ing his kinship theory of genomic imprinting (*3*), individuals in a colony or society are not single-purpose agents but may be torn by opposing interests. For example, genes that program either rapid dispersal of offspring or greater parental care of offspring can result in different outcomes depending on whether the gene is inherited from the father or the mother. Expression of a gene for rapid dispersal of offspring shortens the weaning period, a great advantage to the mother, and so it is more likely that a maternal rather than a paternal copy of this gene will be expressed.

The common language of the meeting was evolutionary game theory, which assumes that a particular type of behavior (strategy for interacting with other members of a group) is more likely to spread within the group if it leads to success (*4*). Mathematicians developed game theory about 50 years ago to explain the economics of human societies. Despite its popularity, game theory was slow to catch on among skeptical economists. It was not until evolutionary biologists applied game theory to explain behavioral traits in social animals—such as sentinels providing the alarm call for their threatened colony and putting themselves at risk of being spotted by the predator (an unselfish behavior)—that mainstream economists became more receptive to game theory.

Evolutionary game theory (*5*) can explain a diverse spectrum of social behaviors—such as, conflict, cooperation and coordination—confirming, as Robert May (Oxford University, UK) stressed in his address, that very simple rules can explain the complex behavior of societies (*6*). With a few party hats and cunningly simple games such as "the Centipede game" (*7*) (see the figure), Andrew Colman (University of Leicester, UK) clearly demonstrated that game theory enables irrational behavior in humans to be observed. There are few better examples for demonstrating how irrational behavior can actually benefit economic exchange than the "Public Goods" game. Four persons are given $10 each by the experimenter, and asked (independently) to invest any part of it into a common pool. The experimenter then doubles this common pool and distributes it evenly among the four players. If all players invest their whole sum, they can double it. But the temptation to freeload is strong because players get back only half of their own offerings. Nevertheless, a substantial number of the players contribute a lot. But if the game is repeated for a few more rounds, the players learn quickly to defect; soon, all contributions are negligible—and so are the earnings, of course. The whole game changes dramatically, however, if the players can, at the end of each round, punish their less generous coplayers by fining their accounts. This punishment is economically irrational, because the fines return to the experimenter, not to the punisher; in fact, the rules request that punishers have to pay half as much as the fine they impose. In his talk, Ernst Fehr (University of Zurich, Switzerland) showed that, nevertheless, the tendency to engage in this costly (and irrational) form of punishment is widespread, and its effect is beneficial: Players invest for fear of being punished (*8*). As Mark Twain put it, "the surest protection against temptation is cowardice."

Punishment is a newcomer to the long list of possible factors influencing cooperation among individuals, which includes kinship and reciprocal altruism (where an act of generosity is returned either by a recipient or a third party). Reciprocal altruism has been demonstrated in animals as diverse as stickleback and cichlid fish, chimpanzees, and undergraduates (*9*). The possibility that cooperation is based on reciprocal altruism (that is, whatever we do, we expect some sort of return) becomes less likely as the size of the group increases because, in larger groups, the interactions among individuals are more numerous and more complex. This is particularly intriguing as group size may well have been the decisive factor enabling *Homo sapiens* to displace its Neanderthal ancestor (*10*)—larger groups meant pressure for selection of genes that favored intricate neural pathways (*11*) and the greater communication capabilities of language (*12*).

The development of human language is a recent evolutionary transition. Language consists of words and the grammar rules that arrange them. Words are stored in a person's mental lexicon, whereas rules are generated by a computational grammar book that enables us to produce an infinite number of sentences. Understanding how language evolved is one of the great challenges still facing evolutionary biologists. By building models of language that interface with linguistics, computer science, and learning theory, we soon should be able to explain how natural selection enabled the emergence of our universal language capabilities.

Early philosophers—such as, Hobbes, Rousseau, and Hume—realized that economic exchange is dominated less by rational deliberation and more by a set of instincts (human nature). Now we are ready to design experiments, encompassing both natural and social science, to test models of human nature, thus allowing these two scientific worlds to merge.

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PERSPECTIVES: CHEMISTRY

Stretched Water Is More Reactive

George C. Schatz

Two reports in this issue on pages 958 and 961 (*1*, *2*) present important new results on a topic of long-standing interest to chemists, namely how reagent vibrational motions influence the dynamics of chemical reactions. This topic is particularly important for "activated" reactions, in which a potential energy barrier must be overcome for the reaction to occur. The barrier can sometimes be overcome more efficiently by exciting vibrational modes of the reagents than by supplying the same amount of energy in the form of heat. Branching between different products can also be controlled by vibrational excitation. Thus, the control of chemical reaction rates by vibrational excitation has been a long-sought goal in chemistry (*3*). There has also been much interest in determining the amount of excitation in the vibrational modes of the products, which provides a signature of the path by which the reaction occurs.

We often think of barriers to chemical reactions in terms of a simple diagram showing the energy along the reaction path from reagents to products (see the first figure). The barrier along this path limits the reaction rate. If the reagent energies are governed by a thermal (Boltzmann) distri-

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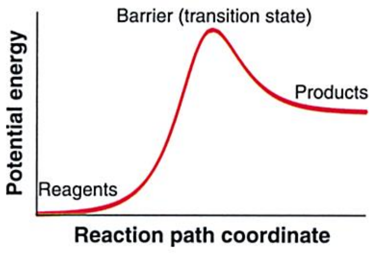
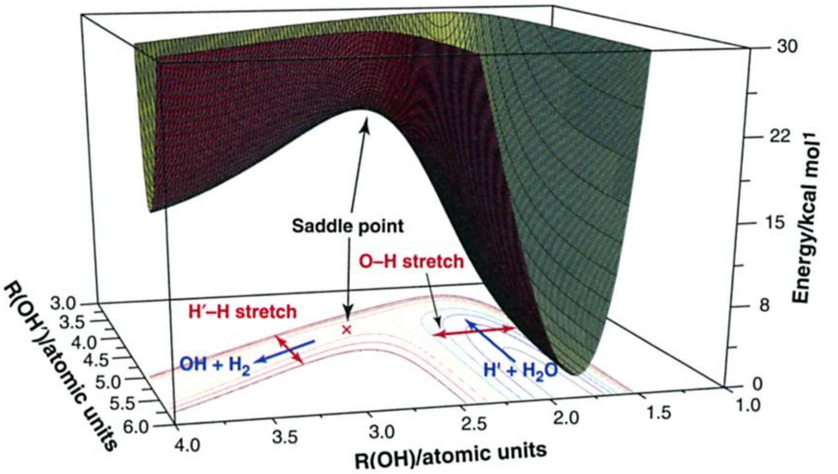
bution, then the probability that the system will have enough energy to get over the barrier drops off exponentially with barrier height. This leads to the well-known Arrhenius formula for the reaction rate.



Energy along reaction path for a typical activated endothermic reaction.

In this simple picture, motion from the reactants to the products is governed by a single coordinate. In reality, however, this motion involves many degrees of freedom, corresponding to the vibrations and rotations of the reacting molecules in addition to the translational motion that brings the species together. Vibrational motions play an important role in the reaction considered in (*1*, *2*), $H + H_2O \rightarrow OH + H_2$. To visualize the effect of vibrational motion in this reaction, the second figure presents contours of the energy surface that determines the forces on the atoms while reaction occurs. The four-atom system has six internal degrees of freedom, but only two are included in the figure: the O–H bond that breaks and the O–H′ distance associated with the attacking H atom (labeled H′). This is an endothermic reaction so the products lie above the reactants. Also, there is a 22 kcal/mol barrier that corresponds to a saddle point on the surface.



Potential energy for the $H + H_2O$ reaction as a function of the O–H and O–H′ distances. The atom labeling is H′ + H–O–H″ → H′–H + O–H″. The energy function, which has been minimized with respect to the coordinates not plotted, is based on electronic structure calculations (*10*) that are very similar to those presented in Fig. 1 of (*2*). At the top, a perspective plot of the surface is shown. Contours of the same surface are shown at the bottom. Blue arrows on the contour plot indicate motion along the reaction path in regions corresponding to the approaching reagents and the departing products. Red arrows indicate directions associated with O–H stretch vibration in the reagents and H′–H stretch vibration in the products.

The figure shows how vibrational modes can influence the reaction dynamics. In the $H + H_2O$ (reagent) region, motion along the bottom of the potential energy valley brings the reactants together, whereas the O–H stretching motion in water is perpendicular to the reaction path. In the $OH + H_2$ (product) region, the reaction path corresponds to H_2 separating from OH, and the perpendicular vibration is the H′-H stretch.

The barrier on the potential surface occurs at a geometry more like the products than the reactants. The O–H stretch excitation in the reagent valley pushes the system toward this barrier. The real picture is more complicated, however, because the four additional internal degrees of freedom that are not plotted can also influence reaction. In addition, O–H stretch motion is a superposition of the two stretch modes of water, and it is not possible to excite the OH stretch alone in a conventional photolysis experiment.

A reaction is considered "mode-specific" if it is preferentially accelerated by exciting some vibrational modes but not others. The $H + H_2O$ reaction has served as a prototype for mode-specific bimolecular reactions for nearly 20 years. Early theoretical predictions (*4*) of mode-specific behavior in this reaction stimulated the first mode-specific experiments by Crim and co-workers (*5*), who studied states with three or more quanta of OH stretch excitation, and by Zare and co-workers (*6*), who emphasized states with one quantum of excitation. These experiments demonstrated the effect, but important issues remained open. They are finally addressed in (*1*) and (*2*).

Strazisar *et al.* (*1*) consider an isotopic counterpart of the reverse reaction, $OH + D_2$. They use crossed molecular beam experiments to determine the distribution of vibrational states of the HOD product. The results indicate that the energy is preferentially released into the O-D stretch mode, with much less excitation of the HOD bend. The results are in excellent agreement with recent theoretical predictions (*7*) but are substantially different from earlier theory, indicating that the energy surfaces used in the earlier studies were inaccurate.

Zhang *et al.* (*2*) present quantum dynamics simulations of the $H + H_2O$ reaction using energy surfaces that are much more accurate than in earlier studies. The resulting high-quality estimates of cross sections for H atom abstraction and exchange reactions are used to test experimental measurements. In addition, new estimates of mode-specific reaction rate coefficients are provided that are in excellent agreement with the results of Crim and coworkers. These estimates again show that O–H stretch excitation efficiently pushes the system over the barrier to reaction, whereas bend excitation is much less efficient. The enhancement in rate coefficients associated with O–H stretch excitation is so large that the dominant state contributing to the thermal rate coefficient has two quanta of O–H stretch excitation. In other words, vibrational excitation "beats" the Boltzmann factor for this reaction.

The two studies provide a consistent picture of the role of vibrations in the $H + H_2O$ reaction. We learn that this reaction is strongly mode-specific, with much larger enhancements in reactive cross sections or rate coefficients for excitation of the stretch modes than for that of the bend modes. Perhaps this should not be surprising for reactions involving water, because the O–H stretch mode connects in a straightforward manner to motions leading to reaction. Similar behavior has been found in other reactions involving molecules with OH or CH stretch modes, such as $Cl + H_2O$ and H + HCN (*8*). These studies provide important guidance to current efforts to observe vibrational excitation effects for reactions in liquids and on surfaces (*3*, *8*, *9*).

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