Hydration of Sodium in Water Clusters

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Hydration of sodium in water clusters, $Na(H_2O)_n$, $1 \leq n \leq 8$, is investigated using nonlocal pseudopotentials and local-spin-density functional theory, with exchange-correlation gradient corrections. Addition of water molecules to an Na atom results in a successive decrease in the ionization potential, with a marked reduced variation for $n > 4$. This reflects the formation of a molecular shell about the Na for $n \sim 4$, accompanied by expulsion of the metal valence electron from the hydration cavity and its delocalization in a "surface Rydberg-like state."

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Energetics, structure, dynamics, and spectroscopy of solvation in bulk liquids and clusters (in particular, polar molecular ones) are subjects of continued research endeavors pertaining to fundamental properties of electrons and ions in liquids, chemical reactions, biological processes, and the size dependence of electron localization modes and stability of solvated species in finite clusters [1,2]. While the properties of excess electrons in water clusters have been thoroughly investigated experimentally and theoretically [1,2(a),2(b),2(d)], it is only most recently that measurements of the ionization potentials (IP's) of alkali atoms (M = Na and Cs) in size-selected water clusters, $M(H_2O)_n$, $1 \leq n \leq 30$, have been made [3,4]; these reveal a monotonic decrease in the IP's for $0 \leq n \leq 4$, from IP[Na] = 5.13 eV and IP [Cs] = 3.89 eV to IP$[M(H_2O)_n] = 3.2 \pm 0.1$ eV (M = Na or Cs) for $n \geq 4$. Interestingly, the limiting value for $n \geq 4$ coincides with the estimated IP of an excess electron solvated in bulk water [1,3,4].

We report results of a study of the electronic and geometrical structures for $Na(H_2O)_n$ clusters [5], $1 \leq n \leq 8$, showing that increasing the hydration number results in delocalization of the sodium $3s$ valence electron. Moreover, the origin of the characteristic change in the rate of variation of the IP's for $n > 4$ is related to formation of a hydrated Na^+ species, with the electron delocalized outside the Na^+ hydration cavity.

The electronic structure of the system is calculated self-consistently using the Kohn-Sham (KS) formulation of the local-spin-density functional (LSD) method, with norm-conserving nonlocal pseudopotentials [6] for oxygen and sodium, and a local one for hydrogen (the cutoff radii used are 1.45 a.u. for oxygen, 2.5 and 2.75 a.u. for sodium s and p, respectively, and 0.95 a.u. for hydrogen. We use a dual-space plane-wave representation, with the Kleinman-Bylander decomposition [7] of the pseudopotentials performed in real space [8,9]. We emphasize that while a plane-wave representation is used, we do not employ a supercell, i.e., the system does not interact with any of its images [9]. Convergence was found to require a value of $E_{pwc} = 62$ Ry as the plane-wave kinetic energy cutoff. In each case the structure of the system was obtained via a steepest-descent method on the Born-Oppenheimer potential energy surface, starting from several judiciously chosen starting configurations. For the LSD part the per particle correlation energy of the uniform electron gas is taken after Ceperley and Alder [10]. Exchange [11] and correlation [12] gradient corrections (XCGC) were applied perturbatively (i.e., post-LSD) [11,13].

We remark first on the quantitative agreement between our calculations and experimental data for several molecular constituents of our system. In particular, for H_2O, using $E_{pwc} = 62$ Ry, the calculated atomization energy, OH distance, θ(HOH) angle, and dipole moment are 10.80 eV, 0.956 Å, 107.4°, and 1.67 D, respectively, while calculation with $E_{pwc} = 96$ Ry yields 10.58 eV, 0.960 Å, 105.4°, and 1.69 D, respectively, compared to the experimental values [14] of 9.51 eV, 0.957 Å, 104.5°, and 1.855 D. The calculated OH stretch and HOH angle-bending frequencies (3713 and 3944 cm^{-1} for the former and 1575 cm^{-1} for the latter) are also in adequate agreement with the measured ones [14]. Furthermore, for $(H_2O)_2$ the calculated binding energy of the dimer, using $E_{pwc} = 62$ Ry is 0.213 eV, the distance between the oxygens is 2.96 Å, and the dipole moment is 2.56 D, in very good agreement with our calculations using $E_{pwc} = 96$ Ry, and with measured values [14] (0.234 eV, 2.98 Å, and 2.60 D, respectively). In this context we remark that, in accord with previous experience [15], a proper description of hydrogen bonding in our systems requires gradient corrections (e.g., LSD calculations without gradient corrections yield a dimer binding energy of 0.398 eV and a distance of 2.68 Å between the oxygens, which are inferior in comparison to the results including XCGC given above). We also note the excellent agreement between the calculated dissociation energies of $Na(H_2O)^+$ and $Na(H_2O)$ (1.06 and 0.27 eV, respectively, see Table I), and the corresponding experimental estimates [3(a)] (1.04 and 0.28 ± 0.04 eV), as well as the accurate predictions for the vibrational frequencies [calculated Na-O stretch frequencies in $Na(H_2O)^+$ and $Na(H_2O)$, 318 and 237 cm^{-1}, compared to a measured [3(a)] 305 ± 15 cm^{-1} for the former and a previously

TABLE I. Energetics of neutral $Na(H_2O)_n$ and ionized $Na^+(H_2O)_n$ clusters, $1 \leq n \leq 8$, using LSD XCGC (energies in eV). $\epsilon_{e\text{-}Na^+}$ and $\epsilon_{e\text{-}H_2O}$ are the individual contributions to the energy of the HOKS orbital (given by ϵ_{HOKS} which includes also a kinetic energy contribution) due to interactions with the Na^+ ion and the water molecules in $Na(H_2O)_n$. The energy gap between the HOKS orbital, occupied by the metal valence electron, and the water eigenvalue spectrum is given by δ. Δ and $\Delta+$ are the energies required to remove a water molecule from the neutral and ionized clusters, respectively (experimental values and error estimates after Ref. [3(a)] in parenthesis). IP is the adiabatic ionization potential of the neutral clusters (experimental values, in parenthesis, after Ref. [3]). For $n=6$ results are given for three structures; see Ref. [17]. Δ and $\Delta+$ for $n=8$ correspond to $\{E(8)-[E(6)+2E(H_2O)]\}/2$, where $E(n) \equiv E[Na(H_2O)_n]$.

n	$\epsilon_{e\text{-}Na^+}$	$\epsilon_{e\text{-}H_2O}$	ϵ_{HOKS}	δ	Δ	$\Delta+$	IP
1	−6.44	0.82	−2.68	5.90	0.27	1.06	4.62
					(0.28 ± 0.4)	(1.04)	(4.38 ± 0.03)
2	−5.87	−0.75	−2.53	5.62	0.31	0.73	4.20
					(0.28 ± 0.04)	(0.86 ± 0.04)	(3.80 ± 0.05)
3	−5.41	−1.45	−2.30	5.94	0.30	0.71	3.79
					(0.37 ± 0.15)	(0.69 ± 0.05)	(3.48 ± 0.06)
4	−4.35	−3.41	−2.12	6.08	0.40	0.84	3.35
					(0.32 ± 0.2)	(0.60 ± 0.05)	(3.20 ± 0.10)
5	−4.00	−3.61	−2.01	5.52	0.26	0.49	3.12
					(0.53 ± 0.24)	(0.53 ± 0.05)	(3.20 ± 0.10)
6(4+2)	−3.66	−3.78	−1.95	5.58	0.29	0.47	2.94
					(0.46 ± 0.24)	(0.46 ± 0.05)	(3.20 ± 0.1)
6	−3.93	−3.89	−2.02	5.83	0.29	0.29	3.17
6b	−3.66	−4.47	−2.03	5.23	0.26	0.28	3.09
8	−3.58	−4.23	−1.97	5.27	0.26	0.36	2.91

calculated [16] value of 226 cm^{-1} for the latter, respectively].

These comparisons, as well as others for H_2, Na_2, O_2, NaH, and NaO where quantitative agreements with experiments were obtained [9], support our confidence in our ability to faithfully describe the energetics and dynamics in molecular systems such as those studied here.

Optimized low energy structures of $Na(H_2O)_n$ clusters and corresponding images of the electron distribution of the highest occupied KS orbital (HOKS), populated by the metal valence electron which for all sizes is separated by a gap $\delta \simeq 5.5$–6 eV from the water eigenvalue spectrum, are shown in Fig. 1. In the course of determining these structures [17] we noted that they are close to those of the corresponding relaxed ionized ones $[Na(H_2O)_n^+]$, with the molecules in the first hydration shell oriented with the oxygen end closer to the sodium atom [5] (calculated values for the energies to remove a water molecule from neutral and ionized clusters, given in Table I, are in good correspondence with experimentally estimated ones [3(a)]. The images in Fig. 1 and the probability distributions in Fig. 2 demonstrate formation of a hydration cavity about the Na atom, and successive delocalization of the Na valence electron about the surrounding water molecules. As indicated in Fig. 2 the probability of finding the electron inside the tetrahedral hydration cavity for

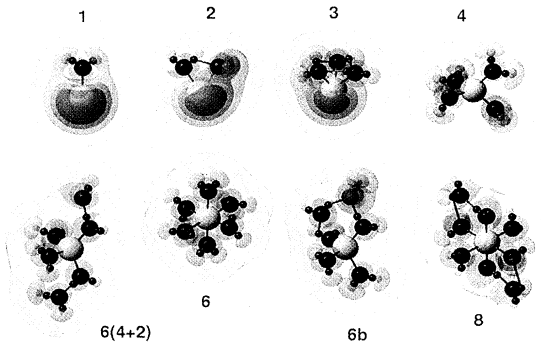

FIG. 1. Atomic configurations [17] and electronic density distribution of the HOKS in $Na(H_2O)_n$ for $n=1$, 2, 3, 4, 6(4+2), 6, 6b, and 8. Large, medium, and small spheres correspond to Na, O, and H atoms, respectively. The lightest shade (light violet) of the iso-density surfaces corresponds to $1 \times 10^{-4} a_0^{-3}$ and darker shades correspond to $5 \times 10^{-4} a_0^{-3}$, $10 \times 10^{-4} a_0^{-3}$, and $20 \times 10^{-4} a_0^{-3}$, respectively. The sodium atom is represented by a large yellow ball, and the oxygen and hydrogen atoms by blue and small red balls, respectively. (Note that for $n > 2$ the largest density is absent due to delocalization of the charge distribution.) H-O and Na-O bonds of $< 5a_0$ are shown as connecting rods.

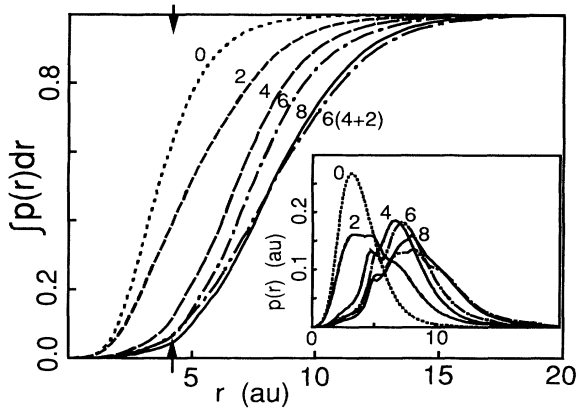

FIG. 2. Accumulative probabilities vs r (in a.u.) corresponding to those shown in the inset. The average r(Na-O) = 4.25 a.u. distance in $Na(H_2O)_n$ is indicated by arrows. Shown in the inset are probability distributions $p(r)$ of the HOKS in $Na(H_2O)_n$, for $n = 0$, 2, 4, 6, 6(4+2), and 8 vs radial distance from the Na atom.

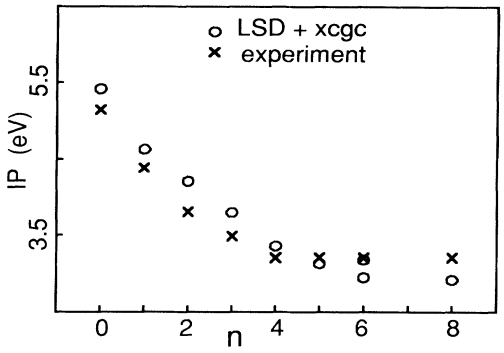

FIG. 3. Experimental (after Refs. [3(a),3(b)]) and LSD XCGC calculated adiabatic ionization energies (in eV) for $Na(H_2O)_n$ ($0 \leq n \leq 8$), plotted vs n. For $n = 6$ results are given for the structures marked 6 and 6(4+2) in Table I (see Ref. [17]).

$Na(H_2O)_4$ [defined as a sphere about the Na of radius r(Na-O) $= 4.25 a_0$, which is the average distance between the Na atom and the oxygen atoms in $Na(H_2O)_4$] decreases to a value of 0.12 (for Na the corresponding value is 0.64). Further addition of water molecules reduces this value to 0.07 for $n = 6$ and 0.05 for $n = 8$. Furthermore, we note that the electron is not attached to a particular water molecule, instead it is spread rather equally about them (in a certain sense the delocalized electron forms a "surface Rydberg state" of the hydrated sodium atom).

The calculated adiabatic IP's (the vertical and adiabatic IP's are close to each other, reflecting a very small structural rearrangement following ionization) shown in Fig. 3 are in good correspondence with the measured ones [3(b)]. Moreover, the calculated and measured values [3(b)] exhibit the same trend versus cluster size; that is, in both, a reduced rate of change of the IP's is exhibited for $n > 4$. This characteristic behavior correlates with the expulsion of the electron from the hydration cavity about the sodium and the surface-delocalized nature of the electron. Further insight is gained from inspection of Table I. In particular, the opposing trends in $\epsilon_{e\text{-}Na^+}$ and $\epsilon_{e\text{-}H_2O}$ is noted, as well as the slower variation of $\epsilon_{e\text{-}Na^+}$ for $n > 4$.

Coupled with our structural results we conclude that the hydration of sodium in small water clusters involves a partial "detachment" of the 3s valence electron from the Na atom, accompanied by delocalization to form a surface Rydberg-like state. This picture correlates with the observation that the limiting value of the IP's for $n > 4$ is essentially the same for both hydrated sodium [3(b)] and cesium [4]. This process may also underlie the different behavior observed for Na and Cs solvated in ammonia clusters [3(b),4], where the decrease in IP upon the addition of ammonia molecules persists beyond 20 molecules, since ammonia clusters have a much reduced tendency to attach an excess electron in a well-bound surface state [18] as a precursor for interior localization in $(NH_3)_n^-$ which occurs for $n \gtrsim 30$ [19] (note the smaller dipole moment of NH_3 as compared to that of H_2O). Consequently it may be expected that a behavior similar in nature to that found for alkali atom solvation in small water clusters may be found in other polar molecular solvents of large enough dipole moment to stabilize well-bound surface states.

While the size evolution of alkali-atom solvation in clusters reveals the nature of precursors to hydration in bulk water, the proximity of the values of the IP's of $M(H_2O)_n$ clusters (M = Na,Cs) for $n > 4$ to that estimated for a single excess electron in bulk water may be a coincidence, since electron hydration in water is known experimentally and theoretically to involve long-range interactions, leading to a $n^{-1/3}$ variation of the IP's [1,20]. This coincidence is related, as discussed above, to the structure and balance of interactions in small $M(H_2O)_n$ clusters. In particular we note that for $n \gtrsim 4$ the contributions to the energy due to interactions of the metal valence electron with the parent Na^+ ion and the water molecules are of comparable magnitudes (see $\epsilon_{e\text{-}Na^+}$ and $\epsilon_{e\text{-}H_2O}$ in Table I). We suggest that as one approaches the bulk limit, where the fully hydrated Na^+ ion and the electron are distant from each other, $\epsilon_{e\text{-}Na^+}$ is compensated by the long-range interaction of the hydrated electron with the polar water medium.

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[17] In addition to the optimized structures of the neutral and ionized $Na(H_2O)_n$ clusters other isomeric structures are possible. From our results, and comparisons to experimental data (see Table I), we may conclude that our optimized structures are among the lowest energy ones. Structures for $n=1$ and 2 are evident from Fig. 1. For $n=3$ and 4 our results (Table I and figures) correspond to a trigonal pyramid (the Na at the apex above the oxygen plane with the H_2O molecules hydrogen bonded), and a tetrahedral structure around the sodium (see Fig. 1), respectively. For $n=5$ the lowest energy structure is based on a tetrahedral arrangement and an H_2O molecule outside it. For $n \geq 3$ other, higher-energy, structures were found: For $n=3$ a planar structure of the ionized cluster (with the 3 oxygens and sodium at the corners of an approximate rhombus) is degenerate in energy with the trigonal one, and for the neutral this structure is slightly higher in energy (by 0.05 eV) and its IP is 3.75 eV; for $n=4$ a square-based pyramidal structure (with the oxygens forming the base, and the H_2O molecules hydrogen bonded) of the ionized and neutral clusters is higher in energy (by 0.34 and 0.1 eV, respectively) than the tetrahedral ones, and its IP is 3.59 eV; for $n=5$ a pentagonal pyramidal structure (with the oxygens at the base) is higher in energy than the optimized one by 0.28 eV for the ionized cluster and 0.04 eV for the neutral one, and its IP is 3.37 eV. For $Na(H_2O)_6$ results for three structures are shown (see Table I). The first two [denoted as 6(4+2) and 6] which for the neutral cluster have the same energy, but the first is more stable for the ionized one (by 0.18 eV), correspond to 4 and 6 molecules in the first hydration shell, respectively. The structure marked 6b, which is the highest in energy, is like 6(4+2) but with the two H_2O molecules outside the first shell hydrogen bonded to each other. Structures such as 6b, which possesses a dipole moment associated with the two outer molecules resulting in enhanced partial localization of the electron, may be involved in the eventual formation of a separated ion-solvated electron pair.

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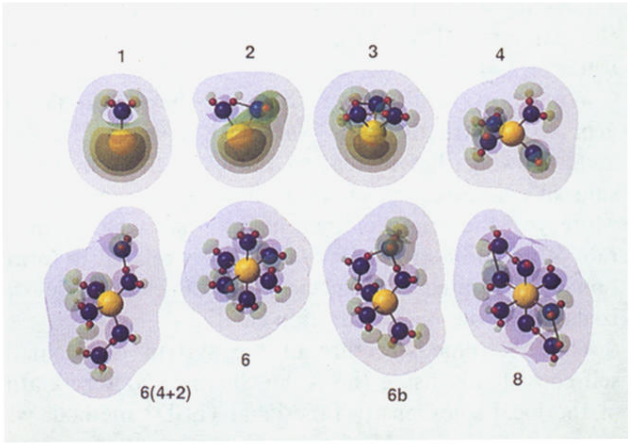

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