conducted in low-density, pioneer vegetation in the desert, such tests need to be repeated in regions with more diverse, dense vegetation. Also, the time scale of future studies should be longer. Kessler and Baldwin's experiments were probably conducted over too short a period to enable them to observe the full behavioral repertoire of all organisms in the food web and the complete range of interspecific interactions. Indeed, anyone undertaking a critical cost-benefit analysis needs to be aware that apparently beneficial interactions are never foolproof and that their outcome may vary between parasitism at one extreme and mutualism at the other, depending on the conditions (*11*). Nevertheless, Kessler and Baldwin have taken an important first step toward unraveling the nature of direct and indirect plant defense.

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A Light-Driven Linear Motor at the Molecular Level

Jean-Pierre Sauvage

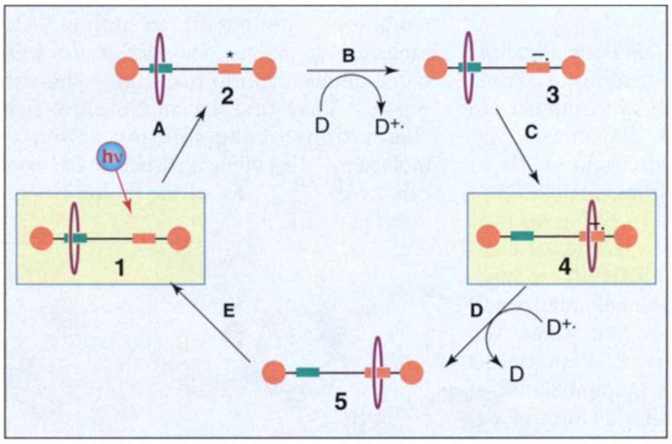
Molecules called catenanes (interlocking rings) and rotaxanes (a dumbbell threaded through a ring) have experienced a spectacular revival during the past 15 years. Until the beginning of the 1980s, they were considered interesting laboratory curiosities but suffered from the fact that they could be prepared in tiny amounts only (*1*), thereby precluding their detailed study or application.

The introduction of templated strategies to construct catenanes and rotaxanes dramatically changed their fate. Within a few years, they became synthetically quite accessible compounds, typically made on a scale of 0.1 to 1 g (*2*). Synthetic chemists could tune their properties by introducing appropriate functions and began to envision a bright future for materials made from these molecules. The post-1980s catenanes and rotaxanes display interesting properties, such as transition metal complexation, photochemistry, photoinduced electron transfer and luminescence, electrochemistry, and electrochromism. A second revolution occurred at the beginning of the 1990s, when chemists proposed that these compounds could form the basis of molecular machines and motors; the time for setting them into motion was ripe (*3*, *4*). New concepts were introduced, such as molecular "shuttles" (*5*), in which a ring moves at will along the string on which it is threaded, and controllable catenanes (*6*), in which a ring undergoes circumrotation within another ring with which it is interlocked. Soon, molecules other than catenanes and rotaxanes were used to build fascinating molecular machines made from synthetic organic compounds or DNA (*7*). Recent examples include rotary motors (*8*, *9*).

On page 2124 of this issue, Brouwer *et al.* show that an asymmetrical rotaxane, based on hydrogen bonding, behaves like a linear motor, reminiscent of the way a piston moves within a cylinder (*10*). The translational motions of the ring along the axle through which it has been threaded can be regarded as the power stroke of a piston in a given direction, followed by a recovery stroke in the opposite direction. The system is particularly remarkable because the "motor" is entirely driven by light (see the figure).

The motion has been demonstrated with a set of various physical techniques, the most important of which is time-resolved transient absorption spectroscopy, which almost allows the "visualization" of the shuttling process as a function of time. Until now, the "fuel" used to set molecular machines in motion was mostly electrochemical, chemical, or photochemical, the latter requiring the consumption of an added compound used as a "sacrificial" agent. In the previous studies, one could also isolate the different states of the machine. The beauty of the present system is that nothing but light is consumed. If the shuttle is pumped with laser pulses at the right frequency, the molecular machine can, in principle, generate mechanical power.

There are at least two reasons for designing, constructing, and studying molecular machines. First, such systems may be able to mimic essential biological processes involving motion, such as the rotary motor adenosine triphosphatase (*11*) or linear motors involved in muscle contraction and stretching (actin/myosin). Second, artificial systems may act as switches or as information storage and processing devices at the molecular level. Remarkable recent



Light-driven "power stroke" of Brouwer *et al.*'s molecular linear motor. In the resting state of the rotaxane (**1**), the ring preferentially interacts with the station on the left through hydrogen bonds. In step **A**, energy input in the form of light generates an excited state on the station on the right (**2**). The excited state has a strong electron-accepting character. In step **B**, it accepts an electron from an external electron donor D to afford **3**, with an extra electron on the station on the right. This negative charge enhances the affinity of the ring for this station. The ring moves to the right (step **C**) to afford **4**. By analogy with a piston, steps **A** to **C** can be considered as the "power stroke." This takes about 1 μs, after which the system returns to its original state ("recovery stroke"). The oxidized donor $D^{+\cdot}$ generated in step **B** is reduced back to D in step **D**, and the unstable species **5** thus generated leads to the starting form **1** by shuttling the ring back to the left. The recovery process is complete within about 100 μs.

The author is at the Institut Le Bel, Université Louis Pasteur, Strasbourg, France. E-mail: sauvage@chimie.u-strasbg.fr

results suggest that molecule-based computers may not be out of reach (*12*) and could be realized within one or two decades.

The concept of a light-induced power stroke on a molecular piston is, in itself, important. In addition, the report by Brouwer *et al.* opens the gate to other potentially valuable applications such as transport of given molecular species (particularly through a membrane), reminiscent of kinesin or dynein traveling along microtubules in cells (*13*).

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Water on the Move

Michael L. Klein

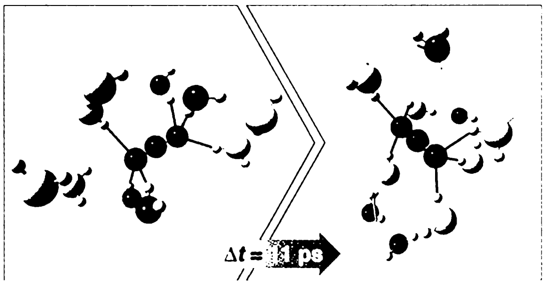
Water has an extraordinary ability to dissolve substances, enabling the transport of nutrients and trace elements vital to life. The polar nature of water and its propensity for forming hydrogen bonds are key to this ability. Insights into the structure and hydrogen bond dynamics of common salts dissolved in water have been gained from diffraction and ultrafast spectroscopy studies (*1–3*), but the dynamic behavior of the water molecules in the solvation shells of dissolved ions is only now being revealed. Computer simulations based on first principles molecular dynamics (Car-Parrinello or CPMD) (*4*) are providing an increasingly important complement to experimental data (*5–7*).

A pair of articles in this issue advances our fundamental understanding of simple ions in water. On page 2118, Kropman and Bakker (*8*) show that the dynamics of water molecules in the solvation shells of halide ions are much slower that those of the surrounding water. In doing so they overcome a substantial experimental challenge, arising from the difficulty of separating the signal from the solvating water molecules from that of the bulk water. And on page 2121, Geissler *et al.* (*9*) propose a new mechanism for the autoionization of water, which has been intractable for experimental and theoretical studies alike.

Kropman and Bakker use nonlinear spectroscopy to separate the spectral response of water molecules hydrogen-bonded to the halides Cl^-, Br^-, and I^- from that of the surrounding bulk water. The water molecules in the solvation shells of these anions move comparatively slowly, with mean lifetimes ranging from 12 to 20 picoseconds (ps) for 1 to 6 mol/liter NaCl solutions and 18 to 25 ps for NaI under similar conditions. CPMD studies have mostly focused on structures rather than lifetimes of aqueous solvation shells (*10*). However, a recent CPMD study of the azide anion (N_3^-) in water (*11*) suggests that the lifetime of its solvent shell (see the figure) is similar to those measured by Kropman and Bakker for halide anions. Their measurements will provide benchmarks against which to test future CPMD simulations.

Geissler *et al.* use CPMD (*4*), combined with transition path sampling (*12*), to unravel the basic mechanism that underlies the autoionization of water (*9*). Autoionization is an extremely rare event in which H_2O spontaneously dissociates into hydronium H_3O^+ and hydroxide OH^- ions. Under ambient conditions, only one in ten million water molecules is ionized. Geissler *et al.*'s technique allows them to track down this rare process. They find that rare electric field fluctuations of the solution acting on molecules surrounding a particular OH bond can drive the transfer of the proton along a chain (or wire) of hydrogen bonds, leading to the formation of separated hydronium and hydroxide ions. If the wire thus formed contains only two bonds, the nascent ions usually recombine within 100 femtoseconds (fs). Detailed analysis suggests that the hydrogen bond wire must contain between three and five bonds if it is to lead to a stable charge-separated state. This perspective on autoionization is new and leads to a prediction that transient (100 fs) populations of hydronium and hydroxide ions should exist in bulk water. The presence of these transient species in water cries out for experimental verification.

There is ample evidence in the literature that the CPMD approach quantitatively reproduces the properties of bulk water under a variety of conditions. The above discussion illustrates that such simulations are now being used with increasing confidence to probe the behavior of ions in solution. There is little doubt of the correctness of Geissler *et al.*'s computations and analysis (*9*), but the robustness of predictions must be assessed with respect to the approximations inherent in the methodology. A number of technical concerns, such as the small system size and absence of quantization of the nuclear motion (*13*), immediately spring to mind.



Dynamics of water molecules in the solvation shell of a dissolved N_3^- ion. Shown are two configurations separated by a time interval Δ*t* of 11 ps. The images were taken from a CPMD calculation (*10*), which used a periodically replicated simulation cell with a single azide anion plus 31 D_2O waters (1.8 mol/liter). Nitrogen atoms are blue. Hydrogen bonds to water molecules in the first solvation shell are drawn as green lines. During the depicted interval, four solvent molecules, whose oxygen atoms are drawn in yellow, replace four hydrogen-bonded water molecules from the solvation shell, whose oxygen atoms are highlighted in red. For visual clarity, most of the water molecules in the simulation cell are drawn as stick figures.

Geissler *et al.* argue that nuclear quantum effects may affect the kinetics of the system but are unlikely to change the mechanistic pathway they identify. The issue of system size is perhaps more troubling. The key finding of Geissler *et al.* is that the hydrogen-bonded wires that make up the transition state ensemble leading to autoionization contain three to five bonds. This conclusion is based on an analysis of a system of water molecules contained in a cube with roughly 1-nanometer edges. The observed three to five hydrogen bond wire is the maximum chain length that can be supported in the sample. Thus, the authors cannot exclude the possibility that in bulk water, even longer wires contribute to the transition state ensemble.

The author is in the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, PA 19104, USA. E-mail: klein@lrsm.upenn.edu