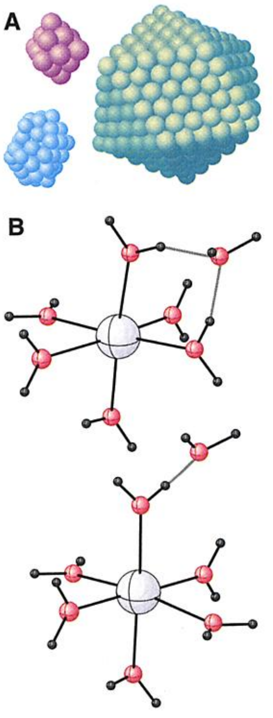
PERSPECTIVES: CHEMISTRY

Cluster Solutions

Anthony Stace

Clusters consisting of finite collections (2 to 1000) of atoms or molecules are easily generated in the gas phase with modern experimental methods. It is often claimed that the study of such clusters may bridge the gap between the properties of single atoms or molecules and the condensed phase (*1*). This objective is rarely realized, however, because the size range over which many physical properties operate far exceeds the range of cluster sizes that can be manipulated and studied in a systematic fashion (see the table). As a result, a considerable gulf remains between cluster and bulk properties (*1*).



Clusters large and small. (A) Atomic clusters. **(B)** Ca^{2+} solvated in water (*3*). Only one water molecule in the second solvation shell is shown.

Perhaps one of the few realistic opportunities for identifying macroscopic behavior in a microscopic system is in the study of ion solvation (*2*). The hydration enthalpy, ΔH_h, of Na^+ (–405 kJ mol^{-1}) is roughly equivalent to the sum of the individual enthalpies of the first six water molecules to attach to a sodium ion in the gas phase. For singly charged ions such as Na^+ and K^+ , the first solvation shell would thus appear sufficient to reproduce the essential thermodynamics of solvation (*2*).

Gas phase studies have shown that in the case of singly charged ions, the first solvation shell is indeed effective at shielding the charge from the remaining solvent molecules. However, any attempt to model ion solvation in clusters must also consider multiply charged ions, which constitute a major fraction of the ions encountered in chemistry and biochemistry. Despite considerable technical difficulties, substantial progress has been made over the past decade (*3*, *4*). Most studies have concentrated on cations such as Cu^{2+} and Mg^{2+}. These studies have shown that for doubly charged ions, the relation between the ion and the solvent is different from that observed for singly charged ions.

On page 1322 of this issue, Wang *et al* (*5*) present results from one of the few experimental studies of solvated di-anions. They use photoelectron spectroscopy (PES) to probe anions and their solvent environments. Size-selected $SO_4^{2-}(H_2O)_n$ and $C_2O_4^{2-}(H_2O)_n$ clusters are irradiated with an ultraviolet laser, and the kinetic energies of the photodetached electrons are measured. Knowledge of the photon energy together with the measured kinetic energies is used to determine the binding energies of the electrons.

A particularly important characteristic of multiply charged anions and one that has a profound effect on photoelectron spectra is the presence of a repulsive Coulomb barrier. In SO_4^{2-}, an electron held in a valence orbital experiences an attractive Coulomb potential that holds it close to the anion core. Once the photodetachment process has been initiated and SO_4^- and e^- start to separate, the electron begins to experience the strong repulsive Coulomb interaction that exists between charged species of the same sign.

Electrons with low kinetic energies (high binding energies) cannot surmount the repulsive Coulomb barrier and so are not detected. Therefore, any low-energy feature in a photoelectron spectrum of, for example, a $SO_4^{2-}(H_2O)_n$ cluster has to represent a new ionization pathway. Wang *et al.* (*5*) observe such a feature beyond $n = 12$ and attribute it to the ionization of neutral water molecules. At the same time, features attributed to photodetachment from the di-anion begin to disappear. Thus, at $n \sim 12$, solvation of the anion is nearing completion, and incoming photons "see" the solvent more than the solute. However, features due to the solute do not disappear completely until $n \sim 30$.

In this study and in related experiments on multiply charged cations (*3*, *4*), the influence of the charge does not tail off once the first solvation shell is established. This behavior contrasts markedly with the conclusion reached concerning the solvation of singly charged ions. Particularly in the case of hydrogen-bonded solvents such as water and methanol, contributions from at least the second solvation shell ($n \sim 20$) must be considered to provide a complete description of the solvation process of multiply charged ions (*6*).

For di-cations in, for example, water, this situation is easy to visualize through the formation of a network of charge-enhanced hydrogen bonds (see the figure). But for anions, the nature of the solvent structure is less easy to appreciate. Anion solvation enthalpies are about half those of cations (Ni^{2+}, $\Delta H_h = -2105$ kJ mol^{-1}; SO_4^{2-}, $\Delta H_h = 1059$ kJ mol^{-1}), and the orientations of water molecules in close proximity to anions will be quite different from those calculated for cations (*7*). The latter naturally lend themselves to the formation of an extended water lattice, whereas anions such as SO_4^{2-} lead to a net reduction in lattice structure (order), as seen from their positive hydration entropies (*7*). Some anions appear to not even dissolve in water clusters: PES experiments on I^- have been interpreted in terms of the anion residing on the surface of a cluster containing up to 60 water molecules (*8*). I^- also has a large positive hydration entropy (*7*).

Two decades of experiments on singly charged ions have made a substantial contribution to our understanding of ion-solvent interactions. The challenge now is to extend this work to multiply charged species, where even basic phenomena such as the anomalous acidity of Sn^{2+} still await a rational explanation. Wang *et al.*'s study illustrates how cluster studies can play a part in solving these mysteries.

The discrete picture of solvation and/or coordination offered by cluster experiments may also have merit in a quite unexpected area. The local environment experienced by metal ions in biological systems

MEASURED PHYSICAL PROPERTIES OF CLUSTERS THAT HAVE BEEN EQUATED WITH BULK BEHAVIOR

Bulk property	Cluster measurement	Size
Work function (conduction band development)	Ionization energy/ electron affinity	~200 atoms
Melting	Electron beam heating	>1,000,000 atoms
Structure (regular)	Mass spectrometry (magic numbers)	~13 atoms
Structure (bulk)	Electron diffraction	~2000 atoms
Solvation	Gas phase thermochemistry	~10 molecules

CREDIT: PANEL B IN THE FIGURE IS ADAPTED FROM (3)

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frequently includes two or three water molecules. Prompted by a Lewis acid-base relationship with the metal ion, water molecules often produce OH$^-$, which then goes on to attack other molecules in close proximity to the metal (*9*). An example is Zn^{2+} in carbonic anhydrase where the resultant OH$^-$ attacks CO$_2$. The coordination of these molecules is more likely to resemble the molecular arrangement determined from cluster studies than the time-averaged picture derived from ions in solution.

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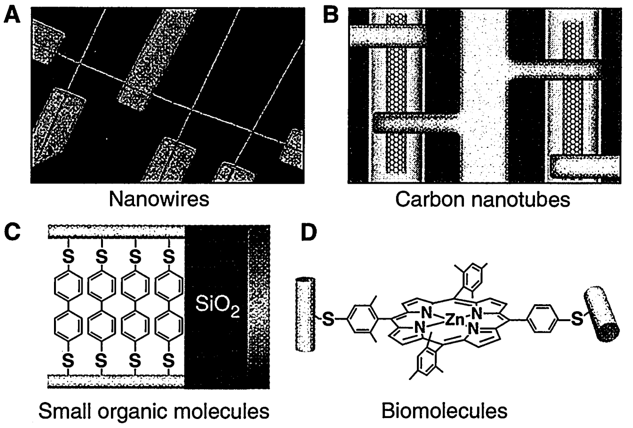
PERSPECTIVES: NANOTECHNOLOGY

Toward Nanocomputers

Greg Y. Tseng and James C. Ellenbogen

The rapid miniaturization of electronics to the micrometer scale has been a key force driving scientific and economic progress over the past 25 years. Nanometer-scale electronics (nanoelectronics) is the closely watched next frontier (*1–5*). Two reports in this issue describe dramatic steps toward the realization of electronic nanocomputers. Bachtold *et al.* (page 1317) demonstrate logic circuits constructed from individual carbon nanotube molecules (*6*). Huang *et al.* (page 1313) have assembled logic circuits from semiconductor nanowires (*7*).

Enhanced online at www.sciencemag.org/cgi/content/full/294/5545/1293



Nanowires
Carbon nanotubes
Small organic molecules
Biomolecules

Approaches to molecular-scale electronics. **(A)** Diodes and transistors based on semiconductor nanowires are assembled with microfluidics to form logic AND, OR, NOR, and XOR circuits and logic functions such as a half adder (*7*). **(B)** Carbon nanotube transistors (*8*) are connected by gold interconnects to construct logic circuits such as a NOT circuit, NOR circuit, static random access memory (RAM) cell, and ring oscillator (*6*). **(C)** Field-effect transistors based on self-assembled monolayers of polyphenylene molecules are combined to create a NOT circuit (*11*, *12*). **(D)** Porphyrin molecules store digital information as electrical charges like dynamic RAM cells (*20*).

In recent years, researchers have reported a variety of molecular-scale wires and switches (*8–21*), including molecular-scale transistors based on carbon nanotubes (*8*) and semiconductor nanowires (*9*). However, the two reports in this issue are the first to advance molecular-scale electronics fully from the single-device level to the circuit level. Both groups developed new methods to meet two key device requirements that previously prevented the realization of transistor circuits. First, the component transistors must produce signal amplification or "power gain" with an output to input ratio much greater than 1. Second, each transistor must be controlled by its own local "gate" contact.

Bachtold *et al.*'s study builds on the same group's earlier discovery that individual semiconducting nanotubes adsorbed between two metal contacts on a silicon substrate behave like the field-effect transistors in today's microcomputers (*8*). However, the controlling gate contact in that experiment consisted of the entire supporting silicon chip. In such a layout, multiple nanotube devices placed on a chip all must be switched simultaneously. Furthermore, the power gain was less than 1 because the silicon oxide insulator between the gate contact and nanotube was relatively thick, preventing sufficient capacitive coupling between the gate contact and nanotube.

To construct nanotube circuits, the group has now used electron beam lithography to pattern local aluminum gate contacts and exposed them to air to form very thin insulating layers on the aluminum leads (*6*). Insulator thickness is reduced substantially, enabling the new nanotube transistors to operate independently with a gain ratio in excess of 10, a remarkable increase. By wiring nanotube transistors together with gold interconnects made by lithography, the authors have constructed a range of logic circuits.

Huang *et al.* also build on their earlier achievements in devices to achieve circuits. Earlier this year, the group demonstrated diodes and bipolar transistors made from nanowires in a crossed geometry (*9*). In the present work, they assemble OR and AND logic circuits with only diodes, but to construct other circuits required the development of nanowire field-effect transistors. The new nanowire transistors are formed by placing two nanowires in a crossed geometry and using thermal heating to generate an insulating oxide between the nanowires. As with Bachtold *et al.*'s nanotube transistors, the nanowire transistors feature local gate contacts with thin insulators and are thus easily integrated into transistor circuits.

With the exception of the contacts, Huang *et al.*'s nanowire circuits are assembled without "top-down" methods such as lithography. Instead, "bottom-up" parallel assembly tools such as microfluidics are used. This feature enables them to build and test relatively large numbers of devices and demonstrate readily reproducible behavior in them. Furthermore, Huang *et al.*'s circuits incorporate at least one natural nanometer-scale metric—the constant, small dimension of the crossing points of the nanowires—suggesting that the entire circuits might be shrunk in a straightforward way to the nanometer scale. This capability is important given that the circuits in both studies are still micrometer-scale systems.

The two reports use very different types of nanometer-scale structures and different techniques for assembly, thus pursuing different routes to building electronic nanocomputers. In the variety and complexity of the circuits they have demonstrated, both surpass two other important results in nanoelectronics announced very recently by Derycke *et al.* (*10*) and Schön *et al.* (*11*, *12*). Derycke *et al.* demonstrated a NOT logic circuit or

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