On the Molecular Basis of Water Hydrolysis. A Detailed ab Initio Study

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A refined study of the water hydrolysis is made at the HF-MP2 level, with full counterpoise correction and many-body analysis. The O−H bond dissociation occurring during water hydrolysis was studied in small water aggregates, from the trimer to hexamer, using fully optimized structures at the HF-MP2 level. The breaking of the O−H bond in these clusters is a complex reaction. It is found that the H-bond coordination pattern for each monomer influences its role during the reaction. From a detailed analysis of molecular properties those roles can be clearly identified. The results obtained show that at least two water molecules should act as promoters of the hydrolysis reaction while the molecules intervening in the concerted double proton transfer can be distinguished in the reactants structure by its large three-body nonadditive interaction. Only one final structure, where the ions act as triple acceptors and triple donors of H-bonds, becomes stable. The role of ion hydration in lowering the barrier for the hydrolysis reaction in these clusters is also discussed.

Introduction

Some gas-phase studies of proton-transfer reactions with stepwise solvation of the reactants have demonstrated that the acid/base behavior of isolated solvent molecules can be dramatically different from their performance as bulk liquids. Water, the classical amphiprotic solvent is a clear example of this: the gas-phase basicity of water is ≈35 kcal/mol below that of ammonia.[1] This difference has been explained as coming from the enormous solvation energies of the products.[1] Nonetheless, in a recent pair of works.[2,3] it is shown that the water hydrolysis in a water pentamer is possible through a concerted double proton transfer. Since five water molecules could not account for the solvent effects that would be responsible for the reaction in liquid phase, there is a need to clarify which are the molecular properties that drive the water hydrolysis reaction.

It is well-known that the water hydrolysis phenomenon is promoted by acids such as metallic cations and "free" protons. Cations that hydrolyze extensively are those that are either small (e.g., Be^{2+}) or are highly charged (e.g., Fe^{3+}, Sn^{4+}), or both, and have a high charge-to-size density.[4] When the catalyst is a proton, the hydrolysis reaction becomes one step in the mechanism of proton transfer and diffusion in aqueous systems, as is strongly supported by some theoretical work.[5−8] Water can behave as an acid moiety itself; is it capable of promoting its self-dissociation? If it is, how does it do it? As Mó et al.[9] pointed out, the acid/base character of a water molecule is closely related to the nonadditive effects of the environment. A close analysis of the geometries of those clusters where hydrolysis occurs could help to answer the previous questions. In this work, we looked into such characteristics and the effect they might have on the O−H bond dissociation mechanism.

So far, the experimental and theoretical work made on this particular reaction agree on pointing to the collective effects as the trigger of water hydrolysis. The X−H bond dissociation {X= O, F, S}, has recently been the subject of several studies. It has been suggested by some authors that the mechanism of ionic dissociation of a water molecule in aqueous solution might be determined, on one hand by the geometrical arrangement of the molecules that take part directly in the process, and on the other, by the cooperative effects.[9] Chipot et al.[10] found in a recent work, that in the protolytic dissociation of the HCl and HF molecules, the number of water molecules directly involved in the mechanism is a factor determining the occurrence of the dissociation process. Lee et al.[11] found similar results for HF, HCl, and H_2S. Furthermore, the relative positions of the additional water molecules are important in determining the subsequent proton-transfer reactions.

In this work we analyze which molecular properties that arise as result of collective phenomena are directly involved in the hydrolysis mechanism. We make use of quantum mechanical methods to sample the potential energy surface of the O−H bond dissociation occurring in water clusters of different sizes. For all of them we have calculated the molecular properties that seem to have a close effect on the role individual water molecules might have as hydrolysis promoters. Up to now, this kind of analysis is missing from current literature that has been devoted to locate the occurrence or not of the hydrolysis process in water clusters. The analysis presented here helps to provide a rationale of the solvent effects acting upon this important reaction. This work offers an analysis for deciding the factibility of occurrence of the reaction in different clusters.

As a result of the breaking of an O−H bond from a water molecule in a cluster, there are several possible rearrangements. Some of them could lead to ionic products, H_3O^+ and OH^-, in their midst while some others could produce a chain of proton transferences leading back to a neutral molecular cluster. With the results presented here we propose a series of conditions that must be fulfilled in order to produce and stabilize the ionic products. We show that there are two crucial aspects that determine either the stabilization of the ionic pair within the cluster or the return to a neutral molecular cluster following coupled transference; the final geometrical arrangement of the cluster and the environmental conditions of the water molecules

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TABLE 1: Predicted Energies in kcal/mol for the Dissociation Processes Using Basis Sets of Different Sizes[a]

basis set	ΔE^b	ΔE^c
6-31G	422.36	39.91
6-31+G	398.49	40.18
6-31G(d)	429.43	46.58
6-31++G	394.41	39.86
6-31G(d,p)	433.62	46.49
6-31++G(d,p)	405.94	46.36
6-31++G(3df,2p)	407.07	46.59
6-311G	418.88	39.63
6-311+G	395.60	39.87
6-311G(d)	425.99	47.30
6-311++G	395.63	39.80
6-311G(d,p)	430.19	47.39
6-311++G(d,p)	406.35	47.41

[a] ΔE corresponds to the differences between the products and the reactants. [b] $H_2O \rightarrow H^+ + OH^-$. [c] $(H_2O)_3 \rightarrow [H_3O^+ - OH^- - H_2O]$.

involved. Results show that once the ionic products are formed and stabilized within a cluster, the role of additional water molecules could be understood in terms of a competing process of ion hydration and water networking.

Method

Standard ab initio calculations were carried out using Gaussian94.[12] There are several technical and practical considerations to be taken into account when selecting an appropriate basis set for the study of bond dissociation: The selected basis set must not be very large in order to allow extensive sampling of the potential energy surfaces and must be flexible enough to accurately describe the hydrogen-bonded systems as well as the expected product, the OH^- moiety. We tested several basis sets in two different situations: the ionic dissociation of a single water molecule, i.e., $H_2O \rightarrow H^+ + OH^-$, and the ionic dissociation of a water molecule in a cyclic trimer, i.e., $(H_2O)_3 \rightarrow [H_3O^+ - H_2O - OH^-]$. Contrary to what has been observed for OH^- in water,[23] when the OH^- moiety occurs within a water cluster, together with the corresponding H_3O^+ ion, it seems there is not such a stringent need for diffuse functions and large basis sets. This can be seen in Table 1, which presents the effect of basis set size on the calculations of the ionic dissociation of an isolated water molecule. It is quite interesting to observe that the convergence in the reaction energy of the latter case is reached as soon as polarization functions are included in the basis set. As we will always work under this condition, and considering that since the extended sampling of potential energy surfaces is intendend, the use of larger basis sets with diffuse functions is not convenient on account of the large computational cost it will represent. The 6-31G(d,p) basis set was selected to sample the potential energy surfaces.

Correlation energy is essential for a proper description of molecular distortions, and we included it at the MP2 level. It produces a $\approx$50% difference in the relative stabilization energy of a neutral cluster against that of the ionic pair. Furthermore, correlation energy has also been emphasized as a necessary requirement for the many-body analysis.[13] Xantheas[14] reported that the MP4 correlation level adds only a small ($\approx$2%) modification to the MP2 interaction energies in close to optimal structures. Nevertheless, since the MP2 correction is so important for geometries far from the equilibrium position,[13] we checked the effect of a higher correlation level (MP4) in structures having large distortions. We found that the MP4-corrected energies obtained for the optimal pentamer, the ionic pair within the pentamer, and the corresponding transition state were all $\approx$9% more attractive than those at the MP2 level, but no appreciable differences appeared in their relative energies. Considering that the general picture of the energetic description for the reaction does not change when the correlation level is raised, and since the computational cost of sampling potential energy surfaces is very high, results were obtained at the MP2 level.

To separate promotion effects from the whole solvation phenomena is not an easy task; there is not a direct form to do it. We think that the better these effects are distinguished from those pertaining to ionic hydration, the easier it will be to understand the important solvent effects water, as a solvent, has on most aqueous acid/base processes.

To differentiate what we will be referring to as promotion effects as compared to solvation ones, we calculated the magnitude and the dependence of the behavior of the former with the size of the cluster, starting from the smaller cluster where only one molecule could act as a promoter for the water hydrolysis reaction; the water trimer. From there, we looked for similar patterns in larger stable structures. Actually, to our knowledge there has not been a complete study of the trends of nonadditive effects and the role they play on molecular distortion in water clusters larger than water trimers.

Once the water clusters were fully characterized at this level, we induced the O−H bond dissociation with two different approaches. First, the length of a selected O−H bond was increased in a stepwise manner along the hydrogen bond coordinate, while fully optimizing all other geometrical parameters in each step. This procedure has already been used for studying the gas-phase proton transfer reaction of nitric acid−ammonia in molecular clusters.[15] As will be discussed later, this procedure was not appropriate for the complete characterization of the reaction since the concerted motion of other protons is always induced and the description of these simultaneously occurring transfers was impaired. Therefore, we also considered a two-dimensional surface in which the movement of each proton is carefully monitored. Both approaches allowed us to sample the region of the potential energy surface where the hydrolysis reaction coordinate lays. In this way, it was also possible to gain some insight on the mechanics of the process. It will be shown that both protocols allow for a proper search of the reaction coordinate.

In the following sections we present the results obtained for the O−H bond dissociation occurring in water clusters, from a cyclic trimer to hexamers. One of the goals of this work was to elucidate the role that molecular properties involved in the mechanism play in this important reaction. Specifically, the many-body analysis of the pentamer allows a close-up view of the role that each water molecule plays in the reaction and the analysis performed for the hexamers will be useful to address the competing effects of ion hydration and water networking. The analysis provides a rationale for the need of a defined number of molecules in the aggregate for the stabilization of ionic products. The conclusions arising from the study made in the larger clusters might be further extended to provide an initial point for the study of this reaction in bulk water.

Results

I. Distortion and O−H Bond Dissociation in Water Clusters. (a) Trimers. As has already been mentioned, the trimer case is analyzed just as a model for what could be the promotion of hydrolysis with little or no solvent effects present. We selected the most stable trimer, the cyclic one. In this trimer every monomer has an identical H-bond donor−acceptor pattern, and no acidic character in the structure is favored. It is interesting

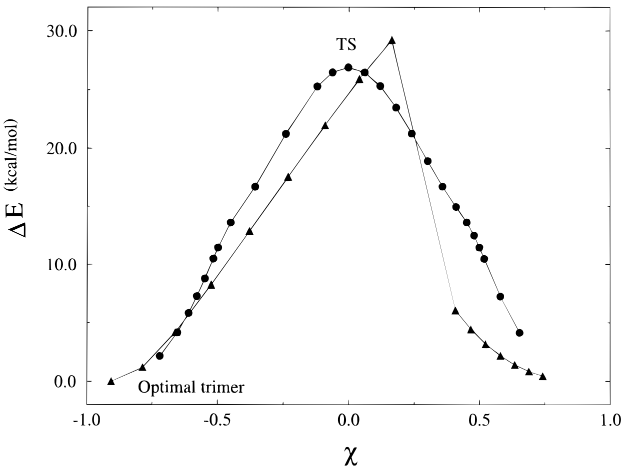

Figure 1. Comparison of the energy curves for the O−H bond dissociation at the MP2 level in the water trimer: (●) for the concerted transference and (▲) for the stepwise elongation of the O−H bond as described in the text. $\chi = R_{O_d-H} - R_{O_a-H}$, where O_d stands for donor oxygen and O_a for acceptor oxygen.

to note that, even in this symmetric structure, three-body nonadditivity is a stabilizing contribution that amounts to 26.2% of the interaction energy. To test the cluster's response to molecular distortions resembling an O−H bond dissociation, one of the hydrogen atoms forming a H-bond was selected and it was gradually elongated in order to induce the ionic pair, H_3O^+ and OH^-, genesis. At a certain point ($R_{OH} = 1.35$ Å), the geometry transforms back spontaneously into a neutral structure as a result of the two other protons in the cycle being transferred.

In a more detailed search it was possible to characterize a transition state between the two neutral molecular clusters representing reactants and products. This transition state lies 26.90 kcal/mol higher in energy than the initial optimal trimer, and its structure corresponds to a planar ring in which all protons are equidistant to the oxygen atoms ($R_{OH} = 1.215 \pm 0.001$ Å).

Starting from this transition state structure, we obtained the reaction route with the intrinsic reaction mechanism algorithm implemented in Gaussian 94.[12] A comparison of both studies, i.e., single O−H bond elongation and the concerted transference can be seen in Figure 1. The comparison is made in terms of χ, the reaction coordinate parameter, defined as $\chi = R_{O_d-H} - R_{O_a-H}$, where d and a mean donor and acceptor, respectively. There we show that single O−H elongation induces a concerted proton transference, leading to a new neutral cluster with no ionic pair produced along the route. It is interesting to observe that for the first stages of the concerted transference there is a steep rise in the energy of the cluster. During this stage it is possible to see that water monomers are moving closer to each other in order to facilitate the proton transfer.

A similar mechanism for proton transference has been reported by Spaeth et al.[16] in pure alkaline metal hydroxides, where this behavior contributes to proton diffusion but does not produce proton conductivity. Furthermore, it is possible to see that at least 40% of the barrier (see Figure 1) comes from the energy required to closely pack the water molecules (from an O−O distance of 2.78 to 2.37 Å). This condition of close packing appears in the crystalline structure of the metal hydroxides but seems difficult to reach in liquid water since the minimum approach distance is 2.40 Å, as can be seen in the O−O experimental radial distribution function.[17]

(b) Larger Cyclic Clusters. The cyclic water tetramer and pentamer have been recently very well characterized by means of theoretical studies[18] and far-infrared vibration−rotation−tunneling spectroscopy.[19] Those works were intended to unequivocally assess the global minimum structure for those clusters, as well as to quantify the nature of the many-body effects in hydrogen-bonded systems such as these. For the cyclic pentamer there is an additional interest, since it appears to be a fundamental structure in the hydration of biomolecules where larger water clusters seem to be concatenated water pentagons.[20]

Employing a method similar to the one described above for the O−H bond elongation in the trimer, we went on studying the tetramer and pentamer structures. As expected, a pattern resembling the one observed for the trimer was found, since the donor acceptor array is the same. Even if the results obtained were not unexpected, it was important to check the occurrence of the same concerted multiple transfer in this structure. Additionally, in larger clusters it is quite common to find cyclic tetramers showing a varied donor−acceptor pattern, which, as will be discussed later, plays an important role in the proton-transfer mechanism.

(c) Noncyclic Structures. By means of a molecular dynamics study of the water solvation structures in liquid water, using a refined analytical interaction potential (NCC), Corongiu et al.[21] found that at room temperature, on average, the most abundant structures correspond to a tetracoordinated and pentacoordinated water molecule. Those structures persist in the MD simulation for time scales ≈1 ps, 2 orders of magnitude greater than water vibrational frequencies. The longest lived structures in that simulation were pentamers. With that in mind we decided to analyze the hydrolysis reaction in stable noncyclic structures that have a certain probability of existing in liquid water due to their size and their O−O distance. However, we would like to emphasize that the conclusions arising from this study might not be directly extrapolated to the bulk liquid but could provide a helpful interpretation of the feasibility of hydrolysis in pure water systems.

For the pentamer, we found a stable structure. This, a pyramidal structure, was fully optimized, and its total interaction energy was −35.23 kcal/mol, compared with the −38.00 kcal/mol for the cyclic configuration. The varied H-bond donor−acceptor pattern has allowed us to look upon the effects of this coordination on the promotion of hydrolysis. As a matter of fact, this pyramidal structure has already been studied in the proton-transfer context.[2,3]

The pyramidal pentamer (5B) has water molecules with three different H-bond interaction patterns, i.e., daa, dda, and da, where d stands for H-bond donor and a for H-bond acceptor, as shown in Figure 2.

Within this structure we explored the feasibility of hydrolyzing two different molecules, W3 and W5. The former is a daa molecule, it is expected that it will hold properly a negative charge. The latter is a daa molecule, whose coordination properties are opposite to those of W3, and therefore we expect a rather different behavior upon distortion.

In W3, the proton (H10) was elongated toward an acceptor molecule, which also has a dda pattern (W2); the process is named route I. For W5, the proton (H6) was moved directly toward a da acceptor (O4 in W4); this would be referred to as route II. In Figure 3 we observe the energy profiles for each case as a function of the difference between the distance of the transferred hydrogen to the donor and to the acceptor oxygens. For the sake of comparison the equivalent profile for the cyclic pentamer is also shown.

For route II a concerted transference occurs with H6 going to W4 and simultaneously H8 going to W3, thus producing a

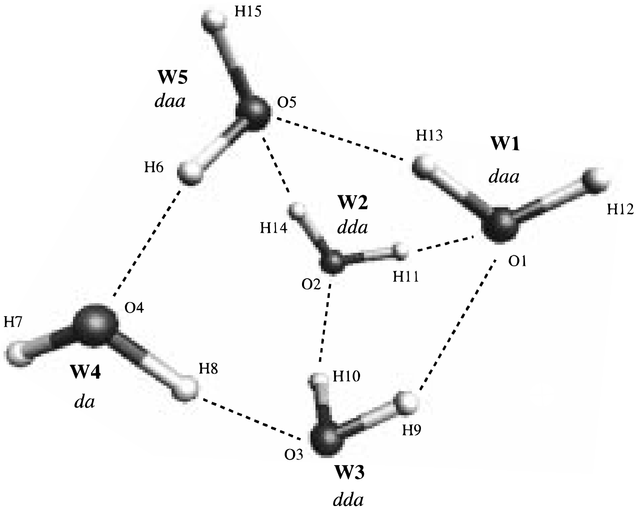

Figure 2. Optimal structure for the water pentamer 5B showing the H-bond donor−acceptor character of the molecules, i.e., donor (d), and acceptor (a). All geometrical parameters can be provided upon request.

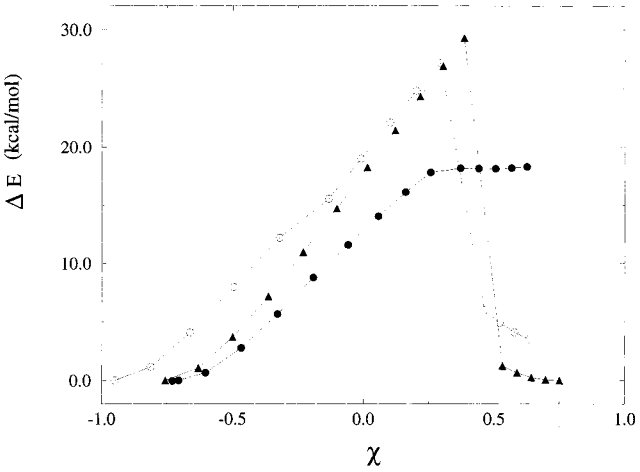

Figure 3. Energy curves for the O−H bond dissociation at the MP2 level in the water pentamers starting from the optimal structure for each cluster: (▲) for the cyclic pentamer; (○) for the route I in pentamer 5B; (●) for route II in pentamer 5B as described in the text. $\chi = R_{O_d-H} - R_{O_a-H}$, where O_d stands for donor oxygen and O_a for acceptor oxygen.

stable ionic pair as the one previously reported by Tozer et al.[3] Each ion formed establishes three strongly favorable interactions with the remaining neutral water molecules; i.e., the ions have a triple donor and a triple acceptor character and all the neutral molecules in the cluster change their original character to a da one (Figure 4). The optimized structure has a C_3 symmetry. A very different scheme appears for route I. Here the multiple transfer that occurred in the cycle formed by W3−W2−W5−W4 did not lead to a stable ionic pair but led back to a neutral molecular cluster. This is the pattern that has been previously observed for the cyclic trimer, tetramer, and the pentamer, and it suggests that concerted multiple transfer is not only a probable process but also a common one.

Since the process we found involves several proton transferences, we decided to consider the reaction coordinate that connects the ionic pair with the optimal pentamer through the multiple transfer being taken into account explicitly. For that, the O−H bond distances of both transferable protons were fixed stepwise, fully optimizing the remaining geometrical parameters. The corresponding surfaces can be seen in Figures 5 and 6. Differences between both surfaces are clear. Those differences could be useful as a key to understanding the role individual water coordination exerts upon the factibility of hydrolyzing a water molecule. In the first case it is possible to see that the concerted motion involves four protons, leading to a rearrangement of a neutral structure. In the second case, there is a transition state and ionic products in a large plateau with a very shallow minimum. Of course, we are really dealing with a four-dimensional problem in a two-dimensional way. A comparison of the one-dimensional curve for route II, in Figure 3, and the proper two-dimensional one, Figure 5, shows a similar behavior. Also, the one-dimensional curve for route I, in Figure 3, is similar to the two-dimensional one, Figure 6. Of course, the actual height of the barrier for the process occurring through route I might not be obtained by means of this partial representation (Figure 6) but due to the similarities observed,

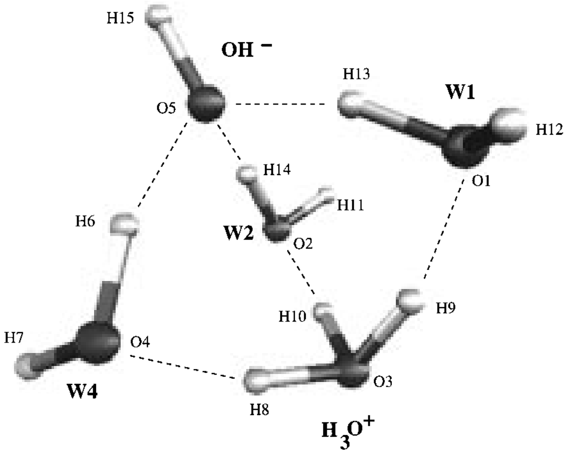

Figure 4. Potential energy surface for the concerted double proton transference in pentamer 5B through route II described in the text.

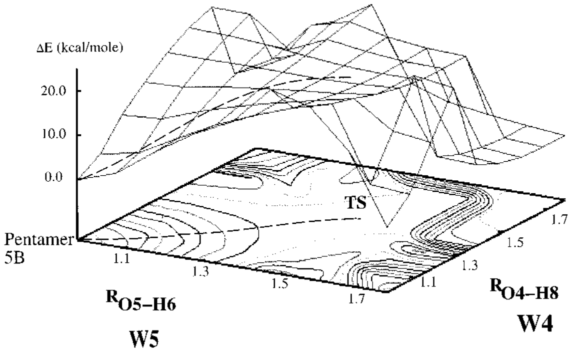

Figure 5. Stable ionic pair structure found starting from pentamer 5B through case II, as described in the text after full optimization.

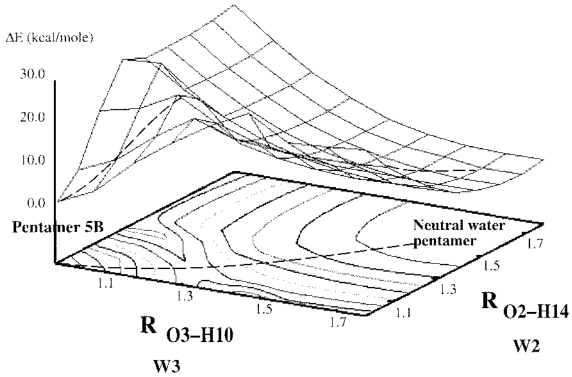

Figure 6. Potential energy surface for the concerted double proton transference in pentamer 5B through route I described in the text. The concerted motion of these two protons conduces to a quadruple transference that leads back to a neutral structure.

it is expected that a complete description of the quadruple transfer might be similar to those described above.

Lee et al.[2] found evidence of the existence of a dissociated water molecule in water clusters through the stabilization of an ionic pair in this pentamer as well as in an octamer. However, we want to emphasize that these ionic products and the transition state cannot be reached by the concerted transference of any pair of protons in the cluster. The different shapes of the surfaces presented in Figures 4 and 5 clearly suggest that certain requirements are crucial for determining the nature of the final state for the process.

It is important to notice that the double transference occurring in the pentamer is not as symmetric as the concerted transference described for the trimer. In this latter case the transition state is located at $\chi = -0.002$, i.e., the midpoint between the donor and the acceptor oxygens. For the pentamer the transition state (with a $\nu^{-1} = -186.83$ cm^{-1}), occurs at $\chi = 0.372$. Even if the proton transferences represent a synchronous proton displacement, it seems that for the pentamer one has to go quite a long way toward the ions for the process to reach a transition structure. Analogous to the trimer case, the shortening of the O−O distance, along the reaction coordinate, is an important modification, even if not as marked as for the trimer, it is still important, from 2.67 to 2.55 Å for O5−O4, and 2.70 to 2.56 Å for O4−O3. This compression seems more likely to occur in liquid water since the shortest O−O distance is not smaller than the average closest neighbor approach measured by means of X-rays or neutron diffraction experiments in liquid water.

Strong geometrical and environmental conditions must be fulfilled in order to obtain an ionic pair as a product and prevent the return to a neutral cluster through concerted multiple transferences and those conditions are found in the following properties of the water cluster: (a) the initial donor−acceptor conditions (DA) of the water molecules that participate in the proton transference; (b) the conformational changes that occur in the cluster during the proton transference; (c) the final structure of the aggregate.

Analyzing the initial DA conditions of the intervening water molecules, the following was found. For case I the participating acceptor and donor molecules (W3 and W2, respectively) are both dda while for case II they are daa and da (W5 and W4). This indicates a different ability of the acceptor molecule for receiving the incoming “extra” proton. W1 and W2 seem to be the molecules that act as promoters: at the beginning, there is a long H-bond connecting them that is easily broken as soon as W5 and W4 move their corresponding protons. These two water molecules later allow the stabilization of the ions formed.

On the basis of the H_3O^+ stabilization through a triple donor coordination, it is possible to see that the process will be favored by the existence of a daa molecule as the final acceptor of the proton. This is the case for route II but not for route I. In route II, W4 connects the initial donor with W3, a dda molecule, but in route I as soon as H10 transference starts, W2, an original dda, breaks the O−H bond with W1 and no other molecule in the cluster has now the required dda character. There is another structural characteristic that clearly differentiates both routes. In route I the breaking of the H-bond between W2 and W1 leads to an opening of the cluster, isolating W1 from the reaction, whereas for route II even if the same H-bond breaks, W1 remains close to the cluster and active in the transference.

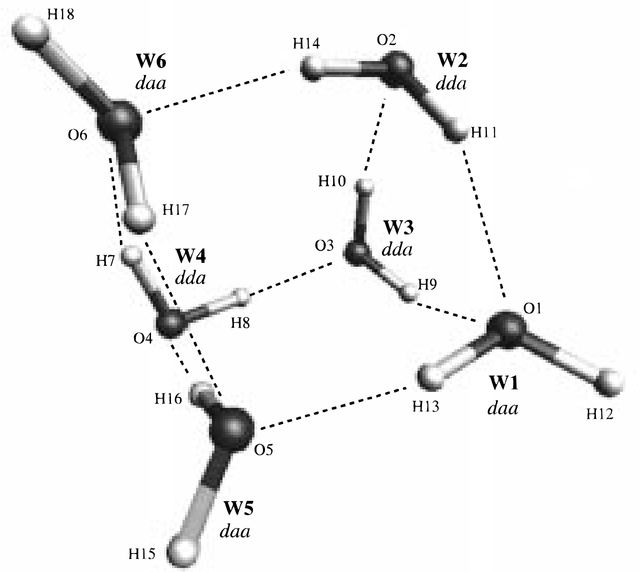

Figure 7. Optimal structure for the water hexamer, showing the H-bond donor acceptor character of each monomer. All geometrical parameters can be provided upon request.

The reaction found for the water hydrolysis process is the same Tozer et al.[3] have already reported with a transition state very close to the products. The height of the energetic barrier is slightly smaller in our case (18.17 vs 19.4 kcal/mol), and this could be only a reflection of the different basis set employed in both works.

Two different aspects of the influence of nuclear quantum effects were analyzed. First the zero point vibrational energy corrections and second, the existence of a normal vibrational mode corresponding to the reaction coordinate. ZPE correction produced a lowering of the barrier from 18.17 to 16.09 kcal at the MP2 level. Again, a comparison with the results reported by Tozer et al.[3] shows a small difference since the same kind of correction lowered their barrier only 1.4 kcal. A second effect analyzed was the existence of a normal vibrational mode in the reactants structure related to the double transference. The normal mode at 3357.9 cm^{-1} corresponds to the simultaneous elongation of the O5−H6 and O4−H8 bonds; the concerted transference of these protons produced the ionic products, as has been described in this section. As a matter of fact, there is no other vibrationally promoted proton transference for this structure.

The initial interest to extend the hydrolysis study up to hexamers was not only to test the transferability of the mechanism found for the pentamer to larger clusters but also the fact that this is also a common cluster size in liquid water. We specifically wanted to test the following: (i) The dependence of the process on the initial coordination pattern of the active molecules (ii) The dependence of the process on the number of H-bonds modified during the hydrolysis mechanism. (iii) The effect of an additional molecule on the cluster containing the ions.

The geometry for the optimal hexamer is, up to now, a matter of strong discussion. There is a common agreement on the fact that 3D cage structures are more stable than planar ones.[22] Of the many possible 3D structures, we selected one that has only two kinds of donor−acceptor monomers, daa and dda, as seen in Figure 7. We will refer to this figure for the ensuing discussion.

Since the complete sampling of the potential energy surface for the transference in this case is not practical, we considered a model for the reaction coordinate representing the concerted double transference. We fixed in a stepwise manner the length of the O−H bond of the two transferred protons and performed a full optimization of the rest of the structure. Since this procedure is equivalent to move along the diagonal line in the

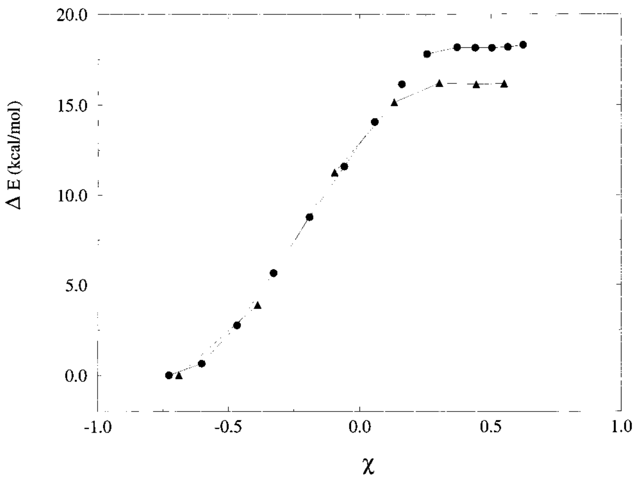

Figure 8. Energy curves for the O−H bond dissociation at the MP2 level in the water pentamer 5B (●) and the hexamer (▲), starting from the optimal structure for each cluster and promoting a concerted double transference as described in the text. $\chi = R_{O_d-H} - R_{O_a-H}$, where O_d stands for donor oxygen and O_a for acceptor oxygen.

two-dimensional surface, we refer to this method as the diagonal optimization. Proton H16 in W5 (daa) was transferred to W4 (dda), and simultaneously, H8 was moved toward O3 (dda). It would seem that the intermediate molecule in the concerted transference is different from the one found in the pentamer, but this is not the case. As soon as the first proton approaches O4 the H-bond that W4 had with W6 is broken, making W4 a da bridge. In Figure 8, the energy profile of this process is shown. It is possible to see that the height of the barrier is ≈2 kcal/mol smaller than that corresponding to the pentamer. This result is surprising since the results of Lee et al.[2] indicate that from pentamer to octamer there is a fast lowering of the barrier (from 14 to 5.5 kcal/mol with the BLYP method). This discrepancy can be due to the known weaknesses of DFT-(BLYP) in treating H-bonded systems. An example of this can be found in the same work,[2] where they present a discrepancy in the pentamer between their HF-MP2 calculations, having a barrier of 19.4 kcal/mol, and the DFT(BLYP) results of 14.0 kcal/mol.

We think that the lowering of the energetic barrier with the subsequent addition of water molecules is a very slow process because, contrary to what is commonly thought, the presence of additional water molecules does not produce more hydrated ions. Once the H_3O^+ and the OH^- get a coordination 3d and 3a, respectively, they no longer behave as "real ions" since the total charge over the available atoms for coordination is much less than the one they present in a water molecule, thus leading to the fact that additional water molecules tend to construct the water network rather than to coordinate the ionic moieties, as can be seen in Figure 9. Tuñón et al.[23] showed that in the stepwise hydration of OH^- there are no hydrogen bonds between the solvent molecules and the hydrogen atom of the ion even with six hydrating molecules. Attempts at forcing this H-bond were unsuccessful in locating a stable structure.

Nonetheless, the effect of additional water molecules interacting with the H-donor or H-acceptor molecules could modify the size of the barrier since their capacities for association are being modified by the additional coordination. To check if hydration of the ions will favor the process, diagonal optimization was carried out starting from fully optimized hexamer structures corresponding to the structure of the pentamer plus a water molecule H-bonded either with W3 or with W5, the molecules that will transform into the ions. The barriers for the formation of the ions were found to be higher than that of the previous hexamer for both cases, thus confirming the hypothesis that additional molecules build up the water network. In agreement with Tuñón's results,[23] we were not successful in obtaining a minimum when the OH^- is H-bonded to a water molecule.

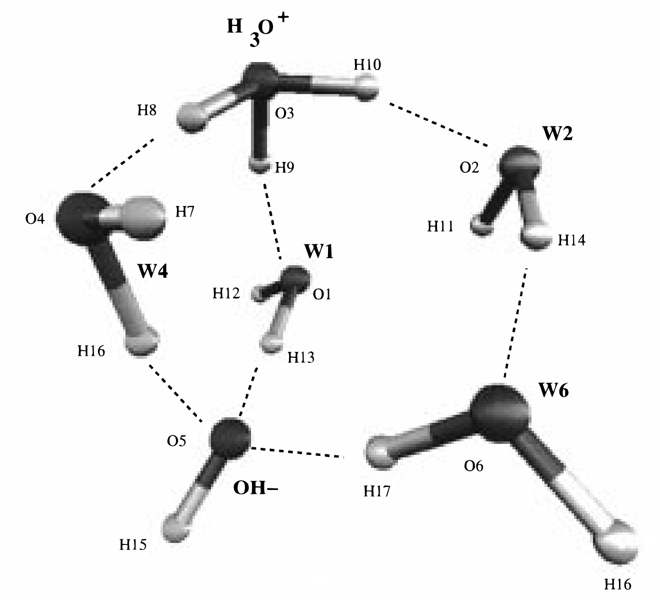

Figure 9. The stable ionic pair structure found starting from hexamer through diagonal optimization, as described in the text, after full optimization.

One could extend this observation and naturally expect that ions will be located at the surface of larger clusters where they are less likely to disrupt the network. Also, it is interesting to note that the difficulty in locating an equilibrium structure for the fourth coordination of OH^- might develop into a vacancy in liquid water. Of course, further investigation is needed to elucidate this point.

Up to now we have confirmed that water hydrolysis is a feasible reaction in water pentamers and hexamers. For smaller cyclic clusters we did not find the desired products, i.e., the ions; this is due to the fact that there are not molecules acting as promoters, since all molecules in the cluster are active participants of the observed multiple tranferences. We have been able to show that hydrolysis reaction is strongly dependent on the coordination pattern of the molecules involved, which is closely related to the individual acidic character of each monomer. But underlying this amount of data is the role of individual molecules during the process of distortion and dissociation of a molecular bond. It is possible to distinguish two groups of molecules in each structure, those that participate in the concerted transference of protons and those that do not. These latter molecules, W1 and W2 in the pentamer or W1, W2, and W6 in the hexamer, act as the promoters of the reaction. How do they do it? And when does its role transform back into that of solvent molecules? These questions can be answered from a detailed analysis of the molecular properties within the cluster.

II. Molecular Basis of the Process. (a) Charge-transfer process. It has been suggested that charge transfer between an ionic solute and the solvent has a significant role in solvation, and particularly in the hydration of the charged species.[24] There are two aspects that could be playing an important role for the latter: the charge transfer to the water molecules in the cluster and the resulting total ionicity of the cluster.

In this work the effect that the charge-transfer phenomenon

TABLE 2: Mulliken's Molecular Charges for the Pentamer 5B When in Its Most Stable Neutral Structure and When It Contains the Ions H_3O^+ and OH^- [a]

pentamer 5B		ionic pair + $3H_2O$			
		Mullikens's		CHELP	
W1	−0.006	H_3O^+	+0.693	H_3O^+	+0.691
W2	+0.006	OH^-	−0.668	OH^-	−0.634
W3	−0.004	H_2O	−0.009	H_2O	−0.019
W4	+0.002	H_2O	−0.006	H_2O	−0.018
W5	+0.002	H_2O	−0.009	H_2O	−0.019

[a] Numbers correspond to Figures 2 and 4.

has upon the dissociation of the O−H bond in the pentamer is explored. In Table 2 we present the total molecular charge of each monomer in the optimal neutral geometry, as well as in the geometry of a cluster having the ionic pair. The analysis was done using the Mulliken charges computed during the ab initio calculations and with the CHELP[25] method since the comparison of both predictions could be useful for elucidating the dependence on the method.

As can be seen in Table 2, there is no appreciable charge transference appearing between the water molecules and the ions in the structures that followed the concerted multiple transfer. However, there is a considerable charge transference between the ions themselves, despite this being a water-mediated interaction. Since charge delocalization gives a good estimate of the molecular involvement, we can see that at least three water molecules are strongly implicated in the O−H breaking, the donor, the acceptor, and the intermediate "proton carrier", while all the other witness molecules provide a solvent-like effect. Our results agree with those of Tuñón et al.[23] who found a similar charge transfer from OH^- to the water molecules in a cluster at the HF-MP2 level. Nonetheless, it was necessary to check if the lack of diffuse functions in the basis set used was responsible for the small charge transference. We performed the same kind of analysis using a 6-311+G(d,p) basis set and, even if it is possible to find larger transference occurring toward water molecules (from 0.019 to 0.04), the overall image was not modified.

(b) Nonadditive Effects. The distortion of the water molecules becomes more feasible when the cluster size increases and the importance of the nonadditive corrections increase with monomer deformation.[26] Pastor and Ortega-Blake[13] found that the intramolecular relaxation of water molecules in a cluster leads to extremely large nonadditive corrections, and they propose the possibility that molecular distortion comes as a consequence of nonadditive effects. This stresses the importance of the coupling between intra- and intermolecular properties. The breaking of an O−H bond in the hydrolysis phenomena is accompanied by a large molecular distortion of the donating moiety and of the neighboring waters. Hence, it is expected that nonadditive effects reflecting cooperativity are a crucial and determining factor in the final stability of the distorted molecular arrangement.

It has been found[13] that the canonical many-body expansion does not converge when the intramolecular relaxation of water is allowed and that an alternative scheme has to be used. This new expansion corresponds to a physical model that considers first the deformation of the monomer in a vacuum and then the interaction of the deformed monomers in the aggregate. In this scheme a zero-order term corresponding to the deformation energy of the monomers is considered separately, leading to a modification of the definition of the two-body interaction energy. This noncanonical many-body expansion is then

$$E_{\mathrm{int}} = E_{1\ldots n} - nE_{\mathrm{o}} = \sum V_{ij} + \sum \delta_i + \ldots + \zeta_n \qquad (1)$$

where E_{int} is the interaction energy of the aggregate of n-molecules with a total energy $E_{1\ldots n}$, the energy of each monomer being E_i, and the deformation energy $\delta_i = E_i - E_{\mathrm{o}}$, where E_{o} corresponds to the energy of the optimal monomer structure. $V_{ij} = E_{ij} - E_i - E_j$ is the modified two-body interaction energy. The three-body nonadditivities ζ_3 is equal to $E_{ijk} - \sum V_{ij} - \sum \delta_i$, and the higher order nonadditive terms are defined according to eq 1. This scheme has the advantage of leading to a convergent series but it has the disadvantage of not being associated with the common partition scheme where the n-body terms can be identified with different energy contributions as exchange, polarization, etc.

In Table 3, we present the many-body analysis for the pyramidal pentamer in its form of reactants and products. All calculations of nonadditivities were done at the MP2 level and with full counterpoise; i.e., the energy of each subsystem ($\langle i \rangle$, $\langle i, j \rangle$, or $\langle i, j, \ldots \rangle$) at the cluster geometry is evaluated in the full basis of the complete cluster ($\langle i, j, \ldots, n \rangle$) considered. This counterpoise correction has proven to be necessary for a proper description of nonadditivities and in a critical manner when correlation energy is included.[13] In particular, the use of a limited basis set, as the one employed here, emphasizes the need of its use. We found that the values of the interaction energies are substantially affected by the correction, but the effect is smaller on nonadditivities and, most importantly, the relative strength of the interaction between clusters, as well as the relative contributions to the many-body expansion are conserved. (The comparison of the results presented in Table 3 with those calculated without the counterpoise correction are available as Supporting Information.)

From Table 3, it is possible to observe that in the reactants structure, the most distorted molecules are those acting as H-bond acceptors. This comes as a result of the cooperativity in the water−water interaction. In the two-body interaction energies section, it can be seen that only two water molecules, W3 and W5, form three strong H-bonds. W1, W2, and W4 are not able to form a proper H-bond between them; as a matter of fact, the H-bond between W1 and W2 is so weak that it could easily be dismissed as such, but the O−O distance (2.9 Å) makes this decision not so simple. It seems that the role of W1 is that of a bridge between W3 and W5. This hypothesis can be tested by means of the three-body nonadditivities. With this criteria we can observe that the three-body term corresponding to W3−W4−W5 is clearly stronger than any of the two others, indicating that these three molecules are strongly intermingled even before any distortion is induced in the structure.

It is important to mention that the same trends are observed for the hexamer, that is, the route that allows for the double transference has a common cooperativity pattern as the one described for the pentamer. There is a trimer having dda and daa molecules with strong H-bonds, and the second largest three-body nonadditivity. The largest three-body nonadditivity corresponds to the W4−W5−W6 trimer, but since this structure is broken with the movement of H16, it can no longer be considered as a suitable candidate for the concerted transference to take place.

Some authors[27] have suggested that the proton transference in liquid water during water hydrolysis is possible due to the favorable interaction that ions establish with water molecules. Certainly, this is a very important factor but not the one that drives the hydrolysis reaction as detailed below.

In Table 3 we present the many-body analysis made for the ionic pair stabilized in pentamer 5B. The two-body interaction

TABLE 3: Many-Body (MB) Expansion of the Intermolecular Interaction (kcal/mol) in the Pentamer 5B and the Optimized Structure Containing the H_3O^+ and OH^- Ions[a]

	pentamer 5B			ionic pair·$3H_2O$	
molecule	E_{int}	MB terms	molecule	E_{int}	MB terms
W1	1.42		W1	2.86	
W2	0.11		W2	2.81	
W3	0.15		H_3O^+	7.12	
W4	1.39		W4	2.37	
W5	1.34		OH^-	0.12	
$\sum\delta_i$		**4.41**		**15.28**	
12	−0.17		1−2	2.27	
13	−3.90		1−H_3O^+	−25.70	
14	−1.82		1−4	2.13	
15	−3.54		1−OH^-	−27.27	
23	−1.56		2H_3O^-	−26.65	
24	−1.63		2−4	2.11	
25	−4.39		2−OH^-	−27.23	
34	−3.03		4−H_3O^+	−25.06	
35	−2.48		H_3O^+−OH^-	−138.09	
45	−3.55		4−OH^-	−26.23	
$\sum V_{ij}$		**−26.06**		**−288.72**	
123	−3.36	0.59	1−2−H_3O^+	−30.36	5.94
124	−0.67	0.03	1−2−4	14.17	−0.39
125	−4.61	0.61	1−2−OH^-	−41.62	4.82
134	−7.19	−1.41	1−H_3O^+−4	−30.60	5.68
135	−7.99	−0.98	1−H_3O^+−OH^-	−183.58	−2.61
145	−6.19	−1.44	1−4−OH^-	−41.62	4.40
234	−5.74	−1.16	2−H_3O^+−4	−30.63	4.68
235	−7.87	−1.04	2−H_3O^+−OH^-	−183.49	−2.57
245	−8.22	−1.49	2−4−OH^-	−41.71	4.34
345	−8.62	−2.44	H_3O^+−4−OH^-	−181.25	−1.48
$\sum\zeta_{ijk}$		**−8.72** (40.28%)			**−23.81** (8.24%)
1234	−10.97	0.01	1−2−H_3O^+−4	−38.52	−0.69
1235	−13.73	0.10	1−2−H_3O^+−OH^-	−222.75	0.43
1245	−13.04	0.07	1−2−4−OH^-	−53.06	−0.17
1345	−20.60	−0.33	1−H_3O^+−4-OH^-	−221.25	0.31
2345	−20.10	−0.32	2−H_3O^+−4-OH^-	−221.46	0.31
$\sum\zeta_{ijkl}$		**−0.47** (1.54%)			**0.20** (0.08%)
12345	−30.82			−248.90	
ζ_{ijkm}		**0.02** (0.07%)			**0.53** (0.22%)

[a] Numbers correspond to Figures 2 and 4. The term in parentheses corresponds to the percent error introduced in the interaction energy if the *n*-body correction is truncated at the previous order, i.e.,

$$\zeta_n\,\% = \frac{\zeta_n}{\sum V_{ij} + \sum\delta_i + \sum\zeta_{n-1}} 100$$

contribution is very attractive, and it is possible to see that each $H_2O-H_3O^+$ interaction contributes ≈−25 kcal/mol while the H_2O-OH^- interactions do so with ≈−27 kcal/mol. The geometrical arrangement the two ions end up with is not the most favorable, but still their attraction is quite large (−138.5 kcal/mol).

In the hydrolysis within the hexamer, the H-bond breaking of W6−W4 is understandable only in terms of the preference a water molecule has to interact with an ion, such as OH^-, than with another water molecule. Here the promotion of hydrolysis by W6 consists of the breaking of the most attractive H-bond in the structure, allowing on one hand the use of W4 as a connector for the concerted double transference and on the other the stabilization of the ensuing anion by means of strong coordination.

This kind of analysis allows us to see a complex interplay for the formation of the cluster with the ions present. The close packing due to three-body nonadditive effects made possible the concerted transference and the breaking of O−H bonds, whereas the later stabilization of the products is facilitated by the extremely favorable pairwise interaction provided by the convenient coordination of the ions in 3d and 3a patterns, as mentioned before.

It is important to note that the two-body interaction energies and three-body nonadditivities allow us to predict which subset of molecules in a cluster have the most favorable conditions for the genesis of ionic products of hydrolysis. This finding could be a useful tool for selecting, in a numerical simulation study of water hydrolysis, those molecules that generate the ions; it could also be thought, that a rare occurrence of these initial conditions in liquid water might be one of the reasons behind a small equilibrium constant for this reaction.

Conclusions

One of the hypotheses of this work was that there are specific molecular properties, consequences of collective phenomena, that can be addressed as direct promoters of water hydrolysis. To properly identify those properties, we have presented here a refined set of calculations of small water clusters that include correlation energies at the MP2 level. Inclusion of the MP4 level produced only a small modification of the interaction energies (+6%) and did not modify the general pattern. The counterpoise correction for the many-body analysis of the interactions was also considered. The quality of these calculations allows us to trust the accuracy of the results.

The route that leads to the ionic products is predetermined by three-body nonadditive effects and by the donor−acceptor character of the molecules that take part in the double-concerted proton transference. The geometrical rearrangements induced by the proton transference itself, prior to the stabilization of the ions, also play a relevant role.

Since most transferences are conducive to a neutral cluster, we think that the small equilibrium constant of the process is in part related to the small probability of having routes leading, via concerted motion, to a dissociation. From seven possible protons to be transferred, i.e., those present as H-bonds in the pentamer, only one combination of double transferences fulfills the geometrical and coordination requirements that lead to ionic products. It is possible to think that the appearance of an ionic pair in larger clusters is crucially dependent on a final situation where the ions have a 3d and 3a character, respectively, and do not have a direct proton link. We found that the process that yields an ionic pair does not modify the general structure of the cluster; i.e., even if the number of H-bonds is modified, no large displacements of the molecules in the cluster occur. Nonetheless, in the pentamer 5B we saw that route I, which leads back to a neutral cluster, and route II, which produces the ionic products, present a difference. The second one keeps a compact structure and the other does not. We can expect this to have a direct consequence in the entropic contribution to the process. In this work we found similar results to those of previous reports that show that water hydrolysis, as the direct event of transferring a proton from one water molecule to a neighboring one, is an unlikely process, since it is immediately reversed. It is important to note that the coupled transfer phenomenon reported by Tozer et al.[3] seems to be of quite common occurrence, appearing also in the simplest molecular arrangement that can provide for it, the cyclic trimer.

The energetic barrier of the process is directly related to the number of water molecules in the aggregate; however, the lowering of this barrier by water addition shows a very slow convergence. For the pentamer, the ionic species have a complete coordination and the additional water molecule in the hexamer goes to form the liquid water network rather than to increase the hydration around any of the ions. We can then expect that full solvation of the ions will occur only after a substantial number of water molecules have been added. We also extrapolated the results to suggest that in larger clusters the ions might be on the surface, where they disrupt less the water network, and that the difficulty in locating a water molecule close to the hydrogen atom in OH^- might develop into a vacancy in the liquid phase. The discrepancy with the results of Lee et al.[2] indicating a fast stabilization of the process can be explained as a consequence of their results being obtained with DFT(BLYP) calculations.

The effect of the O−O distance on the size of the barrier has been carefully studied in a related process: the excess proton exchange in water.[28] In this work it was found that the O−O separation is also relevant for the dissociation process. It is important to notice that this parameter is related to the size of the cluster. Water pentamers and hexamers exhibit closer O−O distances than smaller clusters on account of cooperative effects. So, not surprisingly, it is found that structures with large nonadditivities allow for smaller O−O distances, which are necessary for lowering the O−H dissociation barrier. Hence, the hydrolysis of water by water is not a simple event. There is an initial complex molecular interplay that triggers the reaction. The many-body analysis gives a clear insight into the initial role previously described. A clearer view of the second stage, i.e., the hydration of the products, has to be looked into by construction of larger clusters, which are not as easy to deal with via quantum mechanical treatments and an alternative model has to be used.

It is quite probable that the mechanism found for the hydrolysis in the pentamer is not the same occurring in the liquid phase. It is expected that fluctuations will exert a strong influence on the true mechanism. Nonetheless, we are confident that the molecular properties found to be relevant for the hydrolysis in clusters would play an important role in the reaction that takes place in liquid water.

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Supporting Information Available: Table comparing results of Table 3 with those calculated without the counterpoise correction (2 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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