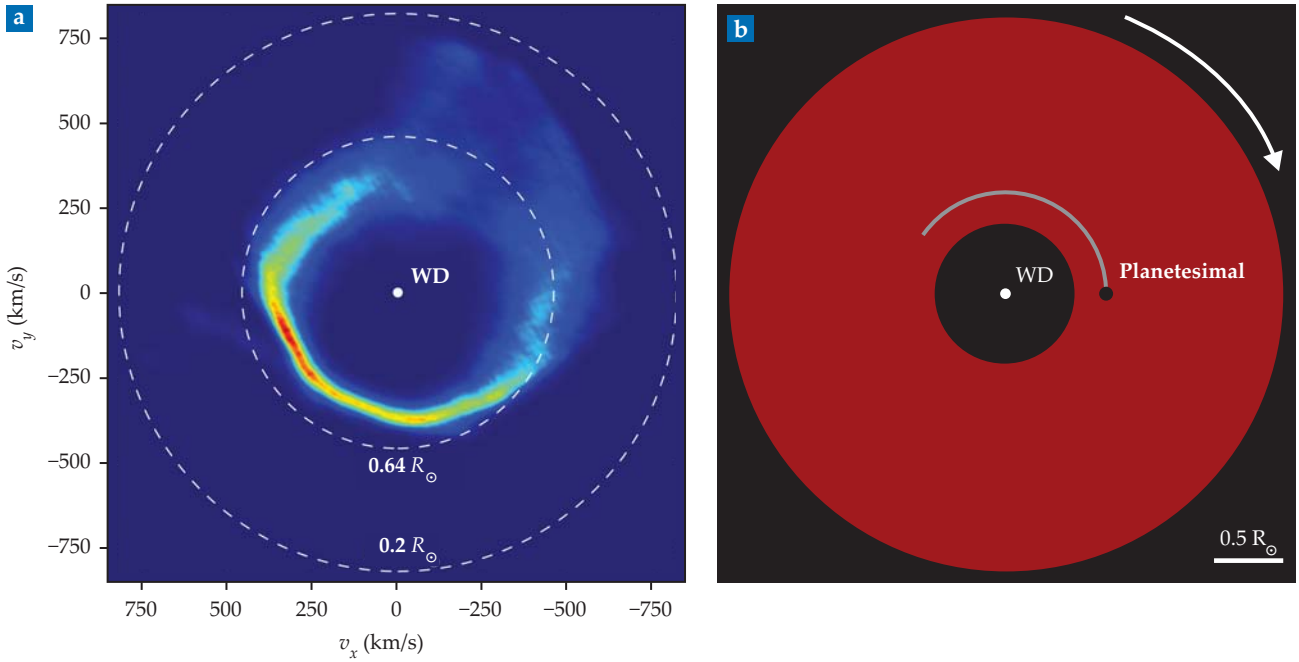

FIGURE 2. THE DEBRIS DISK SURROUNDING THE WHITE DWARF (WD). (a) A map in velocity space shows the pattern of gas swirling in the disk (red is highest flux, dark blue is lowest). The pattern precesses on a time scale of 25 years. The overlaid dashed circles indicate material in orbits at two different distances from the star. The configuration appears inside out because material moves faster in closer-in orbits. The radius of the Sun, $R_\odot$, is 6.96 x 10^8 m. (Adapted from ref. 5.) **(b)** In position space, both the disk and the planetesimal orbit clockwise. The solid red area indicates the region of observed calcium emissions. The gray curved line trailing the planetesimal shows the inferred extent of the gas that generates extra emission. (Adapted from ref. 1.)

A series of calculations led Manser to propose two possibilities for the object's structure. A spherical body as small as tens of kilometers across could be held together by its own gravity provided its density is that of metallic iron, 8 g/cm^3, or higher. Alternatively, an iron-dominated larger body, hundreds of kilometers across, could have a layered internal structure that is strong to avoid being ripped apart. In either case, the original planet would have had distinct layers, like the dwarf planet Ceres. The surviving body could be the iron- and nickel-rich core of a former planet that once orbited much farther away from the star and had its crust and mantle ripped off during the star's explosion. Kenyon observes that "it's interesting to contemplate how the planetesimal got into this mess after having spent most of its previous life far away from its host star."

As of now, astrophysicists know of only seven other white dwarfs that have gas in their disks. Those systems are the next candidates to check for orbiting rocky bodies. Tracking planetesimal behavior over time will help astronomers explain how rocky bodies behave during the final stages of stellar evolution as they form disks around white dwarfs and will also provide the only direct views of planetary inner cores.

Rachel Berkowitz

References

1. C. J. Manser et al., *Science* **364**, 66 (2019).
2. E. Han et al., *Publ. Astron. Soc. Pac.* **126**, 827 (2014).
3. A. Vanderburg et al., *Nature* **526**, 546 (2015).
4. B. T. Gänsicke et al., *Science* **314**, 1908 (2006).
5. C. J. Manser et al., *Mon. Not. R. Astron. Soc.* **455**, 4467 (2016).

Inverted kinetics seen in concerted charge transfer

A counterintuitive phenomenon has now been observed in a new realm.

Just as a round stone rolls faster on a steep slope than on a gentle one, a chemical process speeds up when it's made more energetically favorable. At least, that's what usually happens. But 60 years ago when Rudolph Marcus developed his pioneering theory for electron transfer, he found that in a certain region of parameter space, increasing the driving force—the drop in free energy between the initial and final states—should actually slow the transfer down.[1]

That surprising prediction—the so-called Marcus inverted region—was experimentally confirmed[2] in 1984, and in 1992 Marcus was awarded the Nobel Prize in Chemistry for his theory (see PHYSICS TODAY, January 1993, page 20). Today, Marcus theory is textbook material in chemical kinetics,[3] and inverted regions in electron-transfer reactions are widely observed.

Electron transfer underlies all of oxidation–reduction chemistry, including corrosion, combustion, electrochemistry, and ionic bonding. In photovoltaic cells, the creation and recombination of free

electrons and holes are both examples of electron transfer. Engineering a photovoltaic system to reside in a Marcus inverted region can reduce the rate of recombination and enable the extraction of more energy more efficiently.

But electron transfer by itself doesn't involve the making or breaking of chemical bonds that are necessary for manipulating molecular identity or storing energy as chemical fuel. Now James Mayer, Sharon Hammes-Schiffer (both at Yale University), Leif Hammarström (Uppsala University in Sweden), and their colleagues have observed the signature of a Marcus inverted region in a different type of reaction that does rearrange a molecule's atoms.[4] Rather than the transfer of a single electron, their reaction involves the simultaneous transfer of an electron and a proton—that is, a hydrogen nucleus. Such concerted proton–electron transfer is known to be important in biology, solar fuels, and chemical synthesis.

Up is down

Marcus theory stems from the insight that the rate of a charge-transfer process depends critically on what's going on in the solvent or other surrounding medium. In water and other polar solvents, for example, the negatively charged ends of solvent molecules are drawn to positively charged regions of a solute molecule, and vice versa. When charge is redistributed among one or more solute molecules, the energetically preferred solvent configuration changes.

A full representation of the solvent configuration would require a many-dimensional space, but the key features can be collapsed onto a single coordinate, as shown in figure 1. The initial and final states of the reaction have their lowest free energies for different solvent configurations, and in either state, perturbing the solvent away from its preferred configuration increases the free energy in a way that's well approximated by a parabola.

The law of conservation of energy dictates that charge transfer can proceed only when the initial and final states have the same free energy at the same solvent configuration—that is, at the point where their parabolas cross. In most cases, the crossing point is not at the bottom of the initial-state free-energy curve, so it represents a free-energy barrier the system must surmount. The higher the barrier, the slower the reaction.

The seven final-state parabolas in figure 1 represent a series of hypothetical reactions that are identical in every respect except for the free-energy difference between the initial and final states, also called the driving force. (In the lab, such a series might be approximated by chemically altering the electron donor or acceptor to have different affinities for the transferred electron.) In the normal (noninverted) region of parameter space, shown by the blue parabolas, increasing the driving force lowers the crossing point's free energy and speeds up the reaction. But that trend can't continue indefinitely. Eventually, as shown by the gray parabola, the crossing point reaches the initial state's free-energy minimum; in that case, there's no barrier to the reaction, and the charge transfer is as fast as it can possibly be. At still larger driving forces, as shown by the red parabolas, the free energy of the crossing point starts to rise again, and the charge transfer slows down. That's the Marcus inverted region.

Defying diffusion

Early attempts to experimentally observe the inverted region came up short. As the driving force was increased, the rate of electron transfer initially increased, as expected—but then it leveled off and never clearly decreased. The problem was diffusion: In an electron transfer

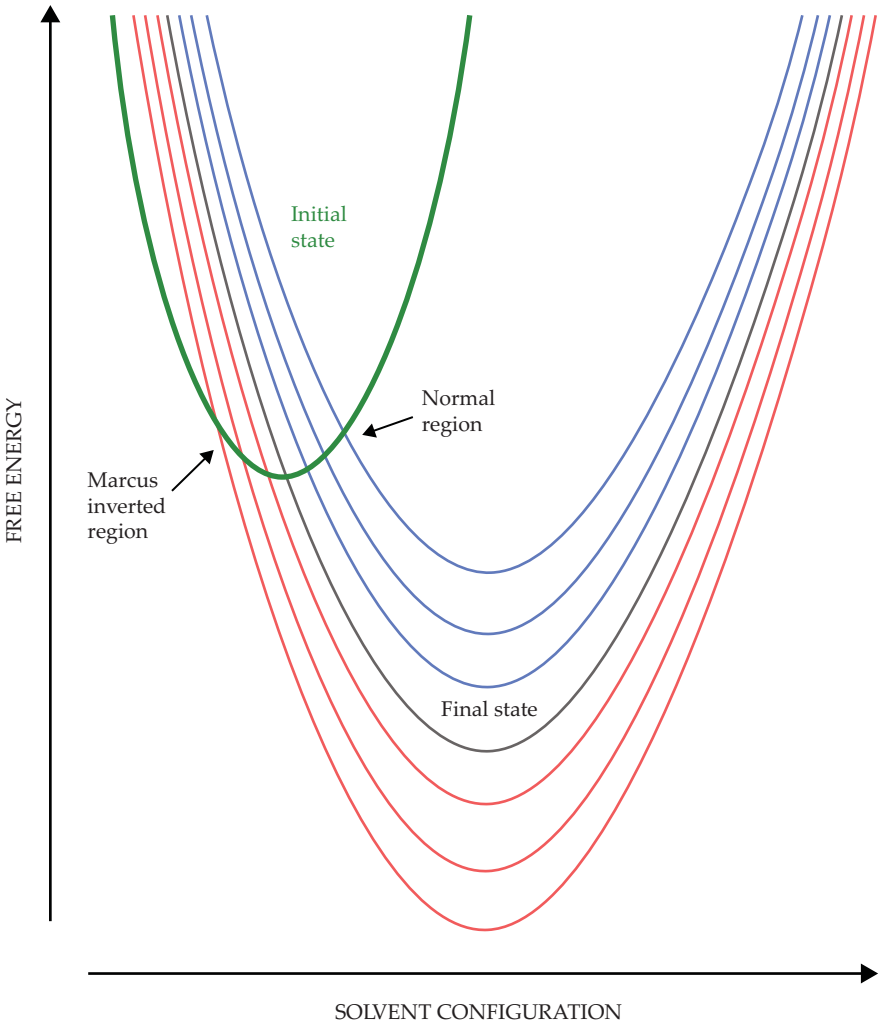

FIGURE 1. ACCORDING TO MARCUS THEORY, a charge-transfer reaction can proceed only at the point where the free-energy curves of the initial and final states intersect. In the normal region of parameter space, lowering the final-state free energy (as represented by the series of blue parabolas) also lowers the free energy of the crossing point, and the reaction speeds up. But in the Marcus inverted region, lowering the final-state free energy (red parabolas) raises the crossing-point free energy, and the reaction slows down.

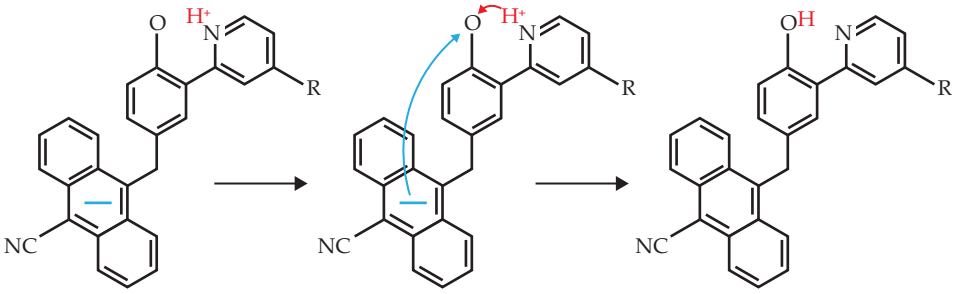

FIGURE 2. IN A THREE-PART MOLECULE called an anthracene-phenol-pyridine, concerted movement of a proton and an electron characterizes the spontaneous relaxation from a charge-separated state to the ground state. Placing different molecular groups at the position marked "R" changes the relative free energies of the initial and final states. The molecules with the larger free-energy changes show slower rates of charge recombination—the signature of a Marcus inverted region.

between two molecules in solution, the measured rate depends not only on the intrinsic transfer rate, as described by Marcus theory, but also on how frequently the donor and acceptor molecules approach each other. When the intrinsic rate is fast, as it is at the onset of the inverted region, the transfer occurs essentially immediately every time a donor and an acceptor get close enough. The rate-limiting step is diffusion, and the intrinsic transfer rate is obscured.

In 1984 John Miller, Lidia Calcaterra, and Gerhard Closs solved the diffusion problem by putting their electron donor and acceptor on the same molecule, connected by a rigid molecular spacer. By guaranteeing that the donor and acceptor would always be in close proximity, they overcame the effect of diffusion and achieved the first unambiguous demonstration of a Marcus inverted region.[2]

In their new paper, Mayer and colleagues also looked at intramolecular charge transfer, this time in a family of three-part molecules called anthracene-phenol-pyridines.[4] Optically exciting an anthracene-phenol-pyridine can give rise to a metastable charge-separated state, as shown in figure 2, with an extra electron on the anthracene unit (the three fused benzene rings in the lower left) and an extra proton, or H^+ ion, on the pyridine (the nitrogen-containing ring in the upper right). To return the molecule to the ground state, the electron and proton both migrate to the phenol unit in the middle. Importantly, the transfer is simultaneous: There's no observable intermediate state in which one of the charges has moved without the other.

The first anthracene-phenol-pyridines were prepared several years ago by Miriam Bowring, then a postdoc in Mayer's group, as part of an effort to push the limits of how fast concerted proton–electron transfer could go.[5] In the unsubstituted molecule (without the CN or R groups in figure 2), she found that the rate of charge recombination was independent of temperature. In a reaction with a free-energy barrier, thermal fluctuations are what push the system over the barrier, so the reaction is faster when the temperature is higher. Temperature independence, on the other hand, meant, tantalizingly, that the researchers had happened upon the zero-barrier reaction that marks the boundary between the normal and inverted regions.

Proton potential

But it wasn't clear that the inverted region would be experimentally accessible. Indeed, theoretician Hammes-Schiffer and her colleagues made the case a decade ago that it shouldn't be.[6] The crux of the argument is that when the H^+ ion moves, it can set a molecular vibration in motion and leave the charge-recombined molecule in a vibrationally excited state. Because a molecular vibration can be approximated by a quantum harmonic oscillator, with a ladder of eigenstates equally spaced over a wide energy range, there's always a state that's close to the right energy for a barrierless reaction. Increasing the driving force, they predicted, should increase the number of vibrational quanta in the final state, with the Marcus inverted region always just out of reach.

Nevertheless, observation of the bar-

rierless reaction was encouraging, and Mayer and colleagues were eager to explore it further. When Bowring presented her results at a conference in Sweden in 2014, their group struck up a collaboration with Hammarström, whose lab was ideally equipped to perform the necessary ultrafast measurements. Giovanny Parada, then a graduate student at Uppsala and now a postdoc with Mayer, also joined the project.

Parada used his synthetic-chemistry expertise to expand the family of anthracene-phenol-pyridines. By attaching different molecular groups at the position marked "R" in figure 2, he could influence the affinity of the H^+ ion for the pyridine and thus tune the charge-recombination driving force over several tenths of an electron volt. Not all the molecules he prepared showed observable charge-separated states, but of those that did, charge recombination was consistently slower in those with higher driving forces. For good measure, the researchers repeated the rate measurements in three solvents of different polarity. They saw the same trend each time.

But what about vibrational excitations—why weren't they blocking access to the Marcus inverted region? It turned out that the charge transfer *was* exciting a molecular vibration, just not with as many quanta as needed to get to the zero-barrier reaction. To see why, Hammes-Schiffer and her student Zachary Goldsmith delved into the quantum details. They found that the wavefunction of the initial charge-separated state had a negligible overlap integral with the vibrational state that would have yielded the zero-barrier reaction. The transition to that state was therefore inhibited. The quantum properties were a consequence of the shape of the potential felt by the proton, so designing molecules with an eye toward that potential could be a route to finding the Marcus inverted region in other concerted charge-transfer systems.

But for now, nobody knows how common or rare the effect might be. The Yale–Uppsala collaboration is on the case, with the theoreticians exploring large regions of parameter space to guide the experimenters' next choice of molecules to study. "We'd like to think that the phenomenon will prove to be widespread," says Mayer, "because then it could be used in more complex systems to tackle challenges such as solar-energy conversion." Because concerted proton–electron transfer is common in biology, in processes such as photosynthesis and respiration, another intriguing question is whether nature already exploits the Marcus inverted region in biological pathways. If so, understanding the inverted kinetics could be key to mimicking those functions in synthetic systems.

Johanna Miller

References

1. R. A. Marcus, *Discuss. Faraday Soc.* **29**, 21 (1960).
2. J. R. Miller, L. T. Calcaterra, G. L. Closs, *J. Am. Chem. Soc.* **106**, 3047 (1984).
3. See, for example, P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, Dover (2006), p. 155.
4. G. A. Parada et al., *Science* **364**, 471 (2019).
5. M. A. Bowring et al., *J. Am. Chem. Soc.* **140**, 7449 (2018).
6. S. J. Edwards, A. V. Soudackov, S. Hammes-Schiffer, *J. Phys. Chem. B* **113**, 14545 (2009).

Flows of volcanic rock and gas ride a carpet of air

The two-phase fluid drives hot gas to its base to lower frictional forces.

FIGURE 1. THE VOLCANO ERUPTION SIMULATOR FACILITY at Massey University in New Zealand produces experimental pyroclastic flows—hot avalanches composed of air, ash, and rock—that allow the study of their dynamical behavior. In this series of images spanning about a second, the bottom meter of a two-layer flow passes a fixed observation point. The arrows denote the boundary between a denser particle layer overridden by dilute, turbulent ash.

Mount Vesuvius erupted in 79 CE with little warning. The volcano's pyroclastic flows—hot avalanches composed of air, ash, and rock—obliterated everything in their path. The Roman cities of Pompeii and Herculaneum and the remains of about 1500 people were later excavated from under several meters of ash. In contrast to the viscous, ambling lava flows of other volcanoes, such as Mauna Loa in Hawaii, pyroclastic flows cruise across land at speeds of about 10–30 meters per second for tens of kilometers without slowing down.

Pyroclastic flows have long perplexed volcanologists. Given volcanic particles' high static friction, they should stay put on slopes of up to 35–45°. But scientists have observed pyroclastic flows traveling over land surfaces with average slopes of just 8° and sometimes even upslope for short distances.

Volcanologists can't easily measure the physical properties of pyroclastic flows in the environment because of the danger to people and the destruction of field instruments. Instead, researchers turn to numerical models. For a few decades, high pore pressure—that is, the pressure in the space between particles—was suspected of modifying frictional forces. But without a clear understanding of how pyroclastic flows generate and sustain pore pressure, scientists couldn't conclusively test the hypothesis. Rather