# Ultracold chemistry: No longer a disappearing act

Until now, researchers have struggled to study reactions whose products they couldn't see.

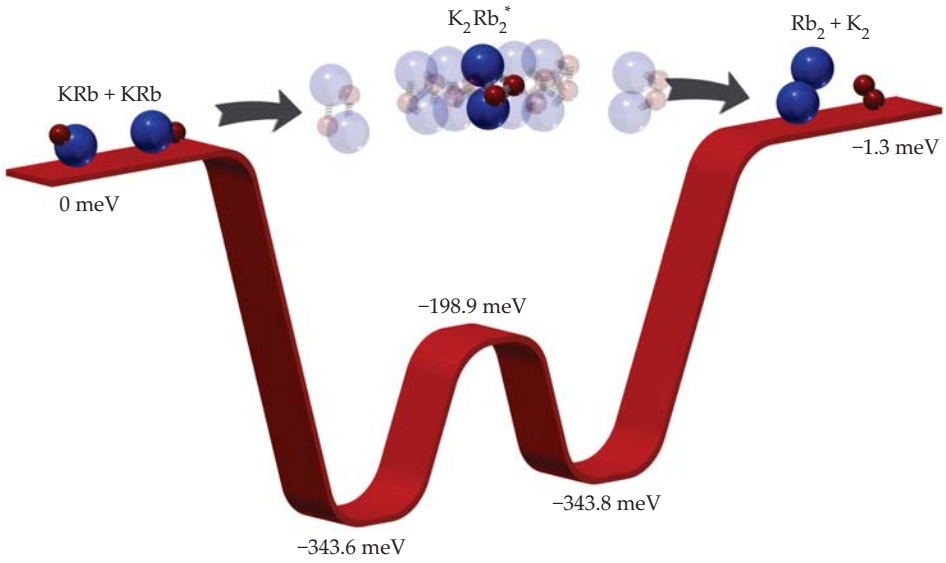


**FIGURE 1. MOLECULES OF POTASSIUM–RUBIDIUM (KRb)** can react to form $K_2 + Rb_2$ by means of a four-atom intermediate complex $K_2Rb_2^*$. Because the reaction releases energy and has no initial energy barrier, it's energetically allowed even at submicrokelvin temperatures. But until now, the reaction products had never been observed. (Courtesy of Ming-Guang Hu.)

A chemical reaction can be divided into three stages: the initial encounter of the reactants, the final emergence of the products, and everything in between. The middle stage—which involves all the making and breaking of chemical bonds, the rearrangement of atoms, and the surmounting of energy barriers—is difficult (although not impossible) to directly observe. Much of it can be reconstructed, however, through a combination of theoretical calculations and a careful look at the speeds, directions, and quantum states of the reaction products. (See, for example, PHYSICS TODAY, February 2019, page 14.)

In the submicrokelvin regime, the nature of the experiments means that that product information is usually inaccessible. Researchers prepare a gas of ultracold molecules—for example, potassium–rubidium, or KRb—in an optical dipole trap, monitor the rate at which the molecules disappear, and infer that the disappearance must be due to a chemical reaction. The trap has an energy depth of less than a nano-electron volt. The presumed reaction products, $K_2$ and $Rb_2$, are produced with far more kinetic energy than that, so they're lost from the trap and from the experiment.

Now Harvard University's Kang-Kuen Ni and colleagues, including PhD student Yu Liu and postdoc Ming-Guang Hu, have found a way to fill that information gap. By adapting velocity-map imaging (VMI), a standard technique of chemical physics, into the ultracold regime, they've detected both $K_2$ and $Rb_2$ fleeing from a trapped ultracold KRb gas.[1] And they've caught a glimpse of $K_2Rb_2^*$, the transient intermediate complex that precedes the product formation. Because of the reactants' low energy and ground quantum state, the intermediate has a lifetime of nanoseconds to microseconds, not femtoseconds, so it can be detected without special ultrafast techniques.

## Sticky molecules

The field of ultracold chemistry stemmed from an unintended discovery just over a decade ago. In the first experiments on ultracold heteronuclear molecules, which Ni worked on as a graduate student under Jun Ye and Deborah Jin at the University of Colorado Boulder, the aim wasn't to study chemical reactions at all.[2] Rather, the researchers hoped to investigate the many-body physics of quantum gases (Bose–Einstein condensates or, in the case of $^{40}K^{87}Rb$, degenerate Fermi gases) with dipole–dipole interactions among the particles. Atoms are readily cooled to temperatures at which quantum effects prevail, but they lack permanent electric dipole moments. So do homonuclear molecules. But heteronuclear molecules fit the bill.

Because direct cooling of molecules proved too much of a challenge, the researchers cooled gases of two different atoms, then used lasers and magnetic fields to coax them together into molecules. Those techniques are best suited to pairs of alkali atoms, such as K and Rb, and bialkali molecules remain the most commonly studied ultracold molecular systems. Experiments on KRb reached 150% of the Fermi temperature[2] in 2008 and 30% of the Fermi temperature last year.[3]

From the many-body physics perspective, the loss of molecules from the trap is a bug, not a feature, because it limits the duration of the experiments. But the researchers noticed that the rate of loss was proportional to the square of the density of the KRb gas—that is, to the rate of bimolecular collisions. They concluded that the losses must be due to molecules colliding and reacting.

The work presented an opportunity to study chemistry in a new quantum regime. In a sense, all chemistry is quantum mechanical because the electrons that make up interatomic bonds must be described by their quantum wavefunctions. But at ambient temperatures, atomic nuclei are well approximated as classical billiard balls; at ultracold temperatures that approximation breaks

down. A new medley of quantum chemical effects—for instance, the requirement that when two identical fermionic molecules react, they must do so via an overall antisymmetric wavefunction—came into play and observably influenced reaction rates.[4] (See the article by Debbie Jin and Jun Ye, PHYSICS TODAY, May 2011, page 27.)

Despite the interest in ultracold chemistry, researchers still hoped to study long-lived molecular gases in which reactions were suppressed. And there seemed to be a way to make them: Whereas the KRb reaction releases 1.3 meV of energy, as shown in figure 1, other bialkali molecules, such as rubidium–cesium or sodium–potassium, must consume energy to react. Because ultracold molecules have little energy to consume, gases of those molecules should be stable. However, experiments soon showed that even those putatively unreactive species disappeared from their traps at almost the same rate as KRb and other reactive molecules.[5]

Theorist John Bohn and colleagues, also at the University of Colorado, have proposed an explanation for that mysterious effect.[6] When two bialkali molecules (such as RbCs) collide, they cling together in a four-atom complex ($Rb_2Cs_2^*$) that persists for long enough that it might collide with a third molecule or absorb a photon from the optical trap.[7] Either of those interactions could break the complex into products with enough energy to escape the trap.

It's a plausible hypothesis, but without any way of observing the complexes or the reaction products, experimenters have had a hard time definitively testing it. And it's raised the question of how well the KRb reaction is really understood: Does it proceed as a direct bimolecular reaction, as previously presumed, or does it rely on Bohn's sticky-complex mechanism as well?

## Products and intermediates

Ni and coworkers' initial idea was to use mass spectrometry to characterize the masses of molecules escaping the trap. But colleagues in physical chemistry urged them to consider VMI. "They convinced us that it was 'easy' and would give us a wealth of information," she says. "We've found the VMI complements mass spec and has been crucial for all of our studies thus far."

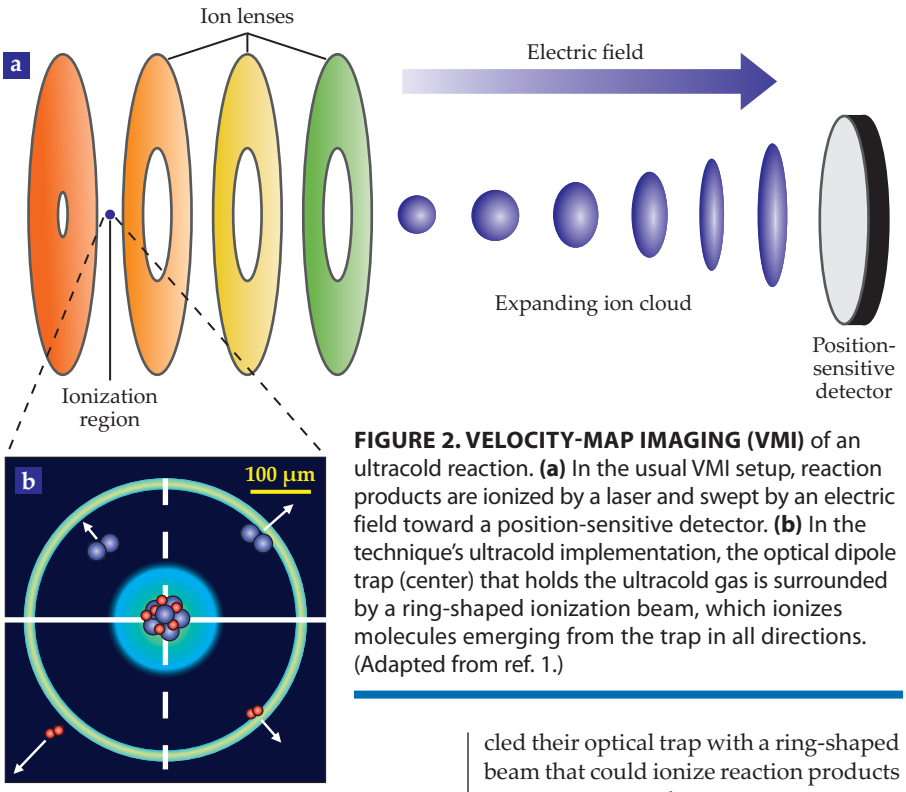


**FIGURE 2. VELOCITY-MAP IMAGING (VMI)** of an ultracold reaction. **(a)** In the usual VMI setup, reaction products are ionized by a laser and swept by an electric field toward a position-sensitive detector. **(b)** In the technique's ultracold implementation, the optical dipole trap (center) that holds the ultracold gas is surrounded by a ring-shaped ionization beam, which ionizes molecules emerging from the trap in all directions. (Adapted from ref. 1.)

Figure 2a shows the structure of a typical VMI experiment. Molecules formed in a reaction are ionized, usually by a pulsed laser, and then swept by an electric field toward a position-sensitive detector. Their time of flight between ionization and detection gives their mass-to-charge ratio, and their positional distribution on the detector gives the transverse component of their velocity. A series of charged plates focuses the ions so that ions created in different locations but with the same velocity strike the same point on the detector. (For more on VMI and its applications, see PHYSICS TODAY, October 2013, page 15.)

Typically, the reacting molecules in a VMI experiment come from molecular beams—thin jets of gas squirted into the reaction chamber—and are continuously supplied by the quadrillions. In contrast, an ultracold KRb gas, which takes the better part of a minute to prepare, contains just a few thousand molecules that react into nonexistence over the course of several seconds.

To make the most of their limited potential signal, Ni and colleagues used an unconventional optical setup, as shown in figure 2b. Rather than focusing their ionization beam to a point, they encircled their optical trap with a ring-shaped beam that could ionize reaction products emerging in any direction.

The mass-resolved data showed clear signatures of both $K_2$ and $Rb_2$. But were they the result of a direct reaction or of a more complicated process involving additional molecules or photons? To find out, the researchers turned to the product velocities extracted from the VMI data. A reaction between two cold, ground-state KRb molecules must conserve both momentum and energy: $K_2$, at just under half the mass of $Rb_2$, should emerge from the reaction at just over twice the velocity, and the sum of the product kinetic energies shouldn't exceed the 1.3 meV released in the reaction. The experimental data revealed that both those constraints were satisfied—good evidence that the reaction proceeds directly, as expected.

But that wasn't all. The mass spectra also showed small peaks corresponding to the masses of $K_2Rb$ and $KRb_2$. The researchers knew those molecules couldn't be formed in a direct reaction: Both product channels $K + KRb_2$ and $Rb + K_2Rb$ are energetically forbidden by hundreds of meV. They suspected the triatomic signals might be the result of the four-atom intermediate complex, $K_2Rb_2^*$, with one of its atoms expelled by the ionization laser. Sure enough, when they lowered the ionization photon energy to just above the complex's ionization

threshold, the $K_2Rb$ and $KRb_2$ disappeared and were replaced by a peak at the mass of $K_2Rb_2^*$.

## More to come

"We were really just hoping to see products," says Ni, "and were not even considering the intermediates at first. But now that we've seen them, there's a lot more to explore." Although she naturally wonders what products VMI might detect emerging from a gas of NaK, RbCs, or any of the other bialkali molecules whose direct reaction is energetically forbidden, Ni notes that those experiments aren't on the agenda—at least not for her group. "All our lasers are specifically optimized to work with rubidium and potassium," she says. "We'd need a whole new set of lasers to study sodium or cesium." But, she notes, further experiments on KRb could provide insight into the reaction mechanisms of other molecules.

The feasibility of Bohn's proposed sticky-complex mechanism, after all, depends critically on how long-lived the $Na_2K_2^*$ and $Rb_2Cs_2^*$ complexes really are. Theory offers a way to predict the lifetime of a molecular complex as a function of the density of states of its available decay channels, but the method remains to be tested in the quantum regime. A direct experimental measurement of the $K_2Rb_2^*$ complex lifetime would be a valuable benchmark for understanding the decays of other similar complexes.

So far, Ni and colleagues have just an order-of-magnitude estimate of the $K_2Rb_2^*$ lifetime—between 350 ns and 3.5 μs—based on the strength of their measured $K_2Rb_2^*$ signal and their best guess of the complex's photoionization cross section. With technical improvements to their experiment, they hope to be able to measure the lifetime directly based on the elapsed time between when the complexes escape the trap and when they're ionized.

**Johanna Miller**


## References

1. M.-G. Hu et al., *Science* **366**, 1111 (2019).
2. K.-K. Ni et al., *Science* **322**, 231 (2008).
3. L. De Marco et al., *Science* **363**, 853 (2019).
4. S. Ospelkaus et al., *Science* **327**, 853 (2010).
5. See, for example, X. Ye et al., *Sci. Adv.* **4**, eaaq0083 (2018).
6. M. Mayle et al., *Phys. Rev. A* **87**, 012709 (2013).
7. A. Christianen et al., *Phys. Rev. Lett.* **123**, 123402 (2019).


# Spin waves control the magnetization around them

The quasiparticles essential for proposed magnonic devices exert a spin-transfer torque of the same magnitude as that of electrons.

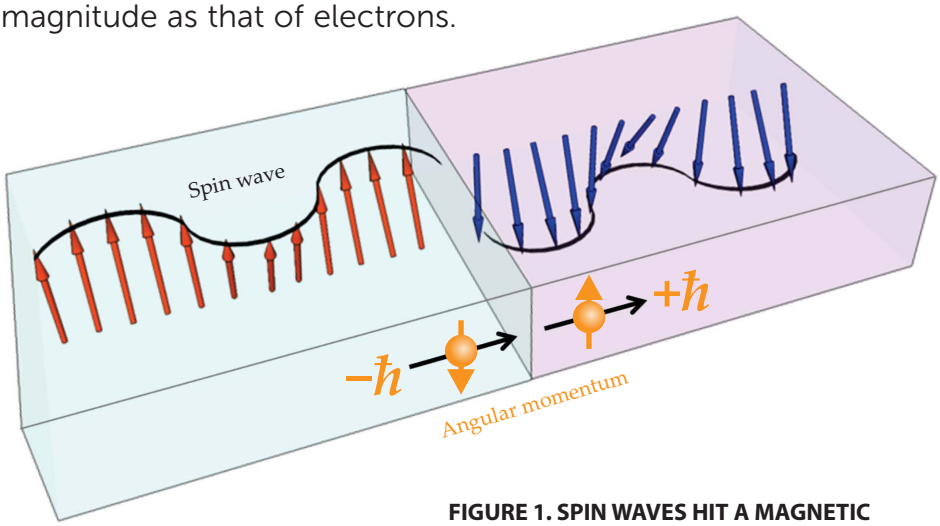


**FIGURE 1. SPIN WAVES HIT A MAGNETIC DOMAIN WALL** (the boundary between the blue and pink boxes) in a magnetic film. As it moves from left to right, the spin wave carries spin and angular momentum (orange) and comprises the collective precession of electron spins (red and blue arrows). At the domain wall the phase and angular momentum of the spin wave flip. (Adapted from ref. 2.)

As electronics get faster and smaller with more densely packed elements, Joule heating from electron motion and the resulting collisions becomes more prominent. Heat limits the performance of electrical devices and requires built-in cooling methods—from fans to heat sinks. A device that transports information without moving electrons would avoid such power dissipation, and so-called magnonic devices would do just that.

In magnonics, spin waves embody and transfer information through the collective precessions of electron spins that transport angular momentum while the electrons stay put. Although related, magnonics is distinct from spintronics, which uses the electron spin as an additional degree of freedom but still relies on electron motion in the form of electrical spin currents.

The spin-wave quasiparticle, known as a magnon, flows and carries spin angular momentum in much the same way that electrons do. In a well-prepared sample, it can propagate as far as centimeters—three orders of magnitude farther than electrical spin currents—and spin waves have already performed as logic gates.[1]

Despite their advantages, magnons are trickier to direct and measure than electrons are. A step toward making magnons more manageable has now been taken by two groups—one led by Luqiao Liu of MIT and the other by Hyunsoo Yang of the National University of Singapore. Their experiments have revealed how magnons both control and are controlled by their magnetic environment. The results suggest a design for all-magnon devices that are free from Joule heating and prove that magnons are capable of applications like manipulating magnetic memory.

## Generating spin waves

The key for both studies was producing strong spin currents. A few techniques can generate spin waves, but they share a basic scheme: Take a material with the electron spins aligned in one direction and flip or disturb one spin state. The interaction between the flipped electron and its neighbors starts the electron spin pre-