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CHEMICAL DYNAMICS IN SOLUTION

Recent advances in ultrafast lasers and in theory have made it possible to study on the molecular level the major role played by the solvent in chemical reactions.

Graham R. Fleming and Peter G. Wolynes

The majority of reactions carried out by chemists take place in liquid solutions. Only within the last 10–15 years, however, has it become possible to study such reactions in molecular detail.

The surge in work on reaction dynamics in condensed phases has been prompted by recent developments in theory, experimental technique and simulation. It is probably fair to say that 20 years ago the level of theory was so low, the experimental techniques so crude and the specific chemical systems so complex that meaningful experiments with straightforward interpretations were very difficult, if not impossible, to conceive. Today we have molecular-level theories of the role of solvent molecules in electron-transfer reactions; advances in ultrafast laser technology allow us to observe directly the motion of reacting molecules¹ (see figure 1) and the results of huge strides in computer simulation are available to aid in the study of complex many-body systems. Prior to these developments, simulation of realistic systems for time periods long enough to overlap with those of actual measurements was not feasible. (Figure 2 shows the time scales involved.) In this article we hope to give a flavor of recent work on the dynamics of solution-phase chemical reactions and to point briefly to prospects for future developments.

How do solvents influence chemical dynamics? For one thing, they provide sources and sinks for energy. When reactants and products are separated by an energy barrier, for example, solvents provide the energy to reach

the top of the barrier, and they enable the new product species to dispose of its excess energy. Solvents also create and impede molecular motion. They determine the energy surfaces on which reactions take place. And they provide a dielectric medium that can stabilize charged species, affecting the rate at which charge is transferred from one place to another.

One simple example of a solvent's impeding motion is the cage effect, first proposed by James Franck and Eugene Rabinowitch in 1934. In a dissociation process $AB \rightarrow A + B$ there is a significant possibility that the surrounding solvent molecules will hinder the separation of the fragments A and B , in which case they may then recombine. Richard Noyes postulated that in the case of the photodissociation of I_2 , this cage effect accounted for the difference between the final yield of separated iodine atoms and the number of iodine molecules initially excited. The development of picosecond lasers raised the possibility of observing the cage effect directly, and experiments on the I_2 system by Tung J. Chang, Geoff W. Hoffman and Kenneth Eisenthal at IBM in 1974 stimulated substantial interest. Many later studies revealed that in this case the gods were not kind—the various time scales inherent in the problem have not yet allowed a direct observation of the cage effect—but much was learned about the flow of vibrational energy between solvent and solute,² and the stage was set for a huge burst of experimental and theoretical activity.

Molecular motion and friction

Theoretical progress in the last decade was driven in large part by advances in the formal theory of nonequilibrium processes, which reached the point that one could make sensible use of the concept of friction at the molecular

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Femtosecond dye laser system at the University of Chicago. Graduate student Sandra Rosenthal makes an adjustment in the copper-vapor-laser dye-amplified system just behind the flowing sample. The system was used to collect the data shown in figure 4. **Figure 1**

level and compute frictional properties from the marriage of intermolecular forces and macroscopic parameters.³ Friction—the influence of the motions of neighboring molecules on the way a molecule moves and exchanges energy and momentum with its surroundings—is a key concept in condensed-phase molecular dynamics. In addition to collisional, or viscous, friction, responsible for impeding molecular motion, there is also dielectric friction, the response of the solvent to changes in the charge or charge distribution of the solute molecules. For example, a lag in the solvent's ability to equilibrate a new charge can impose a frictional drag on an electron-transfer reaction.

Studies of rotational reorientation of molecules in solution have been particularly important in establishing ideas about collisional friction. These studies are based on light scattering, nmr and ultrafast spectroscopy. A large body of work has established a firm link between molecular-level friction and macroscopic viscosity. In general the rate of reorientation is inversely proportional to viscosity, at least in cases where the solute diameter is larger than that of the solvent; and for longer than a picosecond or so, motion is accurately described as small-step diffusion. For small molecules, and over short times, significant amounts of free or inertial motion are possible.

Perhaps one of the most direct ways to observe the influence of solvent friction on a reaction in solution is to study a reaction that has no activation barrier.⁴ Then solvent friction will be the only impediment to the

reaction. One can initiate such a reaction by, for example, placing a molecule in an excited state with a short light pulse; one can then follow the reaction by absorption or emission spectroscopy. The simple organic molecule stilbene provides a test system for both activated and activationless processes. As figure 3 shows, the isomerization of *trans*-stilbene in the excited state into *cis*-stilbene involves an activation barrier, whereas the isomerization of excited *cis*-stilbene into *trans*-stilbene appears to involve no barrier.

In the absence of a barrier there is no time scale separation between reactive motion and the rate of reaction, and so the possibility exists of directly observing the motion of a reacting molecule along the reaction coordinate. (The reaction coordinate is a one-dimensional representation of the multidimensional path connecting reactants and products by the lowest-energy route; the reaction proceeds along the reaction coordinate.) The lack of time scale separation also makes barrierless reactions very fast, and systematic studies have been possible only recently. Studies on *cis*-stilbene isomerization have been carried out by Robin Hochstrasser and Fleming. Figure 4a shows the fluorescence decay of *cis*-stilbene dissolved in isopropanol following excitation with a subpicosecond pulse. That this decay represents progress in the reaction is shown by the fluorescence polarization anisotropy (figure 4b). The optical transition moments of *trans*- and *cis*-stilbene make an angle to one another. Thus as the molecule twists, the transition moment rotates in the

molecular frame, leading to depolarization of the fluorescence. The blue curve in figure 4b shows the behavior that would be expected if the depolarization arose from overall molecular tumbling. The red curve shows the predicted behavior when a 20° rotation of the transition moment is added to the overall tumbling.

The influence of solvent viscosity on this reaction is rather weak: The reaction time increases from 1.0 psec to 1.4 psec as the viscosity is increased from 0.32 centipoise (hexane) to 2.43 centipoise (tetradecane). A quantitative description of this simple prototype reaction will probably require multidimensional consideration of the reaction and consideration of the time dependence of the solvent friction at these very short times.

Activated processes

Most chemical transformations are considerably slower than the molecular motions we have just discussed. This is not because particularly sluggish movements are required but because at the level of an individual molecule most reactions are rare events. At any one time only a small population of molecules are "activated" and participating in chemical reaction events. If the energy of the activated molecules must exceed that of the reactants by E , the reaction rate will be proportional to $e^{-E/kT}$. The fact that many activation energies are much larger than the thermal energy kT explains the dramatic range of reaction rates. The rareness of activated molecules is also a source of frustration in experimental kinetics, because the crucial activated molecules cannot be readily studied due to their low concentration.

In the 1930s researchers realized that by identifying activated molecules as those at a saddle point on the potential energy surface, they could use the methods of equilibrium statistical mechanics to calculate their concentration. Molecules at a saddle point crossing toward the product are likely to continue to fall down the hill and

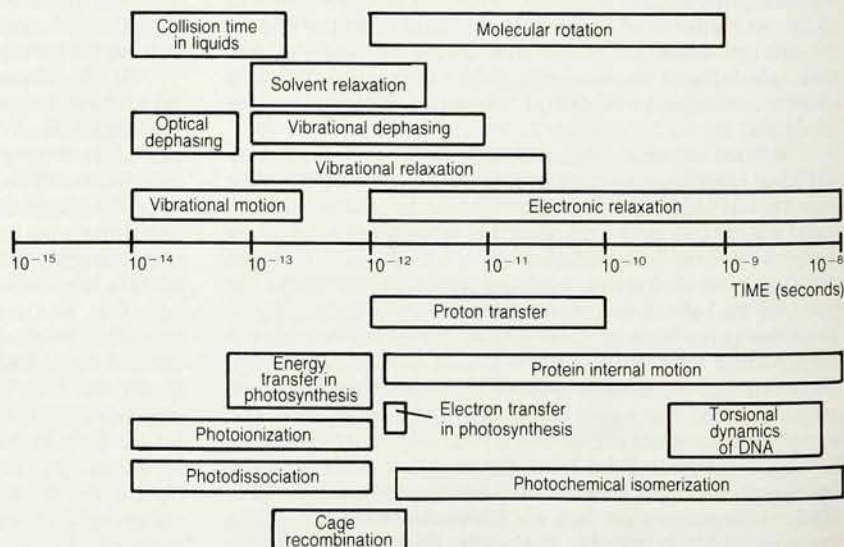
react. The transition-state theory *Ansatz*, or assumption, is that reactive trajectories cross through the saddle point once and only once on their way to the product. This theory then gives an expression for rate constants involving only thermodynamic information about the transition state:

$$k_{\text{TST}} = (\omega_0/2\pi) e^{-F/kT}$$

Here ω_0 is the frequency of motion of reactants in the reactant potential well, and F is the free-energy barrier. Whether the transition-state *Ansatz* is correct depends on the details of molecular motion.

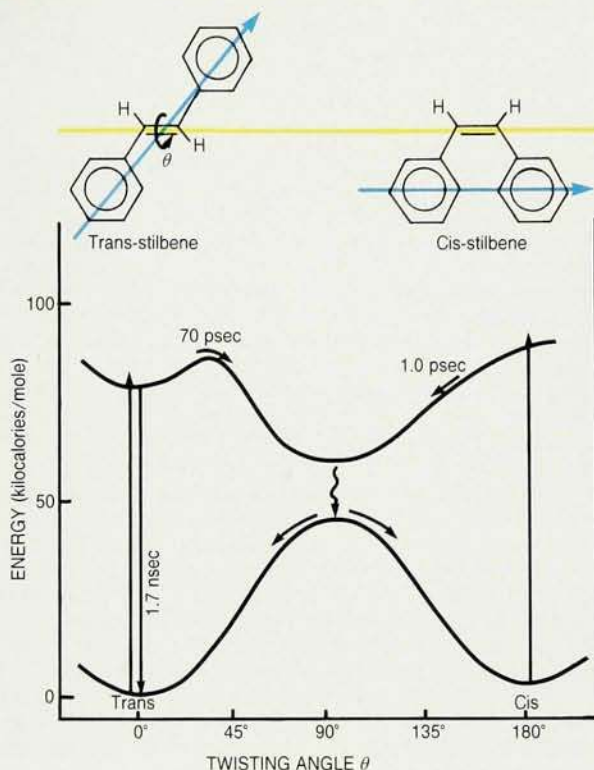
Even for simple chemical reactions, the condensed-phase environment can change the way molecules move through the transition state. The friction and random forces arising from a condensed-phase environment can affect the rare, activated trajectories just as they do the ordinary, nonactivated molecular motions. The role of friction in activated processes was first explored by Hendrik Kramers 50 years ago.⁵ In the late 1970s chemical physicists rediscovered many of Kramers's results, using the formal techniques of nonequilibrium statistical mechanics and linear-response theory. They were also able to connect these theoretical results with experiments.

There are two ways in which friction from the solvent affects motion through the transition state. If the friction is large, the system will undergo Brownian or diffusive motion through the transition state. This will lead to many recrossings of the saddle point, as indicated in figure 5a. Using simple arguments from random-walk theory, one can show that the number of recrossings is roughly proportional to the width of the transition-state region divided by the mean free path for the motion of the reaction coordinate.⁶ The width of the transition-state region here refers to the distance from the saddle point at which the system has lost enough energy to make it



Time scales typical of chemical and biological dynamics. The upper half of the figure illustrates the range of times for a number of elementary relaxation processes. The lower half illustrates the time scales on which some typical chemical processes occur in solution. The box lengths indicate the time ranges. **Figure 2**

Isomerization energy barriers for ground-state stilbene (lower curve) and excited-state stilbene (upper curve). These one-dimensional potential energy surfaces are schematic. A large barrier separates the *cis* and *trans* isomers on the ground-state surface, but not on the excited-state surface. In this one-dimensional model the reaction coordinate involves twisting about the carbon-carbon double bond. The isomerization of either isomer in the excited state to the other isomer is postulated to occur via the same intermediate, for which the twisting angle θ is 90° . The arrow through the structure diagram of each isomer shows the direction of the dipole moment associated with the transition from the ground state to the first excited state. The time constants indicated refer to measurements in hexane solution. **Figure 3**



unlikely that thermal motions will return it to the saddle point. Because the transition-state theory counts each of these recrossings as a reaction event, one must apply a correction factor. This transmission coefficient is inversely proportional to the number of recrossings. In the high-friction case, the transmission coefficient decreases with the friction on the reaction coordinate.

The transition-state *Ansatz* also fails in the limit of weak friction. Some friction is required to activate the system and to trap it after it has left the transition state. If no friction is present, recrossings will occur (figure 5b). For very weak friction, the number of recrossings is inversely proportional to the friction constant, and in this regime the rate coefficient will rise as the friction increases. Indeed, even before Kramers, chemists had thought about this regime in trying to understand how activation, the inverse of trapping, occurs in gas-phase unimolecular reactions.

In general, both of these effects of friction will enter into any condensed-phase chemical reaction. Thus one expects a nonmonotonic relationship between rate and friction, as figure 5c indicates.

Much of the work of the last decade has aimed at collecting experimental data with which to confront these ideas about the effects of friction on reaction rates. This work has led to new insights into the details of molecular reaction events in liquids. Two especially fruitful systems for investigation have been the isomerization of the excited state of *trans*-stilbene as studied through picosecond spectroscopy and the boat-chair interconversion of cyclohexane as studied through nuclear magnetic resonance spectroscopy.⁷

The full range of behavior depicted in figure 5c has been obtained for activated isomerization of excited *trans*-stilbene (figure 3) in experiments ranging from supersonic expansions to low- and high-pressure gases and liquid solutions. Figure 6 shows how the rate of isomerization changes as friction is varied over six orders of magnitude.

(Following the suggestion of Jürgen Troe, we use the inverse diffusion coefficient as the friction measure, so that data from the gas phase and solution can be plotted on a single curve.) The qualitative features of figure 5 are clearly apparent. The "Kramers turnover" occurs on the borderline of gas and liquid, and in solution the reaction rate always decreases as viscosity is increased.

Efforts to describe quantitatively data such as those in figure 6 have led to a number of significant ideas. One of these, addressing the role of the frequency dependence of the friction, was first investigated by Richard Grote and James T. Hynes at the University of Colorado.⁸ They pointed out that the motion through the transition state, even in reactions with moderate barriers, may well be so rapid that not all solvent fluctuation modes will be effective in damping the motion. They showed that in the moderate-to-large friction regime one can generalize the Kramers expression in an elegant way: The expression remains intact but the friction coefficient in it is evaluated at a finite frequency. This frequency is the one associated with the unstable mode at the saddle point and must be self-consistently determined, because it depends on the friction itself. Most of the friction in viscous fluids arises from fluctuations on time scales longer than that of the motion across the transition-state region, and the Grote-Hynes expression, when combined with hydrodynamic modeling, gives results that are consistent with the stilbene experiments.

There are still many puzzles connected with the high-friction regime. Qualitative features of the dependence of reaction rates on friction in this regime can be understood with the Grote-Hynes theory, but rigorous tests are difficult because direct information on frequency-dependent friction is still scanty. The mechanism of friction in very viscous fluids is still the subject of controversy and may be connected with the mysteries of the liquid-glass transition.

The *trans*-stilbene isomerization is in the high-

friction regime in normal liquids, however, in such liquids the cyclohexane isomerization exhibits the entire range of behavior from the low-friction to the high-friction regime. Jiri Jonas and his coworkers at the University of Illinois were able to study this isomerization in a variety of solvents using pressure as an experimental variable. Pressure provides a particularly useful tool for getting at the corrections to transition-state theory because frictional effects are strongly dependent on pressure. It was a great surprise to many people that low-friction effects could be seen in a chemical reaction at liquid-state densities. The expectation was that energy flow from the reaction coordinate into other internal degrees of freedom of the cyclohexane molecule would be so rapid that recrossings of activated molecules through the saddle point would be rare. The high collision rate in dense fluids was thought to ensure that activation and trapping would not be rate limiting. On the other hand, the cyclohexane data can be explained if the intramolecular energy flow is at least partially inhibited, so that the reaction coordinate's coupling to the solvent environment dominates.

Bruce Berne at Columbia University has pointed out that restricted internal energy flows can be understood using chaos theory.⁹ Some trajectories through the transition state have regular, nonchaotic motion, and these trajectories are the ones that can be affected by solvent friction. David Chandler and his coworkers at the University of California, Berkeley, using stochastic dynamics computer simulations, have shown that this is indeed the explanation for the cyclohexane data.¹⁰

Solvation dynamics

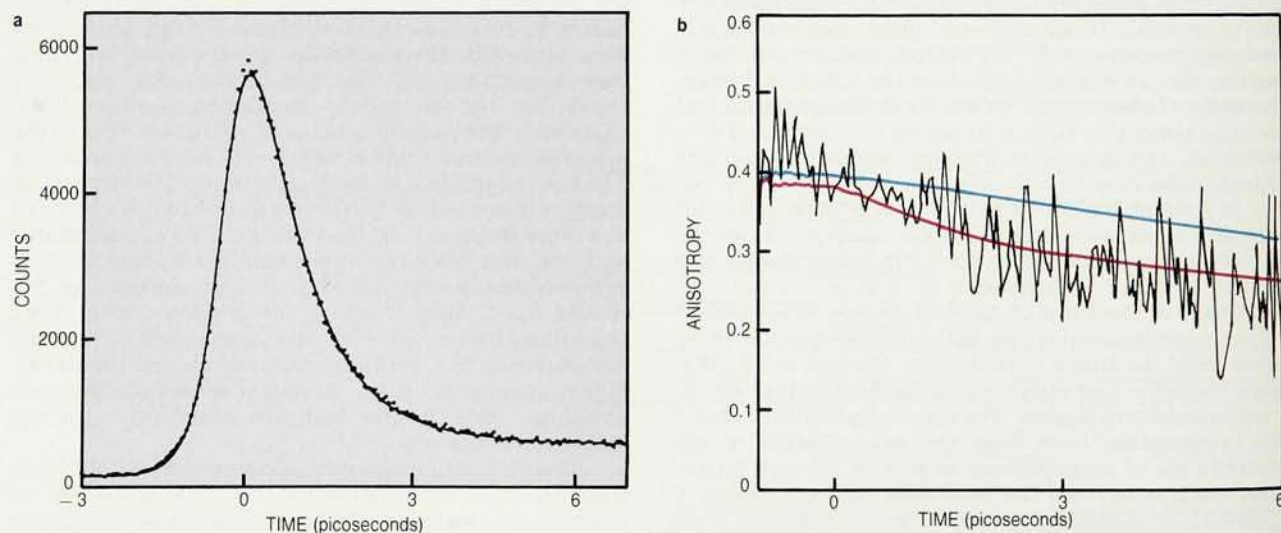
A condensed-phase environment can profoundly change the energetics of a chemical reaction. This is especially true when the reaction involves the transfer of charge, as do the fundamental processes of oxidation-reduction and

acid-base neutralization. The interaction energy of a charged species with a solvent can approach chemical binding energies, and the dynamics of solvation plays a role in charge-transfer reactions. Because the interaction of a charge with the solvent environment is long range, solvation is a collective phenomenon. Recently, picosecond spectroscopy has allowed direct observation of the formation of the solvation sphere around charged solutes.¹¹ These observations rely on the fact that picosecond laser pulses can induce charge transfer or internal charge rearrangement. A variety of other probes, such as nmr spectroscopy, and transport measurements such as electrical conductivity also give information about the dynamics of the solvation shell.

Because solvation is collective and involves long-range forces, it is natural to use continuum theories to explain it. The continuum theory of ionic solvation was first put forward by Max Born 70 years ago. Dynamically, a dielectric continuum is characterized by a frequency-dependent dielectric constant:

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 \epsilon_{\infty}}{1 + i\omega\tau_D}$$

Here ϵ_0 and ϵ_{∞} are the zero-frequency and infinite-frequency dielectric constants, respectively. The time scale τ_D is on the order of the molecular rotation times, as shown by Peter Debye in 1929. The continuum theory gives a surprising prediction for solvation dynamics, however. When the time-dependent continuum electrostatic problem is solved, one discovers that the solvation polarization forms on a time scale called the longitudinal relaxation time τ_L and given by $(\epsilon_{\infty}/\epsilon_0)\tau_D$. For highly polar solvents, this longitudinal time is considerably shorter than τ_D . The reason it is shorter is that charge is separated in the environment by the solute ion, and this separation of charge sets up an electric field that acts to



Fluorescence decay of *cis*-stilbene dissolved in isopropanol, following excitation with a subpicosecond pulse. **a:** Decay of fluorescence from the excited singlet state. The decay results from motion along the reaction coordinate shown in figure 3. **b:** Decay of anisotropy in the polarization of the fluorescence. The blue curve is from a model in which only overall molecular tumbling depolarizes the fluorescence. The red curve includes in addition a 20° rotation of the transition moment on the same time scale as the population decay shown in **a**. **Figure 4**

force quicker return to equilibrium. Although this continuum calculation is straightforward, it was not until the advent of picosecond experiments that the importance of the longitudinal relaxation time scale became well known.

Interest in the time scale of solvation was piqued by a cryptic remark made by Lars Onsager in a discussion at a 1976 conference. In talking about the spectroscopy of the solvated electron, he argued that the solvent far from a localized electron would relax to equilibrium faster than the solvent near the electron, and so the solvation structure around the electron would form from the outside in! It is clear that Onsager knew about the continuum dielectric theory, but we shall never know exactly how he came to this counterintuitive notion about solvation dynamics because he died shortly after the meeting.

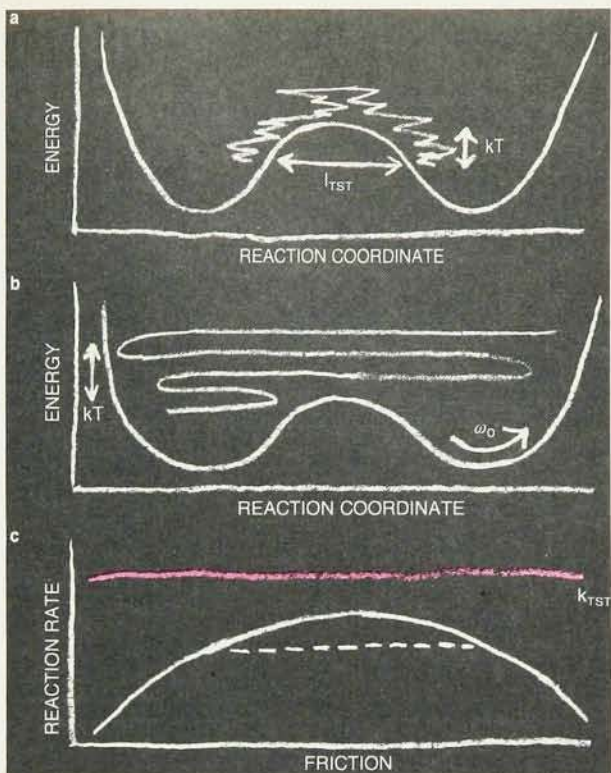
In 1983 Daniel Calef and Peter Wolynes showed how one could develop a molecular theory of solvation dynamics using a generalization of the Vlasov equation from plasma physics.¹² This molecular theory did indeed show the Onsager effect—that is, the solvation structure formed more rapidly far from the ion than close by. Wolynes also developed a more easily used dynamic theory based on the mean spherical approximation to a static solvation structure.¹² This theory leads to a longer time scale for solvation in the nearby shells. These theories have all been developed further, and many new dynamical effects have been included. Translational as opposed to rotational dynamics can often dominate in the first solvation shell, as was intimated in a molecular theory of ion mobility developed by Peter Colonomos and Wolynes.¹³ The work of Biman Bagchi at the Indian Institute of Science in Bangalore has emphasized the importance for the solvation dynamics of translational motion in the dynamical behavior of the first solvation shell.¹³ Translational motions speed up the response of the first shell, and this can lead to the bizarre-sounding result that the overall solvation process calculated by the molecular theory looks like that of the simple continuum model (which considers only rotational motion) only when there is a significant translational component to the response.

Several large simulations of solvation dynamics have been carried out, the most detailed being on water and acetonitrile.¹⁴ The resulting picture is very different from Onsager's conjecture. In both water and acetonitrile the solvation dynamics are dominated by very rapid collective motions in the first shell.

Experimental studies have confirmed many aspects of the molecular description of solvation. Paul Barbara's experiments at the University of Minnesota on solvation in water are in reasonable accord with the simulation results.¹⁵ However, experiments with time resolution adequate to reveal the predicted ultrafast oscillatory behavior have not yet been carried out.

Electron transfer

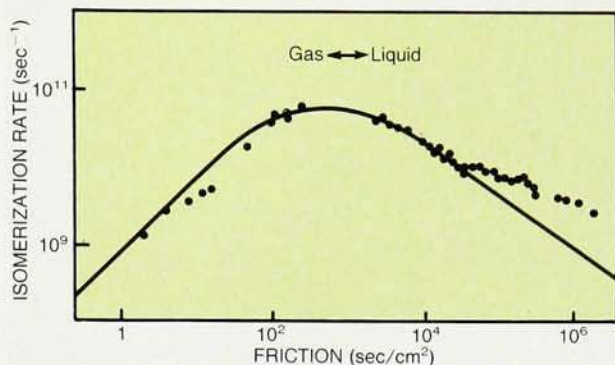
Electron-transfer reactions are among the most interesting reactions in solution, because they involve collective solvation dynamics, activated processes and quantum phenomena. Investigators realized rather early that electron transfer involves quantum mechanical tunneling of the electron itself. We reached an important milestone in our understanding when Rudolph Marcus pointed out that nuclear rearrangements and solvation are also necessary. The charge digs a rather deep potential well by



Reaction barriers. **a:** At high friction, the number of steps that a Brownian walk takes in the transition region is given by $N = (l_{TST}/\lambda)^2$. (Within the width of the transition region l_{TST} , the potential energy is within kT of the barrier height; λ is the mean free path of the Brownian motion.) The fraction of these steps at the crest is λ/l_{TST} , and so the number of crossings of the crest is given by $N_C = l_{TST}/\lambda$. **b:** At low friction and for one-dimensional motion, trapping occurs at the trapping time τ_{trap} , when the reaction coordinate loses kT of energy. Since $\tau_{trap} \xi \langle v^2 \rangle \approx kT$, we have $N_C = (\omega_0/2\pi) \tau_{trap} \propto \xi^{-1}$, where ξ is the friction. **c:** Expected dependence of reaction rate on friction. The transition-state rate k_{TST} is an upper limit for the rate. The dashed curve is the rate for the process when a nonadiabatic correction is included. **Figure 5**

solvating, so that in general the electron may not immediately transfer to the acceptor species, since the acceptor orbital is not in resonance with the differently solvated donor. Nuclei must be rearranged and solvent molecules moved in such a way that the electron has equal energies on the donor and the acceptor for tunneling to occur. The transition state for electron transfer therefore involves nuclear configurations that only partially solvate the donor and prematurely solvate the acceptor ions. The change in solvation energies creates the barrier to reaction.

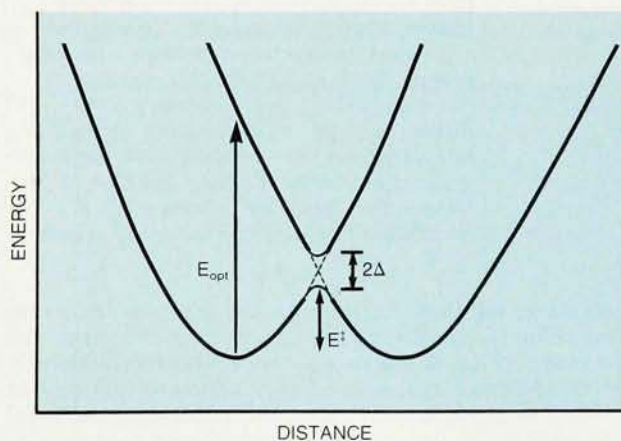
A central notion of Marcus's theory is that one can treat the environment's response to the charge as approximately linear. In that case one can draw a schematic reaction diagram, like the one in figure 7, consisting of intersecting parabolas. Electron tunneling occurs most easily where these curves cross. If the tunnel splitting (2Δ in the figure) is sufficiently large, the process will be adiabatic and the nuclei will follow the lower-energy



Isomerization rate of *trans*-stilbene as a function of friction, showing the Kramers turnover. The solid line is from a calculation by Jürgen Troe and his coworkers at the University of Göttingen.⁷ The deviation at high friction may be due to frequency-dependent friction. At high friction it is also likely that the proportionality between the inverse diffusion coefficient and friction breaks down, even for low-frequency motions. **Figure 6**

surface. But if the splitting is small, the transit will be nonadiabatic and the system will go through the crossing point with only a small probability of electron tunneling; the system will then be found on the excited surface. The problem of a charge interacting linearly with its environment is very similar to the problem of polaron transport in crystalline solids. A school of researchers in the Soviet Union, led by Benjamin Levich and Ravaz Dogonadze, used this analogy fruitfully starting in the late 1950s.

Marcus's assumption of a linear response has some



Marcus energy diagram. In the absence of electron tunneling, the energy surfaces in a reaction diagram are intersecting parabolas. The curves that result from the presence of tunneling are split by 2Δ at the crossing. The probability of remaining on the lower surface is $(\Delta^2/2\pi)\hbar FV$ when Δ is small. Here F is the slope of the unperturbed surfaces and V is the velocity at the crossing. E_{opt} is the energy required for an optical excitation between the two electronic states; E^1 is the energy of the transition state. **Figure 7**

surprising consequences that have been observed experimentally. Because the reaction coordinate involves solvent motions, it can be very similar for chemically different reactants that have similar charge distributions. It is easy to find families of compounds that have potential surfaces that are essentially the same shape but whose minima sit at different energies. The geometry of intersecting parabolas then implies a nonmonotonic relationship between the activation barrier and the exothermicity of the reaction. Normally reactions become faster as they become more exothermic, but Marcus's linear-response assumption predicts that very exothermic electron-transfer reactions will be slow. Unambiguous evidence for this was not discovered until 30 years after publication of his theory.¹⁶ Marcus's theory, incidentally, used a continuum analysis, à la Born, to estimate the activation barriers. Although experiments often exhibit the trends obtained in that continuum calculation, more detailed investigations show deviations requiring microscopic theories. One surprising result of microscopic theories and simulations is that even when molecular effects are important, the linearity assumption is a good one.

How do the details of solvent motion affect the rates of electron transfer? If a single transit of the intersection region in the transition state occurs, the rate given by the transition-state theory is modified by a transmission coefficient reflecting the probability of a change in the electronic state. For small tunnel splittings the rates then depend on the splitting. Classical probability arguments that take into account multiple crossings give a transmission coefficient like the one indicated by the colored line in figure 5c. There is a large plateau in the rate-vs-friction curve (the dashed line in figure 5c) across which the "golden rule" estimate is valid, and there are high- and low-friction regimes in which the results of single-surface dynamics apply. This classical probability argument is correct when the phase of the quantum system becomes randomized between transits of the crossing. This is a good approximation for high damping, but for low damping there are resonance effects that can be taken into account by keeping track of probability amplitudes.

The studies of nonactivated solvation dynamics suggest that the collective reaction coordinate for electron-transfer reactions in solution will usually not be highly underdamped. In this case the single-surface transmission coefficient that applies when there are many crossings will be proportional to τ_L^{-1} , the reciprocal of the longitudinal relaxation time. Michael J. Weaver at Purdue University has made some beautiful studies of electron-transfer reactions that appear to confirm this behavior.¹⁷ Using a series of electron-transfer reactions with similar activation energies but different tunneling matrix elements, he was able to show that nonadiabatic dynamics and solvent dynamics do compete, as theory predicts.

Finally, quantum dynamics plays a role.¹⁸ Arieh Warshel at the University of Southern California has simulated this role using classical dynamics and approximations based on polaron theory. Theorists have also been able to carry out simulations of the liquid that take account of tunneling, using path integral quantum Monte Carlo methods. Figure 8, a picture from studies by Andrew McCammon at the University of Houston and his coworkers, illustrates the quantum paths involved in the rearrangement of the inner sphere in an electron-transfer reaction. Recently Chandler and others have also used the path integral Monte Carlo techniques, to evaluate the role of quantum dynamics in the more distant solvent mole-

cules; they have concluded that the motions of the hydrogen atoms in the solvent can be dominated by tunneling. Measured isotope effects on the rates agree with this.

Future work

On the theoretical side, there remain many challenges in the study of solution-phase dynamics. Clearly, the concept of friction has played a useful organizing role in investigations of rate phenomena in solution. In the future we will be faced with understanding the limits of this concept. Limits will appear in the case of very viscous fluids, where the mechanism of friction may change, and in the regimes where quantum mechanics plays a role. The role of chaotic motion in determining energy flow requires more attention, and here the quantum theory is still far off. Simulation technology has advanced rapidly in the last decade, but challenges remain. Even in classical dynamics, the models used in electron transfer are far from universally adequate. We know from theory that the polarizability of solvent molecules must be important in determining dynamic time scales, yet polarizability has not been included in the simulations directly. While some quantum effects can be treated with the dispersed-polaron methods or path integral methods, many real-time quantum effects, such as resonances, have not yet been explored with simulations in many-body systems.

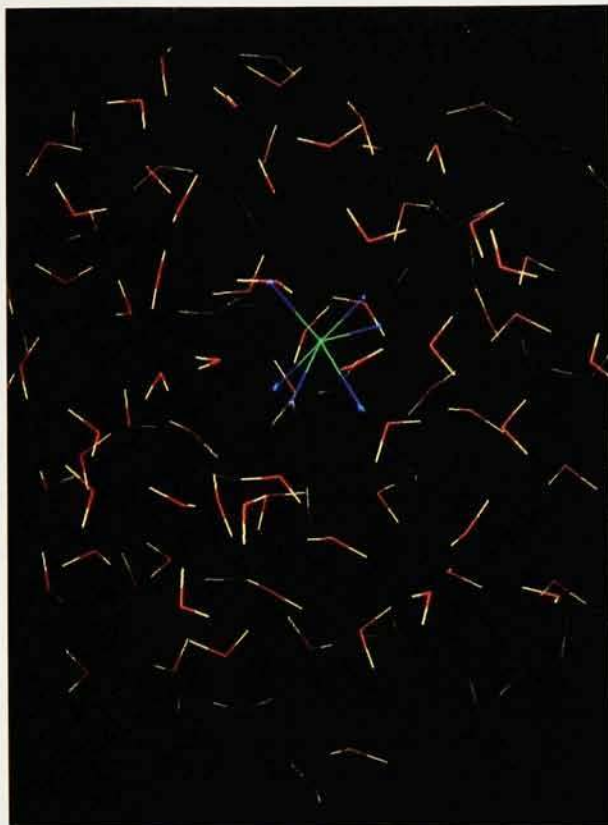
We are certain that other theoretical developments will be necessary, because even in the case of simple isomerizations the confrontation between theory and experiment demanded new ideas. This confrontation has only begun in the more complicated areas of electron transfer and quantum dynamics. There are surely more surprises in store for us.

On the experimental front a number of provocative possibilities are beginning to emerge. It is now possible to control the relative phase of sequences of femtosecond pulses. An exciting outcome of this capability is the potential to control chemical reactions. The combination of phase and timing control will allow us to use pulse sequences to move wave packets selectively from one potential surface to another, thereby, for example, directing the system along one product channel rather than another. Initial applications are likely to be in gas-phase systems. In solutions, molecular dephasing times are so short that pulses at the limit of current technology—6 fsec—will be necessary.

The development of high-repetition-rate amplified laser systems will also enable experimenters to make much greater use of infrared and Raman spectroscopy to follow vibrational energy flows in reacting systems. The greatly increased sensitivity resulting from the high repetition rates should allow direct observation of the motion of solvent molecules during reactions and provide a basis for a molecular understanding of friction.

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Simulation of the inner coordination sphere of the transition state for the redox reaction between $\text{Co}(\text{NH}_3)_6^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$. Chong Zheng at the University of Houston and his coworkers did this calculation using path integral Monte Carlo methods.¹⁸ The quantum delocalization of the ammonia molecules (represented by blue lines) is small but significant for the reaction rate. The red and yellow V-shaped structures are water molecules. **Figure 8**

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