

## Can the pH value of water solutions be estimated by quantum chemical calculations of small water clusters?

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In the study, various water clusters were explored from the point of view of the proton transfer between H-bonded neighbors. A relatively modest approach—the MP2/6-31+ +G(*d*,*p*) level—was chosen as acceptable considering the fact that also larger systems have to be included. The tight ion-pair model (with usually three fixed O–O distances) was adopted for the autodissociation process. First, cluster-estimated pH values rapidly decrease as cluster size increases from 2 to 6. For larger clusters in gas phase, the topology of H bonds plays an important role, varying pH from 7 to 13 in hexamers and from 5 to 15 in octamer clusters. The relationship energy/distance was quantified, too. Enhancing our model with the conductorlike screening model (COSMO) approach brought significant improvement in description of the autodissociation reaction with a stable zwitterionic structure. However, when the O–O restrictions were released, the small barrier for backward reaction disappeared, reforming neutral cluster spontaneously. Also Boltzmann weighting procedure was applied, and for the explored clusters *in vacuo*, the series of pH 25-18-14-13-10 was obtained for cluster sizes *n*=2, 3, 4, 6, 8. Using the COSMO approach, the analogous series is 15-14-12-10-9. The limit of the series is still about two to three units above the experimentally known pH. In order to reach the size-independent (bulk) value, larger clusters are needed. However, the situation is far from hopeless since (as it was proven in the study) four-coordinated molecules are not involved in the proton transfer process directly; they can only be a part of the surrounding environment. © 2006 American Institute of Physics.

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### INTRODUCTION

Water is one of the most amazing chemical substances in the world. It possesses a lot of extreme physicochemical properties such as anomal volume-temperature behavior (which is actually basic for the existence of life on Earth), conductivity, heat capacity, boiling and freezing temperatures, etc. Moreover, its abundance makes it the most common chemical substance on the planet.

On water, many papers are published every year. For instance, in 2003 Keutsch *et al.*<sup>1</sup> published a review article only on water trimer where on more than 40 pages properties of this “cluster” were discussed. In the next paragraphs we would like to mention some basic achievements and recent computational results on properties of water, with accent on the water dissociation process. Even within such a reduced subject it is not possible to mention all performed studies.

Let us start with a single water molecule, since all cluster and bulk properties originate from the molecular behavior. The geometry of water was computed many times and some of the recent and high level estimations were done in Refs. 2–5. In Refs. 4 and 5, also IR spectra were determined. Ground state and excited state geometries and vibrational modes were calculated using time-dependent density functional theory (TD-DFT) by del Puerto *et al.*<sup>6</sup> An experimental study on vibration states of the water molecule was pub-

lished, e.g., by Coudert *et al.*<sup>7</sup> For additional comparison with experimental data an excellent reference<sup>8</sup> on vibronical levels of the water molecule can be used. An examination of molecular structure behind the Born-Oppenheimer approximation is done in the work of Shigeta *et al.*<sup>9</sup> and Csaszar *et al.*<sup>10</sup> A thorough exploration of water potential functions was published in a series of Varandas studies.<sup>11</sup> The entropy contribution at various correlated electronic densities was explored in the work.<sup>12</sup> An analysis of partial charges in the basis set limit was discussed in the study by Astrad *et al.*<sup>13</sup> for a single water molecule and water dimer. An extensive study on charge distribution using various quantum chemical population analysis methods for the water molecule was published recently.<sup>14</sup> The dipole moment value of the water molecule passing from gas phase to liquid was explored by Silvestrelli and Parrinello<sup>15</sup> and values up to three dimensions (3D) with large fluctuations were reported. The results for a combination of a quantum mechanical approach with a polarizable continuum model and molecular simulation techniques are presented in the work by Mendoza *et al.*,<sup>16</sup> where satisfactory agreement of solute-solvent interactions can be found. Another approach to the description of the water molecule in liquid water is given in the study by Moriarty and Karlstrom,<sup>17</sup> where a combined quantum mechanical/Monte Carlo (QM/MC) treatment was applied. 89 water molecules were used in MC method as an external bath for the examination of the neighborhood influence. A similar idea was

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used by Chalmet and Ruiz-Lopez<sup>18</sup> where the water molecule was calculated in an implicit continuum model and in a discrete model at the DFT level, as well as using a quantum mechanical/molecular mechanical (QM/MM) approach. The solvation of the water molecule in liquid water and cyclohexane is the subject of the study.<sup>19</sup> Here, it was also shown that the work for the cavity creation is largely surpassed by the formation of two H bonds in liquid water, whereas it is almost exactly counterbalanced by the establishment of van der Waals interactions in liquid cyclohexane. A development of the analytical pair potential of water is presented in the study by Turi and Borgis.<sup>20</sup> The comparison with quantum molecular dynamics simulations gives a very good agreement with the potential. Solvation sites of the water molecule using two different models (EPM4 and EPM5) were examined in Ref. 21, showing that various sites of water interact with other solvent molecules independently. A quantum chemical approach to the dissociation process in water was presented in the work by Takahashi *et al.*<sup>22</sup> using QM/MM. They showed that the dissociation free energy decreases monotonically as the density increases due to the entropic term ( $-T\Delta S$ ). The explanation of the entropy increase at low densities is connected with the decrease in the translational degrees of freedom brought about by the aggregation of solvent water molecules around the ionic solute.

The changes of the monomer geometry in the dimer formation at high QM levels [CCSD(T) and symmetry adapted perturbation theory (SAPT)] can be found in Ref. 23. The effect of anharmonicities on the thermodynamic description of the water dimer is analyzed in the study.<sup>24</sup> A systematic, high-level *ab initio* investigation of the water dimer has been performed in many studies,<sup>25</sup> where also effects such as accurate basis set superposition error (BSSE) correction, dipole moments,<sup>26</sup> polarizabilities,<sup>27</sup> vibration spectra,<sup>28</sup> vibration-rotation-tunneling (VRT) spectra,<sup>29</sup> and spin-spin constants<sup>30</sup> are discussed. A determination of the stretching modes of the H-bonded OH coordinate in dimer in excited state was published recently. A full six-dimensional (6D) intermolecular surface is explored at the DFT level by Mok *et al.*<sup>31</sup> A full 6D surface was used also by Fellers *et al.*<sup>32</sup> for the determination of vibrational-rotational-tunneling states. A MC approach to enthalpy of the dimer formation was applied in the study<sup>33</sup> at various temperatures. Bandyopadhyay *et al.*<sup>34</sup> have used MC simulations for average structural changes of the dimer. Water rearrangement in dimeric and trimeric structures is examined in Ref. 35.

Investigation of geometry parameters and the potential surface of water trimers can be found, e.g., in Ref. 36. Very interesting is the construction of nonempirical modeling (NEMO) potentials based on the water monomer, which was compared with MP2-R12 calculations on cyclic trimer and tetramer clusters.<sup>37</sup> A three-body interaction potential for water was generated for water trimeric structures with Hartree-Fock (HF) and SAPT methods.<sup>38</sup> Trimer-pentamer clusters at the SAPT and CCSD levels were used for the construction of a similar potential.<sup>39</sup> Recently proton transfer in the cyclic trimer was explored by Kim and Kim.<sup>40</sup>

Higher water clusters (up to  $n=20$ ) were examined at intermediate neglect of differential overlap (INDO),<sup>41</sup>

HF,<sup>42,43</sup> MP2,<sup>44</sup> and DFT (Ref. 45) levels of calculations. An interesting study on structures of hexamer clusters was published by Lee *et al.*<sup>46</sup> According to this paper and the work of Liu *et al.*,<sup>47,48</sup> Kim and Kim,<sup>49</sup> and some others,<sup>50</sup> the most stable hexamers should be structures from the cage family. However, when the zero point vibrational energy (ZPVE) corrections are included the chair conformation becomes slightly more stable<sup>51</sup> and at the Gibbs free energy level (including entropy term), the cyclic conformation represents the most stable arrangement. A comparison of stabilization energies and vibrational modes of heptamers with hexamer and octamer structures was published by Kim *et al.*<sup>52</sup> Octamers were further calculated using a polarization model of molecular interactions by Stillinger and David<sup>53</sup> and a parallel-tempering model for an isothermal-isobaric ensemble was used by Ocasio and Lopez.<sup>54</sup> A great deal of interest was devoted to cubic octamers (but not only them) at various *ab initio*<sup>55,56</sup> levels. It was shown by Kim *et al.*<sup>57</sup> that the less organized cyclic clusters become more stable at temperatures higher than 40 K when entropy contributions are included. Database structures were used for the DFT optimization of 121 water clusters in Ref. 58. Many systematic studies on larger water clusters in the framework of molecular simulations with empirical potentials (e.g., Refs. 59–61) were published, too.

The distribution of water clusters in gas phase was studied by Mhin *et al.*,<sup>62</sup> who showed higher stability of linear trimer and tetramer structures above 400 K. An experimental measurement of small water clusters was described using IR-laser absorption spectroscopy,<sup>63</sup> far IR-VRT spectroscopy,<sup>64</sup> and combined computational Fourier transform infrared (FTIR) techniques.<sup>65</sup>

Concerning the water autodissociation reaction, one of the first quantum chemical calculations came from Warshel,<sup>66</sup> who used the surface constrained soft sphere dipoles model. Although the models based on Langevin dipoles do not reflect the molecular structure of the solvent, they proved to be very successful and were further developed in his group, e.g., Florián and Warshel.<sup>67</sup>

Štrajbl and Warshel<sup>68</sup> presented an interesting QM/MM study of water autodissociation reaction, where the empirical valence bond (EVB) approach developed by Warshel and co-workers<sup>69</sup> is utilized for the creation of a reference potential. The EVB force field was adjusted to reproduce gas-phase B3LYP/6-31+G\* energy surfaces for proton transfers between  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$ , and water molecule. Significant dependence of the potential of mean force (PMF) profiles on the size of the quantum system ( $n=2-7$ ) was observed. The key advantage of the EVB approach is the ability to capture the nonequilibrium solvation barrier, which is impossible within the cluster models.

In this study we concentrate on an interesting and important property of water—its acidity. For various water clusters ( $\text{H}_2\text{O}$ )<sub>*n*</sub>,  $n=2, \dots, 21$ , a specific proton transfer energy surface was constructed so that the formation of ion pairs on neighboring molecules is enforced. Such a surface can be considered as an upper estimation of a possible ion-pair activation barrier due to necessary O–O distance restrictions. Similar theoretical studies dealt with water *pK* using

CPMD,<sup>70,71</sup> with the periodic box of 32 water molecules. Their estimation of  $pK$  is very good ( $13 \pm 1$ ). Also Kuo *et al.*<sup>72</sup> reported a similar autodissociation process in some isomers of the dodecahedral cage cluster  $(H_2O)_{20}$  using the B3LYP functional. Lee *et al.*<sup>73</sup> and Jensen *et al.*<sup>74</sup> presented studies where a stable minimum on potential energy surface (PES) of  $(H_2O)_5$  with an ion pair was localized. This pentamer and octamer zwitterions were reproduced obtaining a fairly good agreement with the above-mentioned papers.

## COMPUTATIONAL METHODS

Geometry optimizations as well as PES calculations were carried out with the MP2 method and 6-31++G( $d,p$ ) basis set using GAUSSIAN 98 (Ref. 75) suite of programs. This level of theory was chosen after thorough testing calculations performed on the dimer and trimer water molecules. The relatively modest MP2 approach yields results which are of comparable quality to more demanding methods such as CCSD(T) or CASPT2 with Dunning's aug-cc-pvtz and aug-cc-pvqz basis sets (see Results). For the large clusters consisting of 12 and 21 monomers, the ONIOM (Ref. 76) method was used. In this model, the high layer system was treated at the MP2/6-31++G( $d,p$ ) level and contained two central molecules involved in the proton transfer plus their closest H-bonded neighbors. The low layer was described at the HF/6-31G( $d$ ) level. The starting geometry for the largest cluster was taken from the work of Hartke.<sup>61</sup> In each cluster, the proton transfer along the shortest H bond was examined (the two monomers involved in this H-bond interaction are further called "central dimer"). The considered reaction coordinate (labeled  $Ri$ ) was the O–H distance between the oxygen atom of the forming  $OH^-$  anion and the transferred proton. The one-dimensional PES for the proton transfer from one water molecule to another was constructed by the relaxed scan method. However, it was found that some geometry constraints had to be imposed in order to prevent "neutralization" of the formed  $H_3O^+ - OH^-$  ion pair. For sufficiently large  $Ri$  values, one of the two remaining hydrogen atoms of  $H_3O^+$  tended to be released from the cation moiety reestablishing a neutral arrangement. (This behavior was also observed in Ref. 68, where the authors assigned the point beyond which the neutralization occurred as a transition state.) In this way, the oxygen-oxygen distances between  $H_3O^+$  and its H-bonded neighbors were kept fixed during the scan. This resulted in three fixed distances (or less, if there were less than three H-bonded neighbors). As a consequence of the O–O distance restrictions, the ion pair is forced to remain localized on the neighboring molecules. In our model and for the selected clusters, the ion pair remained unseparated by other water molecules. The only exception is the pentamer "zwitterion," see the discussion below. Such a separation can increase the stability of the cluster, as is known from literature.<sup>77</sup> The "tight ion-pair" model did not lead to stable geometries of zwitterions for the studied clusters. This means that there is no local minimum on the PES corresponding to the ion-pair structure. Instead, the second inflection point on the PES (with a positive second derivation) was utilized as a reference structure defining the prod-

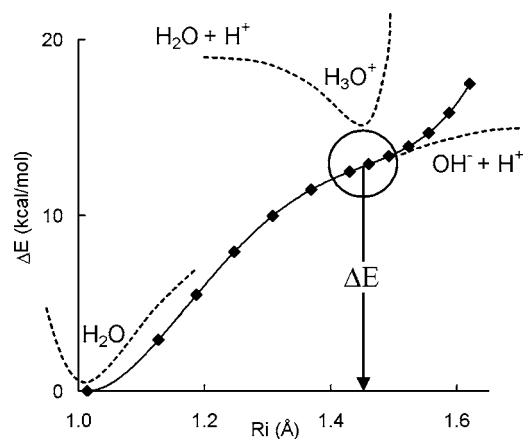


FIG. 1. Definition of reference energy. In the circle, the second inflection point on the PES is marked where the zwitterionic structure should appear as a superposition of two potential curves:  $H_2O \leftrightarrow OH^- + H^+$  and  $H_2O + H^+ \leftrightarrow H_3O^+$ .

uct state of the ion-pair formation reaction (cf. Fig. 1). Details of the proton transfer PES in the water dimer and trimer (discussed below) are depicted in Figs. 2 and 3.

The exact location of this point was obtained by fitting the determined PES with a double Morse potential:

$$E = d_0 + d_1[1 - \exp(-a_1(x - r_1))]^2 - d_2[1 - \exp(-a_2(r_2 - x))]^2 \quad (1)$$

followed by the analytic evaluation of the requested point. Using the above formula we assume that the PES can be combined from the  $HO^- - H^+$  interaction (first term) and the much weaker  $H^+ - OH_2$  term, as depicted in Fig. 1. In this view the second inflection point has a clear physical meaning and can be regarded as an activation barrier for the subsequent proton transfer in the ion-pair separation process.

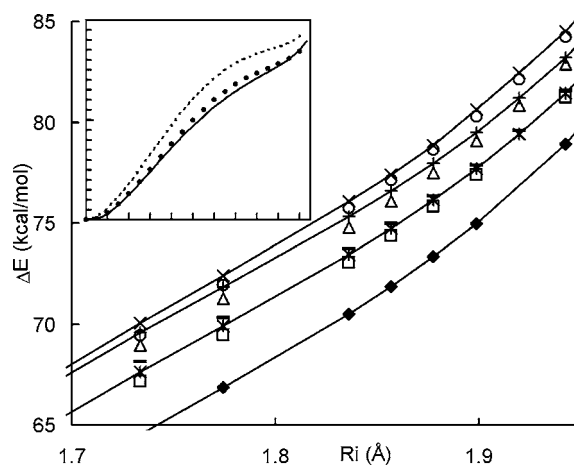


FIG. 2. The PES of proton transfer in water dimer ( $\Delta E$  as a function of the reaction coordinate  $Ri$ ). Single-point calculations at various *ab initio* methods on the MP2/6-31++G( $d,p$ ) relaxed-scan geometries. For each curve, the  $E$ (minimum) is set to zero (in kcal/mol and Å):  $\times$ —CASPT2/aug-cc-pvqz,  $\circ$ —CASPT2/aug-cc-pvtz,  $+$ —CCSD(T)/aug-cc-pvqz,  $\triangle$ —CCSD(T)/aug-cc-pvtz,  $\text{X}$ —MP2/aug-cc-pvqz,  $\square$ —MP2/aug-cc-pvtz,  $—$ ...MP2/6-31++G( $d,p$ ), and  $\blacklozenge$ —B3LYP/6-31++G( $d,p$ ). The insert displays the complete PES curve [the range is  $Ri = (0.95, 2)$  Å]:  $—$ —CASPT2/aug-cc-pvqz,  $\cdots$ —CAS-SCF/aug-cc-pvtz, and  $----$ —HF/aug-cc-pvtz.



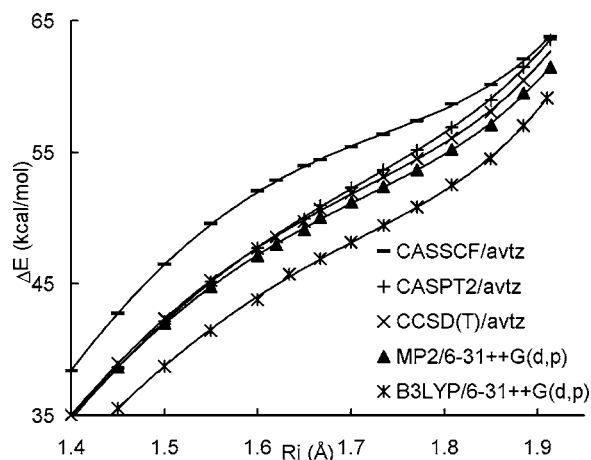


FIG. 3. Detail of proton transfer PES of water trimer ( $\Delta E$  as a function of the reaction coordinate  $R_i$ ). Single-point calculations on the MP2/6-31++G( $d,p$ ) optimized geometries.

In order to make the second inflection more apparent, another series of relaxed scans was performed. Here, the other O–H distance (between the oxygen atom of the forming  $H_3O^+$  and the transferred proton) was used, labeled  $R_w$ . Both energy curves overlap in a relatively broad range around the first inflection point. Thus, the two scan curves can be sewed together and utilized in the fitting procedure. Then the values of free energy (at  $T=298$  K) for the geometries corresponding to both neutral minima and second inflection points are calculated using the (MP2/6-31++G( $d,p$ )) harmonic oscillator and NVE microcanonical ensemble of ideal gas for the determination of thermal and entropy terms. Having determined  $\Delta G_b$  for the proton transfer along the given H bond,  $pH_b$  can be evaluated according to the formula

$$pH_b = -\log[H_3O^+] = -\log \frac{K_v}{2} = \frac{1}{2} \left( \frac{\Delta G_b}{RT \ln 10} \right). \quad (2)$$

The subscript  $b$  is introduced in order to emphasize that this  $pH$  is the result of the two states'  $\Delta G_b$  difference without any other corrections. This equation with such a  $\Delta G_b$  definition is the key point of our study. It is clear that the  $\Delta G_b$  is only an approximation of the correct value of the standard free energy of the autodissociation reaction. A partial justification of using  $\Delta G_b$  comes out from the fact that energy, which is necessary for further proton motion (e.g., from this reference state to infinity), is negligible or at least significantly lower than  $\Delta G_b$ . Also note that the  $pH$  defined in Eq. (2) should be understood as a value corresponding to a system of noninteracting clusters of water. We do not assume that this is the actual picture of the bulk. However, it would be interesting to explore if, and for which cluster size, this “cluster-based”  $pH$  approaches the  $pH$  of (bulk) water.

An estimation of the  $pH$  value of the cluster is achieved by adding the energy difference between the given conformer ( $i$ ) in neutral (nondissociated) form and the global minimum (gmin): ( $\Delta G_0(i) - \Delta G_0(\text{gmin})$ ) to  $\Delta G_b$ . This is the simplest way of considering the fact that the examined cluster is not the global minimum. The “additive”  $pH$  value calculated with corrections on total energy is labeled  $pH_a$ . In the

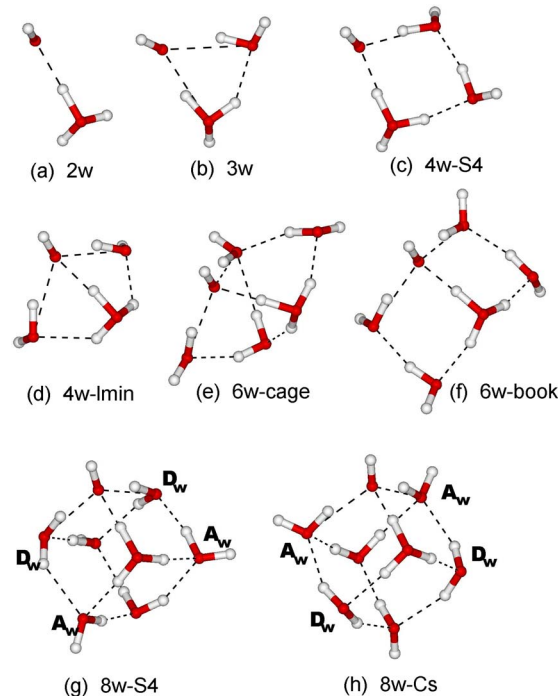


FIG. 4. Ion-pair structures for PES explored clusters ( $n=2-8$ ). The geometries correspond to the second inflection point on the proton transfer PES. These clusters were used for the construction of the linear energy/geometry formula in Eq. (3). (g) and (h) demonstrate the difference in H-bond topology between clusters 8w-S4 and 8w-Cs.

case of the global minimum conformer,  $pH_a = pH_b$  holds. Another subscript  $w$  is introduced below for the energy-weighted cluster.

The polarizable continuum model (PCM) in the version of conductorlike screening model<sup>78</sup> (COSMO) of Klamt and Schuurmann as implemented in GAUSSIAN03, revision c02, was used for the estimation of solvation effects of the implicit bulk water environment. The same MP2/6-31++G( $d,p$ ) level of theory was used for geometry optimizations and frequency calculations.

## RESULTS AND DISCUSSION

### Calculations on the water dimer

The water dimer has only one stable conformation, which belongs to the  $C_2$  point group of symmetry. Calculations on this well-studied system were done in order to calibrate our computational model and compare its performance with some more accurate *ab initio* methods. First, it was realized that the oxygen-oxygen distance must be kept fixed during the proton transfer. In the case of the *fully relaxed* scan with  $R_i$  as the reaction coordinate, the structure breaks down at a certain point where one of the protons of the acceptor water is split off and neutralizes the forming  $OH^-$  anion. Choosing  $R_w$  as the reaction coordinate without fixing the  $R_{(O-O)}$  distance brings just both molecules close to each other (the  $R_i$  distance does not change significantly), but no ion pair is created.

The resulting ion-pair structure for the dimer is depicted in Fig. 4(a) [all pictures in Fig. 4 show the (tight) ion-pair structures of the respective clusters]. The potential energy

TABLE I. Ion-pair formation energy of the water dimer calculated at different levels of theory on the MP2/6-31++G(*d,p*) optimized PES.

Method/Basis	aug-cc-pvqz	aug-cc-pvtz	6-31++G( <i>d,p</i> )
CASPT2	74.12	73.19	
CCSD(T)	72.86	72.31	
MP2	71.32	70.33	71.33
B3LYP			67.56

surfaces obtained for various methods are compared in Fig. 2. All points were calculated on the MP2/6-31++G(*d,p*) optimized structures using aug-cc-pvqz/pvtz basis set. It can be seen that except for the HF and CASSCF levels, all dynamically correlated methods including CCSD(T) (with two frozen core orbitals) and multireference CASPT2 yield very similar PES curves (the configuration space was composed of two *A'* frozen core orbitals, ten *A'*, and three *A''* active orbitals for the CASSCF and CASPT2 calculations). The quantitative differences between the methods used are shown in Table I. The difference between CASPT2/aug-cc-pvqz and MP2/6-31++G(*d,p*) is 2.8 kcal/mol, while the same difference in the case of B3LYP/6-31++G(*d,p*) is 6.5 kcal/mol. Concerning the size of the basis set, the CASPT2 ion-pair formation energy is slightly increased (by 1 kcal) when passing from the triple to the quadruple zeta quality basis. The same holds for MP2 and CCSD(T). However, the results obtained for MP2 energies with 6-31++G(*d,p*) and aug-cc-pvqz bases are practically identical (within 0.1 kcal/mol).

Free energy difference between the minimum and the second inflection point of the PES was calculated to be 69.4 kcal/mol [MP2/6-31++G(*d,p*), cf. Table II]. It means that if bulk water could be described as an ideal gas of water dimers,  $pH=25.4$  should be obtained.

### Trimers

The global minimum structure of the trimer is a nonsymmetric triangular cluster [its ion-pair form is in Fig. 4(b)]. It should be noted that the three-monomer ring suffers from sterical strain (a ring with too small valence angles) and therefore rarely appears at low-lying minima of larger clusters.<sup>43</sup> Another minimum in the form of a linear chain with energy about 7.5 kcal/mol higher is also known.

In the PES construction, all three O–O distances were fixed at the optimized-minimum values during the proton

transfer. The free energy difference between the neutral minimum and the structure of its corresponding second inflection point is 50.6 kcal/mol, which yields according to Eq. (2) the  $pH_b$  value of 18.5. While this number is still far from the bulk water value, it is interesting that the addition of one molecule reduces the proton transfer energy by almost 19 kcal/mol.

Figure 3 displays the energy curves obtained by different *ab initio* methods. Generally, the same conclusions on the applicability of the MP2 method can be drawn as in the case of the water dimer. Based on these two systems, the MP2/6-31++G(*d,p*) method was found to be sufficiently accurate for the exploration of the PESs of water clusters. Concerning the B3LYP method, it appears that it underestimates the barrier height by roughly 6–7 kcal/mol compared to the CASPT2 method (active space definition for CASPT2: 3 core, next 7 closed, and 8 active orbitals).

### Tetramers

The PES for the proton transfer in two different tetramer clusters was investigated. The first one was the global minimum [Fig. 4(c), labeled 4w-S4], which has almost square planar arrangement with S4 symmetry. The second explored structure was a local minimum in Fig. 4(d) (labeled 4w-lmin), with total energy about 6.2 kcal/mol higher. This system can be regarded as a water dimer with two adjacent molecules. Since there are only two molecules H-bonded to the  $H_3O^+$  cation in 4w-S4, two frozen O–O distances were found sufficient for the PES construction here. In the case of 4w-lmin, there are three such molecules coordinated to  $H_3O^+$  and therefore also three O–O distances had to be fixed. Nevertheless, the free energy necessary for the proton transfer is slightly lower in the 4w-lmin structure ( $\Delta G_b = 35.1$  kcal/mol and  $pH_b = 12.8$ ) than in 4w-S4 ( $\Delta G_b = 38.2$  kcal/mol). The resulting  $pH_a$  values are 14.8 for 4w-lmin and 14.0 for the 4w-S4. Besides these two structures, two other cyclic clusters with similar energies of neutral structures (cf. Fig. 6 and Table III) were used later. Notice that the formation of the ion-pair structure is by about an additional 15 kcal/mol less demanding when passing from trimer to tetramer clusters.

### Pentamers

The global minimum of the pentamer has the shape of a planar pentagon. The simulation of the proton transfer failed here and the structure broke down into a 3D conformation

TABLE II. Selected geometry parameters (in Å) and energies (in kcal/mol) obtained for PES calculations.  $R_{(O-O)}$  is the oxygen-oxygen distance in the central dimer. Values in italics are based on  $\Delta E$  (not  $\Delta G$ ) values.

Cluster	2w	3w	4w-S4	4w-lmin	6w-book	6w-cage	8w-S4	8w-Cs	12w	21w (surf.)	21w-mod-1
$R_{(O-O)}$	2.911	2.796	2.756	2.721	2.622	2.641	2.685	2.585	2.585	2.726	2.511
$\Delta G_b$	69.4	50.5	38.2	35.1	19.1	19.3	24.9	12.9	12.5	25.3	4.4
$\Delta G_0$	0	0	0	5.2	1.1	3.3	0	3.3	9.8	0	15
$\Delta G$ total	69.4	50.5	38.2	40.3	20.2	22.6	24.9	16.2	22.3	25.3	19.5
$pH_a$	<b>25.4</b>	<b>18.5</b>	<b>14.0</b>	<b>14.8</b>	<b>7.4</b>	<b>8.3</b>	<b>9.1</b>	<b>5.9</b>	–8	>9	>7
$pH_b$	25.4	18.5	14.0	12.8	7.0	7.1	9.1	4.7	4.6	>9	>7

TABLE III. Estimation of  $pH_w$  of water tetramer clusters (energies in kcal/mol, distances in Å). The  $pH_b$  values were obtained from Eq. (2) based on  $\Delta G^n(i)$  values weighted over all H bonds according to Eq. (6). The weighting factor of the conformer  $w(i)$  is defined in Eq. (7).

Cluster code	S4	Cl	A	lmin
$pH_b$	<b>14.01</b>	<b>14.20</b>	<b>13.85</b>	<b>12.063</b>
$\Delta E_0$	0	1.16	7.74	6.17
$\Delta G_0$	<b>0</b>	<b>0.33</b>	<b>4.22</b>	<b>5.21</b>
$w(i)$	$6.4E-01$	$3.6E-01$	$5.1E-04$	$4.4E-04$
$pH_w$	<b>14.09</b>			

where the  $H_3O^+$  is three coordinated [cf. Fig. 5(a)]. This problem could only be resolved at the cost of fixing all O–O distances, but this causes cruel deviation from any realistic models. It is also connected with severe convergence problems. However, it can be stated that ion-pair formation in planar clusters, and generally in any clusters where the forming  $H_3O^+$  is only two coordinated, is energetically more demanding (compared to the three-coordinated cation).

Another non-planar pentamer cluster was studied with total energy about 3.2 kcal/mol (cf. Table IV) above the global minimum [5w-cage in Fig. 5(a)]. This particular structure has also been of interest in previous theoretical studies on ion-pair formation.<sup>73,74</sup> It is the smallest cluster that allows the creation of a “nearly stable water zwitterion,” where the ion pair is separated by a single “layer” of water molecules. Smith *et al.*<sup>79</sup> calculated the free energy difference between the zwitterionic cluster and the global minimum to be 24.9 kcal/mol at the MP2/6-311++G(*d,p*) level. An acti-

TABLE IV. Estimation of  $pH_w$  of water pentamer cluster.

Cluster code	Ring	Cage	Book	Spiro
$pH_b$	<b>13.03</b>	<b>10.57</b>	<b>8.94</b>	<b>16.11</b>
$\Delta E_0$	0	1.93	2.88	5.63
$\Delta G_0$	<b>0</b>	<b>3.26</b>	<b>3.53</b>	<b>5.26</b>
$w(i)$	$9.9E-01$	$4.0E-03$	$2.6E-03$	$1.4E-04$
$pH_w$	<b>13.01</b>			

vation barrier for neutralization (backward reaction) is less than 0.1 kcal/mol and vanishes completely when ZPVE and thermal contributions are considered. This cluster is not suitable for our model with tight ion pair due to the insufficient  $H_3O^+$  stabilization. Proceeding with the transfer along the shortest H bond [marked as “1” in Fig. 5(a)] leaves the  $H_3O^+$  only two coordinated, and the structure breaks down during the construction of the proton transfer PES. Only with all O–O distances fixed, activation barrier of 30.7 kcal/mol was obtained. The second shortest H bond (marked as “2”) represents a better choice for the  $H^+$  transfer since  $H_3O^+$  is now three coordinated. During the course of this transfer, the originally two-coordinated  $OH^-$  is neutralized by the proton from the H bond “1” and the same zwitterionic structure as described by Smith *et al.* is formed [Fig. 5(b)]. This is the only case in our study where the ion pair was separated by a neutral water molecule. The proton transfer PES displays a local minimum corresponding to the zwitterionic state [Fig. 5(c)]. Since this zwitterionic state was obtained under the tight ion-pair model restrictions (three out of ten O–O distances fixed), its energy ( $\Delta G_b=28.9$  kcal/mol) is larger compared to the fully optimized zwitterion ( $\Delta G_b=19.4$  kcal/mol). Such a difference is not surprising since the energy of the optimized zwitterion benefits from a significant structural relaxation (all O–O distances are approximately 0.2 Å shorter compared to the neutral structure). The role of electrostatic energy in the relaxed (ion distance  $R=3.106$  Å) and unrelaxed ( $R=3.174$  Å) geometries was also explored. Based on the point charge interaction (with  $z=\pm 1$ ), it was found that the energy difference between the two geometries is about 2.3 kcal/mol, clearly demonstrating the role of structural relaxation.

The “model-dependent deviation” caused by fixing O–O distances was also evaluated for octamer cubelike zwitterions of  $C_{3v}$  symmetry (described also in Ref. 79). In this case the difference between optimized and restricted zwitterions was found to be much smaller compared to the pentamer case, namely, 1.9 kcal/mol.

## Hexamers

Hexamer clusters generally represent a very important class of clusters since they form transitions from planar to spatial structures. Water hexamers appear in many conformations, which have almost identical energies (within tenths of kcal/mol) with dramatically different structures ranging from rings to three-dimensional cages. These clusters have been the subject of numerous theoretical and experimental studies, i.e., the recent work of Chesnut<sup>80</sup> and Losada and

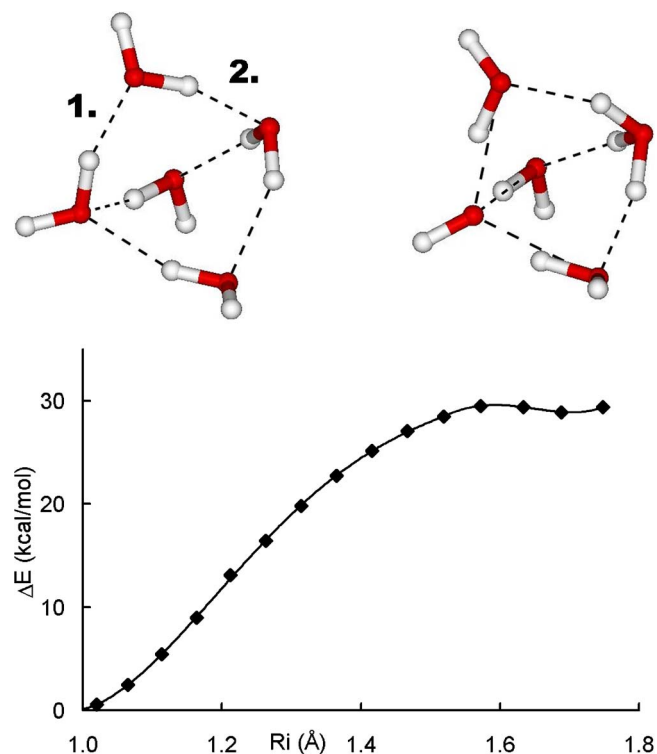


FIG. 5. Pentamer 5w-cage conformer: (a) neutral and (b) zwitterionic structures, which correspond to the global and shallow local minima on the proton transfer PES (c).



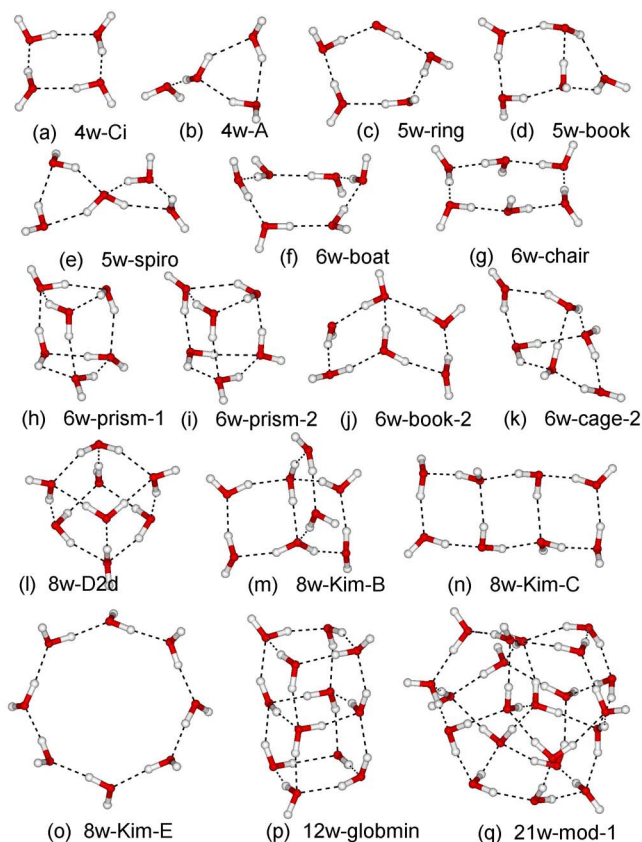


FIG. 6. Additional clusters used in the weighting procedure for a more accurate estimation of the  $pH_w$  value.

Leutwyler<sup>51</sup> should be mentioned. The lowest-lying conformers from several chosen clusters are displayed in Figs. 4 and 6. The differences of their electronic energy, enthalpy, and Gibbs free energy are shown in Table V. Note that the nearly planar (2D) clusters with 6w-boat and 6w-chair arrangements become more stable than 3D structures at higher temperatures due to the entropy term.

The determination of the proton transfer PES in the global minimum 6w-boat structure [Fig. 6(f)] led to unrealistic energies in analogy with the cyclic pentamer. The prism-type clusters [Figs. 6(h) and 6(i)] are also not appropriate for the PES construction since the three-membered rings are unstable, open during the proton transfer, and transform into the 6w-book shape [Fig. 4(f)]. Note that the 6w-book isomer has a different H-bond topology than the “book” described in Ref. 51, which is used later in our study for the statistical evaluation of  $pH_w$  [6w-book-2 in Fig. 6(j)].

The 6w-book and 6w-cage structures [Figs. 4(e) and

4(f)] are closely related. In both clusters, the two original hydrogen atoms of the forming  $H_3O^+$  cation are H bonded, which makes oxygen in  $H_3O^+$  to be a better proton acceptor. Simultaneously, oxygen in  $OH^-$  particle becomes a more efficient proton donor since it accepts two additional H bonds. In this way, the water molecules adjacent to the central dimer contribute significantly to the decrease of  $\Delta G_b$ . This feature can be easily understood since the increased electron density in the H bonds formed is connected with the weakening of the (covalent) O–H bonds. This was previously described by Kuo *et al.*,<sup>72</sup> who performed a systematic study on H-bond topology in  $(H_2O)_{20}$  based on the regular dodecahedron cluster. Their notation, introduced for the description of H-bond patterns in Ref. 12, was modified in the present paper:  $A_w(D_w)$  means three-coordinated water molecule, which accepts (donates) two H bonds, respectively [cf. Fig. 4(g)]. The symbol  $4_w$  denotes a four-coordinated molecule. Using this convention, the central dimers in 6w-book and 6w-cage belong to the  $A_wD_w$  topology class. The  $A_wD_w$  pattern was found, in accord with Kuo *et al.*, to be energetically most favorable for the proton transfer.

The central H bond in 6w-book is significantly stronger compared with the isolated dimer, which is also apparent from its shortening from 1.943 Å (isolated dimer) to 1.626 Å. This leads to a substantial decrease of the proton transfer (free) energy. The transfer now requires  $\Delta G_b = 19.1$  kcal/mol, in comparison with 69.4 kcal/mol in the case of an isolated dimer. Including the additive energy corrections to the global minimum, the final value of  $pH_a = 7.4$  was obtained. Such a number would represent an excellent agreement with the experimental value for bulk water. However, this is clearly a rather fortuitous result. Later it will be shown that the 6w-book does not represent the global minimum for hexamer clusters at  $T = 298$  K, and its contribution to the weighted hexamer  $pH_w$  is not so important.

Computations on the 6w-cage cluster give an almost identical free energy of the proton transfer ( $\Delta G_b = 19.3$  kcal/mol). This structure is topologically related to 6w-book and it can be converted to 6w-book by breaking its longest H bond. Due to the larger energy difference from the global minimum, the resulting  $pH_a$  value for 6w-cage is slightly higher, approximately 8.3.

## Octamers

The cubelike structures with various arrangements of hydrogen atoms represent clusters with the lowest energies. A systematic search performed by Belair and Francisco<sup>56</sup> re-

TABLE V. Estimation of  $pH_w$  of water hexamer clusters.

Cluster code	Boat	Chair	Book	Book2	Cage2	Prism2	Cage	Prism1
$pH_b$	<b>13.14</b>	<b>12.79</b>	<b>6.55</b>	<b>11.02</b>	<b>10.34</b>	<b>9.44</b>	<b>7.61</b>	<b>10.84</b>
$\Delta E_0$	2.33	1.00	0.98	0.53	0.39	0	1.98	1.75
$\Delta H_0$	1.65	0.46	0.64	0.23	0.12	0	1.59	1.61
$\Delta G_0$	<b>0</b>	<b>0.52</b>	<b>1.10</b>	<b>1.18</b>	<b>2.37</b>	<b>2.58</b>	<b>3.58</b>	<b>3.84</b>
$w(i)$	5.7E-01	2.4E-01	8.9E-02	7.8E-02	1.1E-02	7.3E-03	1.4E-03	8.8E-04
$pH_w$	<b>12.24</b>							

TABLE VI. Estimation of  $pH_w$  of water octamer clusters.

Cluster code	S4	D2d	Ci	C2	Kim-B	Cs	Kim-C	C1-c	C1-a
8w-									
$pH_b$	<b>10.08</b>	<b>10.49</b>	<b>7.96</b>	<b>8.39</b>	<b>14.26</b>	<b>11.50</b>	<b>4.51</b>	<b>6.34</b>	<b>8.66</b>
$\Delta E_0$	0.05	0	3.26	3.27	7.96	4.21	7.75	4.38	4.57
$\Delta G_0$	<b>0</b>	<b>0.87</b>	<b>2.61</b>	<b>2.64</b>	<b>2.78</b>	<b>3.32</b>	<b>3.29</b>	<b>3.46</b>	<b>3.52</b>
$w(i)$	$7.8E-01$	$1.8E-01$	$9.5E-03$	$9.1E-03$	$7.2E-03$	$3.0E-03$	$2.9E-03$	$2.3E-03$	$2.1E-03$
	C1-b	Kim-E	C1-e	C1-d	C1-f	C1-g	C4-a	C4-b	
$pH_b$	<b>9.13</b>	<b>12.56</b>	<b>5.69</b>	<b>4.93</b>	<b>7.86</b>	<b>5.90</b>	<b>15.75</b>	<b>15.45</b>	
$\Delta E_0$	4.54	14.41	7.05	6.99	7.26	8.03	11.79	12.13	
$\Delta G_0$	<b>3.59</b>	<b>4.15</b>	<b>5.43</b>	<b>5.64</b>	<b>5.75</b>	<b>6.37</b>	<b>9.09</b>	<b>10.26</b>	
$w(i)$	$1.8E-03$	$7.1E-04$	$8.2E-05$	$5.7E-05$	$4.8E-05$	$1.7E-05$	$1.7E-07$	$2.4E-08$	
$pH_w$	<b>10.12</b>								

vealed 14 topologically distinct cubic octamer structures. Cubic patterns also appear in most of the global minima of the larger (up to  $n=20$ ) clusters.<sup>43</sup> The relative order of octamer minima depends on the temperature and the type of thermodynamical potential considered, cf. Table VI. The global minimum  $\Delta G(298)$  is represented by the 8w-S4 structure [Fig. 4(g)]. This is in contrast with the findings of the paper by Kim *et al.*,<sup>57</sup> where the HF method favors noncubic clusters at room temperature. Structures from Ref. 57 were recalculated in this study and those which remain stable at MP2/6-31++G( $d,p$ ) level are labeled 8w-Kim-B, -C, and -E [letters are taken from the original paper, see Figs. 6(m)–6(o)] and are used in the subsequent part. The relative energies of neutral structures ( $\Delta E$  and  $\Delta G$ ) are collected in Table VI.

The  $\Delta G_b$  energy for the proton transfer in the 8w-S4 cluster was determined to be 24.9 kcal/mol, yielding  $pH_b = 9.1$ . This value is significantly higher than that for the above mentioned 3D hexamer clusters with the same  $A_w D_w$  topology. Besides the global minimum, the PESs of the proton transfer for some other structures were explored, too. The 8w-D2d [Fig. 6(l)] was not studied since it has exactly the same topology as 8w-S4. Based on considerations from Ref. 56, the 8w-Cs structure [Fig. 4(h)] represents a better candidate for the “low- $pH$  cluster” since the shortest H bond is just 1.576 Å long, while the corresponding H bond in the 8w-S4 cluster is 1.711 Å. In accord with this topology criterion, calculations revealed that the ion-pair formation in 8w-Cs requires only 12.9 kcal/mol ( $pH_b = 4.1$ ). So that the 8w-Cs cluster, despite lying 3.3 kcal/mol higher in energy than 8w-S4, yields a considerably lower  $pH_a$  value of 5.9. The origin of such a low  $pH_b$  can be explained in terms of the topology of the central dimer neighborhood. While the central dimers in both 8w-S4 and 8w-Cs belong to the same  $A_w D_w$  class, their neighboring monomers have “topologically opposite” characters in the two clusters. The  $OH^-$  particle in 8w-Cs has two  $A_w$  neighbors, which are better proton donors (based on polarization effects caused by  $OH^-$ ) than the two  $D_w$  monomers occupying these sites in 8w-S4, cf. Figs. 4(g) and 4(h). Similarly, the  $D_w$  water represents a better proton acceptor than the  $A_w$ . Therefore the effect of the  $A_w D_w$  pattern of the central dimer is further amplified in the 8w-Cs structure, while it is partially damped in the 8w-S4 cluster.

Using the present notation, the topology of the central dimer area has the form  $A_w A_w - A_w D_w - D_w D_w$  in the 8w-Cs cluster compared to  $D_w D_w - A_w D_w - A_w A_w$  in the 8w-S4 cluster.

### Cluster of twelve water molecules (12w)

The significance of the H-bond topology was further explored in a particular 12w cluster [Fig. 7(a)] which was designed as an extension of the 6w-book structure (actually it consists of two merged 6w-book clusters). Since the MP2/6-31++G( $d,p$ ) treatment used for smaller clusters was too demanding for the PES calculations here, the ONIOM [MP2/6-31++G( $d,p$ ):HF/6-31G( $d$ )] was chosen instead. The “high” ONIOM layer contained one-half of the cluster (one 6w-book motif).

Compared to the original 6w-book results, the decrease in free energy necessary for the ion-pair formation is quite significant (6.6 kcal/mol, which is about 30%, see Table II). Another remarkable result is that the O–O distance in the central dimer is the same as in the 8w-Cs cluster. The 8w-Cs and 12w clusters also share identical  $A_w A_w - A_w D_w - D_w D_w$  topology pattern, but their geometries are based on different structures (tetragonal versus pentagonal arrangements). The close topology relation is reflected in similar  $\Delta G_b$  of the proton transfer, which is 12.5 kcal/mol (only 0.4 kcal/mol less than in the 8w-Cs). So the  $pH_b$  value of the 12w cluster is 4.6. The energy difference ( $\Delta E$ ) between the presented 12w cluster and the dodecameric global minimum [cluster “12A” according to Maheshwary *et al.*,<sup>43</sup> here shown in Fig. 6(p)] is 9.8 kcal/mol when both clusters are reoptimized at the MP2/6-31++G( $d,p$ ) level. Including this energy difference in the  $\Delta G_b$  of the proton transfer, the  $pH_a$  value can be estimated to be about 8. The other 6w-book fragment of this cluster has the central dimer O–O distance slightly larger (2.858 Å compared to 2.619 Å) due to a less favorable central dimer topology, which is  $D_w A_w - A_w D_w - D_w A_w$ .

### Structure “21w”

The idea of modeling properties of bulk water from small clusters has one major drawback, namely, that all molecules lie on the cluster surface and their coordination number is usually 3 or less. The smallest cluster with one water molecule completely covered inside the “envelope” of other



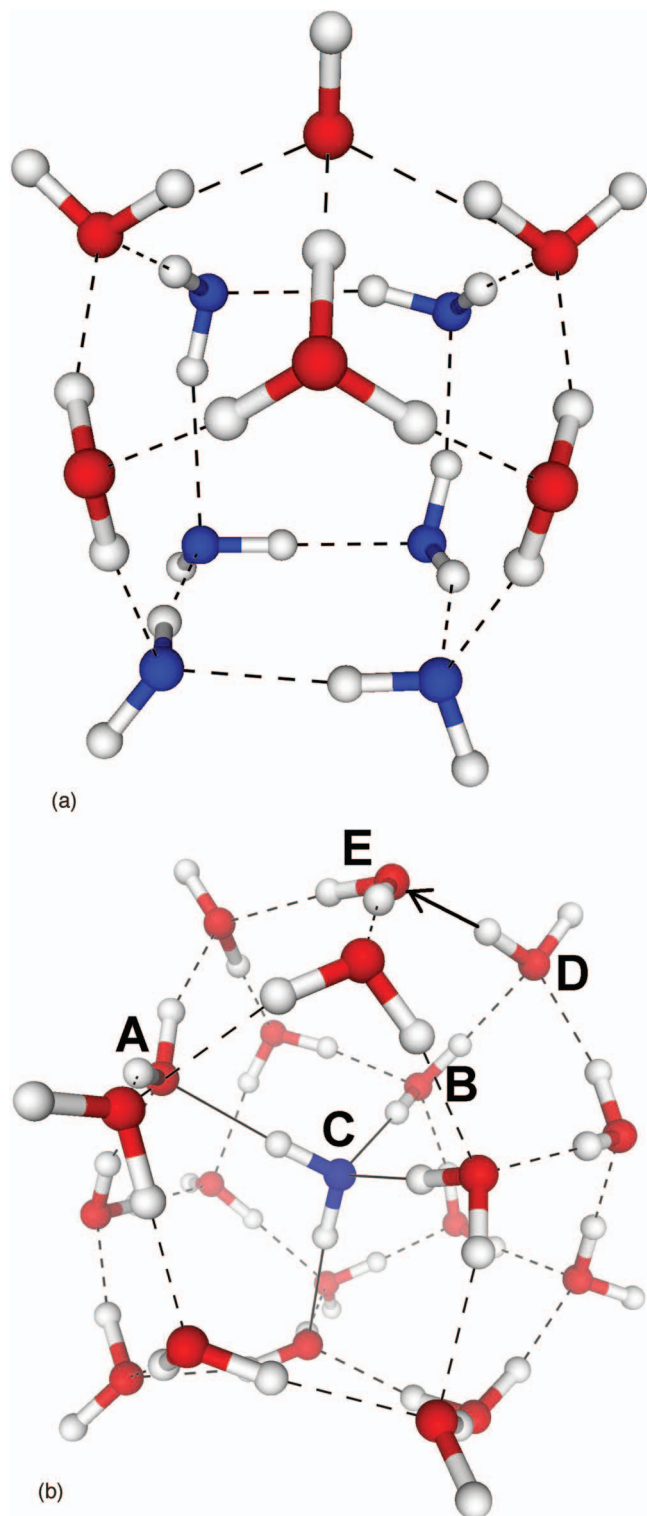


FIG. 7. (Color) Explored 12w and 21w water clusters: (a) The “high” [MP2/6-31++G( $d,p$ )] ONIOM layer consists of the 6w-book pattern (red). (b) Three different coordinates of the proton transfer: (i) from C to A, (ii) from B to C, and (iii) from D to E (along the shortest H bond on the surface).

water molecules consists of 17 molecules, as was shown by Hartke,<sup>60</sup> who used an empirical force field TTM2-F potential. The structure 21w [Fig. 7(b)] is the deepest minimum found in Ref. 60 for  $n=21$  and it was chosen for this study particularly because it consists exclusively of five-molecule

cycles. Its structure allows studying ion-pair formation “inside” the cluster, in the presence of four-coordinated water environment.

The possibility of the proton transfer both from and to the central water molecule was studied, as can be seen in Fig. 7(b). Also another proton transfer on the cluster surface along the shortest H bond was performed. The ONIOM method was employed in the same way as in calculations of the 12w cluster—the high layer contained the central dimer plus its H-bonded neighbors (eight molecules for simulations of the processes involving the central water molecule and six molecules for the processes on the surface).

Interestingly, there is only a negligible difference in the proton transfer PES for the transfer from the central water molecule to the surface [from molecule C to A in Fig. 7(b)], forming a central  $\text{OH}^-$  anion, and for the opposite transfer (from B to C), where a central  $\text{H}_3\text{O}^+$  particle is formed. The energy difference between these two ion-pair clusters is about 0.5 kcal/mol. Both proton transfers require  $\Delta E = 35$  kcal/mol, resulting in the  $p\tilde{H}_b$  value of 12 (tilde means that the  $pH$  was determined from  $\Delta E$  only). A remarkable elongation of the only hydrogen bond where proton is *accepted* by the oxygen atom forming the central  $\text{H}_3\text{O}^+$  was observed during the proton transfer. Its initial length of 1.83 Å increased to 2.15 Å in the zwitterionic structure (the other three O–O distances of the closest neighboring oxygen atoms with  $\text{H}_3\text{O}^+$  were kept frozen according to the model definition). The elongation can be partially regarded as a reaction to the imposed restrictions. Similarly, the H bond *donated* by  $\text{OH}^-$  was lengthened from 1.82 to 2.00 Å in the  $\text{C} \rightarrow \text{A}$  transfer. This indicates that the weakening of these particular H bonds further contributes to the increase of  $\Delta E$ .

When the ion pair is formed on the cluster surface [transfer from D to E in Fig. 7(b)] between three-coordinated molecules,  $\Delta E$  of this proton transfer is lower by about 10 kcal/mol. These results have important consequences, showing that four-coordinated water is energetically much less favorable for ion-pair formation than three-coordinated molecules (at the cluster surface). This also confirms the well-known fact that both  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  exhibit strong hydrophobic characters.

The fact that the energy of the “surface” transfer (25 kcal/mol) is twice as large as in the case of the 12w cluster can be explained by the topology differences. The topology of the central dimer area in the 21w cluster can be described as  $D_w A_w - A_w D_w - D_w A_w$ . Only one out of four neighbors of the central dimer is arranged in a way that effectively contributes to the  $\Delta E/\Delta G$  decrease.

It was possible to rearrange H bonds around the central dimer into a topology resembling the structure of the 12w cluster:  $A_w A_w - A_w D_w - D_w A_w$ . The optimized geometry of this modified cluster [21w-mod-1 in Fig. 6(q)] exhibits a very short central dimer O–O distance, 2.511 Å, which is by 0.28 Å shorter than in the original 21w cluster and even by 0.074 Å shorter than in 12w. The subsequent proton transfer requires only 4.4 kcal/mol. This observation is in accord with conclusions from Ref. 72 on the  $(\text{H}_2\text{O})_{20}$  clusters, where a certain arrangement of the H-bond network resulted in a spontaneous autodissociation. However, the neutral 21w-

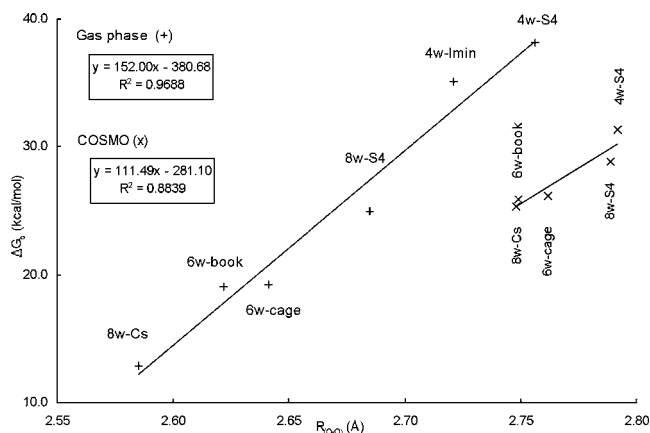


FIG. 8. Relation between Gibbs free energy  $\Delta G_b$  and  $R_{(O-O)}$  distance in central dimer for gas-phase and COSMO models.

mod-1 structure has about 15 kcal/mol higher energy than the original 21w structure, and therefore its influence on the  $pH_w$  of 21w clusters is negligible.

### Relation between geometry of the cluster and the $\Delta G_b$ value

For the examined clusters, correlation was found between the  $R_{(O-O)}$  distance of the central dimer and the  $\Delta G_b$  value for the ion-pair formation process in a given cluster (see Table II and Fig. 8). The least-squares fit of the data obtained for tetramer, hexamer, and octamer clusters yields the following linear relation:

$$\Delta G_b = 152.00R_{(O-O)} - 380.68. \quad (3)$$

The smallest 2w and 3w clusters were not used for the construction of Eq. (3), since they are relatively exceptional due to no or too few adjacent water molecules, and moreover, all the O–O distances were kept fixed during the proton transfer. The largest absolute deviation is 2.5 kcal/mol in the 8w-S4 cluster.

The most important consequence of this correlation can be seen in the possibility to estimate the  $\Delta G_b$  and thus the  $pH_b$  for the proton transfer without explicitly constructing the ion-pair formation PES. The only information needed is the optimized structure of the neutral cluster. However, this formula should be used with care, since only a reduced set of possible topologies of the central dimer was considered for its construction. The  $\Delta G_b$  obtained from the fitted formula [Eq. (3)] was also compared with the energy from the PESs of 12w and 21w clusters (determined with a slightly different ONIOM method). In the case of the 12w cluster, the difference between the calculated and fitted  $\Delta G_b$  values is 1.4 kcal/mol. A substantially worse agreement was obtained in the case of the 21w cluster, where the calculated  $\Delta E = 35.0$  kcal/mol corresponds to the fitted  $\Delta G_b = 44.6$  kcal/mol for transfers involving a central water molecule. Similarly, the calculated energy of  $\Delta E = 25.3$  kcal/mol for the transfer on the cluster surface is related to the fitted value of  $\Delta G_b = 35.8$  kcal/mol. For the 21w-mod1 cluster, the calculated  $\Delta E = 4.4$  kcal/mol and fitted  $\Delta G_b = 1.8$  kcal/mol values do not match too well either.

First, an explanation can be sought in a slightly different method, which has to lead to a different quantitative energy/distance ratio. Second, the different topology of the 21w clusters from 4w molecules can partially deviate. Third, the pronounced hydrophobic character of ion particles in the water cavity surely causes further changes in the above-mentioned ratio. Finally, some differences can be linked with the different types of rings. While basically only the four-membered rings (for nonplanar structures) appeared in 8w cluster, the 21w cluster is composed of five-membered rings where sterical tension is diminished. This fact was also not incorporated in the fitted relationship [Eq. (3)]. The ring size can represent another important criterion for the  $pH$  convergence with cluster size. The most frequent six-membered ring were not included in the explored clusters since small conformers (e.g., adamantanlike 10w cluster) are not stable and calculations of larger structures are computationally too demanding.

### Boltzman distribution of various clusters

A physically correct approach for calculating  $pH$  values has to include averaging over all conformers of a given cluster size. This is feasible only for the smallest clusters since the number of conformers rapidly grows with the cluster size. Restricting the statistical ensemble to the energetically lowest minima should still provide a good approximation, at least for moderate cluster sizes. Due to the known energy/structure relationship, the autodissociation free energy  $\Delta G_b$  can be estimated based on the optimized geometry of the clusters. The probability  $w(b)$  of ion-pair formation for every H-bonded pair of molecules in any cluster can be calculated using Eq. (3) from the Boltzman distribution function  $BD(b)$  according to the following (assuming equilibrium was achieved):

$$w(b) = Z_i^{-1} \exp\left(-\frac{\Delta G_b}{RT}\right), \quad (4)$$

where  $Z_i$  denotes the partition function (or rather a normalization factor):

$$Z_i = \sum_b \exp\left(-\frac{\Delta G_b}{RT}\right). \quad (5)$$

The weighted ion-pair formation energy  $\Delta G^n(i)$  for an arbitrary conformer  $i$  of the cluster size  $n$  is the sum of contributions from each H bond:

$$\Delta G^n(i) = \sum_b w(b)\Delta G_b. \quad (6)$$

Now we need sufficiently large ensemble of the  $n$ -mer conformers in order to find the Boltzman distribution function  $BD(c)$ , which determines the probability of occurrence of these conformers:

$$w(i) = Z_n^{-1} \exp\left(-\frac{\Delta G_0^n(i) - \Delta G_0^n(\text{gmin})}{RT}\right), \quad (7)$$

where  $\Delta G_0^n(i)$  is the free energy of the neutral conformer  $i$  and  $\Delta G_0^n(\text{gmin})$  is the free energy of the  $n$ -mer global mini-

TABLE VII. Comparison of gas-phase and COSMO results at the MP2/6-31++G( $d,p$ ) level (in kcal/mol and Å).

Structure	2w	4w-S4	6w-cage	6w-book	8w-Cs	8w-S4
$\Delta G$ gas phase	69.4	38.2	19.3	19.1	12.9	24.9
$\Delta G$ COSMO	41.0	31.3	28.8	25.9	25.3	26.2
$pH_b$ COSMO	15.0	11.5	10.6	9.5	9.3	9.6
$R_{(O-O)}$ gas phase	2.911	2.756	2.641	2.622	2.585	2.685
$R_{(O-O)}$ COSMO	2.854	2.792	2.789	2.749	2.748	2.762

num. Finally, the weighted ion-pair formation free energy  $\Delta G^n$  is obtained as

$$\Delta G^n = \sum_i w(i) \Delta G^n(i), \quad (8)$$

with weighting based on the distribution of the neutral clusters, ion-pair energy  $\Delta G^n(i)$ , and  $i$  running over all conformers (including the global minimum). This  $\Delta G^n$  can be substituted into Eq. (2), which yields the “statistically” correct  $pH_w$  value for the given cluster size  $n$ .

Results for the tetramer, pentamer, hexamer, and octamer clusters are summarized in Tables III–VI, respectively. The first conclusion from this procedure is that weighting over various H bonds in the cluster does not change  $\Delta G^n(i)$  substantially. The explanation of this can be seen in the linear dependence of  $\Delta G_b$  on  $R_{(O-O)}$ , while the weighting factor is exponentially dependent on  $\Delta G_b$ . The difference between  $pH_b$  calculated from the lowest  $\Delta G_b$  and  $\Delta G^n(i)$  (weighted over  $b$ ) was at most 0.07 units. It means that only a few shortest H bonds need to be considered in the determination of  $\Delta G^n(i)$ . Weighting over clusters becomes important when there are conformers with free energy [of the neutral structure  $\Delta G_0^n(i)$ ] very close to the global minimum and a relatively different  $\Delta G^n(i)$ . Otherwise, the relative weight of higher-lying clusters decays rapidly—it is 0.18 for the cluster with  $\Delta G_0=1$  kcal/mol above the global minimum and only 0.006 when the difference  $\Delta G_0^n(i) - \Delta G_0^n(\min)$  is 3 kcal/mol.

In the case of the trimer clusters, already the first higher-lying local minimum can be neglected since it is about 7.5 kcal/mol, higher. Nevertheless, applying the described procedure we arrive at  $pH_w=16.20$ . Notice that using the structure-energy formula [Eq. (3)] causes a deviation of 2.3 units, since the computationally determined  $pH_a$  value is 18.5.

All low-lying conformers of the tetramer clusters are easy to compute. Nevertheless, only the two square structures [4w-S4 and 4w-Ci in Fig. 6(a)] contribute to the  $pH_w$  value substantially. The  $pH_w$  was found to be 14.09 (see Table III).

The  $pH_w$  for pentamers was determined by a cyclic conformer [labeled 5w-ring in Fig. 6(c)]. The other clusters [Figs. 5(a), 6(d), and 6(e)] do not contribute to the  $pH_w$  value significantly. The  $pH_w$  was calculated to be 13.01, which is almost identical to the  $pH_a=13.03$  of the 5w-ring. Note that the weight  $w(i)$  of the 5w-cage cluster discussed above is 0.004.

For hexamer clusters, the number of low-lying minima with significantly different  $pH_b$  values is relatively large as

can be seen from Table V. For example, the free energy difference between 6w-book and 6w-boat is just 1.1 kcal/mol, while their  $pH_a$  values differ by 7 units! Therefore an error of 1 kcal/mol (method, basis set, anharmonic corrections, etc.) can completely change the resulting  $pH_w$ . Omitting some of the low-lying conformers could have the same effect. Therefore all topologically favorable clusters of all important hexamer classes (book, cage, prism, and circle) have to be included. Clusters such as 6w-book-2, 6w-cage-2, and 6w-chair [Fig. 6(g)] were added in this step. The final  $pH_w$  value obtained for the water hexamers at  $T=298$  K is 12.24.

Interestingly, the problem with ensemble completeness is much less severe for octamer clusters as the global minimum 8w-S4 is energetically well separated from other isomers (except for 8w-D2d, which yields an almost identical  $pH_a$ ). For the purpose of the weighting procedure, all 14 cubelike octamers were included (structures can be found in Ref. 56), and also the structures 8w-Kim-B, -C, and -E from Ref. 57 [Figs. 6(m)–6(o)]. The results are summarized in Table VI. It is known that the cyclic and noncubic conformers become more favorable at higher temperatures due to entropy reasons, but these transitions occur above 289 K (in contrast to the hexamer). For example, the cyclic 8w-Kim-E is still 4.1 kcal/mol higher than the global minimum at  $T=298$  K. Under these conditions the resulting  $pH_w=10.12$  is only 0.04 units higher than the  $pH_a$  of 8w-S4. Note again that this value differs from the computationally determined  $pH_b(8w-S4)=9.1$  due to the deviation in of the fitting formula.

## COSMO

In this section we describe an approach to estimate the effects of the bulk phase, which was performed within the polarizable continuum model. Calculations using the COSMO method were done on the reduced set of the water clusters from the previous part. The most important results are summarized in Table VII.

Considering the continuum model, differences among various clusters of the same size are strongly reduced. Further, convergence towards the experimental  $pH$  value with increasing number of water molecules is smoothed and improved, e.g., changes in the central dimer O–O distances [cf. Fig. 9(a)]. The same follows for the ion-pair formation energies [Fig. 9(b)]. In the dimer case, the dissociation energy is significantly reduced (from 71 to 42 kcal/mol) due to the model of implicit solvent. In the hexamer case, the ion-pair energy of gas phase is already comparable with the COSMO calculations, which points to the fact that the most essential



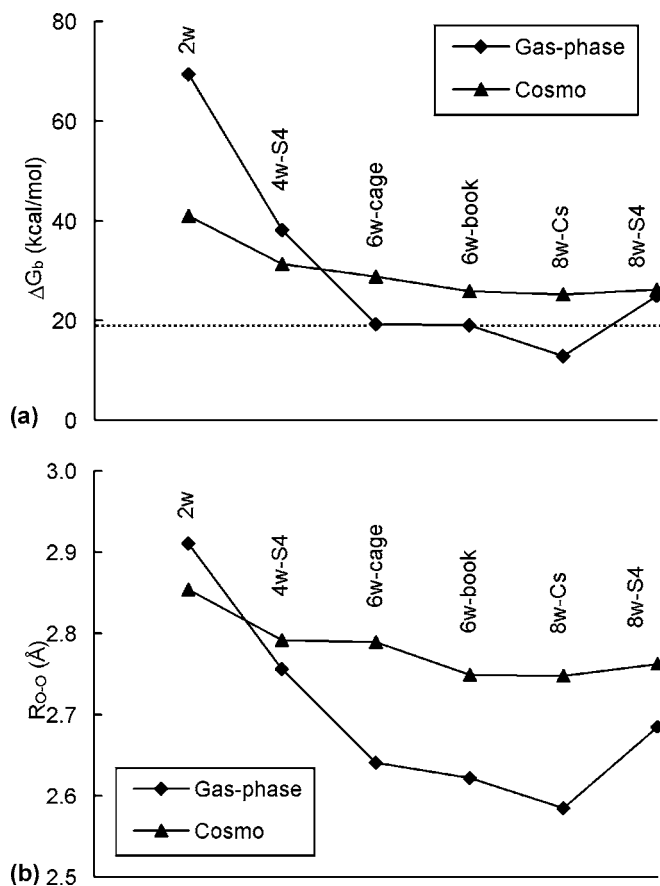


FIG. 9. Changes of (a) the  $R_{O-O}$  distance in neutral cluster and (b) the ion-pair formation energy  $\Delta G_b$ . The dashed line in (b) marks the value which corresponds to  $pH=7$ .

environment is present; both water molecules of the central pair are three coordinated. As mentioned above, the differences between various clusters are substantially smaller. For example, comparing 8w-Cs and 8w-S4 clusters in gas phase, the difference in the ion-pair energy is about 13 kcal/mol, while in the COSMO model this difference decreased to 3 kcal/mol. It is apparent that clusters under the influence of implicit water environment display smaller differences between various topologies, since the polarized continuum effectively simulates H-bond interactions with the neighborhood. In this way the results can be apparently considered to be more “size dependent” rather than “shape dependent.” A seemingly slower convergence (passing from 2w to 8w clusters) was achieved. It can be, however, regarded as a result of smaller differences between individual clusters of the same size since COSMO substantially damps various fluctuations caused by different “shapes” of the surface.

Unlike in gas phase, the PES of the autodissociation in the COSMO framework exhibits a regular activation barrier and subsequent stabilization of the ion-pair products in a local minimum. However, these “zwitterions” originated from the tight ion-pair model always neutralize when the O–O distances are relaxed.

## CONCLUSIONS

In the study, various water clusters were explored from the point of view of the proton transfer between H-bonded

neighbors. A relatively modest approach—the MP2/6-31++G(*d,p*) level—was chosen as acceptable considering the fact that also larger systems have to be included. The tight-ion-pair model (with usually three fixed O–O distances) was adopted for the autodissociation process.

- The first thing that can be noticed is a fast  $pH$  decrease when cluster size increases from 2 to 6. For large clusters in gas phase, the topology of H bonds plays an important role, varying  $pH$  from 7 to 13 in hexamers or from 5 to 15 in octamer clusters.
- The important relationship between energy/distance was quantified (in the form of a linear equation) for the given method and basis set, which enables a fast estimation of  $pH$  values within the considered set of clusters. Nevertheless, this still represents the weakest point and it should be taken with care since in the case of substantially different topologies (e.g., containing 4<sub>w</sub> molecules) it can lead to pronounced deviations.
- Considering the weighting procedure, it is worth mentioning that a complete exploration of larger clusters is practically impossible since there are either too many different families of clusters (based on different structural patterns or the arrangement of oxygen atoms in space) as well as too many various topologies in the given family (arrangements of H bonds).
- For larger clusters, there is a great amount of the diverse ion-pair formation energies  $\Delta G_b$ . The formation can be even spontaneous in some cases, which has been demonstrated in several papers.<sup>72,77</sup>
- Since the  $1/RT$  equals 1.6 kcal at 298 K, the weights of energetically distant local minima quickly become negligible. For the water octamer, we have shown that the correct consideration of the local minima changes the  $pH$  value only by 0.2. However, local minima may become significant for larger clusters. Moreover, considering the autodissociation process to be infinitely fast for some higher-lying cluster, the ratio of cluster distribution is changed and we can get out of equilibrium and thus outside the Boltzmann distribution.
- Enhancing our model with the COSMO approach brought significant improvement in the description of the autodissociation reaction with a stable zwitterionic structure. However, when the O–O restrictions were released, the small barrier for backward reaction disappeared, reforming neutral clusters spontaneously. The polarizable continuum model also smoothed the differences between various topologies and cluster families (as was demonstrated in Fig. 9).
- Averaging the explored clusters *in vacuo*, the series of  $pH$  25-18-14-13-10 was obtained in the range of dimer to octamer clusters. Using the COSMO approach, the same series is 15-14-12-10-9. It shows that we are still two units from the experimentally known  $pH$  and probably larger clusters (by about 20 water molecules) are needed to reach the size-independent (bulk) value.

However, the situation is far from hopeless since the  $4_w$  type molecules are not involved in the autodissociation process as we demonstrate here.

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