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CLUSTER SOLUTIONS

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].

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, DH_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 $C_2O_4^{2-}$

(H₂O)_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 SO₄²⁻, 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 SO₄²⁻ 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 SO₄²⁻ (H₂O)_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 ~ 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 ~ 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 ~ 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 (Ni²⁺, D_Hh = -2105 kJ mol⁻¹; SO₄²⁻, D_Hh = 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 SO₄²⁻ 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 Sn²⁺ 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 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 Zn²⁺ in carbonic anhydrase where the resultant OH⁻ attacks CO₂. 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.

DIAGRAM: 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.

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

Legend for Chart:

A - Bulk property
B - Cluster measurement
C - Size

A

B
C

Work function (conduction band development)

Ionization energy/electron affinity
-200 atoms

Melting

Electron beam heating
>1,000,000 atoms

Structure (regular) Structure (bulk)

Mass spectrometry (magic numbers) Electron diffraction
-13 atoms -2000 atoms

Solvation

Gas phase thermochemistry
-10 molecules

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