Electronically excited water aggregates and the adiabatic band gap of water

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The authors report results for the electronic properties of the S_1 singlet excited state of $H_3O^+[OH(H_2O)_{(n-2)}]^-$ aggregates, where $n=2-5$ is the number of water molecules. The energy of the excited state was defined relative to the ground state of neutral water clusters. Results for ionized aggregates are also reported. The results are based on configuration interaction with single excitations geometry optimizations followed by density functional theory and time dependent density functional theory calculations. Emphasis was placed on the relationship between electronic properties of the aggregates and the adiabatic band gap of liquid water. The authors' predictions for the adiabatic energy gap of water clusters are in the 6.01–6.55 eV range. These values are ~0.9–0.4 eV below the experimental adiabatic band gap of liquid water (6.9 eV). Comparison with experimental information for water is reported for several properties of interest including vertical and adiabatic ionization energies, excitation energies, photoemission thresholds, and conduction band edge. The results provide a description, at the molecular level, for the electronic properties of water aggregates that is consistent with the current picture for the band gap of bulk water [J. V. Coe, Int. Rev. Phys. Chem. **20**, 33 (2001)]. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Electronic properties of water are not very well understood.[1,2] They are, however, of fundamental importance in investigating the chemical reactivity and dynamics of electronically excited states in aqueous solutions,[3,4] and in explaining several unique properties that characterize the water hydrogen bond (HB) network. A longstanding issue concerns the fact that hydrated electrons in liquid water are produced by photoabsorption at ~6.5 eV.[5–9] This energy is significantly lower than the threshold energy for photoelectron emission (PET) by liquid water (9.9 eV,[2] 10.06 eV,[10,11] and 9.3±0.1 eV[12]) and ~6 eV below the first ionization potential of the gas phase water molecule (12.62 eV).[13] Several works pointed out that the ability of water to reorganize about charged species as well as the reactive nature of electronically excited water molecules should be taken into account in explaining electronic properties of water.[14–16] Moreover, they indicate that an adiabatic route for accessing the conduction band of liquid water can be defined and that the bottom of the conduction band is characterized by the reorganization of the water molecules around the H_3O^+ and OH radical species as well as by the presence of a delocalized or

quasi-free electron. The energy associated with this process corresponds to the water adiabatic band gap, and it is estimated as ~6.9 eV.[14,15]

Although some experimental[14–16] and theoretical[17] works on the water adiabatic band gap have been reported, the structure and electronic properties of photoexcited states of water associated with the adiabatic band gap deserve further investigation. On the other hand, it is generally accepted that some of the complex behavior characterizing the water HB network is already present in small water aggregates.[3] Therefore, the study of water clusters can be very useful in understanding, from a microscopic point of view, the electronic properties of bulk water.

In this article we report a theoretical investigation of the electronic properties of small water clusters. Our main interest is to study how the energetic properties of electronically excited water aggregates can be related to the electronic properties of liquid water, such as the photoelectron emission threshold, the conduction band edge, and the adiabatic band gap. The presently adopted procedure relies on *ab initio* configuration interaction with single excitations[18] (CIS) geometry optimizations for the S_1 singlet excited state of water aggregates. The energetic properties of the optimized structures were analyzed by density functional theory (DFT),[19] and excitation energies were calculated by time dependent density functional theory (TDDFT).[20] For the water monomer and dimer, results based on symmetry adapted cluster

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configuration interaction with single and double excitations[21–23] [SAC-CI(SD)] are also presented. Some recent works on excited water clusters were reported.[24,25] However, they focused, essentially, on vertical excitation processes.

The article is organized as follows. Initially, computational details (Sec. II) are presented. In the same section we introduce the definition and appropriate notation for properties relevant for the discussion. In Sec. III we report results for several electronic properties of water aggregates, including vertical excitation and ionization energies, energetics of the e^- anionic defect, and adiabatic energy gap in water clusters. We conclude by placing emphasis on two aspects: (1) the importance of taking into account the reactive nature of electronically excited water and the structure relaxation of the water molecules upon photoexcitation; (2) the interest in carrying out cluster studies for a better understanding of the electronic properties of bulk water.

II. COMPUTATIONAL DETAILS

Optimized ground state (S_0) and singlet lowest excited (S_1) structures were determined by *ab initio* configuration interaction with single excitations (CIS).[18] A discussion on the reliability of CIS excited state structures has been recently reported.[26] It was concluded that, in general, CIS optimized geometries are usually close to those predicted by equation of motion CCSD (Ref. 27) and are in good agreement with experimental information. The optimizations were carried out with the double augmented d-aug-cc-pVDZ basis set.[28] Harmonic frequencies were evaluated at the same level (CIS/d-aug-cc-pVDZ).

Different excited conformers corresponding to local minima on the S_1 potential energy surface were identified. They are characterized by the presence of the hydronium (H_3O^+), the OH radical, and a delocalized electronic density that can be associated with the microsolvated electron (see next session for details). Single-point energy DFT calculations were then performed with the BHandHLYP functional[29,30] as implemented in the GAUSSIAN 03 suite of programs.[31] The BHandHLYP exchange-correlation functional is defined as $0.5E_x^{HF}+0.5E_x^{LSDA}+0.5\Delta E_x^{Becke88}+E_c^{LYP}$, where E_x and E_c are exchange and correlation functionals, respectively. The choice of this functional was oriented by recent works on hydrogen bonding[32,33] and ionized water clusters[34,35] indicating that BHandHLYP provides an adequate description of the structure of water and related systems. This was explained by partial correction of the self-interaction error[19] due to the admixture of "exact Hartree-Fock (HF) exchange."[34] Excitation energies of water clusters were determined by TDDFT (Ref. 20) with Dunning's d-aug-cc-pVTZ basis set.[28] Full active SAC-CI(SD) calculations for $n=1,2$ were carried out with the d-aug-cc-pVDZ (optimizations) and d-aug-cc-pVTZ (single-point energy) basis sets.

We will focus the present discussion on the first excited singlet S_1 states. An extensive search on the potential energy surface (PES) of excited states is not affordable for large water aggregates. Therefore, our procedure to identify local minima on the S_1 excited state potential energy surface was directed to structures characterized by the presence of the three species associated with the conduction band edge for the water adiabatic band gap,[14] namely, H_3O^+, the OH radical, and the hydrated electron. A similar approach was applied by Sobolewski and Domcke to study zwitterionic and biradical forms of the water pentamer.[36] It should be observed that by adopting the present procedure, we can identify the structures of the excited aggregates on the S_1 PES although no information on the dynamics of the microscopic process leading from S_0 to S_1 is provided.

To discuss the importance of structure reorganization upon excitation, we will introduce the following notation. $E(S_i;S_j)$ means that the S_j state energy is calculated in the geometry of the state S_i. For example, $E(S_0;S_0)$ or simply E_0 is the ground state energy calculated in the ground state geometry of the singlet reference state S_0. For a given number of water molecules (n), the ground state reference system was taken as the most energetically stable conformer. In addition, we will represent by $E(S_j;S_j \leftarrow S_i)$ the excitation energy from S_i to S_j in the geometry of the singlet state S_j. Ionization of the S_i state in the S_i geometry will be simply represented as $E(S_i;+)$. The energy of an optimized ionized aggregate $[E(+,+)]$ will be represented as $E(+)$.

The relative (or adiabatic) excitation energy E_R for the $S_1 \leftarrow S_0$ transition can be written as

$$E_R(S_1) = [E(S_1;S_0) - E_0] + E(S_1;S_1 \leftarrow S_0), \quad (1)$$

where E_0 is the ground state reference energy and $E(S_1;S_1 \leftarrow S_0)$ is the $S_1 \leftarrow S_0$ excitation energy calculated at the optimized structure of the excited state S_1. The reorganization (or relaxation) energy associated with the $S_1 \leftarrow S_0$ excitation is $E(S_1;S_0) - E_0$. The relative ionization energy for the S_1 excited state optimized structure will be represented as $E_R(S_1;+)$ and can be written as

$$E_R(S_1; +) = [E(S_1; +) - E_0]. \quad (2)$$

The adiabatic ionization energy can be calculated by $E_R(+;+) = [E(+;+) - E_0]$ and will be simply represented as $E_R(+) = [E(+) - E_0]$.

Energetic properties related to vertical processes, the anionic e^- defect, and the adiabatic energy gap of water clusters are reported and their calculation for the water pentamer is illustrated in Fig. 1. The quantities represented by $V_{0,v}$ and V_0 correspond to the energy to transfer an electron from the vacuum to the lowest unoccupied molecular orbital of the aggregate. For the vertical process (left side of Fig. 1) $V_{0,v} = E(S_0;S_1 \leftarrow S_0) - IP$, where $IP = E(S_0;+) - E(S_0)$ is the vertical ionization potential. For the adiabatic process describing the relaxation of the water molecules around the H_3O^+ and OH species (middle of Fig. 1), $V_0 = E_R(+;S_1) - E_R(+)$. The last quantity can be considered as analogous to the conduction band edge of liquid water (V_0), which is defined as the energy to take a zero kinetic-energy gas phase electron to the bottom of the conduction band of the condensed phase as a delocalized or quasi-free electron.[14] However, it should be observed that V_0 for liquid water describes the energetic stabilization of a quasi-free electron interacting with the hydrogen bond network. In a small cluster, only a few dangling
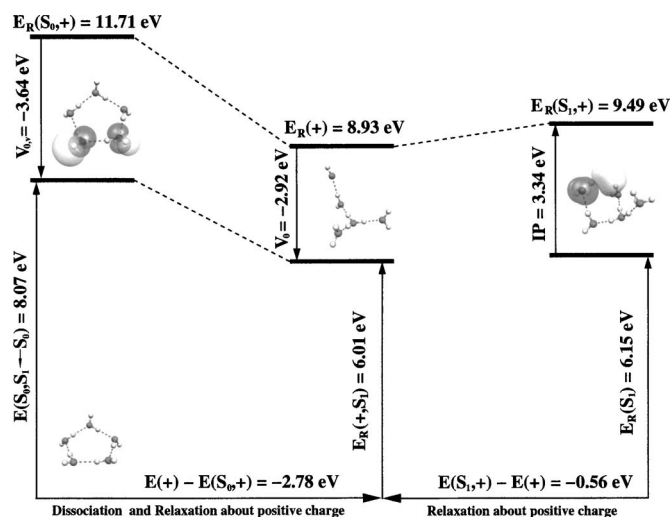
FIG. 1. Electronic properties as a function of the "solvent" coordinate for a water pentamer. (a) The left side arrows indicate vertical excitations (no relaxation). $E(S_0;S_1 \leftarrow S_0) = 8.07$ eV; $IP = E(S_0;+) - E(S_0) = 11.71$ eV; $V_{0,v} = E(S_0;S_1 \leftarrow S_0) - IP = -3.64$ eV. (b) Middle vertical arrows correspond to relaxation around the cationic defect (H_3O^+). $E_R(+;S_1) = [E(+;S_0) - E_0] + E(+;S_1 \leftarrow S_0) = 6.01$ eV; $V_0 = E_R(+;S_1) - E_R(+) = -2.92$ eV; $E_R(+) = E(+) - E_0 = 8.93$ eV. (c) Right side vertical arrows indicate the energetics of relaxation around the e^- anionic defect. $E_R(S_1) = [E(S_1;S_0) - E_0] + E(S_1;S_1 \leftarrow S_0) = 6.15$ eV; $IP = E_R(S_1;+) - E_R(S_1) = 3.34$ eV; $E_R(S_1;+) = E(S_1;+) - E_0 = 9.49$ eV. The horizontal arrows correspond to $E_R = E(+) - E(S_0;+)$ (-2.78 eV) and $E_R = E(S_1;+) - E(+)$ (-0.56 eV) relaxation energies.

hydrogen atoms are available and the interaction of the microhydrated electron with the H_3O^+ and OH species cannot be *a priori* discarded.

Optimized structures corresponding to the ground (S_0) and lowest (S_1) singlet states are reported in Figs. 2–4. Ionization of the excited clusters followed by geometry relaxation leads to the ionized structures reported in Figs. 2–4. For $n = 3 - 5$ several isomers (local minima on the S_1 surface) were identified. Electronic density difference isosurfaces, corresponding to the difference between the total CIS unre-

laxed density of the excited state and of the HF ground state in the geometry of the S_1 complex, are represented in Figs. 2–4. These isosurfaces provide a qualitative picture of the charge reorganization upon photoexcitation. For a given n, the energies relative to the ground state reference system (most energetically stable conformer) are also reported in Figs. 2–4, where the relative energies in brackets are corrected for $T = 298$ K and include zero point vibrational energies (ZPVEs).

III. RESULTS AND DISCUSSION

A. Vertical excitations and the optical energy gap of water clusters

Vertical excitation energy $E(S_0;S_1 \leftarrow S_0)$, IP, and $V_{0,v}$ for water clusters are reported in Table I. For a given number of water molecules, these clusters correspond to the most stable structures. Vertical excitation energies can be compared with other results from the literature.[24,37,38] For the water monomer, our result (7.76 eV) is ~0.3 eV above experimental information (7.4–7.5 eV).[38] An excellent agreement between our calculation (7.76 eV) and the semiempirical estimate of Chipman (7.78 eV)[24] is observed. For the water dimer, we predict that $E(S_0;S_1 \leftarrow S_0)$ is 7.68 eV, which is also in good agreement with a value reported by Chipman (7.91 eV).[25] A very good agreement between TDDFT and SAC-CI(SD) results for the vertical excitation energies of the water monomer and dimer is observed. In addition, a comparison between SAC-CI(SD)/d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ and SAC-CI(SD)/d-aug-cc-pVTZ//SAC-CI(SD)/d-aug-cc-pVDZ vertical excitation energies indicates that quite similar geometries are predicted by the two methods. From the TD-DFT results for the S_1 vertical excitation energies of water clusters, a 0.44 eV blueshift is observed from the water monomer ($n = 1$) to the water pentamer ($n = 5$). This value is ~0.5 eV lower than the predicted blueshift of the S_1 vertical excitation energy (~1 eV) observed for bulk water.[39] The
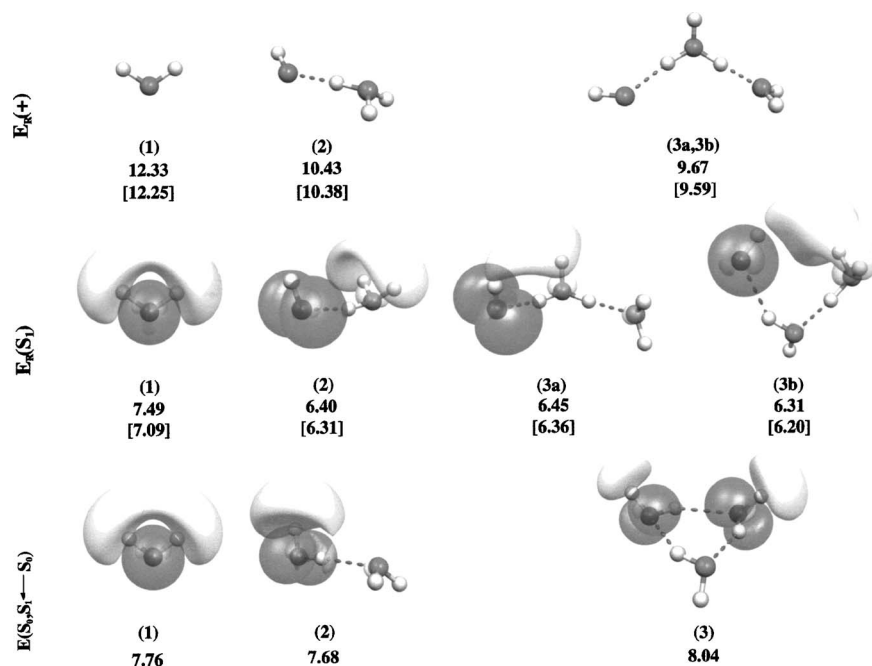

FIG. 2. CIS/d-aug-cc-pVDZ optimized structures for the ground state, singlet excited states, and ionized states of water aggregates ($n = 1 - 3$). Values are vertical excitation energies $[E(S_0;S_1 \leftarrow S_0)]$ and adiabatic excitation and ionization energies $[E_R(S_1)$ and $E_R(+)]$. Energetic properties were calculated at the BHandHLYP/d-aug-cc-pVTZ level. Bracketed values are thermally corrected energy differences (ZPVE included). Data in eV. The isosurfaces correspond to electronic density differences of -0.002 e Å^3 (dark) and $+0.002$ e Å^3 (white).
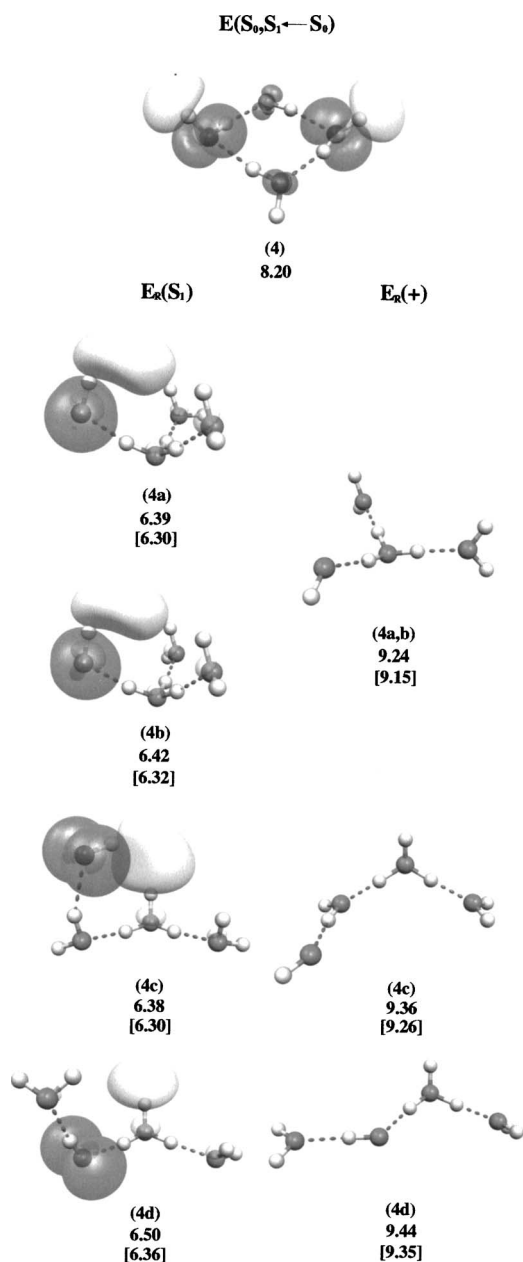
FIG. 3. CIS/d-aug-cc-pVDZ optimized structures for the ground state, singlet excited states, and ionized states of water aggregates ($n=4$). Values are vertical excitation energies $[E(S_0; S_1 \leftarrow S_0)]$ and relative or adiabatic excitation and ionization energies $[E_R(S_1)$ and $E_R(+)]$. Energetic properties were calculated at the BHandHLYP/d-aug-cc-pVTZ level. Bracketed values are thermally corrected energy differences (ZPVE included). Data in eV. The isosurfaces correspond to electronic density differences of -0.002 e Å^3 (dark) and $+0.002$ e Å^3 (white).

FIG. 4. CIS/d-aug-cc-pVDZ optimized structures for the ground state, singlet excited states, and ionized states of water aggregates ($n=5$). Values are vertical excitation energies $[E(S_0; S_1 \leftarrow S_0)]$ and relative or adiabatic excitation and adiabatic ionization energies $[E_R(S_1)$ and $E_R(+)]$. Energetic properties were calculated at the BHandHLYP/d-aug-cc-pVTZ level. Bracketed values are thermally corrected energy differences (ZPVE included). Data in eV. The isosurfaces correspond to electronic density differences of -0.002 e Å^3 (dark) and $+0.002$ e Å^3 (white).

~ 1 eV blueshift of the first absorption band in condensed phases relative to the isolated water molecule has been usually related to Rydbergization effects[40–42] or attributed to excitons of molecular origin.[43,44] The idea behind Rydbergization is that in condensed phases a Rydberg state is energetically destabilized by repulsive interactions of the delocalized electron distribution with the surrounding molecules.[41] It should be expected that this effect is weaker in gas phase water aggregates.

Vertical ionization potentials of the water aggregates are close to 12 eV. The result for the water monomer (12.46 eV)
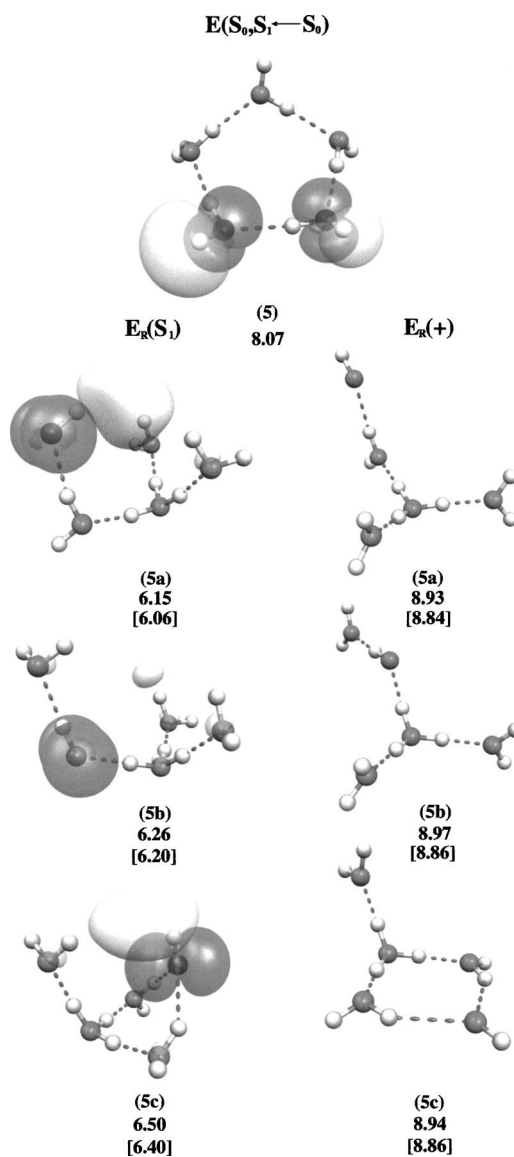
is in good agreement with the experimental value of Dutuit *et al.* (12.62 eV).[13] For the water dimer our prediction (11.64 eV) is 0.46 eV below the experimental value (12.1 eV) reported by Tomoda *et al.*[45] IPs for water clusters ($n=2–5$) are ~ 1.6 eV above the experimental PET of liquid water (9.9 eV,[2] 10.06 eV,[10] and 9.3 ± 0.1 eV[12]). The reduction of the PET from the clusters to liquid water is related to electronic and thermal broadening. Electronic broadening is associated with the splitting of the orbital energies due to hydrogen bond interactions. Thermal broadening is related to disorder and thermal activation in liquid phase.[46] Therefore, the downward shift of the electron binding energies in liquid water relative to the gas phase clusters can be explained by the presence of liquid configurations with lower (weaker) interaction energies.[47,48]

TABLE I. Vertical excitations and optical energy gap in water clusters. Geometry optimizations were carried out at the CIS/d-aug-cc-pVDZ level. DFT energies and TDDFT excitation energies were calculated at the BHandHLYP/d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ level. SAC-CI(SD) results for $n=1,2$ are shown in brackets.

n	1	2	3	4	5
E_0	−76.422 007	−152.851 629	−229.289 290	−305.729 222	382.164 651
$E(S_0;+)$	−75.964 020	−152.423 864	−228.850 824	−305.290 051	−381.734 348
$E(S_0;S_1 \leftarrow S_0)^a$	7.76[7.81;[b] 7.74[c]] (7.4–7.5;[d] 7.78;[e] 7.61[f])	7.68[7.88;[b] 7.84[c]] (7.53;[g] 7.91[h])	8.04	8.20	8.07
IP[i]	12.46 [12.61;[b] 12.57[c]] (12.62[j])	11.64 [11.82;[b] 11.79[c]] (12.1)[k]	11.93	11.95	11.71
$V_{0,v}^{l}$	−4.70 [−4.80;[b] 4.83[c]]	−3.96 [−3.94;[b] 3.95[c]]	−3.89	−3.75	−3.64

[a]$E(S_0;S_1 \leftarrow S_0)$ is the optical energy gap.
[b]SAC-CI(SD)/d-aug-cc-pVTZ//d-aug-cc-pVDZ.
[c]SAC-CI(SD)/d-aug-cc-pVTZ//SAC-CI(SD)/d-aug-cc-pVDZ.
[d]Experimental data from Cheng *et al.* (Ref. 38).
[e]Semiempirical estimate from Chipman (Ref. 24).
[f]From Cai *et al.* (Ref. 37).
[g]From Chipman (Ref. 24).
[h]From Chipman (Ref. 25).
[i]IP$=E(S_0;+)-E_0$.
[j]Experimental value from Dutuit *et al.* (Ref. 13).
[k]Experimental value from Tomoda *et al.* (Ref. 45).
[l]$V_{0,v}=E(S_0;S_1 \leftarrow S_0)-$IP.

For vertical excitations, $V_{0,v}$ range from −4.70 eV (monomer) to −3.64 eV (pentamer). Recent investigations on the electronic structure of liquid water indicate that V_0 should be significantly smaller (−0.17 eV) (Ref. 17) or even close to zero. However, it should be observed that our present estimates indicate that $V_{0,v}$ decreases slowly with increasing cluster size, making difficult a comparison with bulk values. In addition, the definition of V_0 by Coe *et al.*[14] also involves the relaxation of the water molecules around a cationic defect (H_3O^+). Although this feature may not be relevant for bulk water, this seems to be not the case for small water clusters (see also Sec. III C).

B. The e^- anionic defect in water clusters

1. Structure and vibrational frequencies

Several recent studies discussed vertical excited states of water clusters.[24,25] However, the structure reorganization induced by the excitation of water clusters is much less known. Adiabatic excitations of water clusters are relevant for a better understanding of the structure and energetics of anionic defect states, including the microhydrated electron. Starting from a water cluster with n water molecules, photoexcitation may lead to the S_1 excited state structure corresponding to $H_3O^+[OH(H_2O)_{(n-2)}]^-$. The CIS optimized structures (local minima on the S_1 PES) are reported in Figs. 2–4. An analysis of the electronic density differences (also reported in Figs. 2–4) strongly indicates that these aggregates are characterized by the presence of the H_3O^+ cation, the OH radical, as well as by a delocalized electronic distribution which can be associated with a microhydrated electron (e^-). These structures will be associated with the e^- anionic defect in water aggregates. In liquid water, the anionic defect is usually represented as $H_3O^+(aq)+OH(aq)+e^-(aq)$.[14,15,41]

The energetic stabilization of a microhydrated electron is a highly cooperative effect involving the reorganization of the HB network and specific electron-dipole and electron-

hydrogen interactions.[49] Different experimental[50,51] and theoretical[49,52–55] investigations on the O–H stretch frequency shift induced by the interaction with an excess electron in water were reported. In comparison with pure water, it was found that the interaction of water molecules with an excess electron leads to a $\nu_{O–H}$ redshift distributed over a wide range of values ($\sim 0-500$ cm^{-1}), depending on the size and structure of the clusters.[52] Although our present interest is mainly oriented to electronic properties, we report (Table II) some information on the structure and vibrational properties of the OH species in the excited (S_1) and ionized ($+$) aggregates. As shown in Table II, the O–H bond lengths ($d_{O–H}$) for excited states are not very dependent on the cluster size and their values are scattered in the 0.950–0.965 Å range. For the ionized aggregates, 4d and 5b show slightly increased O–H bond lengths (~ 0.97 Å) in comparison with the remaining structures. Table II also reports $\delta d_{O–H}$, which is the difference between $d_{O–H}$ in the excited and ionized aggregates. With the exception of structures 2, 4d, and 5b, $\delta d_{O–H}$ is in general quite small. O–H harmonic vibrational frequencies for the excited states exhibit a significant dependence on the cluster size and structure. This dependence reflects specific interactions of the OH species with H_3O^+, H_2O, and the microhydrated electron. Higher frequencies (~ 4000 cm^{-1}) are observed for the structures where the OH hydrogen atom is free (2) or interacting with water molecules (4d and 5b). Significantly lower O–H frequencies are observed for the structures where the OH species interacts with the charge distribution associated with the microhydrated electron (3a-3b, 4a-4c, 5a, 5c). For ionized clusters, with the exception of conformers 4d and 5b, O–H frequencies are quite similar (~ 4000 cm^{-1}). This is related to the fact that the OH species is a terminal group in all the ionized structures with the exception of 4d and 5b, where it interacts with one water molecule. Comparison between vibrational frequencies of the excited and ionized clusters shows, again, that the nature (blue or red) or magnitude of the frequency

TABLE II. Data for the O–H bond length ($d_{O–H}$ in angstrom) and harmonic vibrational frequency ($\nu_{O–H}$ in cm^{-1}) of the OH species in excited (S_1) and ionized (+) aggregates.

	(S_1)		(+)			
	$d_{O–H}$	$\nu_{O–H}$	$d_{O–H}$	$\nu_{O–H}$	$\delta d_{O–H}$[a]	$\delta \nu_{O–H}$[b]
2	0.950	4101	0.960	3968	−0.010	133
3a	0.958	3863	0.958	3992	0.000	−129
3b	0.952	3968	0.958	3992	−0.007	−24
4a	0.965	3678	0.957	4005	0.008	−327
4b	0.965	3671	0.957	4005	0.008	−334
4c	0.958	3781	0.956	4020	0.002	−239
4d	0.957	3984	0.975	3634	−0.018	+350
5a	0.959	3738	0.956	4027	0.003	−289
5b	0.956	3976	0.970	3719	−0.014	+257
5c	0.965	3612	0.957	4012	0.008	−400

[a]$\delta d_{O–H}$ is the difference between $d_{O–H}$ of the OH species in ionized and excited states.
[b]$\delta \nu_{O–H}$ is the difference between the O–H stretch frequencies of OH species in ionized and excited states.

shift is related to specific interactions involving the OH species in the aggregates. For example, only for structures 2, 4d, and 5b, a $\nu_{O–H}$ blueshift is observed when we move from the ionized to excited aggregates. For all the other conformers, $\nu_{O–H}$ is redshifted. Although strong deviations from harmonic behavior of the PES describing the OH interactions with the microhydrated electron should be expected, the present predictions for the $\nu_{O–H}$ redshift from ionized to excited aggregates are in agreement with the trend observed when $\nu_{O–H}$ frequencies in negatively charged water clusters are compared with those in neutral water clusters.[53] A specific feature characterizing the $\nu_{O–H}$ redshift induced by hydrogen-electron interactions is that the O–H distance is almost constant, indicating that these interactions modify, essentially, the curvature of the PES.

2. Energetics of the e^- anionic defect in water clusters

Data on the energetics of the e^- anionic defect in water clusters are reported in Table III. Quite similar $[E(S_1;S_1 \leftarrow S_0)]$ vertical excitation energies are predicted by TDDFT and SAC-CI(SD) for $n=1,2$. More importantly, a comparison between TDDFT and SAC-CI(SD) results for $n=2$ clearly indicates the reliability of CIS geometries and BHandHLYP excitation energies for the larger aggregates. With the exception of the water monomer, excitation energies $[E(S_1;S_1 \leftarrow S_0)]$ are not very dependent on the number of water molecules in the aggregates, although some dependence on the conformer geometry is observed. For example, $E(S_1;S_1 \leftarrow S_0)$ is 3.73 and 2.56 eV for conformers 4b and 4c, respectively. The smallest value of $E(S_1;S_1 \leftarrow S_0)$ is for the

TABLE III. Energetics of the e^- anionic defect in water clusters. Geometry optimizations were carried out at the CIS/d-aug-cc-pVDZ level. DFT energies and TDDFT excitation energies were calculated at the BHandHLYP/d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ level. SAC-CI(SD) results for $n=1,2$ are shown in brackets.

n	$E(S_1;S_0)$[a]	$E(S_1;+)$[b]	$E(S_1;S_1 \leftarrow S_0)$[c]	$E_R(S_1)$[d]	$E_R(S_1;+)$[e]	IP[f]
1	−76.408 551	−75.966 295	7.12 [7.10;[g] 7.02[h]]	7.49[7.46[g,h]]	12.40[12.55;[g] 12.60[h]]	4.91 [5.09;[g] 5.14[h]]
2	−152.731 888	−152.459 583	3.14[3.40[g,h]]	6.40[6.58;[g] 6.55[h]]	10.67[10.77;[g] 10.74[h]]	4.27[4.19[g,h]]
3a	−229.186 903	−228.922 231	3.66	6.45	9.99	3.54
3b	−229.139 545	−228.904 991	2.24	6.31	10.46	4.14
4a	−305.629 042	−305.373 112	3.67	6.39	9.69	3.30
4b	−305.630 516	−305.373 828	3.73	6.42	9.67	3.25
4c	−305.588 889	−305.362 184	2.56	6.38	9.99	3.61
4d	−305.597 686	−305.366 126	2.92	6.50	9.88	3.38
5a	−382.036 994	−381.815 862	2.68	6.15	9.48	3.34
5b	−382.037 937	−381.818 521	2.81	6.26	8.42	3.16
5c	−382.065 968	−381.820 666	3.81	6.50	9.36	2.86

[a]$E(S_1;S_0)$ is the electronic energy (in hartree) at the geometry of the S_1 excited state.
[b]$E(S_1;+)$ is the electronic energy (in hartree) of the ionized cluster at the geometry of the S_1 excited state.
[c]$E(S_1;S_1 \leftarrow S_0)$ is the $S_1 \leftarrow S_0$ excitation energy at the S_1 geometry. Data in eV.
[d]$E_R(S_1)=[E(S_1;S_0)−E_0]+E(S_1;S_1 \leftarrow S_0)$. This quantity is the adiabatic excitation energy and places the energy of the anionic defect relative to the ground state energy E_0. Data in eV.
[e]$E_R(S_1;+)=E(S_1;+)−E_0$. This quantity places the energy of the ionized aggregate (at the geometry of the anionic defect) relative to E_0. Data in eV.
[f]IP$=E_R(S_1;+)−E_R(S_1)$ is the vertical ionization potential of the (electron) anionic defect. Data in eV.
[g]SAC-CI(SD)/d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ.
[h]SAC-CI(SD)/d-aug-cc-pVTZ//SAC-CI(SD)/d-aug-cc-pVDZ.

TABLE IV. Adiabatic energy gap in water clusters. Geometry optimizations were carried out at the CIS/ d-aug-cc-pVDZ level. DFT energies and TDDFT excitation energies were calculated at the BHandHLYP/ d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ level. SAC-CI(SD) results for $n=1,2$ are shown in brackets.

n	$E(+)$[a]	$E(+;S_0)$[b]	$E(+;S_1 \leftarrow S_0)$[c]	$E_R(+)$[d]	$E_R(+;S_1)$[e]	V_0[f]
1	−75.969 033	−76.419 082	7.5[7.5;[g] 7.31[h]]	12.33(12.60)[i]	7.58	−4.75
2	−152.468 202	−152.747 656	3.59	10.43(10.81–10.90;[j] 10.42;[k] 10.7[l])	6.42	−4.02
3	−228.933 942	−229.179 610	3.38	9.67(9.86[k])	6.36	−3.31
4a,4b	−305.389 833	−305.614 711	3.17	9.24	6.29	−2.95
4c	−305.385 186	−305.581 499	2.09	9.36(9.54[k])	6.11	−3.25
4d	−305.382 264	−305.605 961	3.20	9.44	6.55	−2.89
5a	−381.836 483	−382.021 523	2.12	8.93	6.01	−2.92
5b	−381.835 030	−382.037 563	2.91	8.97	6.36	−2.60
5c	−381.836 162	−382.045 135	2.97	8.94	6.22	−2.72

[a]$E(+)$ is the electronic energy (in hartree) of the optimized ionized structure.
[b]$E(+;S_0)$ is the electronic energy (in hartree) of the neutral structure (by electron reattachment) at the geometry of the ionized structure.
[c]$E(+;S_1 \leftarrow S_0)$ is the $S_1 \leftarrow S_0$ excitation energy of the neutral system calculated at the optimized geometry of the ionized cluster. Data in eV.
[d]$E_R(+)=E(+)-E_0$. This quantity places the energy of the ionized structure relative to E_0 and corresponds to the adiabatic ionization energy. Data in eV.
[e]$E_R(+;S_1)=[E(+;S_0)-E_0]+E(+;S_1 \leftarrow S_0)$. This quantity is the adiabatic energy gap. Data in eV.
[f]$V_0=E_R(+;S_1)-E_R(+)$. This quantity is the analogous of the conduction band edge. Data in eV.
[g]SAC-CI(SD)/d-aug-cc-pVTZ//CIS/d-aug-cc-pVDZ.
[h]SAC-CI(SD)/d-aug-cc-pVTZ//SAC-CI(SD)/d-aug-cc-pVDZ.
[i]Experimental value from Tomoda *et al.* (Ref. 45).
[j]Experimental value from de Visser *et al.* (Ref. 60).
[k]Theoretical calculations from Barnett and Landman (Ref. 62).
[l]Theoretical calculations from Novakovskaya and Stepanov (Ref. 61).

3b conformer (2.24 eV) and the largest excitation energy is 3.81 eV (5c). This dependence is possibly associated with specific structural features of the excited aggregates. Interestingly, some of the conformers with higher excitation energies (4a, 4b, and 5c) also exhibit lower ν_{O-H} frequencies (see Table II). The ground state electronic density of the optimized S_1 structures should reflect the presence of the OH⁻ and H_3O^+ species in interaction with water. The electronic density differences isosurfaces (Figs. 2–4) indicate that upon excitation, the promotion of an electron from the p orbital of the OH species leads to a diffuse electron density distribution that is stabilized by the interaction with the hydrogen atoms of the aggregate. This excitation energy can be related to charge transfer to solvent (CTTS) precursor states.[56,57] Theoretical results for CTTS energies in hydrated hydroxide anion clusters were reported.[58,59] Random phase approximation B3LYP calculations of Lee *et al.*[59] estimate CTTS energies for clusters of OH⁻ with one, two, and three water molecules as 3.48, 4.04, and 4.68 eV, respectively. These values are slightly blueshifted in comparison with our results (Table III) for the excitation energies of $H_3O^+[OH(H_2O)_{(n-2)}]^-$ aggregates ($n=3-5$). This tendency is possibly related to the presence of H_3O^+ that will favor electron delocalization and energetical stabilization of the excited state.

The energetics of the adiabatic excitation process can be described by the quantity $E_R(S_1)=[E(S_1;S_0)-E_0]+E(S_1;S_1 \leftarrow S_0)$, which places the S_1 excited state relative to the reference state E_0. $E_R(S_1)$ (see Table III) shows a weak dependence on the number of water molecules in the aggregate. The smallest value (6.15 eV) corresponds to the 5a conformer. The largest adiabatic excitation energy is 6.50 eV for the 4d and 5c conformers. The weak dependence of $E_R(S_1)$ on the cluster size (or the number of water molecules) may

indicate that the energetics of the adiabatic excitations is mainly controlled by local or short-ranged interactions. The energetics of anionic defects in liquid water was discussed by Coe and collaborators.[14,15] These authors placed the e^- anionic defect in the bulk 5.3 eV above pure water. The same authors also reported a value of ~7 eV for the anionic defect associated with an excited p state of e^-(aq).[14] Our results correspond to the lowest $S_1 \leftarrow S_0$ excitation and are in agreement with the minimum photon energy required to produce hydrated electrons from pure water (~6.5 eV).[5–9]

Table III also reports results for $E_R(S_1;+)=E(S_1;+)-E_0$. This quantity places the energy of the ionized aggregate (at the geometry of the S_1 state) relative to E_0. From $E_R(S_1;+)$, the vertical ionization potential of the anionic defect (IP) can be estimated as $IP=E_R(S_1;+)-E_R(S_1)$. Values of IP range from 4.27 eV (water dimer) to 2.86 eV (5c pentamer conformer). These IPs correspond to the energy needed to vertically remove the microhydrated electron from the excited aggregate and can be compared with the PET of hydrated electrons in water (PET ~ 2.4 eV).[14]

C. Adiabatic energy gap in water clusters

Ionization of the excited S_1 aggregates followed by geometry optimization leads to the local minima ionized $(+)$ structures also reported in Figs. 2–4. Our results for the energetics of these ionized structures are presented in Table IV.

The relative energies of the ionized structures are given by $E_R(+)=E(+)-E_0$. This quantity places the energy of the optimized ionized structures relative to E_0 and corresponds to the adiabatic ionization energy of the aggregate. With the exception of the structure related to the water dimer, for which $E_R(+)$ is 10.43 eV, $E_R(+)$ exhibits a weak dependence

on the number of water molecules. $E_R(+)$ are 8.93 and 9.67 eV for the 5a and 3b conformers, respectively. For the water monomer and dimer, experimental results for $E_R(+)$ are available.[45,60] Theoretical results were also reported for small water clusters.[61,62] For the water monomer, our prediction (12.33 eV) is $\sim$0.3 eV below experiment.[45] This difference between theory and experiment is quite similar to the one observed for the vertical ionization energy (see Table I) and reflects the fact that, for the water monomer, the vertical and adiabatic ionization energies are very close.[45] Our result for the water dimer (10.43 eV) is in good agreement with experimental information (10.81–10.90 eV) (Ref. 60), and it is quite similar to a theoretical prediction (10.42 eV).[62] A good agreement between our results and the theoretical values reported by Barnett and Landman[62] for the ionized structures 3 and 4c is also observed.

Electron reattachment to the ionized structures provides a route for calculating $E(+; S_1 \leftarrow S_0)$, which is the $S_1 \leftarrow S_0$ excitation energy of the ground state neutral aggregate calculated at the optimized geometry of the ionized cluster. The $E(+; S_1 \leftarrow S_0)$ excitation energy shows some dependence on the geometry of the optimized conformers. For example, it is 3.17 eV for conformers 4a and 4b and 2.09 eV for conformer 4c. A similar dependence of $E(+; S_1 \leftarrow S_0)$ on the geometry is also observed for conformers 5c $[E(+; S_1 \leftarrow S_0) = 2.97$ eV] and 5a $[E(+; S_1 \leftarrow S_0) = 2.12$ eV]. This trend is the same as that previously observed for $E(S_1; S_1 \leftarrow S_0)$.

A fundamental quantity also reported in Table IV is the adiabatic energy gap for a water cluster, which can be defined as $E_R(+; S_1) = [E(+; S_0) - E_0] + E(+; S_1 \leftarrow S_0)$. A major difference between $E_R(+; S_1)$ and $E_R(S_1)$ (see Sec. III B 2) should be made precise. $E_R(+; S_1)$ only involves the reorganization of the water molecules around the hydronium $(H_3O)^+$ and OH species. However, $E_R(S_1)$ also involves the relaxation of the water molecules around the microhydrated electron. This aspect was stressed by Coe *et al.* in their definition of the adiabatic band gap of water.[14] Our results for $E_R(+; S_1)$ or for the adiabatic energy gap of small water clusters range from 6.01 eV (5a) to 6.55 eV (4d). These values can be compared with experimental (6.9 eV) (Ref. 14) and theoretical (6.83 eV) (Ref. 17) results for the liquid water band gap. The qualitative agreement between our predictions and the results for the liquid phase is an indication of the reliability of the present cluster calculations in describing some basic features characterizing the electronic properties of water.

The quantity (V_0) can now be estimated as $V_0 = E_R(+; S_1) - E_R(+)$. In agreement with our previous predictions [Sec. III A], V_0 decreases slowly with increasing cluster size. In comparison with the results reported in Table I, slightly smaller values are predicted by the above expression. For example, when $n=4$, $V_{0,v} = -3.75$ eV from $V_{0,v} = E(S_0; S_1 \leftarrow S_0) - IP$, whereas it is -3.25 eV (4b) from $V_0 = E_R(+; S_1) - E_R(+)$. These differences are possibly related to the feature that in small water clusters, structure and electronic reorganization around the H_3O^+ cation modifies the energetics of electron attachment to the aggregates.

IV. SUMMARY AND CONCLUSIONS

Ab initio CIS/*d*-aug-cc-pVDZ calculations were carried out to investigate the S_1 singlet excited state structures of $H_3O^+[OH(H_2O)_{(n-2)}]^-$ aggregates. The energetics of the excited structures were then investigated by DFT calculations at the BHandHLYP/*d*-aug-cc-pVTZ level. A very good agreement between several electronic properties of water aggregates and experimental information was observed for ionization energies and photoelectron emission thresholds. Further support on the reliability of the present approach to investigate the electronic structure of excited water clusters has been provided by full active SAC-CI(SD) calculations for $n=1,2$.

One important conclusion concerns the relationship between the electronic properties of the aggregates and the adiabatic band gap of water. The importance of taking into account the relaxation of the water molecules for predicting electronic properties of water should be stressed. This is summarized in Fig. 1, where the energetic properties of the excited and ionized aggregates related to the water pentamer are represented as a function of the "solvent" coordinate describing dissociation (bond breaking and formation) and relaxation or structure reorganization around microhydrated species. Therefore, we provide evidence that several relevant quantities characterizing the behavior of water upon photo-excitation can be assessed by the calculation of the electronic properties of small aggregates. Specifically, the adiabatic route to the conduction band of liquid water[14] can be investigated through the analysis of the structure and electronic density reorganization induced by the photoexcitation of water clusters. Our estimates for the adiabatic energy gap of the aggregates (6.01–6.55 eV) are in keeping with experimental (6.9 eV)[14] and theoretical (6.83 eV)[17] results for the band gap of liquid water.

We also report results for a quantity V_0, which is analogous to the conduction band edge of liquid water. Our calculations indicate that this quantity is strongly size dependent, making difficult a comparison with bulk values. However, although the calculation of V_0 illustrates the limitations of a cluster approach, it seems reasonable to conclude that the study of excited water clusters can improve our understanding of the electronic properties of the bulk phase. Finally, we believe that this work reports, for the first time, an investigation of the electronic properties of small water aggregates that supports the picture proposed by Coe *et al.*[14] for the adiabatic band gap of liquid water.

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