

Molecular vibrations offer control over electron transfer

A targeted low-energy excitation can dramatically alter the course of charge separation in a molecule.

Fundamental to many biomolecular reactions, such as photosynthesis, is the transfer of electrons from one part of a large molecule to another. Mimicking those reactions in the lab—for example, to harness the Sun's energy to create solar fuels—requires researchers to replicate and control those electron-transfer processes in synthetic systems.

That's easier said than done. Although electron transfer is perhaps the most fundamental of all chemical processes, it's often frustratingly difficult to understand. Rudolph Marcus's pioneering theoretical work in the 1950s and 1960s well describes many simple systems and won him the 1992 Nobel Prize in Chemistry (see *PHYSICS TODAY*, January 1993, page 20). But a full quantum understanding of all the factors that influence an electron as it navigates the complex energy landscape of a large molecule remains elusive.

Now Julia Weinstein of Sheffield University in the UK, Anthony Parker and Michael Towrie of the Central Laser Facility at Rutherford Appleton Laboratory, and their colleagues have taken a step toward experimental control over

electron transfer.¹ Using an IR laser pulse to excite a vibrational mode of a molecule in solution, they were able to entirely switch off one of the molecule's electron-transfer pathways. Although their experiment focused on one specific system with no immediate applications, such switching could eventually be used to steer a reaction between different sets of products.

Double-slit analogy

How can a molecular vibration—a slight motion of atomic nuclei—have such a dramatic effect on electron transfer? Electrons are orders of magnitude lighter than nuclei, and the widely used Born-Oppenheimer approximation dictates that their motions can be described separately. When electronic and nuclear dynamics do couple to each other, their mutual influence is usually small.

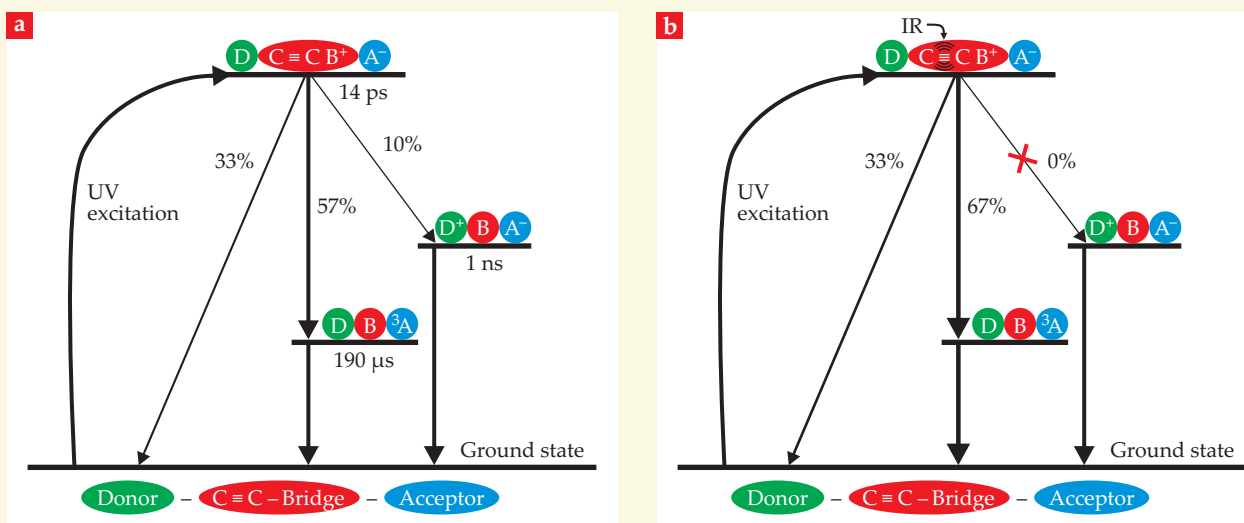
The possibility of a much larger effect was predicted by David Beratan (Duke University) and Spiros Skourtis (University of Cyprus), who, over the past decade, showed theoretically that electron transfer can be analogous to what happens in a double-slit experiment.²

They considered a system in which the electron can't tunnel directly between its initial and final states but must proceed via a sequence of intermediate quantum orbitals. When two or more such paths (which needn't be spatially separate) connect the initial and final states, the overall rate of electron transfer depends on the constructive or destructive interference between them. A small change in phase of one of the paths—which, the theorists postulated, could result from a molecular vibration that couples to one path but not the other—can alter the interference and thus switch the electron transfer on or off.

A proof-of-principle experiment came in 2009, when Tulane University's Igor Rubtsov and colleagues examined electron transfer in a hydrogen-bonded complex of two molecules: an electron-rich donor and an electron-poor acceptor.³ When they used an IR laser pulse to excite a handful of vibrational modes in the region of the hydrogen bonds between the molecules, they reduced the overall amount of electron transfer from donor to acceptor by a few percent.

Targeted excitation

In the new work, Weinstein and colleagues look at electron transfer in a sin-



Electron transfer in an organometallic molecule made up of an electron donor D, a bridge B, and an electron acceptor A. Exciting the molecule with a UV laser pulse sends it to a short-lived charge-transfer state DB^+A^- , which decays in one of three ways: to the ground state, to a triplet state DB^3A , or to a charge-separated state D^+BA^- . (a) Normally, all three processes are present. (b) But when the carbon-carbon triple bond in the bridge is vibrationally excited with an IR pulse, decay to the charge-separated state is switched off.

gle organometallic molecule made up of a donor D and an acceptor A connected by a bridge B. As shown in the figure, UV excitation sends the molecule to a charge-transfer excited state DB^+A^- , which decays into one of three product states: the ground state DBA, a spin-triplet state DB^3A , or a fully charge-separated state D^+BA^- . (Both DB^3A and D^+BA^- eventually decay to the ground state.) Although all three of those decay channels involve an electron transfer, the formation of the charge-separated state D^+BA^- is most analogous to the flow of charge between distant regions of a biomolecule and thus is of greatest interest.

The excited state and the three product states all have different vibrational spectra, and both DB^3A and D^+BA^- are relatively long-lived. So by exciting the system with an ultrashort UV laser pulse and spectroscopically probing it a short time thereafter, the researchers could observe the formation and decay of each product state. As shown in panel a of the figure, 33% of the molecules decayed to the ground state, 57% to the triplet state, and 10% to the charge-separated state.

Next, the researchers added an IR pump pulse between the UV excitation and the spectroscopic probe. They'd designed their molecule so that the electron transfer they were interested in—from the donor to the bridge—had to pass through a carbon-carbon triple bond, whose characteristic vibrational frequency was well separated from those of the molecule's other bonds. By tuning the IR pump to just the right frequency, they could excite a vibration in the triple bond while leaving the rest of the molecule undisturbed.

Quantifying the effects of IR on the product-state yields was not quite straightforward. Not every excited-state molecule absorbs the IR pump, so the raw yields for the IR-pumped system include some molecules that were vibrationally excited and some that were not. Once the researchers had processed their data to account for those cases, they found that for the vibrationally excited molecules only, the yield of the triplet state was increased from 57% to 67%, as shown in panel b. Yield of the charge-separated state was decreased by the same amount: from 10% to zero. "That was a great surprise," says Milan Delor, the paper's lead author. "Based on previous work by other groups, we were expecting the effect to be small. We had to check the calculations many, many times to be convinced of what we were seeing!"

Switching off and on

All three of the decay channels of Weinstein and colleagues' molecule lead back to the same ground state, but one could imagine a similar system in which different channels produce different products. For example, the charge-separated state could initiate a redox reaction that produced a solar fuel. From that perspective, the ability to switch off electron transfer to a charge-separated state is interesting, but it's also important to be able to switch it on: A small energy input, in the form of the IR pump, could make a large difference in the amount of energy stored as fuel. Rubtsov and colleagues, whose 2009 proof of principle involved a reduction in the electron-transfer rate, have recently demonstrated that enhancement of electron transfer is also possible.⁴ They found a system in which IR-pumped molecules exhibit 28% faster charge separation. But the overall enhancement was small, because very little of the pump power was absorbed.

Better theoretical understanding should help in the quest to design molecules with more useful electron-transfer properties. It's still not clear exactly what mechanism was at work in Weinstein and colleagues' molecule: Which sequences of orbitals, if any, destructively interfere to switch off electron transfer to the charge-separated state, or is something entirely different going on? Preliminary calculations by Anthony Meijer, a coauthor on the paper, show two electronic states whose energies cross as the carbon-carbon triple bond is elongated. But modeling the molecule's electronic properties is tricky, thanks to its interactions with the surrounding solvent and the heavy-metal atom contained in the bridge.

As Parker explains, "Theory initially predicted this effect to be possible. We have shown it experimentally; now, as in a game of Ping-Pong, hopefully theorists will give us the ball back and say, 'This is the way it worked, and we predict a molecule that looks like this should also work'—and the cycle continues."

Johanna Miller

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