

lower x-ray brightness, however, makes for rather poor signal to noise.

The large-aperture x-ray telescopes needed to achieve good photon statistics along lines of sight to typical quasars are not expected before the next decade. For a given aperture, however, the sensitivity of an x-ray grating spectrometer improves as the square of the wavelength. "That's why we're now concentrating our search for WHIM lines on higher redshifts, while we're waiting for bigger telescopes," says Nicastro.

Andrzej Soltan (Copernicus Astronomical Center, Warsaw) and coworkers recently reported complementary evidence for the WHIM in the diffuse cosmic x-ray background.⁶ Because the WHIM's mean density is only a handful of protons per cubic meter, its bremsstrahlung—which increases as density squared—would be too faint to see anywhere except near galaxies, where its density is expected to be highest. And that, indeed, is what Soltan and company find.

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A New Look at Electrons in Water Clusters Solves a Longstanding Riddle

Influenced by cluster size and temperature, an electron can attach to the surface or be trapped internally.

In 1962, Edwin Hart and John Boag of Argonne National Laboratory saw a novel absorption peak in the spectrum of water that had been blasted with high-energy electrons. They identified that peak as evidence for electrons in solution—solvated electrons. An individual water molecule, though, does not accept an electron. That means the solvation phenomenon is a cooperative one involving a number of molecules. To learn about the forces responsible for bulk solvation, chemists turned to tiny anionic (negatively charged) water clusters with tens of molecules or fewer. Cluster studies also enable scientists to explore how very small systems are fundamentally different from their bulk cousins.

By 1984, anionic clusters of water molecules had been successfully created in the lab. By decade's end, they had been subjected to theoretical and experimental studies. The result of those explorations was an inconclusive answer to a seemingly straightforward question: Are the electrons in modest-sized clusters bound to the surface or do they live inside? The puzzle was solved only recently when Daniel Neumark, his postdoc Jan Verlet, and colleagues from the University of California, Berkeley, formed distinct types of anionic-cluster isomers.¹ One, a metastable form, had properties consistent with surface binding; another suggested internal solvation.

Two states living side by side

In the mid 1970s, Harvard University's Dudley Herschbach conceived the idea that studying charged water clusters would be a good way to learn

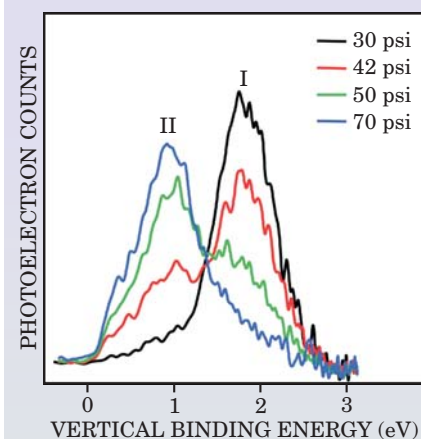
about bulk solvation. But Herschbach's group did not succeed in producing anionic water clusters. That feat was accomplished by Helmut Haberland, Doug Worsnop, and colleagues at the University of Freiburg, Germany, in 1984.²

Within a few years of the Haberland paper, Uzi Landman (Georgia Institute of Technology), Joshua Jortner (Tel Aviv University), and colleagues reported path-integral simulations that predicted the existence of surface states of excess electrons on smaller water clusters; the researchers also compared the energetics of electrons localized on the surface of a cluster with those that are inside.³ The centerpiece of their approach was an effective electron-cluster interaction potential deduced with the help of scattering data. Landman and company concluded that for clusters with at most 32 water molecules, the surface state was energetically favored. Clusters with 32–64 molecules were in a transitional regime, and larger clusters favored internal electrons. For the clusters with electrons inside, the theorists predicted, the vertical binding energy would scale with the number of cluster molecules n and, when plotted against $n^{-1/3}$, would lie on a straight line. (In this usage, "vertical" means that an electron has been liberated, but the remaining neutral species has not had time to relax to its ground state.)

In the late 1980s, Kit Bowen (a former student of Herschbach's), James Coe, and others at Johns Hopkins University put the theoretical predictions to the test.⁴ In their study of electrons solvated in water clusters with n ranging from 2 to 69, they

passed argon gas over water to scoop up clusters, and shot electrons into the carrier gas to make the cluster anions. After separating the clusters by mass, the group liberated electrons with laser photons of fixed energy and then measured the kinetic energies of the freed electrons. The difference between photon and kinetic energies is the vertical binding energy.

Bowen and company saw, when $n \geq 11$, the scaling behavior predicted for internal electrons. Moreover, the linear intercept was in good accord with the vertical binding energy for bulk solvated electrons. They did not see any transition at large n and concluded that they were looking at internally solvated electrons akin to the



Increasing pressure, as these $(D_2O)_{50}$ data dramatically illustrate, changes the relative abundances of anionic isomeric states. The isomer labeled I has properties consistent with an internal electron, and the properties of isomer II suggest an electron localized on the surface. The lowest pressure, 30 psi, corresponds to 2.1×10^4 Pa. (Adapted from ref. 1.)

electrons solvated in bulk. On the other hand, the vertical binding energies that Landman and colleagues calculated for surface states agreed with those measured by Bowen's team. That suggested to some that the Bowen group had seen surface states.

The ambiguity in the Bowen experiment had not been resolved when, seven years later, Mark Johnson and Patrick Ayotte of Yale University analyzed spectra of excited anionic water clusters.⁵ Johnson and Ayotte couldn't resolve the ambiguity either: The positions of absorption maxima suggested surface states, but the trend of excited-state energies with n was smooth and toward the bulk value.

Late last year, Neumark's group looked at anionic water and heavy water (D_2O) clusters with n as high as 200. (The group had worked with D_2O in earlier excitation studies; heavy water's excited-state lifetime is significantly greater than that of H_2O .) In an experiment similar to Bowen's but including runs with higher pressures of carrier gas, they identified three distinct classes of isomeric states for clusters with 11 or more molecules. Two of those are most relevant to the issue of surface versus internal states. The clusters with the higher vertical binding energy (isomer I) were the same species seen earlier at Johns Hopkins: Neumark and company likewise interpreted them as being internally solvated states; some researchers, though, think that interpretation is not airtight.

The newly observed clusters (isomer II) with lower binding energy, ac-

cording to Neumark and colleagues, are states for which the electron resides on the surface. The Neumark interpretations are in qualitative agreement with the analysis of Landman and colleagues and have an intuitive appeal. For large clusters, at least, one would expect that the energy debt an electron pays to distort the water-cluster network and go inside would be paid back with interest by Coulomb interactions with water dipoles. Thus, it would take more energy to liberate an internally solvated electron.

Frozen clustered

High pressure leads to cold water clusters because higher-pressure argon adiabatically expands and cools more before electrons attach to the clusters it carries. The figure on page 21 shows what happens with a change in pressure of the argon gas that carries a particular cluster. At relatively low pressure, the clusters exist predominately as isomer I, but isomer II becomes ever more prevalent at higher pressures. Neumark and company suggest that an electron on the surface of a cold, relatively rigid cluster finds it difficult to effect the reorganization necessary to penetrate inside. For this reason, it's no surprise to find the isomer-II surface state more prevalent in the high-pressure runs.

Independent electronic-excitation studies reported last October by Neumark's group and by a team led by Ahmed Zewail (Caltech) provided further evidence that isomer I is related to the bulk solvated state: The excited state lifetimes are extremely short

and depend on cluster size.⁶ In the course of making adjustments to produce larger clusters of isomer I, Neumark and coworkers caught their first glimpse of the isomer-II state with its lower vertical binding energy.

The more recent work of the Neumark group also included excitation studies and revealed that isomer-II states have longer lifetimes reasonably independent of cluster size. An electron sitting on the surface of a cluster, Neumark explains, would not couple to the solvent network as strongly as an internal electron surrounded by water molecules. Thus, the size independence is qualitative evidence for surface states.

It was the hint of a new structure seen in October that inspired Neumark and colleagues to attempt an experiment that could convincingly demonstrate the existence of novel isomeric states. "We'd like to claim credit for some grand plan," says Neumark, "but we found the surface states more or less by accident."

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What's Making Earth Hum?

New evidence suggests that winter storms over the oceans provide the energy that sets Earth freely oscillating at its fundamental frequencies.

Seven years ago, seismologists discovered¹⁻³ that Earth is vibrating in a discrete set of frequencies between 2 and 7 mHz. The peak frequencies coincide with the spheroidal fundamental modes predicted by a model of Earth. To find these fundamental normal modes, which are masked by earthquakes, seismologists had to look exclusively at data from quiet sites. They also needed the broadband, low-noise seismometers available since the 1980s.

Decades ago, seismologists had seen the so-called microseismic noise at frequencies that peak near 0.2 Hz. Microseisms are known to be caused

by ocean-wave interactions, which generate pressure fields that do not wane with ocean depth. The same mechanism cannot explain the generation of the much lower frequency normal modes. Some researchers had speculated that these fundamental oscillations were instead caused by atmospheric turbulence interacting with the solid Earth. Recently, Junkee Rhie and Barbara Romanowicz of the University of California, Berkeley, presented evidence that the oceans play a role.⁴ Their analysis shows that the normal-mode oscillations originate in the Northern Pacific during the boreal winter and in the southern

oceans in the austral winter.

The discrete normal modes occur continuously, so they cannot be caused by intermittent large earthquakes. Nor can they result from an accumulation of many small earthquakes; there's not enough energy to drive the observed oscillations.

The source must be near Earth's surface because the fundamental modes are all Rayleigh waves, which propagate largely at the surface. Some researchers suggested that the oscillations are caused by random atmospheric pressure fluctuations distributed uniformly over both land and sea surfaces. The normal-mode amplitudes increase in January and July—times of particularly strong atmospheric disturbances.⁵ Researchers have calculated that random atmospheric fluctuations can generate seis-