chemistry

*The award honors three pioneers in the field of chemical reaction dynamics; their work has given rise to chemical lasers and offers the possibility of precisely guiding reactions*

ON 15 October, the 1986 Nobel prize in chemistry was awarded to John C. Polanyi of the University of Toronto for his pioneering work in the use of infrared chemiluminescence in studying the dynamics of chemical reactions; and to Dudley R. Herschbach of Harvard University and Yuan T. Lee of the University of California, Berkeley, for their development of the molecular beam method for studying those reactions.

Among physical chemists, the prize has been greeted with enthusiasm. "It's a very gratifying moment," explains Stanford University chemist Richard N. Zare, who earned his Ph.D. under Herschbach. Not only has the work of Herschbach, Lee, and Polanyi been seminal in the study of reaction dynamics, he says, but the field of reaction dynamics has in turn come to pervade chemistry as a whole. "People don't just talk about reaction rates anymore," says Zare. "They talk in terms of reaction pathways—the quantum details of molecular interactions, the states, the angles, the translational energies. And what this starts to buy you is control: we aren't there yet, but we seem to be heading towards a time when we can make reactions move in any direction we want."

Polanyi's interest in reaction dynamics runs in the family: in the 1930's, his father Michael Polanyi helped create the widely used transition state theory of reaction rates. John Polanyi's own work on chemiluminescence dates from the mid-1950's, when he and his first graduate student, Kenneth Cashion, began their studies of the reaction  $\text{H} + \text{Cl}_2 \rightarrow \text{HCl} + \text{Cl}$ . Since this reaction is known to be strongly exothermic, Polanyi reasoned that a newly created hydrogen chloride molecule would come out of the reaction vibrating and rotating furiously. As it subsided toward the ground state, moreover, the hydrogen chloride would emit its energy as a cascade of infrared photons. Thus the term "infrared chemiluminescence." And this is exactly what Polanyi and Cashion observed: their infrared spectrometer revealed that some 50% of the liberated energy in the reaction was deposited as very

high-level vibrations in the hydrogen chloride molecule.

Polanyi and Cashion published their work in 1958. That same year, as it happens, Arthur L. Schawlow and Charles H. Townes had sparked a vigorous discussion in the physics community with their suggestion that light could be amplified if it is passed through a medium where the atoms and molecules were in a highly excited,



**John C. Polanyi:** *His data provided a deep theoretical insight into the dynamics.*

nonthermal state—a so-called population inversion. This was the principle of the laser, for which Schawlow and Townes were later to share a Nobel prize in 1964. Polanyi, for his part, was quick to realize that the hydrogen chloride reaction provided exactly such a population inversion. In 1960, he pointed out that this reaction, or a similar reaction, might provide the basis of what he called a "chemical laser." That suggestion led directly to the first demonstration of a chemical laser in 1965, by George C. Pimentel and

J. V. V. Kasper at Berkeley. Hydrogen halide reactions are still among the most efficient and powerful chemical lasers known; the hydrogen fluoride laser, in fact, has been seriously considered for possible use in a "Star Wars" Strategic Defense system.

"One can certainly question the uses that chemical lasers are being put to," says Polanyi, who was founding chairman of the Canadian Pugwash group and who has written many articles on arms control and the dangers of nuclear war. "But there's no denying that the work has had practical applications."

In the three decades since that first detection of the hydrogen chloride emissions, Polanyi has continued to develop the chemiluminescence technique. His data on the distribution of energy states in product molecules, and on how those distributions depend on the state of the reactant molecules, have often been the first of their kind. Furthermore, his detailed maps of the so-called energy surface of a reaction—the potential energy of the interacting atoms as a function of their interatomic distances—have given theorists a simple and elegant way of understanding the process as a whole.

Meanwhile, Herschbach and Lee's work on molecular beams was has provided a natural complement to Polanyi's results. Whereas Polanyi focused largely on the vibrational and rotational states of product species, the molecular beam experiments could determine their angular distribution and velocity. As Herschbach himself says, "With the combination, the whole picture is much strengthened."

Herschbach began his work at the Lawrence Berkeley Laboratory in the early 1960's, before moving to Harvard in 1963. "[By that time] we knew a lot about how the electronic structure of molecules determines their geometry," he told *Science* shortly after the prize was announced. "But the essence of chemistry is transformation—the rearrangement of bonds among reacting molecules. And we had only the vaguest ideas about how that worked. So from the outset, we wanted to develop a picture of reactions analogous to the chemists' picture of molecular structure."

Herschbach was not the first to use molecular beams in pursuit of that goal—the technique had originally been demonstrated in the mid-1950's—but he was the first to fully exploit its potential. Essentially, it is the same approach used by generations of nuclear and particle physicists. Instead of studying reactions in bulk matter, where the molecular motions are random and the details of individual interactions are submergled into one average reaction rate, the

researcher fires the reactant molecules at one another in two separate, well-collimated streams. At the crossing point the molecules interact, giving rise to product species that then fly outward into detectors; thus, the experimenter can monitor the molecular interactions one by one.

In the case of Herschbach's first experiments, for example, the reactants were potassium atoms and methyl iodide ( $\text{CH}_3\text{I}$ ); the beams were formed by the simple expedient of placing a sample of each material in a small oven, heating it, and allowing the resulting gas to escape through a slit. The products were potassium iodide (KI) and a methyl group ( $\text{CH}_3$ ); by measuring the distribution of potassium iodide molecules as a function of angle, Herschbach was able to show that the reaction takes place if and only if the incoming potassium atom strikes the opposing molecule on the iodide end, and then bounces backward.

"Those earliest experiments were delightfully crude," recalls Herschbach. The detector was simply a hot tungsten wire, which produced an electric current when struck by potassium iodide molecules. Unfortunately, he says, it also produced a current when struck by elastically scattered potassium atoms. (This arose from the fact that alkali atoms and alkali halide molecules are both very easy to ionize, which had been a prime reason for choosing the potassium-methyl iodide reaction in the first place.) Hersch-



**Dudley R. Herschbach:** "He has this great physical insight."

bach therefore added a detector made of platinum wire, which responded only to potassium atoms, and which allowed him to obtain the potassium iodide flux by subtraction.

"Later," he says, "we learned that if we improved the vacuum enough, the adsorbed gases and such would come boiling off the platinum wire, and pretty soon it would also start responding to both species. So I like to tell people that the experiment never would have worked if we'd had a really clean vacuum system!"

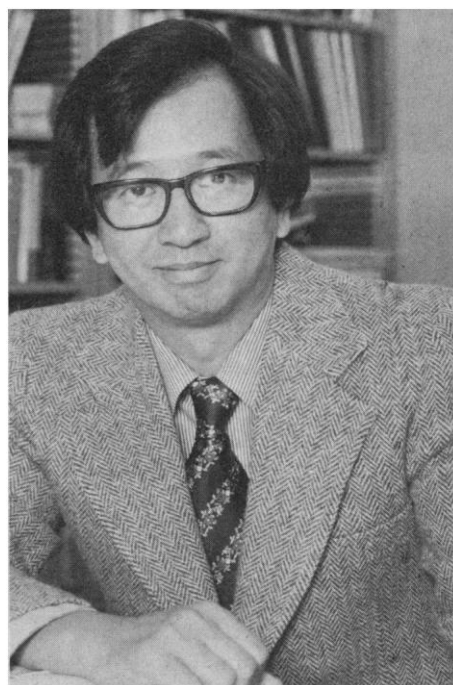
The molecular beam technique has improved considerably since then. And of course, refinements are still being made. But by all accounts, the really critical advance came in the years 1967 and 1968, when Herschbach hired a 31-year-old, Taiwanese-born research fellow who had only recently finished his Ph.D. work at Berkeley. Yuan T. Lee—whom Herschbach calls "an astonishing experimental genius"—proceeded to replace the hot wire detector with an exquisitely sensitive mass spectrometer of his own design. With this "universal" machine, the Harvard team was then able to analyze reaction products in much more detail than before. More importantly, Herschbach, Lee, and their colleagues could now go beyond compounds containing alkali atoms. In principle, they could study anything.

"Lee is the one who really implemented molecular beam chemistry," says Richard Bernstein of the University of California, Los Angeles, who is coauthor of a standard textbook in the field. "His universal machine took the technique from being an exotic curiosity and transformed it into a laboratory workhorse."

In 1968, Lee left Harvard for the University of Chicago, and from there he returned to Berkeley in 1974. Along the way he has built a series of increasingly more sophisticated molecular beam machines, with which he has studied a wide variety of reactions. Indeed, Bernstein credits Lee's group at the Lawrence Berkeley Laboratory with having developed the best molecular beam instrumentation in the world. In recent years, for example, Lee has devised a technique for working with very large molecules such as hydrocarbons, and has begun pioneering explorations of combustion and atmospheric chemistry.

Meanwhile, says Bernstein, Herschbach deserves credit not just for his work on molecular beams per se, but for his contributions as a theorist. "He has this great physical insight," says Bernstein, "a rare ability to devise simple models that can account for the main features of the reaction in a way that is easy to understand."

A conversation with Herschbach provides



**Yuan T. Lee:** "He is the one who really implemented molecular beam chemistry."

ample evidence of that ability—and illustrates why he is so highly regarded as a teacher. "One of the first things we looked at with the universal machine was the hydrogen chloride reaction," he recalls. Since Polanyi had already analyzed that reaction in his studies on chemiluminescence, the Harvard researchers were eager to link up with that work. When they did so, however, they were astonished to find that the distribution of product molecules was very similar to what they had seen in their potassium-methyl iodide experiments, even though the molecular structures in each case seemed very different.

"That's when we began to realize which aspects of the bonding are important to the reaction, and which aren't," says Herschbach. Ultimately, this line of thinking led to the recognition that chemical reactions are governed by a relatively small number of very general mechanisms. The potassium iodide and hydrogen chloride reactions, for example, proceed by what Herschbach calls the "harpoon" mechanism: one molecule sneaks up on the other, spears its target with a valence orbital, and hauls it in.

"It's very striking," says Herschbach. "The 19th century way of writing down reactions—using arrows and chemical symbols such as H or Cl—is misleading. The equations don't generalize, and you can't see the similarities. But if you look at reactions with eyes attuned to the relevant electronic structures, the similarities pop out. It's the closest thing we have to universals in chemistry." ■ **M. MITCHELL WALDROP**