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, according 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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References

1. J. R. R. Verlet et al., *Science* **307**, 93 (2005).
2. H. Haberland et al., *J. Chem. Phys.* **81**, 3742 (1984).
3. R. N. Barnett et al., *Phys. Rev. Lett.* **59**, 811 (1987); R. N. Barnett et al., *J. Chem. Phys.* **88**, 4429 (1988).
4. J. V. Coe et al., *J. Chem. Phys.* **92**, 3980 (1990).
5. P. Ayotte, M. A. Johnson, *J. Chem. Phys.* **106**, 811 (1997).
6. A. E. Bragg et al., *Science* **306**, 669 (2004); D. H. Paik et al., *Science* **306**, 672 (2004).

What's Making Earth Hum?

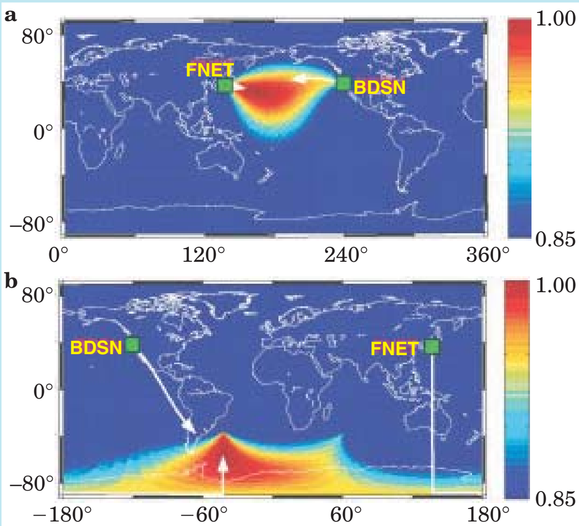
New evidence suggests that winter storms over the oceans provide the energy that sets Earth freely oscillating at its fundamental frequencies.

Seven years ago, seismologists discovered[1–3] 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-



Dominant directions of arrival of surface Rayleigh waves, as detected by seismometer arrays in California (BSDN) and in Japan (FNET) in the winter **(a)** and summer **(b)**. The color coding indicates the amplitude of the arrays' response to waves arriving from a given point, expressed as a fraction of the maximum amplitude. The waves appear to originate in the northern Pacific **(a)** and in the southern oceans **(b)**. In **(b)**, the arrow from FNET appears discontinuous because of the map projection. The cusps are another artifact of that projection. (Adapted from ref. 4.)

mic spectra consistent with those observed.[6–8]

In their recent work, Rhie and Romanowicz used two arrays of seismometers, one in California and the other in Japan. The Berkeley researchers assumed that a Rayleigh wave arrived at each array from some arbitrary direction. They looked for the direction in which the signals recorded on the stations of the array showed the greatest coherence. As seen in the figure, the Rayleigh waves appear to come from the very regions where strong winter storms roil the seas. Rhie and Romanowicz speculate that Earth's normal-mode oscillations are generated by nonlinear interactions between atmosphere, ocean, and sea-floor, probably through the conversion of storm energy to low-frequency "infragravity" ocean waves[9] that interact with sea floor topography. Identifying the exact mechanism is a work in progress.

Toshiro Tanimoto of the University of California, Santa Barbara, has proposed a similar scenario.[10] Estimating the size of sea-floor pressure from existing measurements, he finds sufficient energy in these perturbations to excite the observed seismic signals.

Kiwamu Nishida and Yoshio Fukao of the University of Tokyo have completed a preliminary analysis that, like the Berkeley study, suggests that normal-mode oscillations are excited in the ocean areas in northern and southern winters. The results do not necessarily mean, says Fukao, that Earth's oscillations are caused by oceanic sources rather than atmospheric loads on the sea surface. "We do not know which is more efficient as the excitation mechanism," he adds. Both Fukao and Romanowicz think that the coupling of ocean waves to the sea floor may occur near shore or perhaps at the continental shelves.

Exploiting the noise

By studying Earth's normal-mode oscillations, researchers can learn more about the coupling of the atmosphere, oceans, and solid Earth. Seismologists are learning to embrace the noise signals they once regarded strictly as an impediment, especially in the microseismic frequency band above 0.1 Hz. They have, for example, learned that they can extract information about Earth's crust by analyzing the propagation of noise signals between two seismic stations.[11] The noise in historical seismic data is also being used to track long-term variations in wave climate.

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References

1. K. Nawa, N. Suda, Y. Fukao. T. Sato, Y. Aoyama, K. Shibuya, *Earth Planets Space* **50**, 3 (1998).
2. N. Suda, K. Nawa, Y. Fukao, *Science* **279**, 2089 (1998).
3. T. Tanimoto, J. Um, K. Nishida, N. Kobayashi, *Geophys. Res. Lett.* **25**, 1553 (1998).
4. J. Rhie, B. Romanowicz, *Nature* **431**, 552 (2004).
5. G. Ekstrom, *J. Geophys. Res.* **106**, 26483 (2001).
6. N. Kobayashi, N. Nishida, *Nature* **395**, 357 (1998).
7. T. Tanimoto, J. Um, *J. Geophys. Res.* **104**, 28723 (1999).
8. Y. Fukao et al., *J. Geophys. Res.* **107**, 2206 (2002).
9. For more on infragravity waves, see S. Webb et al., *J. Geophys. Res.* **96 (C2)**, 2723 (1991).
10. T. Tanimoto, *Geophys. J. Int.* **160**, 276 (2005).
11. N. M. Shapiro, M. Campillo, L. Stehly, M. H. Ritzwoller, to appear in *Science*. ■