

## When does a molecule make up its mind?

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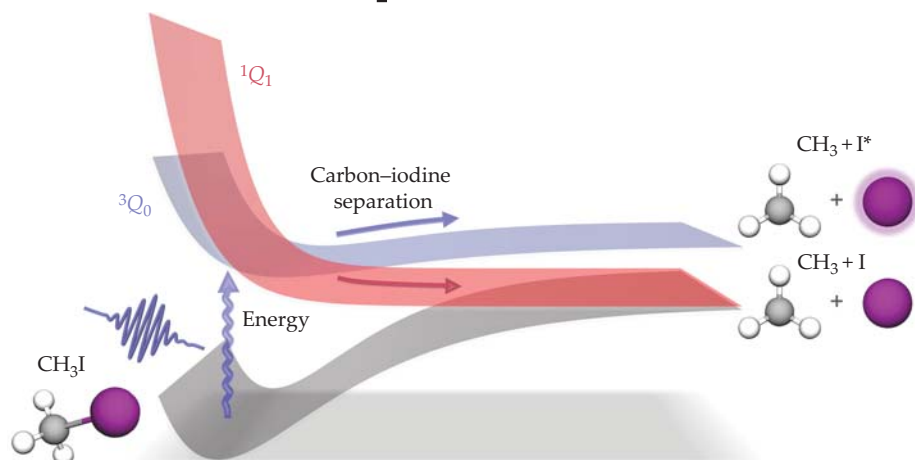
When a molecule reaches a point in its configuration space where the energies of two quantum states cross, it has a choice to make: It can continue along in the state it was in, or it can cross over to the other one. Understanding what happens at those crossroads—known as conical intersections—has been a long-standing challenge in chemical physics. In some molecular systems, most molecules make the switch; in others, most don't. And there's no reliable means of predicting which systems are which.

The problem is that everything happens so fast. Electrons and nuclei alike rearrange rapidly at a conical intersection. Their motions become strongly coupled, and the Born–Oppenheimer approximation—the principle that nuclear and electronic degrees of freedom can be treated separately—breaks down. Because the Born–Oppenheimer approximation is the foundation of nearly all conventional quantum chemical calculations, theorists are left with few tools for describing dynamics at conical intersections. And experimental studies on such rapid time scales aren't much easier.

Now, Kristina Chang of the University of California, Berkeley, her advisers Daniel Neumark and Stephen Leone, and their colleagues have developed a system of ultrafast lasers that can directly observe molecules passing through a conical intersection.<sup>1</sup> In an experiment on the widely studied prototype molecule methyl iodide ( $\text{CH}_3\text{I}$ ), they measured the time scale of the molecule's choice. Their results agree well with what theorists predicted for the system two years ago<sup>2</sup>—a promising sign that theorists and experimenters alike are well on their way to understanding molecular decisions.

## Life choices

Conical intersections are thought to be critical to many of the ways in which molecules convert or make use of energy, especially in living things. Examples include



**FIGURE 1. METHYL IODIDE ( $\text{CH}_3\text{I}$ ),** when excited from its ground state (gray) into the  $^3Q_0$  state (blue), quickly encounters a choice. One-quarter of the molecules cross into the  $^1Q_1$  state (pink), which dissociates into a methyl radical ( $\text{CH}_3$ ) plus a ground-state iodine atom; the rest stay in the  $^3Q_0$  state, which yields  $\text{CH}_3$  plus excited-state  $\text{I}^*$ . Although the outcome is well known, experiments on the ultrafast time scale of the molecular decision are needed to uncover the details of the dynamics. (Courtesy of Kristina Chang.)

photosynthesis, human vision, and DNA's mechanism for resisting UV damage.

Nature has evolved a genetic code consisting of just four DNA bases: adenine, cytosine, guanine, and thymine. Plenty of other molecules exist that could fit just as easily inside DNA's double helix. For example, 2-aminopurine is structurally identical to adenine except for the placement of an  $\text{NH}_2$  group, and it pairs with thymine just as well as adenine does. Nature's choice of adenine over 2-aminopurine seems to have come down to how the molecules respond to UV light.

When adenine absorbs a UV photon—a frequent occurrence in our sunlit world—it returns to its ground state within a picosecond; 2-aminopurine, on the other hand, takes tens of thousands of times as long.<sup>3</sup> The longer a molecule remains in an excited state, the more opportunity the excitation energy has to initiate a reaction that can lead to a genetic mutation. In fact, biologists sometimes use 2-aminopurine as a substitute for adenine in experiments when they want to induce mutations deliberately.

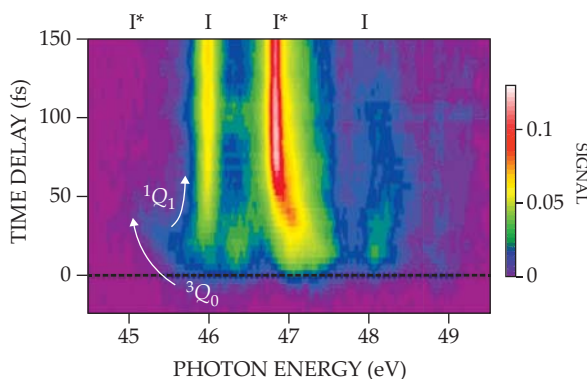
Adenine's short excited-state lifetime is attributable to a conical intersection that efficiently funnels molecules from the excited state to the ground state. It's

not much of an exaggeration, therefore, to say that life on Earth as we know it owes its existence to conical intersections.

But just because a conical intersection can funnel molecules between states doesn't mean it always does. After all, a molecule can pass through a conical intersection and remain in the same state where it started. A more complete understanding of conical intersections is needed to explain why biomolecules behave the way they do. But because biomolecules themselves have many cumbersome degrees of freedom, researchers studying conical intersections often focus on  $\text{CH}_3\text{I}$ , one of the simplest organic molecules with a mere four chemical bonds, one of them different from the rest.

## Speedy spectroscopy

The basic dynamics of  $\text{CH}_3\text{I}$  are well known. When the molecule is excited with UV light at around 277 nm, the carbon–iodine bond invariably breaks. Of the newly freed I atoms, about one-fourth are formed in their ground state, and the remaining three-fourths are in an excited state  $\text{I}^*$ . (Any excess energy goes into either  $\text{CH}_3$  vibrations and rotations or the kinetic energy of the two fragments as they fly apart.)



**FIGURE 2. ATTOSECOND TRANSIENT** absorption spectroscopy shows two distinct excitations of dissociating methyl iodide molecules. Although the 45–46 eV excitation quickly becomes quantum mechanically forbidden for molecules remaining in the  $^3Q_0$  state, the split with the  $^1Q_1$  state is still visible. (Adapted from ref. 1.)

Figure 1 depicts what's going on. The excitation takes the molecules into the  $^3Q_0$  state, right on the brink of a conical intersection with the  $^1Q_1$  state. Molecules that remain in  $^3Q_0$  yield  $I^*$  atoms; those that cross into  $^1Q_1$  yield ground-state I.

Neumark's and Leone's labs specialize in ultrafast chemistry, the study of the rearrangements of atomic nuclei on time scales of femtoseconds (see *PHYSICS TODAY*, December 1999, page 19) and motions of electrons on time scales of attoseconds (see *PHYSICS TODAY*, April 2003, page 27). In 2014 they and then-student Annelise Beck developed the technique of attosecond transient absorption spectroscopy for probing rapid molecular movements.<sup>4</sup>

Many other attosecond techniques can be complicated to interpret (see, for example, *PHYSICS TODAY*, January 2018, page 18). In contrast, transient absorption spectroscopy is much like any other form of absorption spectroscopy: By detecting which energies of incident light a sample absorbs, researchers infer what molecular states it contains. Because the incident light is a pulse that lasts just attoseconds, the measurement can be made with exquisite temporal precision.

A study of the  $CH_3I$  conical intersection proceeds as follows. An initial UV pulse excites a population of molecules into the  $^3Q_0$  state to start them on their journey to carbon–iodine dissociation. After a tunable time delay of tens to hundreds of femtoseconds, the dissociating molecules are blasted with a broadband attosecond pulse that probes their states. If all the molecules are still in the same state, they haven't yet passed through

the conical intersection. But if they're split into two subpopulations of different energies, then they have.

That experiment has been performed before,<sup>5</sup> but it didn't observe the molecules passing through the conical intersection. The sticking point was the initial UV pump pulse. Because of the combination of power and wavelength needed to excite the  $CH_3I$  molecules, it wasn't possible to make the pulses any shorter than 100 fs, far longer than the time scale the researchers

were hoping to measure. An experiment's time resolution isn't strictly limited by its pulse duration—it's possible to use 100 fs pulses to measure times somewhat shorter than 100 fs—but the passage through the conical intersection was still too fast to be meaningfully detected.

### Time to split

"Short, intense UV pulses are difficult to generate," explains Chang, "because we have to make them via the up-conversion of longer wavelengths. The conversion process is often inefficient, so we get UV pulses that are too low in energy to do any kind of useful measurement."

Chang and her colleagues addressed the challenge head-on by developing a new optical setup that made the frequency conversion more efficient. With a free-standing crystal of the nonlinear optical material beta barium borate, they frequency-tripled an ultrashort near-IR pulse. The result: a UV pulse with sufficient power to excite a  $CH_3I$  population, but with a duration of just 20 fs.

The resulting attosecond transient absorption spectroscopy data are shown in figure 2. The attosecond pulse excites two distinct transitions in the dissociating molecules, one in the range of 45–46 eV, the other around 47–48 eV. By the time the dissociation is complete—that is, when the pulse is exciting the unbound I atoms—the lower-energy transition on the  $I^*$  state is quantum mechanically forbidden.

But prior to about 50 fs, a weak blue streak veering off to the left, from molecules remaining in the  $^3Q_0$  state, is visible, as is the much stronger yellow streak

from those crossing into the  $^1Q_1$  state. By fitting the data, the researchers pinpoint the onset of the splitting to  $15 \pm 4$  fs, in good agreement with the theorists' prediction<sup>2</sup> of 13 fs.

"Fifteen femtoseconds is less than a fifth of the carbon–iodine dissociation time of 80–100 fs," says Chang. "That means the molecule makes its 'decision' early on in the reaction of whether to switch states at the conical intersection or not." That conclusion might seem obvious from the way figure 1 is drawn—if the molecules are excited so close to the conical intersection, they should have no choice but to pass through it immediately—but that detail of the system had never before been confirmed experimentally.

The next step is to repeat the experiment with other molecules to see how conical-intersection passage times vary with chemical structure. When iodine is part of a bulkier organic molecule, for example, it dissociates in a similar way and passes through a similar conical intersection, but the outcome varies significantly. Only one-fourth of  $CH_3I$  molecules switch states at the conical intersection and produce ground-state I atoms. But in isopropyl iodide (which contains three carbon atoms), two-thirds of molecules make the switch, and in tert-butyl iodide (with four carbon atoms), more than 90% do.<sup>6</sup>

Could that trend be connected to an observable difference in the dynamics of how the molecules pass through the conical intersection? Ultimately, after all, chemical physicists are interested not just in when molecules make up their minds but in what they decide and why. By systematically studying the relationships between structure, dynamics, and outcome, Chang and colleagues hope to work toward an understanding of how molecular choices influence both chemistry and biology.

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