

WATER WATER EVERYWHERE

WITH COMPUTATIONS PROVIDING THE
ABILITY TO INTERPRET INNOVATIVE
LABORATORY STUDIES, WATER
DIVULGED SOME OF ITS SECRETS



Ken Jordan,
University of Pittsburgh

PHOTO CREDIT:
Justin Merriman/Pittsburgh Tribune-Review



It's in the oceans, rivers and lakes, the sky, bathtubs and drinking glasses. For most of us, water is a taken-for-granted part of our lives. Nevertheless, after more than a century of scientific study, water still holds many secrets.

“Water has properties that differ from any other substance,” says Ken Jordan, professor of chemistry at the University of Pittsburgh, “and these properties play an important role in enabling life as we know it. Just one example is that water has a very high ability to store heat energy, otherwise day-night and seasonal temperatures would fluctuate much more radically than they do. We still don't fully understand what makes water so effective at this.”

Water divulged a few of its secrets in 2004, with *Science* magazine listing a flurry of scientific papers on water's structure and chemical behavior as among the top 10 scientific breakthroughs of the year. These new findings, said *Science*, “could reshape fields from chemistry to atmospheric sciences.”

Jordan collaborated on a number of these projects, and also in follow-up studies reported this year. He's a specialist in theoretical and computational chemistry, well known for his work on water clusters — groups of water molecules linked together. “There are huge gaps in our understanding,” he says, “of how water molecules interact with each other.” For much of the work cited in *Science*, Jordan and his team at Pitt relied on Rachel, PSC's 128-processor HP Marvel, a system well suited for the quantum-level computations involved.

“There's two common themes in these projects,” says Jordan. “One is water. The other is the power of computer modeling when coupled with state-of-the-art experimental studies.” Several of these projects explore long-standing questions about what happens when an extra electron or proton interacts with water clusters, changes that can affect many chemical processes. In all these projects, Jordan's computational work has complemented and added to what can be learned in the laboratory.

<<The Magic Number

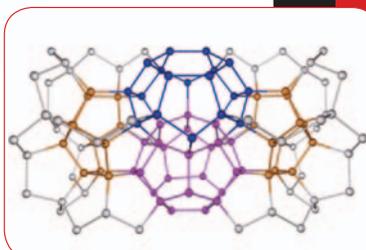
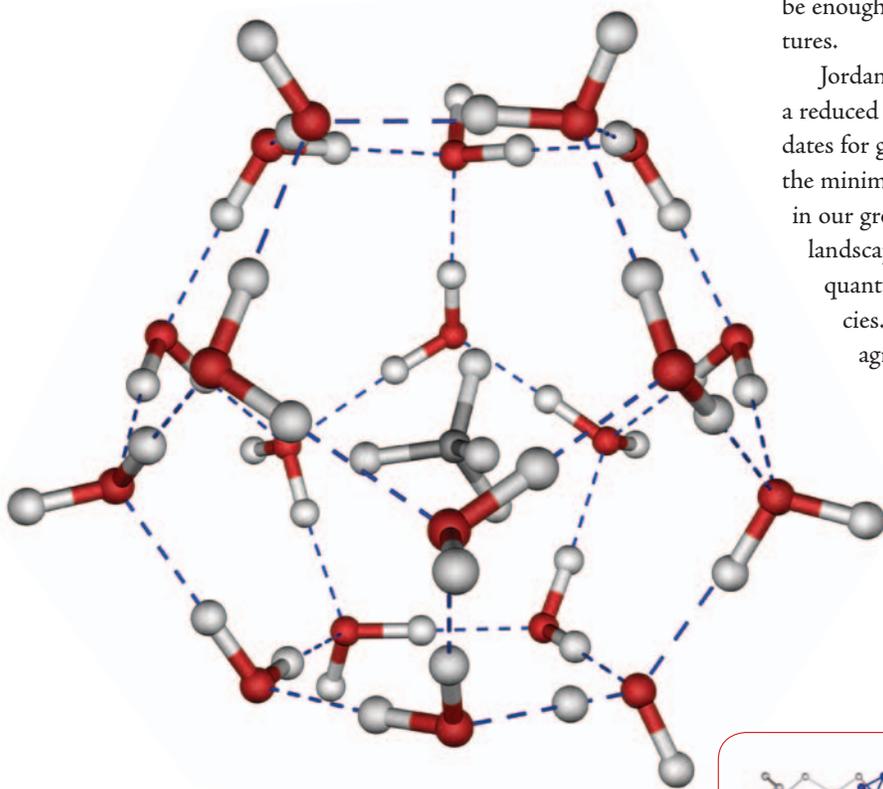
This graphic, representing recent findings by Jordan and collaborators, shows water's magic number cluster as a dodecahedron with the proton on the surface. Twenty H_2O molecules are bound together by hydrogen bonds (dotted lines). One H_2O (purple) is in the center of dodecahedral cage, and the excess proton is associated with an H_3O^+ ion on the surface (blue).

Spectral Signatures

Vibrational spectroscopy is a powerful tool for identifying subtle differences in molecular structure. Much like middle-C on the piano vibrates at a higher frequency than the B below it, different arrangements of molecules vibrate at different frequencies.

In clusters of water molecules, vibrational spectroscopy can register subtle differences in how the H₂Os link up with each other. Clustering occurs through “hydrogen bonds” — links between hydrogen of one water molecule and oxygen of another. Weaker than the covalent bonds that yoke two hydrogens and an oxygen to form water, hydrogen bonds happen as electronic charges — positive for hydrogen, negative for oxygen — on different water molecules interact.

Inevitably some of the hydrogens are left dangling — and these, as you might expect, vibrate at higher frequency than the hydrogens involved in a hydrogen bond. Due to these differences, each of many possible configurations for the same number of water molecules has its own vibrational frequencies, its “spectral signature” — which can be determined with sensitive laboratory techniques.



Methane Hydrate

Much of the natural gas on Earth is created from organic deposits on the ocean floor and held there in crystalline structures of frozen water up to 100 meters thick. Known as methane hydrate, these crystals form from dodecahedral clusters of water (red & white, dotted lines show hydrogen bonds), which create a cage around a single methane molecule (CH₄, gray & white). This same arrangement of waters forms the “magic number” cluster. The water lattice for these hydrates often includes two types of cages (blue & magenta).

BETTER UNDERSTANDING OF THE “MAGIC NUMBER” CLUSTER MAY HELP TO UNLEASH A MAJOR SOURCE OF UNTAPPED ENERGY

From a sample of water clusters of the same mass at low temperature, Jordan’s collaborators at the University of Georgia and Yale University record spectral signatures. The challenge then is to interpret them. “Is the experiment seeing the global minimum?” says Jordan. “Or is it probing an ensemble of many low-energy structures?” To address that question, Jordan’s team applies theory and calculates “the global minimum” — the geometrical arrangement that has the lowest potential energy. This structure is the most stable arrangement of the cluster and the one that most populates the vibrational frequency spectra at low temperature.

To find the global minimum, however, is easier said than done. For a cluster of 21 waters, Jordan estimates there are easily 10²⁰ minima — that’s 100 million-trillion possible structures that may form transiently, of which only one is the global minimum. Even years of computing on the world’s most powerful system wouldn’t be enough to calculate the frequencies of all these structures.

Jordan’s team first uses “model potentials” to identify a reduced set of structures that comprise the likely candidates for global minimum. “You can’t possibly examine all the minima,” explains Jordan. “We have a research effort in our group to develop fast algorithms that survey the landscape.” Within this reduced set, they then use quantum-chemistry methods to calculate frequencies. “We can then see which calculated spectrum agrees best with the experimental spectrum.”

Wet Electrons, Protons & Magic Numbers

This ability — practical only with advanced systems like Rachel — to look at a large number of minima and compute the associated vibrational spectra, which can then be related to laboratory data, has made possible many of the new findings about water. One of the questions that recent work has addressed is the nature of the “wet electron.”

Also called the hydrated electron, this phenomenon — an extra electron added to water — has been widely studied because of its importance in “electron transfer” processes in photosynthesis and in the body, where electrons flit molecule-to-molecule, sparking the reactions of metabolism. Most of what’s been known about the wet electron involves bulk water — as opposed to clusters. New work by several experimental groups used sophisticated spectroscopic methods to analyze an extra electron attached to water clusters. These studies developed information at a level of detail beyond what’s been possible before. Some of this work relied on computational studies by Jordan’s group.

Another of water’s mysteries has been the structure of “magic number” clusters. Mass spectrometry shows that a cluster of 21 water molecules — with one extra proton (H^+) — is much more stable than clusters with either 20 or 22 water molecules. “There’s something imparting special stability,” says Jordan, “and that’s often associated with a special geometrical arrangement.” Studies over the past 30 years have postulated a dodecahedron, a cage of 20 water molecules, with an H_2O in the middle. But where’s the extra proton? Does it go with the central H_2O or on the surface of the cluster?

Using Rachel, among other computational resources, Jordan’s student Richard Christie did calculations to complement laboratory teams at Yale and the University of Georgia. “There were these exciting experimental results,” says Jordan, “and the question was how to explore the needed range of structures quickly enough to rapidly publish a joint experimental/theoretical paper.” Running on 16 of Rachel’s processors required about two days of computing to arrive at spectral signatures for one minima.

The results have settled the question. The magic number proton is on the surface. “This debate has been going on for many years,” says Jordan, “but we’ve found pretty definitely that the proton sits on the surface of the dodecahedron.” This answer, as is usual, brings new problems to resolve. “There’s still a question about how fast the proton can move around. It’s not a finished story.”

Resolving questions about the magic-number cluster, notes Jordan, has implications for a major source of untapped energy. Methane hydrates — a structure that includes dodecahedral cages of water enclosing molecules of methane, aka natural gas. Research in the last decade has found that huge deposits of methane hydrate lie on the ocean floor, and there are major research efforts underway to find how to harness this methane. Jordan’s group is working with four laboratory groups in California looking at relationships between water clusters and the similarly structured gas hydrates.

In 2005, as a follow-up to their 2004 report on the magic-number cluster, Jordan and his collaborators at Georgia and Yale published exciting results involving an extra proton in smaller water clusters, often referred to as the “hydrated proton.” Research over many years identified two competing arrangements. “One,” says Jordan, “is where the proton is associated with a single water molecule, and that gives H_3O^+ — often called the Eigen form, for the Nobel scientist who proposed it. The other form is with the proton equally shared between two waters — $H_5O_2^+$, called Zundel.”

With innovative spectroscopic techniques and Jordan’s calculations to interpret the data, the researchers for the first time identified clear spectral signatures for the two structures. By adding water molecules one by one, they found striking shifts in the frequencies — indications of movement back and forth between the Eigen and Zundel forms as well as the importance of structures that are intermediate between these two limiting forms.

“It gives us a handle,” says Jordan, “on how sensitive the spectra are to the environment.” The extra proton is fundamental to the chemistry of acids and this finding, which no one expected, has wide implications. What especially intrigues Jordan is that when water reveals secrets it seems to hint at even deeper ones. “To me that’s the most interesting science — when you discover hidden questions you didn’t anticipate when you started.” (MS)

>>More information: <http://www.psc.edu/science/2005/jordan>