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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PERSPECTIVES: CHEMISTRY

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*).

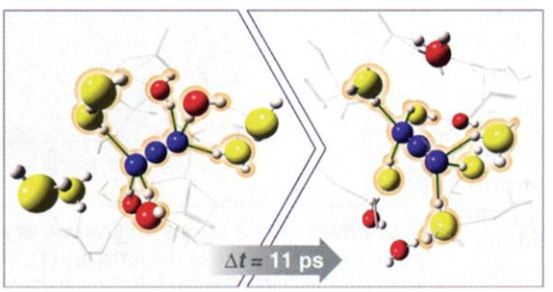
A pair of articles in this issue advances our fundamental understanding of simple ions in water. On page 2118, Kropman and Bakker (*8*) show that the dynamics of water molecules in the solvation shells of halide ions are much slower that those of the surrounding water. In doing so they overcome a substantial 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.

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.



Dynamics of water molecules in the solvation shell of a dissolved N_3^- ion. Shown are two configurations separated by a time interval Δt 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.

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It is likely, however, that the neglect of nuclear quantum effects and the small system size will only influence the quantitative details of the kinetics and not negate the basic mechanism. The calculation of Geissler *et al.* offers both a new perspective on autoionization in water and a challenge. The brave experimentalist who picks up the gauntlet and identifies the predicted transient species will write the next chapter in this story.

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RETROSPECTIVE

Herbert A. Simon, 1916–2001

Edward A. Feigenbaum

Herbert A. Simon, winner of the 1978 Nobel Prize in Economics, died on 9 February at the age of 84. He was Richard King Mellon Professor of Computer Science and Psychology at Carnegie Mellon University. In an era when universities assiduously preserve the names of their new buildings for generous donors, the new Computer Science Building at Carnegie Mellon University is instead named for Simon and another renowned computer scientist, Allen Newell.

The hallmark of Simon's remarkable career is the extent of his cross-disciplinary contributions: from economic theory to psychology to behavioral science to computer science. Before his Nobel Prize, Simon had already won the A. M. Turing Award, the top accolade for computer science, prompting computer scientists to refer to him as "our Nobel Prize winner." But psychologists also awarded him their top honor, the Distinguished Scientific Contribution Award, and they too claimed him as their own.

As his graduate student, in awe of his enormous knowledge and the range of his contributions, I once asked him to explain his mastery of so many fields. His unforgettable answer was, "I am a monomaniac. What I am a monomaniac about is decision-making." Studies and models of decision-making are the themes that unify most of Simon's contributions.

He challenged the assumptions of mid-20th century economic theory, the so-called Rational Economic Man model. This model assumed the omniscience of human decision-making: that humans recognize all of their possible choices and the consequences of selecting each. Simon, the empiricist, observed that Rational Economic Man does not exist. The cognitive ability of people to recognize alternatives and calculate optima is in fact quite limited. He argued that economics could not be built upon a foundation of assumptions concerning human behavior that were patently false.

As a substitute, he introduced assumptions of bounded rationality and the concept of "Satisficing" Man, who cannot maximize or minimize because the computational demands of doing so are beyond his capability. Satisficing man makes choices that are satisfactory—good enough, rather than the best. In the early 1950s, Simon introduced his theory with two classic papers in which he argued that objects (real or symbolic) in the environment of the decision-maker influence choice as much as the intrinsic information-processing capabilities of the decision-maker. In his book *The Sciences of the Artificial* (*1*), with his usual expository skill, he made this idea easy to grasp. His metaphor was the ant on the beach: The ant makes her way from a starting point to a food source along an intricate path. But the path appears to be complex only because of the patterns of the intervening grains of sand, not because of any complex information-processing by the ant.

Collaborating with James March, Simon applied the search model of problem-solving to the study of how organizations make decisions and how they innovate. Their book, *Organizations* (*2*), is the foundation of modern organization theory. March, Richard Cyert, and others extended Simon's theory to microeconomic phenomena in the influential book, *A Behavioral Theory of the Firm* (*3*).

Simon, the theorist, sought to give these abstractions a concrete expression from which precise predictions of human problem-solving behavior could be made. Simon tried using mathematics but found its language was not rich enough to express the complexity of the problem-solving processes he was attempting to model. With Allen Newell in 1955, he discovered the right language: the language of the digital computer. Newell, Simon, and J. C. Shaw of RAND invented a powerful programming language for describing complex symbol processing. They used their new language to model problem-solving processes such as proving theorems in logic. This marked the start of the field of artificial intelligence and Simon considered this contribution to be his finest. Many computer simulation programs of human cognition followed. Newell and Simon's 1972 book, *Human Problem Solving* (*4*), is perhaps the most important book on the scientific study of human thinking in the 20th century.

For the last 25 years of his life, Simon continued to experiment and build computer models of cognition. He designed models of human expertise, scientific discovery (he modeled how certain historically great discoveries of science were actually made), and human memory. He worked for decades on models of the processes through which symbols are learned, recognized, retrieved, and forgotten.

If one were to read a single book that would encompass the essential Simon, I would suggest the slim volume *The Sciences of the Artificial* (*1*), written for a broad scientific audience. In an elegant and lucid way, Simon explains the principles of modeling complex systems, particularly the human information-processing system that we call the mind.

There is no better epilogue for Herbert Simon than that imparted by one of his Carnegie Mellon University colleagues: As Herb Simon struggled to recover from complications of surgery a few days before his death, this author of nearly a thousand papers and 27 books finished a manuscript he was writing and gave instructions to his daughter about its publication.

The author is professor emeritus of computer science, Stanford University. He was a student of and later a research collaborator with Herbert A. Simon.

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