

## PULSE, PUMP &amp; PROBE

Roald Hoffmann

The essential change implicit in the arrow in a chemical reaction,  $A + B \rightarrow C + D$ , may be rapid, it may be slow. I drop a small chunk of potassium into water, and the show is over in less than a second. The majestic copper beech outside my window was not noticeably smaller yesterday, but a photograph of it 75 years ago shows it just 10 feet high. Many biochemical reactions went into that slow growth. They tell me the universe is 15 billion years old, they tell me that the primary photochemical act in vision—a change in shape of a retinal molecule—transpires in 200 femtoseconds. (One femtosecond, fs, is  $10^{-15}$  seconds—the name of the unit a relatively rare intrusion of a nice Scandinavian root into a scientific nomenclature generally too anxious to impress in Greek and Latin.) I sort of trust the former, I believe the latter, and in this third *Marginalia* on the new kinetic chemistry, I would like to tell you why.

When events happen in the time frame defined by our senses, we can easily gauge their rapidity. We have no trouble hearing the difference between a pulse rate of 55 and 155 beats per minute. And we can make out, a bit less distinctly, the number of years elapsed between a frame of Ingrid Bergman in her early *Intermezzo* and late *Autumn Sonata*. But as we move to shorter and longer time intervals we must abandon the direct and sometimes fallible evidence of the senses and rely on instruments and theory.

## Snappy Shots

Let's talk about very quick chemical reactions, those seemingly over before the eye blinks. It seems obvious that if we are to understand them, we must take a quick series of snapshots. How naturally we lapse into the language of photography! Since the end of the 19th century the technology has been in place for producing still images separated in time by intervals much shorter than the eye can resolve. So Étienne-Jules Marey in 1894 showed us sequences of a cat righting itself as it falls. Earlier still, in 1878 Eadweard

Muybridge set up a dozen cameras along a track, trip wires opening their shutters for two-thousandths of a second. Leland Stanford's bet that all four hooves of a horse are off the ground at some point in a gallop was thus proved. And in our century, Harold E. Edgerton's strobe flash caught a bullet passing through an apple.

A little thought about each of these photographic experiments reveals that they depend on signals (typically light at some frequency), a device for recording them (a photographic film), and most important, a precisely sequenced timing of two or more events (the trip-wire, stroboscopic lighting). Muybridge's "experimental setup" would not have resolved Leland Stanford's bet unless the trip wires indeed tripped the shutters expeditiously, the shutter speed were short enough to define the horse and the light level were sufficient to record the event on the film used. The circumstances of the measurement—the distance between the trip wires, the shutter speed, the light—all had to be matched to the speed of the galloping horse, so to say. A similar setup would teach us nothing about the bullet and the apple.

In the experiments I will describe below, people "freeze" the pieces of a molecule as bonds form or break up in the course of chemical reaction, or as the molecule is perturbed in some way. A typical bond length is 1.5 angstroms ( $\text{\AA}$ ;  $1\text{\AA} = 1 \times 10^{-10}$  meters), and we might want to see it changed to 2.5  $\text{\AA}$ . This in a reaction where the formerly bonded pieces might be going off at speeds something like 1,000 meters per second (m/s) relative to each other. How long does it take for the molecular fragments to travel 1  $\text{\AA}$ ? Only  $1 \times 10^{-13}$  s, or 100 fs. Light pulses that could freeze such motion had better be well defined, and in duration substantially shorter still.

The reason I speak of pulses is that this is the way it must be done if we are to learn something of molecules reacting—more in the spirit of Edgerton's stroboscope than Muybridge's trip wires. There is as yet no mechanical shutter that can open or close on the femtosecond time scale, nor can a photographic film form images of angstrom-level resolution. The logic of the experiments I will describe is that of the interaction of short, precisely timed pulses of light with matter.

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