The Nature of a Wet Electron

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A comprehensive state-of-the-art *ab initio* study is performed on the wet electron—an electron interacting with a small cluster of water molecules—in the water hexamer system. Predictions include two previously unknown distinctive geometries which bind the excess electron as internal and external states, photoemission ionization energies in agreement with experiment, identification of generic electrophilic sites involving dangling hydrogen atoms, and the tendency of all hydrogen atoms to be saturated in hydrogen bonding or in interaction with the excess electron. An emerging insight is the capability of electrophilic sites to be actuators of electron transport pathways in biomolecular systems.

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Studies of electrons bound to molecular systems are important for the ultimate understanding of phenomena associated with electron transfers, radial chemical reactions, and polarons [1–8]. One classic and fundamental prototypical system involves the interactions of an electron with water molecules. Solvated electrons (i.e., electrons immersed in liquid water) are believed to be trapped in a cavity space bounded by six water molecules [2]. Such electrons have been the subject of intensive investigation since their transient optical spectra were first identified [3]. From spin echo modulation analyses, Kevan [2] inferred that an electron is hydrated by six water molecules in an octahedral configuration with one O-H bond in each water molecule oriented toward the electron. The existence of such a configuration suggests that it is also possible for an excess electron to be bound to an *isolated* water cluster. Such an electron is often referred to as a “wet” electron.

Since an electron is not bound to a single water molecule, the localization of a wet electron is believed to depend on cluster size. From quantum path-integral calculations using model interaction potentials, Barnett *et al.* [4] suggested that anion water clusters, $e + (H_2O)_n$, with $n = 8-64$, can exist with a novel surface state of an excess electron. In recent mass spectrometer experiments various gas-phase water cluster anions were observed [5,6], but for the case of $n < 10$, clusters with only $n =$ 2, 6, and 7 were identified with certainty. Of particular interest is the case of $n = 6$ (water hexamer anion), since the solvated electron is also coordinated to six water molecules. Except for photoemission ionization energies (IE’s), little is known experimentally about the water hexamer anion. Moreover, because of the complexities of dealing with a fully quantum mechanical problem, *ab initio* theoretical investigations of this system have been limited [7,8]. Indeed, to our knowledge, an optimized geometry and electronic structure of the water hexamer anion, as well as the nature of the interaction forces in the system, have yet to be reported.

In this paper, we present the first extensive *ab initio* theoretical investigation of an excess electron interacting with the electrons and nuclei of six water molecules. To ensure accuracy and reliability we employ two *ab initio* computational methods which are state of the art, respectively, in quantum chemistry and condensed matter physics. Specifically, as a quantum chemical approach, the post Hartree-Fock theory including electron correlation based on the Möller-Plesset second order perturbation theory (MP2) is used with a Gaussian-type basis set including diffuse basis functions (6-311++G** basis set) [9]. As a condensed matter physics approach, density functional theory (DFT) is employed with separable pseudopotentials [10] and a gradient-corrected exchange potential to the local part of the density functional [11] using a plane wave basis set [12] in an iterative minimization relaxation scheme [13]. The results of both methods lead to a consistent and novel picture of a wet electron with possible implications for novel *through-space* (as opposed to *through-bond*) pathways in electron transport.

We begin by placing six water molecules in Kevan’s octahedral geometry shown in the left panel of Fig. 1 [2]. Although this geometry is strictly for a solvated electron, it is a reasonable starting point for the hexamer anion as well. Allowing all the atoms and electrons to relax, we obtain the *triangular-ring* structure shown in the center panel of Fig. 1 [14]. This relaxed structure is different from the octahedral geometry in a significant way: The OH bonds no longer point directly toward the center of the cluster. The relaxation allows hydrogen bonding between adjacent molecules by forming two triangular rings. This structure, however, is only a local minimum energy geometry. We have discovered that a lower energy geometry (by 0.26 eV in MP2 and 0.35 eV in DFT) is the *prism* structure shown in the right panel of Fig. 1 [15].

The nature of the excess electron is illustrated in Fig. 2. Here are plotted valence electron charge distributions of

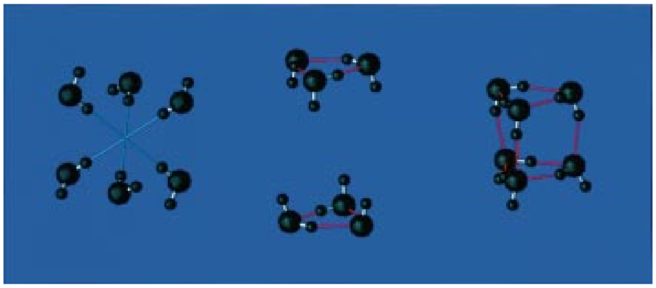

FIG. 1 (color). Possible hexamer anion geometries: octahedral structure of a solvated electron from Ref. [2] (left), *triangular-ring* structure (center), and *prism* structure (right). Oxygen and hydrogen atoms are indicated, respectively, as large and small black spheres. The red lines indicate hydrogen bonding.

the highest occupied molecular orbitals (HOMO) for the *triangular-ring* and *prism* structures, respectively. In the *triangular-ring* structure the electron is well localized inside the cluster and acts to bridge the two rings. Within a sphere encompassing the six oxygen atoms we find 57% of the excess electron. This electron has somewhat of an *s* orbital-like distribution, which is similar in spirit to the predictions made in calculations of the condensed phase [16] and of the hexamer at Kevan's geometry [8]. It differs in that the electron density is described by six maxima distributed among very specific H atoms. These are "dangling" H atoms that are *not* involved in hydrogen bonding. A similar effect is manifested in the electron density distribution for the *prism* structure shown in the right panel of Fig. 2. The dangling H atoms acts as electrophilic sites attracting the excess electron. This is certainly a reasonable result, since H atoms involved in hydrogen bonding are loosely speaking already "saturated" electrophilic sites. All of the H atoms in an anionic cluster, therefore, appear to be involved either in hydrogen bonding or in an interaction with the excess electron. As further evidence of these effects, we show in Fig. 3 the results for two other cluster geometries. These geometries were obtained from the nearly isoenergetic ground state structures of the *neutral* hexamer [17]. One of these (top panel) is a *prism-derivative* structure [18], and the other (bottom panel) is a *cyclic* structure [19]. Both clusters are characterized by excess electron HOMO states that are resonances. They are stable in their neutral configurations. They both clearly show that the excess electron, even in resonant states, is attracted to the dangling H atoms. Furthermore, the surface states observed in the medium-sized water clusters by Barnett *et al.* [4] are related to the electrophilic cluster sites, with the dangling H atom sites acting as actuators of these surface states. Kevan's structure of the electron bound in liquid water also demonstrates that the dangling H atoms are the actuators of the internal states.

Of all the geometries we have studied, we find that only the *triangular-ring* and *prism* structures bind an excess electron. Both the *triangular-ring* and *prism* structures are metastable. At the level of the MP2/6-311++G** theory, the anionic *prism* structure is higher ($\sim$0.5 eV) in energy than the neutral *cyclic* hexamer with the electron at infinity. The significant difference between the electron distribution of the *triangular-ring* and *prism* structures is reflected in a significant difference in our predicted IE's, which are 0.5 and 0.1 eV, respectively [20]. The agreement with the experimental IE's, which are 0.5 and 0.2 eV [5], is notable. This indicates that the observed IE's arise from two separate classes of cluster geometries rather than two states of the same cluster. However, the experimental photoemission signal is found to be much stronger at 0.5 than at 0.2 eV. This might appear to be evidence against the *prism* geometry having a ground state energy lower than that of the *triangular-ring* geometry. But a simple analysis of the appropriate Fourier components of the excess-electron wave functions shows that the *triangular-ring* HOMO state has a much larger photoemission cross section than the *prism* HOMO

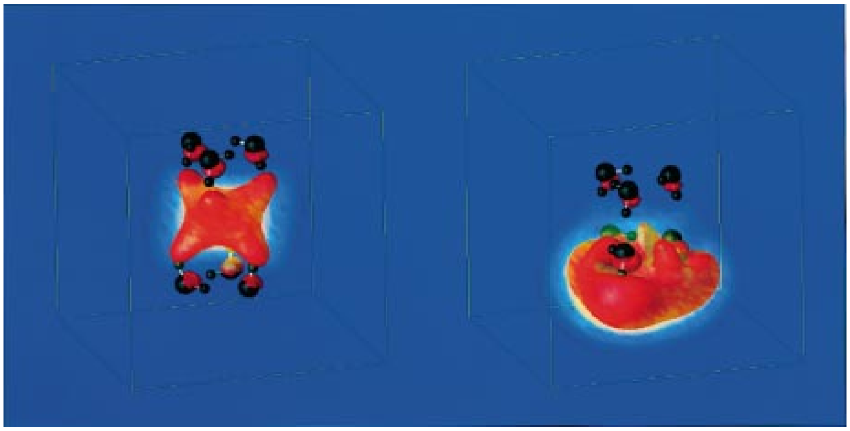

FIG. 2 (color). HOMO electron density distributions for the *triangular-ring* structure (left) and *prism* structure (right). Low to high densities are represented by blue to red clouds.

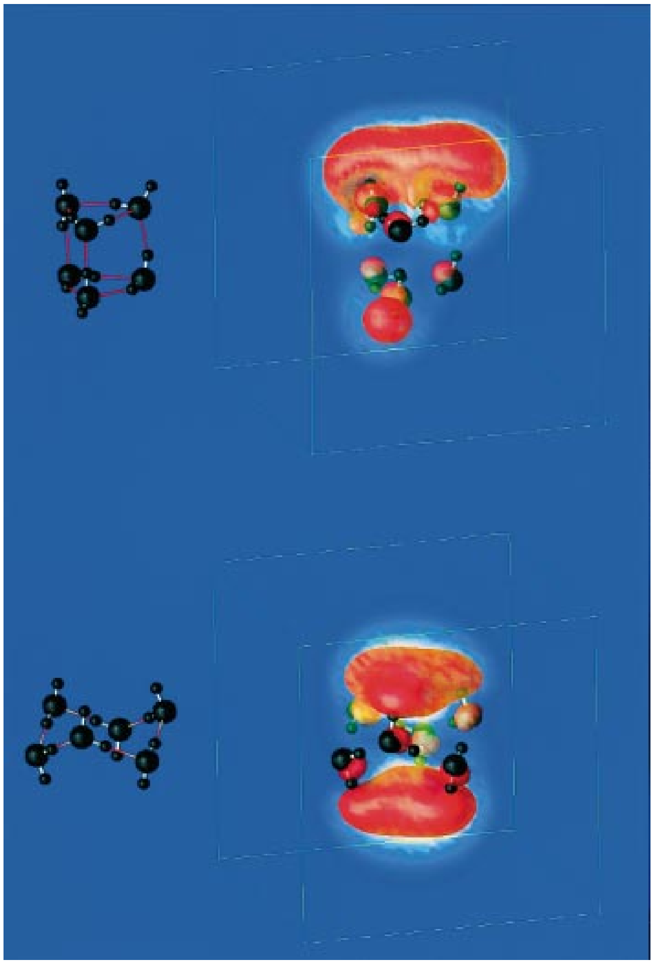

FIG. 3 (color). HOMO electron density distributions for the *prism-derivative* structure (top) and *cyclic* structure (bottom) in resonance states. Same convention as in Fig. 2.

state (by $\sim 10^3$), which leads to consistency with the photoemission spectrum.

Our overall results can be understood using a simple heuristic based on the energetics of hydrogen bond formation and the nature of the excess electron-hydrogen ($e^{\cdots}$H) interactions. The $e^{\cdots}$H interaction is strongly cooperative in that the electron density favors clustered dangling H atoms. This is reflected in the energy difference between the *prism* and *prism-derivative* structures. The $e^{\cdots}$H interaction induces the *prism* structure, which is less stable (0.2 eV) in the neutral state than the *prism-derivative* structure, to become more stable (0.1 eV) in the anionic state. It also induces the *triangular-ring* structure, which is highly unstable in the neutral state, to become stable in the anionic state. Thus the $e^{\cdots}$H interaction emerges as an important force, comparable to the hydrogen-bonding interaction. However, since the energies increase in going from *prism* to *triangular-ring* to Kevan's structure, the $e^{\cdots}$H interaction is weaker than the hydrogen bonding. Since all H atoms in the anionic clusters are involved in either hydrogen bonding or $e^{\cdots}$H interactions, this saturation accounts for the isoenergetic nature of the anionic clusters. Moreover, the competition between the interactions generates more diverse conformers than in the neutral states. As a consequence, deionization of anionic clusters could be used to facilitate the formation of novel neutral conformers that are not easily accessible. The case of the *prism* structure is such an example.

Finally, an interesting insight emerging from this *ab initio* study is related to the *generic* electrophilic nature of the dangling H atoms. This nature should prevail even in more complex molecular environments. It is well known that water molecules can be embedded or attached to biomolecular systems. Conceptually, dangling H atoms on strings or networks of such water molecules would allow an electron to hop between them and thereby actuate a pathway for electron transport [21]. As an example, in azurine dimers from *pseudomonas aeruginosa* [22] two water molecules bridging azurin monomers have been identified as being involved in the electron transfer between the Cu(I) and Cu(II) redox centers in the respective monomers. Although the conformation of these water molecules is not known, in this system it is reasonable to expect one or two dangling H atoms in the cluster. The results of our work would then suggest that through-space electron transport between monomers could then take place through these electrophilic sites. Of course, we have not included the effects of dynamics or solvents which are beyond the scope of this work. Nevertheless, the *generic* electrophilic nature of the dangling H atoms should be fairly robust, and it would be exciting if it proves possible to harness this property to affect novel *through-space* pathways for electron transport in addition to the traditional *through-bond* pathways.

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[14] The distances from the cluster center (Ct) to H, H$'$, and O atoms are 2.85, 3.34, and 3.47 Å, respectively. Here, H and H$'$ denote the H atoms at the shorter and longer distances from Ct, respectively.

[15] The shortest interoxygen distances are 2.92 Å (upper triangle), 2.86 Å (lower triangle), and 2.92 Å (between two triangles). The MP2/6-311++G** energy is $-457.860\,88$ hartress.

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[18] The shortest interoxygen distances are 2.80–2.89 Å (upper triangle), 2.91–2.98 Å (lower triangle), and 2.70–2.87 Å (between two triangles).

[19] The distances from Ct to H, H$'$, and O atoms are 2.26, 2.72, and 2.59 Å, respectively [20]. The photoemission IE's (or vertical electron detachment energies) have been calculated by subtracting the total energy of the anionic species from that of the neutral species at the optimized geometry of the anionic structure.

[20] The photoemission IE's (or vertical electron detachment energies) have been calculated by subtracting the total energy of the anionic species from that of the neutral species at the optimized geometry of the anionic structure.

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