

An *ab initio* study of the $(\text{H}_2\text{O})_{20}\text{H}^+$ and $(\text{H}_2\text{O})_{21}\text{H}^+$ water clusters

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The study of the minimum Born–Oppenheimer structures of the protonated water clusters, $(\text{H}_2\text{O})_n\text{H}^+$, is performed for $n=20$ and 21. The structures belonging to four basic morphologies are optimized at the Hartree–Fock, second-order many-body perturbation theory and coupled cluster level, with the 6–31G, 6–31G*, and 6–311G** basis sets, using the parallel ACES III program. The lowest energy structure for each n is found to be the cage-like form filled with H_2O , with the proton located on the surface. The cage is the distorted dodecahedron for the 21-mer case, and partially rearranged dodecahedral structure for the 20-mer. The results confirm that the lowest energy structure of the magic number $n=21$ clusters corresponds to a more stable form than that of the 20-mer clusters. © 2009 American Institute of Physics. [doi:10.1063/1.3231684]

I. INTRODUCTION

Elucidating the structure of protonated water clusters via experimental studies has been a challenge over the decades. One of the questions raised by those studies concerns the observed prominent stability of the 21-mer cluster over the neighboring ones. The series of experiments started by Lin¹ indicates the increase in the stability for the $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster under various experimental conditions.^{2–10} It was assumed that the unusual stability is caused by the specific clathrate structure, the oxygens of the 20 water molecules arranged in the dodecahedron cage, with a neutral water molecule trapped inside the cage, and a proton residing on the surface as the H_3O^+ Eigen form.² The next important experimental step toward establishing the structure of the 21-mer cluster was taken by Wei *et al.*¹¹ Those authors attempted to get an insight into the structures of the 20-mer and 21-mer protonated water clusters by analysis of reactions with trimethylamine (TMA) molecules. Because the maximum intensity peak for the 21-mer occurs when 10 TMA molecules are attached to the cluster, the researchers concluded that the cluster possesses ten dangling hydrogens not engaged in any hydrogen bond, which would agree with a dodecahedron cage containing the H_3O^+ cation. The weakness of this experiment is that the presence of TMA molecules may significantly change the structure of the water clusters. Being aware of this issue, two groups performed gas phase infrared spectroscopy measurements, obtaining the infrared spectra of the protonated water clusters of a particular size. On the basis of probing the OH stretches, Miyazaki *et al.*¹² demonstrate the development of the $(\text{H}_2\text{O})_n\text{H}^+$ structures for $n=4–27$, concluding that two substantial changes occur. The first occurs around $n=10$, transforming the chainlike structures into more complicated two-dimensional (2D) net forms. The second is a rearrangement of 2D structures into three-dimensional ones, occurring near the “magic number” $n=21$. The experimental study performed by Shin *et al.*¹³ fo-

cuses on changes in the intensity and location of the free OH bands. The assignment of the four bands from the energy range of 3600–3800 cm^{-1} to the different locations of the free OH group, i.e., acceptor-water, acceptor-donor (AD)-water, and acceptor-acceptor-donor (AAD)-water, allows them to establish the structure of the protonated water clusters of the different size ranges. Again, the chain structures are favorable for $n \leq 11$. For $11 \leq n \leq 20$, both AD-water and AAD-water are present. For $n=21$ the former one disappears, indicating that all the dangling hydrogens belong to the AAD-waters. This agrees with the predicted dodecahedron structure with an internal water molecule. However, many questions remain unanswered.

An attempt undertaken by Shin *et al.*¹³ to prove the existence of the Eigen form was not successful. Also, experiments do not clarify whether the proton is located inside the cage or on its surface. Moreover, the precise structure of the clusters is not established, and the unusual stability of the 21-mer is not fully explained. To add yet more uncertainty, some experiments^{12,14} show the existence of the doublet in the dangling OH stretching region of the vibrational spectrum for the $(\text{H}_2\text{O})_{21}\text{H}^+$ cluster, and thus, the presence of both AD-water and AAD-water molecules in the structure. Nevertheless, this incongruity seems to be due to different experimental conditions, as their variations can convert the spectral doublet into a single feature.¹⁴

The presence of so many uncertainties in such an important area of chemistry has long since drawn the attention of theoretical researchers. A variety of theoretical methods has been applied to this intriguing subject.^{9,13–26} The clathratelike structures consisting of 20 oxygens and filled with one water molecule were found to be the lowest energy structure in the majority of the applications, most of them being the distorted pentagonal dodecahedron model. Less agreement concerns the position of the proton, which is located either inside the cavity^{9,19,23} or on the surface.^{13,14,17,21,22,24,26} Also, although most studies predict that the proton exists in the Eigen form,^{13,14,16,17,19–23} some of them show the Zundel form as energetically equal⁹ or point to intermediate forms.²⁶ In order

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to explain the unusual stability of the magic number 21 cluster, its energetic comparison with the neighboring clusters were carried out in most studies. Some studies show evidence of the increased stability of the 21-mer cluster.^{9,15,22} However, the arguments are not strong and may indicate that the larger stability is caused by the entropic factor, as some authors suggest.²⁷ Furthermore, there are studies which show the importance of including the temperature dependence in calculations,^{9,14,19,21,23,25,26} suggesting that due to their fluxionality, finite temperature effects are very important in elucidating the problem of the magic number cluster enhanced stability.

However, there are relatively few studies of the electronic structure of the water clusters near the magic number by *ab initio* methods,^{13,14,17,20} some offering verification of the results coming from experiments or simulations.^{13,14} The relatively large size of these systems makes such applications computationally demanding if a sufficient accuracy is to be achieved. An even greater challenge is the characteristic of the potential energy surfaces, with an extremely large number of close-lying minima,²⁴ many of them separated from each other by high energy barriers, which additionally raises the costs of calculations. Thus, the quality of starting structures is crucial in seeking for a global minimum during an optimization procedure, which suggests sampling the potential energy surface (PES) first by some simulations or molecular dynamics methods. An interesting observation is made in the study of Khan,²⁰ who postulates that the prismatic structure has the lowest energy for both 20-mer and 21-mer clusters. This is a rather solitary result as, to the best of our knowledge, only one study indicates the presence of clathrate structures resembling the pentagonal prismatic form.²³ Nevertheless, Khan²⁰ emphasizes that such a structure is not likely to exist under experimental conditions.

Although there are arguments negating pertinence of the protonated water cluster global minima obtained in 0 K temperature to the issue of the cluster stability near the magic number 21, the treatment of the quasirigid 0 K structures is still the starting point. The previous *ab initio* electronic structure calculations were performed at relatively low levels of theory and there is still some question about the impact of the accuracy on the results, even if the temperature effects are not taken into consideration. The goal of the present study is to remove this uncertainty by performing high-accuracy electronic structure calculations for the 20- and 21-mer clusters, including the geometry optimization at the second-order many-body perturbation theory [MBPT(2)] and coupled-cluster singles and doubles (CCSD) level, and the CCSD(T) single-point energy calculations. All calculations are made possible by the recent development of the parallel ACES III program.²⁸

II. METHODS

The calculations are performed at four levels of accuracy. The first, used to sample the largest number of candidates for low energy minima, is the self-consistent-field (SCF) method with the 6-31G and 6-31G* basis sets. The lowest minima found at that level are subsequently studied at

the MBPT(2) level with the 6-31G* (20- and 21-mer) and 6-311G** (21-mer) basis sets. For the 21-mer cluster, the geometry optimization is also performed at the CCSD level. Additionally, single-point CCSD(T) energies are computed at the CCSD optimized geometries. All CC calculations employ the 6-31G* basis set. The MBPT(2) calculations correlate all orbitals, while the 1s orbitals are frozen in the CC calculations. All geometry parameters are fully optimized without any constraints.

Some of the initial guesses used in the geometry optimization calculations come from previous theoretical calculations. The basin-hopping algorithm and anisotropic site potential results²² provide clathrate structures with an internal H₂O molecule (the distorted dodecahedron for the 21-mer case).²⁹ The prismatic and cubic isomers also use starting structures obtained previously.²⁰ However, since they do not lead to minima, the hydrogen positions are rearranged in such a way that the minimum structures are converged. For some of the 21-mer structures, different starting points are tried, originating from previously found low energy minima for the 20-mer clusters, testing for different locations of the additional water molecule. Also different locations of the proton are considered, positioning it either near the center or on the surface for different classes of clusters of each size. The convergence criterion requires that root mean square values of forces be below 0.0001 units. Also, each stationary point determined at the SCF level is verified by analytical vibrational frequency computations. If no imaginary frequencies larger than 1.0 cm⁻¹ are present, the structure is considered to be a minimum. To improve slow convergence, especially poor at the SCF level, presumably caused by flat energy surfaces near minima, after each of several cycles the new geometries are computed with respect to the Hessian calculated at the SCF/6-31G level. This algorithm helps to converge all structures to the convergence criterion desired, even though for most calculations such Hessians are approximate as they are computed at a different level of theory.

III. RESULTS AND DISCUSSION

This section is organized as follows. First we evaluate the quality of the theoretical methods used, then discuss the Hessian calculations, present the obtained structures, and finally relate our results to the problem of the location of the proton, the existence of the Eigen and Zundel forms, and the enhanced stability of the 21-mer clusters.

The analysis of the effect of the basis set quality is based on SCF and MBPT(2) results. At the SCF level, the 6-31G and 6-31G* basis sets are compared. For the 21-mer clusters, the energy order remains unchanged, and the relative energies themselves change by 3.5–5.7 kcal/mol. Slightly larger changes, reaching about 8 kcal/mol, and a different energy order are observed for the 20-mer clusters. Although the absolute values of the zero-point energies (ZPEs) are much higher in the larger basis set, increasing by about 15 kcal/mol, the relative ZPEs determined at the SCF level change little, differing by less than ~1 kcal/mol. The 6-31G basis is obviously unsuited to calculations including correlation due to the absence of polarization functions. To estimate the

TABLE I. The relative energies of the $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters (in kcal/mol) optimized at the different levels of theory. The values in parentheses include ZPE corrections. The details are in the text.

Method	Structure			
	Dodecahedron	Cage	Prismic	Cubic
SCF/6-31G	0.0	6.3(4.1)	17.0(15.9)	21.2(20.3)
SCF/6-31G*	0.0	9.8(8.2)	12.7(13.3)	15.5(15.9)
MBPT(2)/6-31G*	0.0	14.2	11.0	13.2
MBPT(2)/6-311G**	0.0	13.6	15.4	18.6
CCSD/6-31G*	0.0	13.1	10.8	12.8
CCSD(T)/6-31G** ^a	0.0	13.7	10.5	12.5

^aThe single-point CCSD(T) energy computed at the CCSD geometry.

validity of the 6-31G* basis set, we perform the MBPT(2) geometry optimization in the 6-311G** basis set. Still, the relative energies of the clusters change by 0.6–5.4 kcal/mol. Moreover, the small energy differences among the cage, prismic, and cubic clusters occurring at the MBPT(2) level cause the energy order of those three isomers to be different for the 6-31G* and 6-311G** basis sets. Hence, in order to establish very accurate values of the relative energies, a basis set of the quality of 6-311G** or better should be employed.

The results obtained with the 6-31G* basis set at the various levels of theory show that the differences between the SCF and MBPT(2) methods vary between 1.7 and 6.4 kcal/mol, changing the energy order for some clusters. The comparison between the CCSD and MBPT(2) methods indicates much smaller discrepancies, not exceeding 1.1 kcal/mol. Even smaller differences occur when single-point CCSD(T) energies are computed. Thus, since the increase in the computational cost required by the CCSD method does not provide a comparable improvement in accuracy, the MBPT(2)/6-311G** method seems to be the most efficient choice for the structural determinations of protonated water clusters.

For systems having very complicated PES it becomes critical to differentiate between the minimum and the saddle point. To achieve this goal, we always perform the full analytical Hessian calculations at the SCF level. This allows ruling out several structures corresponding to saddle points. The structures confirmed to be the minima are subsequently used as starting points at the higher levels of theory. Assuming that the optimization procedure does not overcome any energy barrier and does not converge to a different stationary point, the geometries obtained at the higher levels of theory are also minima. This assumption turns out to be valid for each case when the Hessian is calculated at the higher level of theory. These are the full analytical Hessian calculations for all 21-mer structures obtained at the SCF/6-31G* level, and the two 21-mer analytical Hessian calculations performed at the MBPT(2)/6-31G level.

Values of the ZPE corrections, although important for very accurate calculations, are not critical in establishing the energy differences between the isomers, as they never change the relative energies by more than 2.2 kcal/mol. Similarly, the two MBPT(2) Hessian calculations for the 21-mer dodecahedron and cage structures show the value of the

relative ZPE differing from the one obtained at the SCF level by only 1.1 kcal/mol. Thus, one should not expect any meaningful changes in results if the ZPE corrections are included at all levels of theory studied in the present paper.

The four lowest energy structures are considered for 21-mer clusters, each of them belonging to four basic morphologies. Their relative energies are presented in Table I, and their structures are shown in Fig. 1. These are the dodecahedron cage containing the neutral water molecule, the cage built from 21 water molecules, and the structures derived from the 20-mer cubic and prismic forms. Among the 21-mer clusters, the lowest energy structure is the dodecahedron, the same structure as the global minimum obtained by Hodges and Wales.²² It is consistent at all levels of theory employed, as the energy gap between the next structure is at least about 10 kcal/mol, except for the least accurate SCF/6-31G level, for which it equals 6.3 kcal/mol. The other three structures are located much closer to each other and their energy order changes at the different levels of theory. For the MBPT(2)/6-311G** method, these three isomers are energetically within 5.0 kcal/mol, the cage being lowest, followed by the prismic and cubic structures. It should be noted that our prismic and cubic structures are different from those obtained by Khan.²⁰ The structures presented there are constructed by attaching a water molecule to the corresponding 20-mer structures in such a way that it is connected by a single hydrogen bond. Our attempts to find such structures resulted in obtaining saddle points. After this failure, we tried

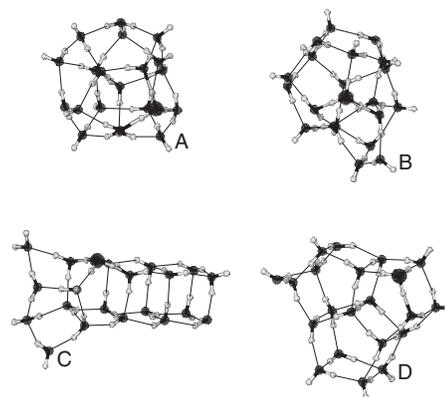


FIG. 1. Structures of the $(\text{H}_2\text{O})_{21}\text{H}^+$ clusters obtained at the MBPT(2)/6-311G** level [(a): dodecahedron, (b): cage, (c): cubic, (d): prismic]; the oxygen of the H_3O^+ cation is enlarged.

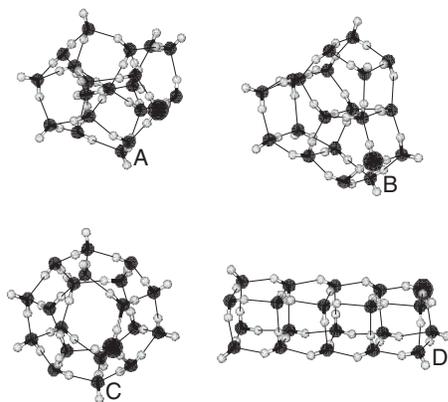


FIG. 2. Structures of the $(\text{H}_2\text{O})_{20}\text{H}^+$ clusters obtained at the MBPT(2)/6-31G* level [(a): cage, (b): prismatic, (c): dodecahedron, (d): cubic]; the oxygen of the H_3O^+ cation is enlarged.

to modify prismatic and cubic structures, obtaining minima. In these cubic and prismatic structures the additional water molecule is bonded by two hydrogen bonds. They have lower energy than the saddle point structures originally obtained. For the case of the cubic isomer, it strongly rearranges the structure of the terminal cube which accommodates the additional water molecule. In the context of the experimental studies, it is important to notice that the dodecahedron structure consists of only the AAD-waters. The other structures contain at least one AD-water molecule. As already mentioned, the experiments of Shin *et al.*¹³ exclude the presence of AD molecules for the 21-mer, and thus, the cage, prismatic, and cubic structures do not exist under those experimental conditions. However, the spectral doublet observed under different experimental conditions¹⁴ may be attributed to the presence of those structures, which seem to exist under certain experimental conditions.

Figure 2 presents the four lowest energy structures obtained for the 20-mer clusters: cage, dodecahedron, prismatic, and cubic morphologies. In Table II, the relative energies of these clusters are presented. The structure referred to as the cage is, in fact, similar to the dodecahedron. The major part of its 19-mer cage is built from the pentagonal units and it is filled with a water molecule. Similarly as for the 21-mer clusters, it is the same structure as the global minimum calculated by Hodges and Wales.²² The prismatic and cubic structures have the same oxygen framework as the clusters presented by Khan,²⁰ but they differ by the orientation of water molecules.

At the MBPT(2)/6-31G* level, the cage structure corresponds to the lowest energy, followed by the prismatic,

TABLE II. The relative energies of the $(\text{H}_2\text{O})_{20}\text{H}^+$ clusters (in kcal/mol) optimized at the different levels of theory. The values in parentheses include ZPE corrections. The details are in the text.

Method	Structure			
	Cage	Prismatic	Dodecahedron	Cubic
SCF/6-31G	3.1(4.4)	17.0(17.6)	0.0(0.0)	27.6(29.6)
SCF/6-31G*	0.0	9.1	5.4	16.9
MBPT(2)/6-31G*	0.0	3.8	7.7	10.5

dodecahedron, and cubic clusters. As compared to the 21-mer clusters, the energy difference between the lowest energy structure and the rest of the isomers is much smaller for the 20-mer clusters. The four isomers are energetically within 10.5 kcal/mol. This would suggest that the existence of the prismatic and cubic morphologies is more likely to occur for the 20-mer clusters.

Our results differ from those obtained by Khan.²⁰ He finds the prismatic structures to be the global minimum for both 20- and 21-mer clusters, whereas in our calculations the lowest minima corresponding to the prismatic forms are higher than the global minima. This discrepancy may be due to the higher level of theory employed in our study, or be a result of using the more appropriate initial guess structures.

One of the questions raised is the location of the proton. Our calculations are consistent with most theoretical studies, locating the proton on the surface for both the 20- and 21-mer clusters. All of our attempts to obtain a structure with an internal proton failed; it consistently migrated toward the surface.

Regarding the question whether the proton exists in the Eigen or Zundel form, all of our structures contain the cation much closer to the Eigen form. In order to estimate the structure of the Eigen and Zundel forms, optimizations of the protonated water dimer and tetramer have been performed. For the Eigen structure obtained by the MBPT(2)/6-311G** optimization of the $(\text{H}_2\text{O})_4\text{H}^+$ cluster, the OO distance is 2.55 Å (1.01 and 1.54 Å for OH distances). For the Zundel structure calculated at the same level of theory for the $(\text{H}_2\text{O})_2\text{H}^+$ cluster, the OO distance is 2.38 Å, with a hydrogen located in the middle. There are differences in the surroundings of the proton between the particular 20- and 21-mer clusters. The OH bond lengths within the H_3O^+ cation vary between 0.99 and 1.07 Å, with their lengths being inversely proportional to the corresponding hydrogen bonds with oxygens of the neighboring water molecules. For two structures, the OH and hydrogen bonds have almost the same lengths among themselves, 1.02 and 1.50 Å for the 21-mer dodecahedron, and 1.03–1.04 and 1.53–1.55 Å for the 20-mer cage cluster, values which are very close to the parameters of the Eigen form. The other morphologies contain more or less distorted Eigen forms. For the 21-mer cage, 20-mer dodecahedron, and 21-mer cubic structures, there are two shorter hydrogen bonds (1.40–1.50 Å) and a longer one (1.58–1.70 Å). For the 20-mer cubic structures, one hydrogen bond is shorter (1.53 Å), with the other two equal to 1.64 Å. Finally, for both prismatic structures all three hydrogen bonds differ from each other by about 0.11–0.13 Å. The largest similarity to the Zundel structure occurs for the 21-mer cage structure, with the OH and hydrogen bonds equal to 1.05 and 1.40 Å, respectively. Nevertheless, it is still far from the Zundel structure obtained for the protonated water dimer.

Unfortunately, the question about the experimentally observed enhanced stability of the 21-mer clusters is the most difficult one for the *ab initio* 0 K calculations. Nevertheless, some arguments can be provided. An estimate of the stabilization effect exhibited when 20 or 21 separated water molecules and a proton merge into one structure is performed at

the MBPT(2)/6-31G* level by subtracting the energy of the separated water molecules, calculated at the geometry optimized for the isolated water molecule, from the total energy of the lowest energy 20- and 21-mer clusters. Indeed, it shows that the 21-mer structure is energetically favorable, as the stabilization energy is 18.4 kcal/mol larger than for its 20-mer counterpart.

Finally, we would like to emphasize the importance of one feature of the medium-sized protonated water clusters in the context of mass-spectrometry experiments. It is the enormous number of different structures separated by almost negligible energy differences, which is clearly shown in the study of Hodges and Wales.²² In order to verify if this picture remains unchanged at the SCF level, we used the six lowest 21-mer structures obtained by Hodges and Wales²² as the initial geometries for the SCF/6-31G optimization, ending up with five nonunique minimum structures, all of them within the 2.7 kcal/mol energy distance. This is an argument that a vast majority of minimum structures found by Hodges and Wales²² indeed are minima, even if the PES is verified by more sophisticated electronic structure methods. Hence, whenever mass-spectrometry experiments are interpreted, the number of different structures within some energy range should be considered, not only a limited number of lowest energy structures. For example, this is pertinent to the experiment of Wei *et al.*,¹¹ where the highest intensity peak must come from all possible structures capable of bonding ten TMA molecules. Although the largest number of structures bond ten TMA molecules, causing that peak to be the most intense, the lowest energy structure may not be one of them. Of course such a thorough study, determining all minima within some energy range, is extremely difficult and expensive for high-level *ab initio* electronic structure methods. Thus, it is not surprising that our global minima for the 20- and 21-mer clusters, similarly to many previous studies,^{13,22,24} do not agree with the experimental findings of Wei *et al.*¹¹ The lowest energy structures for both classes of clusters have nine dangling hydrogens. The structures that would be consistent with this experiment are those which are higher in energy. These are the dodecahedron 20-mer and cage 21-mer structures, which have 11 and 10 dangling hydrogens, respectively. The other structures considered have five to eight dangling hydrogens.

IV. CONCLUSIONS

In this *ab initio* study, the protonated water clusters consisting of 20 and 21 water molecules are treated by high-level electronic structure theory, including SCF, MBPT(2), and CC methods. The low energy minima are obtained at those levels of theory. The results indicate that among the single reference methods studied in the present paper, the MBPT(2) approximation is sufficient in terms of relative accuracy. The Hessian calculations proved to be a valuable tool in verifying the calculated stationary points of PESs and to exclude the structures corresponding to saddle points. The ZPE corrections obtained on the basis of the Hessian calculations are relatively small and do not affect the problem significantly.

The lowest energy structure obtained for the 21-mer clusters is the distorted dodecahedron filled with the neutral H₂O. For the 20-mer clusters it is also the cage structure filled with the neutral molecule, with the cage resembling the distorted dodecahedron. No low energy structures with the central H₃O⁺ ion and no structures containing the (H₂O)₂H⁺ cation being close enough to the Zundel form are found. The analysis of the results shows that the lowest energy 21-mer structure is energetically much better separated from the other structures than it is for the 20-mer clusters. Our calculations confirm the existence of the minima for the prismatic and cubic structures, which are more likely to form for the 20-mer clusters. The estimation of the stabilization energy shows that the lowest energy magic number cluster is about 18 kcal/mol more stable than its 20-mer cluster counterpart.

In most respects our calculations are consistent with previous results, indicating that more accurate electronic structure calculations do not reveal anything substantially new to the problem. Furthermore, it seems that further understanding of still unanswered aspects of the protonated water clusters near the magic number would rather require including different thermodynamic factors, like temperature effects, which is still an extremely difficult challenge for the *ab initio* electronic structure methods applied to systems of the size comparable with that considered in this paper.

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