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Structures of Anion–Water Clusters: $H^-(H_2O)_n$, $n = 1$–3

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The structures of hydride ion–water clusters with up to three water molecules have been computed using accurate ab initio techniques. The water molecules are not distributed symmetrically around the anion. Rather, they cluster on one side of the anion so as to retain a measure of hydrogen bonding. The calculated binding energies (including zero-point energies) for successive addition of water molecules to the hydride ion are 17.4, 14.8, and 13.7 kcal/mol.

Molecular clusters are traditionally considered to be aggregates having properties which lie between those of the gaseous and condensed phases. It is still an open question as to whether clusters are effective models of the condensed phase or represent an entirely new state of matter. In either case, however, much valuable information can be extracted from studies of molecular clusters, including data on the nucleation process as well as information on the many-body interactions between the "solvent" and "solute" species. In fact, knowledge of the nature and magnitude of these interactions is the cornerstone of many models describing condensed-phase systems.

The question at hand is whether by successive addition of "solvent" molecules to a "solute–solvent" cluster one approaches the limiting values of the collective properties of the condensed phase. This will be strongly influenced by the spatial arrangement of the "solvent" molecules around the "solute". The arrangement depends upon the nature, magnitude, and selectivity of the solvent–solute and solvent–solvent interactions which are intrinsic to the molecular species in the system. Clearly, the existence, magnitude, and sign of the electronic charge on the solute molecules are a key factor in determining the disposition of solvent molecules around the solvated species.

In the case of dilute ionic solutions the solvent molecules surround the ion completely, arranged in more-or-less tightly bound shells, so-called "solvation shells". In order to ascertain the factors which govern the structure of water around simple negative ions in aqueous clusters, we have determined the optimum geometries of the first few water molecules around the hydride ion, H^-. The hydride ion is the first member of a series of anions (F^-, Cl^-, OH^-, etc.) that we plan to study. Although the hydride ion is not stable in solution, hydride ion–water clusters correspond to stable minima on the ground-state potential energy surfaces for the proton abstraction reactions:

$$H^- + n(H_2O) \rightarrow H^-(H_2O)_n \rightarrow OH^-(H_2O)_{n-1}H_2 \rightarrow$$
$$OH^-(H_2O)_{n-1} + H_2$$
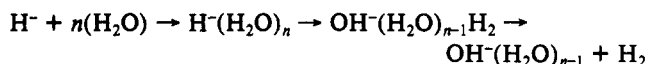
The detailed features of these potential energy surfaces and their variation with the degree of solvation will be presented elsewhere.

Clusters of the H^- with 1, 2, 5, and 11 water molecules have been observed during molecular beam experiments,[1a–c] and the enthalpy of hydration for the first water molecule was experimentally measured[2a] to be 17.3 ± 1.2 kcal/mol. The enthalpy

for addition of the second water was *estimated*[1c] to be 10–15 kcal/mol by comparison with experimental values for F^-. Charge reversal experiments[3a,b] indicated that the structure of the $n = 1$ cluster, $H^-(H_2O)$, differs significantly from the well-known D_{3h} structure of $(H_3O)^+$ in which all of the hydrogens are equivalent.

We have performed MP2 calculations on the $H^-(H_2O)_n$ clusters, for $n = 1$–3, with the new basis sets optimized for correlated electronic structure calculations.[4,5] The basis set used in the present calculations consists of the correlation-consistent polarized valence double-zeta set[4] augmented with additional functions necessary to describe anionic system.[5] All calculations were carried out with the GAUSSIAN 90[6] program suite. We have found correlation effects to be very important in describing the structures and energetics of the $H^-(H_2O)_n$ clusters.

We calculate the binding energy of the $H^-(H_2O)$ cluster

$$H^-(H_2O) \rightarrow H^- + H_2O$$

to be 17.4 kcal/mol, which compares well with the measured[2a] and previously calculated[2b] values of 17.3 ± 1.2 and 16.0 kcal/mol, respectively. For calibration, we compute a binding energy of 5.3 kcal/mol and an O–O bond length of 2.92 Å for the $(H_2O)_2$ dimer, both of which are in excellent agreement with the measured values of 5.4 ± 0.2 kcal/mol[7a,b] and 2.976 ± 0.03 Å.[8] Furthermore, we observe only minor quantitative changes in the computed values of the above quantities with expansion of the basis set, i.e., upon using the augmented triple- and quadruple-zeta basis sets.[4,5]

The optimum geometries of the hydride ion–water clusters containing up to three water molecules are displayed in Figure 1. The $n = 1$ cluster has C_s symmetry; i.e., all four atoms lie in the same plane. The calculated $H–H^-$ distance is 1.433 Å. The calculated geometry of the $n = 2$ cluster is quite unusual. Not only are both water molecules on the same side of the hydride ion but also the two $H–H^-$ distances differ, one being 1.433 Å (the same as in the $n = 1$ cluster) while the other is 1.607 Å. As can be seen, the two water molecules are oriented with respect to each other so as to retain a measure of hydrogen bonding. For example, the O–O distance is 3.157 Å while the O–H–O angle is 165.7°. For comparison, in the water dimer the calculated O–O distance is 2.92 Å and the corresponding O–H–O angle is 180°.

The same structural pattern is found for the $n = 3$ cluster: all three water molecules are located on the same side of the ion and are hydrogen bonded to each other. Now, however, the optimal
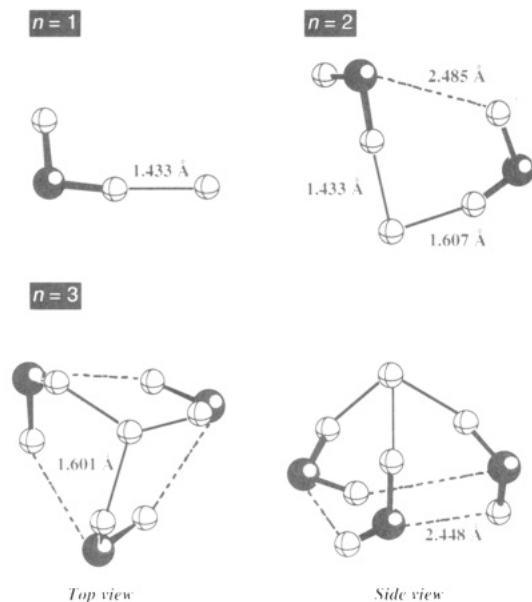
Figure 1. Optimal structures for the $H^-(H_2O)_n$ clusters, for $n = 1$–3, from MP2 calculations with an aug-cc-pVDZ basis set.

geometry has C_3 symmetry with all H–H^- distances equal to 1.601 Å, all O–O distances for the hydrogen bonds equal to 3.134 Å, and all O–H–O hydrogen bond angles equal to 165.8°.

The calculated geometries of the water molecules in the clusters do not exhibit large variations from the calculated geometry of the monomer, namely, $R_{OH} = 0.965$ Å and $\theta_{HOH} = 103.8°$. The bond angles of the water molecules in the clusters vary from 98.3° to 100.3°. For the O–H bond lengths we distinguish between those participating in hydrogen bonding between the water molecules, for which the computed range is 0.967–0.970 Å, and those bonded to the ion for which the range is 1.003–1.035 Å.

The calculated binding energies (including zero-point energy corrections) for successive addition of water molecules to the anion–water clusters

$$\Delta E_{n,n-1} = E_n - (E_{n-1} + E_{H_2O})$$

vary little for the first three members of the series. As noted above, the first water molecule is calculated to be bound by 17.4 kcal/mol ($\Delta E_{1,0}$). The second water molecule is somewhat less bound, $\Delta E_{2,1} = 14.8$ kcal/mol. (As noted above, $\Delta E_{2,1}$ has been estimated[1c] to be 10–15 kcal/mol.) Finally, the binding energy of the third water molecule is calculated to be 13.7 kcal/mol.

The structural motif reported here for the H^-–water clusters is in general agreement with the average structures observed for Cl^-–water clusters in molecular dynamics simulations[9] using many-body interaction potentials. Simulation of dilute ionic solutions with these same potentials predicts that the waters in the first hydration shell are, on the average, symmetrically distributed around the ion. In solution, the water molecules of the first solvation shell bond more effectively with the molecules in the second solvation shell than with themselves. In the absence of the second solvation shell, however, the structure of anion–water clusters appears to be very different than that of the anion and its first solvation shell.

Calculations are currently underway for the $F^-(H_2O)_n$ and $OH^-(H_2O)_n$ systems. For the $n = 1$ and 2 fluoride– and hydroxide–water clusters, we observe structural trends similar to the ones reported here for the hydride–water clusters.

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^{31}P–^{113}Cd and ^{31}P–^{29}Si CP/MAS-NMR in Inorganic Semiconductors

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Cross-polarization of insensitive nuclei (^{29}Si and ^{113}Cd) from abundant ^{31}P spin reservoirs is demonstrated for the first time. Besides offering remarkable gain in detection sensitivity, these experiments provide unique spectral editing opportunities. By replacing the 90° preparation pulse with a rotor-synchronized DANTE sequence, the magnetization associated with resolved ^{31}P sites can be transferred selectively to directly bonded rare-spin nuclei. Through a series of such experiments, it is possible to assign individual P and Si resonances in silicon phosphide (SiP) and to construct the complete ^{31}P–^{29}Si connectivity map.

Introduction

Much of the power of MAS-NMR has come from the ability of exploiting cross-polarization for facile signal detection and spectral editing for insensitive and rare-spin nuclei.[1] To date, protons have almost invariably constituted the abundant-spin reservoir for cross-polarization experiments, although, most recently, ^{19}F has found increasing use.[2–4] To our knowledge, there has been only a single CP study using any other nucleus (^{31}P) as the abundant-spin magnetization reservoir, but even that study benefited from the presence of highly abundant ^{1}H spins (which were detected).[5] Thus, to date solid-state NMR spectroscopy of inorganic materials that are devoid of protons has been mostly