CHEMISTRY

Researchers Unravel a Chemical Reaction

Experimenters use lasers and molecular beams as atom-sized rulers to make a fundamental scientific discovery

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ON the blackboard of his Stanford University office, Richard Zare draws a chemical reaction showing an atom and a molecule colliding to form a new molecule. But the atom and the molecule don't actually have to collide in order to react, Dr. Zare says: Just passing close to one another can be enough to set off the process.

"How close is close enough?" he asks. Until a few months ago, nobody knew.

Knowing how something like distance affects a molecular reaction is very basic to chemistry, explains Zare, but the answer has eluded chemists for years because of the difficulties involved in actually making the measurements. Chemists can control molecular beams – streams of molecules used for making precise measurements of molecular properties – only to within a tenth of a millimeter (a few thousands of an inch). That's a million times larger than the size of most molecules.

"If I had a high-speed camera and could somehow take a picture, I could tell," says Zare. It would have to be a very fast camera, he adds, because chemical reactions take place in femtoseconds (a billionth of a millionth of a second). Instead, Zare has spent the last decade in his basement laboratory developing another way of measuring reaction distance – a method that works by using light as a ruler.

The experiment runs inside a steel vacuum chamber in the back of the Zare laboratory. In the middle of the chamber a beam of barium atoms collides at right angles with a beam of hydrogen-iodide molecules. When an individual atom of barium glances past a hydrogen-iodide molecule, the iodine jumps from the hydrogen to the barium, sending the newly formed barium-iodide molecule spinning and vibrating. The amount of spin and vibration depends on how close the barium and the iodide were when the reaction took place.

When they spin at different speeds, molecules absorb slightly different frequencies. The experiment uses a tunable laser to measure the spin of the barium-iodide molecules as they are created. Although the technique, known as laser spectroscopy, has been used for years, the spectra that Zare needs must be incredibly precise. "This thing pushes the frontiers of instrumentation to make it work," he says.

Looking at the spectrum of the barium iodide, it is possible to find those molecules that are vibrating the least, called the "v equals zero state." Several pages of mathematics in a notebook show how to convert the frequency absorbed by the "v equals zero" molecule into a quantity Zare calls the "impact parameter," a measure of how close the path of a barium atom would come to the hydrogen-iodide molecule if they had not reacted.

To describe the experiment is to belittle its complexity. For example, "barium is a metal," says Patrick H. Vaccaro, a postdoctoral associate in the laboratory. "To make a beam you have to heat it up to 1000 degrees centigrade [1800 F] to make it a gas."

In order to determine the impact parameter, it is necessary to know the speeds of the particles in both beams. For "technical reasons," says graduate student Athanassios A. Tsekouras, each beam must be measured with a different technique: The barium beam's speed is found with a second laser by measuring its Doppler shift, the same technique used by police radar guns to determine the speed of cars. It is too difficult to measure the Doppler shift of the hydrogen iodide beam, so Zare's research group developed a way to measure it mechanically, by breaking the beam into pulses with a rotating shutter and then building a stopwatch that clocks how long it takes each pulse to travel a certain distance.

It takes 36 hours to run the experiment, says Dr. Christine A. Leach, another group researcher. "We take shifts," she says. A computer collects the more than 200,000 data points necessary to complete the measurements.

"Probably, if you wanted to go into an empty room and set this up, it would cost $200,000," says Dr. Vaccaro. But "it's not like you call up Sears and order an experimental chamber," he stresses: Most of the experiment had to be built from scratch; much of what could be purchased had to be modified.

For example, at first the power of the laser beam wasn't stable enough to make the ultra-precise measurements that the experiment required. "We struggled with this problem for about a year before coming up with a satisfactory solution," says Vaccaro.

Finally the group built an "optical feedback" circuit that watched the beam and made it brighter whenever it started to get dim. "The circuit had to be designed, constructed, and debugged in the lab, which is another reason that all this takes so long," he says.

Another problem was developing techniques for handling the hydrogen iodide, which "eats for breakfast" metals like stainless steel and molybdenum, Zare says. One of the things the gas destroyed was a carefully machined nozzle inside the vacuum chamber; it took a month to find a metal that could stand up to the gas and make a new one. "Chemistry is always so much fun!"

But the work has paid off: Surprisingly, all of the "v equals zero" barium-iodide molecules were created when the barium and the iodide were nearly the same distance apart, about 4 1/2 angstroms. (An angstrom is a little larger than a hydrogen atom.)

A few years ago, the Zare group investigated the barium-iodide molecules created in the "v equals eight" vibrational state, and found that they all came from another specific distance, roughly 2 1/2 angstroms, says Mr. Tsekouras. Combining the results of the two experiments, one interpretation is that reactions at different distances make different products, Zare says.

Although the result may seem obvious, says Zare, until they performed the experiment, nobody knew what the result would be. "This is the first measurement of its sort – the first time on any chemical reaction," he says. "It probably won't be done on many more: It's too hard!"

Zare's work builds on molecular-beam research that won Harvard University professor Dudley R. Herschbach the 1986 Nobel Prize in chemistry; not terribly surprising, since Zare was one of Dr. Herschbach's students.

"What Zare has done is take it quite a lot further because he has the full resolution of rotation vibration states. It's certainly a major landmark in the development of our ability to characterize the molecular events," says Herschbach. "This picture will allow us to understand a very wide range of reactions."

Eventually, Herschbach says, that understanding will play an important role in countless scientific and technical endeavors. "This is actually the most practical investment we can make. Nature speaks in many tongues, all of them foreign. What the basic scientist is doing is trying to unravel some of the vocabulary and grammar." Without that understanding, he says, "we can put all the human effort and money to solve some particular problem; we can't make progress unless we can understand nature's [way of doing things.]"

"The reaction itself may be of no particular interest, but if it is particularly well suited to let you test ideas," the results can be applied to many situations, he adds.

And indeed, barium and hydrogen iodide are especially well suited for this experiment, Zare says. Since both are such massive particles, virtually all the vibration and spin in the barium-iodide molecule produced comes from their off-center collision; because of that fact, measuring the vibration and spin of the resulting molecule gives scientists information about the reaction distance.

"This system was not chosen arbitrarily," says Zare. "But it has a consequence: The spectrum of barium iodide is extremely difficult to understand and interpret. . . . It looks like spectroscopic spaghetti."

Because of the technical and intellectual challenges, doing this sort of research "requires a commitment on the part of the researcher," says Zare. "There has been over a decade of work to get this answer. It has already exceeded several graduate student lifetimes. They got their PhDs working on this project, but they didn't finish the project."

But beyond commitment, says Zare, the project requires a consistent source of funding. "That is so hard today, because everybody is interested in commercialization and near-term payoff," says Zare. All the project's funding comes from the National Science Foundation; much of his time is spent writing grant proposals, rather than doing science.

Nevertheless, he says, it's worth it: "We think we are getting a really new understanding of how chemical reactions occur," says Zare. "It just changes your view of what happens."

JOHN VAN PELT – STAFF

The Zare Experiment

For the first time, chemists have been able to measure how the distance of two particles affects the outcome of a chemical reaction.

In the experiment, a beam of barium atoms (green) intersects with a beam of hydrogen iodide (purple and white), forming a molecule of barium iodide (green and purple).

The outcome of each molecular collision depends on how close the particles are when they react.

Using a laser, chemists can measure the amount of spin in the barium iodide molecules that have the least amount of vibration. They can then calculate the maximum distance at which the reaction can take place.

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Three Possible Results