

# Application of the SCC-DFTB Method to $\text{H}^+(\text{H}_2\text{O})_6$ , $\text{H}^+(\text{H}_2\text{O})_{21}$ , and $\text{H}^+(\text{H}_2\text{O})_{22}$

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The low-lying potential energy minima of the  $\text{H}^+(\text{H}_2\text{O})_n$ ,  $n = 6, 21$ , and  $22$ , protonated water clusters have been investigated using two versions of the self-consistent-charge density-functional tight-binding plus dispersion (SCC-DFTB+D) electronic structure methods. The relative energies of different isomers calculated using the SCC-DFTB+D methods are compared with the results of DFT and MP2 calculations. This comparison reveals that for  $\text{H}^+(\text{H}_2\text{O})_6$  the SCC-DFTB+D method with H-bonding and third-order corrections more closely reproduces the results of the MP2 calculations, whereas for the  $n = 21$  and  $22$  clusters, the uncorrected SCC-DFTB+D method performs better. Both versions of the SCC-DFTB+D method are found to be biased toward Zundel structures.

## Introduction

Excess protons in aqueous environments play an important role in many chemical and biological processes.<sup>1–15</sup> Yet the nature of excess protons in liquid water has been hard to pin down experimentally. Computer simulations<sup>1–3</sup> reveal that there is a rapid interconversion between Eigen [ $\text{H}_9\text{O}_4^+$ ]<sup>16,17</sup> and Zundel [ $\text{H}_5\text{O}_2^+$ ] type species.<sup>18,19</sup> Recent experimental work on protonated water clusters has allowed one to isolate the Zundel and Eigen species and to obtain their vibrational signatures.<sup>5</sup> The  $\text{H}^+(\text{H}_2\text{O})_{21}$  magic number cluster, in particular, has been the subject of numerous experimental and theoretical studies.<sup>3–8</sup> Theoretical studies on protonated water clusters of this size are challenging due to the large number of local minima on their potential energy surfaces.<sup>20–33</sup> Although ab initio MP2 calculations accurately describe protonated water clusters, they are too computationally demanding to use in exhaustive searches of the stationary points on the potential energy surfaces or for performing Monte Carlo or molecular dynamics simulations for clusters the size of  $\text{H}^+(\text{H}_2\text{O})_{21}$ . Traditional density functional methods are computationally faster but are known to incorrectly order the isomers of water clusters, in part due to the failure to recover long-range-dispersion interactions.<sup>34–36</sup> Model potentials<sup>25–28</sup> and effective valence bond (EVB) methods<sup>29–33,37</sup> have been developed to describe excess protons in water. The effective valence bond methods, in particular, hold considerable promise, but they are not yet at the point that they accurately reproduce the relative energies of isomers obtained from MP2 calculations.

This leads naturally to interest in whether alternative approaches such as the self-consistent-charge density-functional tight-binding (SCC-DFTB) method<sup>38–46</sup> can provide a semi-quantitatively accurate description of the potential energy landscapes of protonated water clusters. In the present study, two versions of the SCC-DFTB method are applied to the  $\text{H}^+(\text{H}_2\text{O})_6$ ,  $\text{H}^+(\text{H}_2\text{O})_{21}$ , and  $\text{H}^+(\text{H}_2\text{O})_{22}$  clusters, in conjunction with the basin-hopping Monte Carlo method<sup>32,47–57</sup> to locate the local minima. The results are compared with those of Becke3LYP<sup>58</sup> density functional theory and MP2 calculations.

## Methodology

**Electronic Structure Calculations.** The SCC-DFTB method is based on a second-order expansion of the Kohn–Sham total energy<sup>59</sup> in terms of the charge density fluctuations, with the Hamiltonian matrix elements being evaluated using a minimal basis set of pseudoatomic orbitals, along with a two-center approximation.<sup>38–46</sup> In addition, in the SCC-DFTB+D approaches considered here, the total energy also includes damped atom–atom  $C_6/R^6$  terms to account for dispersion interactions.<sup>39</sup> The energy is expressed as

$$E^{\text{SCC-DFTB+D}} = \sum_{i\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}^0 + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + E_{\text{rep}} + E_{\text{dis}} \quad (1)$$

where the  $H_{\mu\nu}^0$  are a Hamiltonian matrix elements evaluated in terms of atom-centered basis functions  $\phi_\mu$ , and the coefficients  $c_\mu^i$  give the atomic contributions of the  $i$ th Kohn–Sham orbital.  $\Delta q_\alpha$  and  $\Delta q_\beta$  are charge fluctuations associated with atoms  $\alpha$  and  $\beta$ , respectively, and  $E_{\text{rep}}$  accounts for short-range repulsion. In the original version of the SCC-DFTB method, the  $\gamma_{\alpha\beta}$  function was approximated as

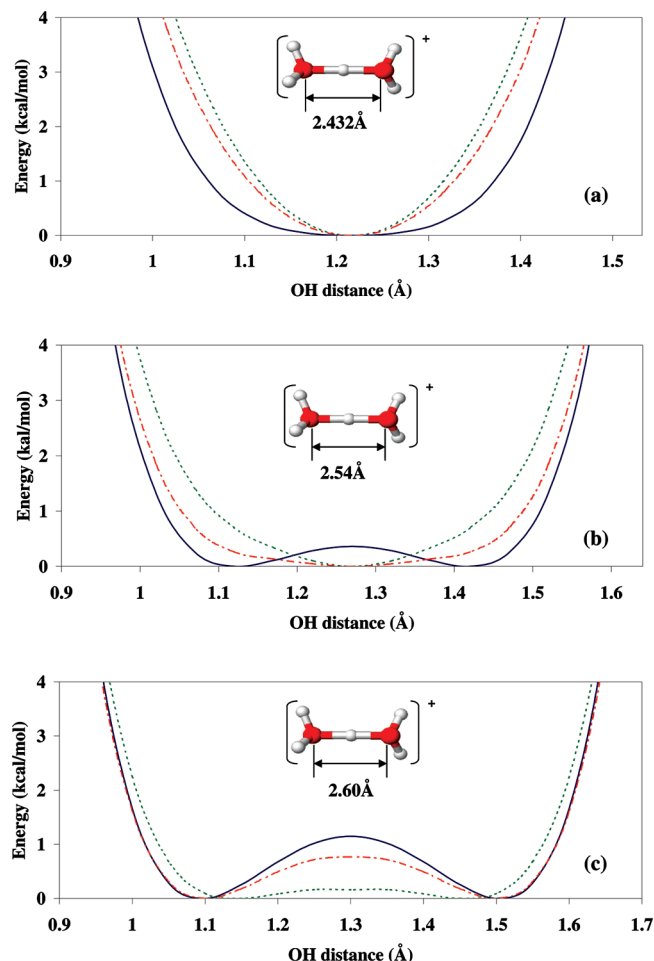
$$\gamma_{\alpha\beta} = \frac{1}{R_{\alpha\beta}} - S_{\alpha\beta} \quad (2)$$

where  $S_{\alpha\beta}$  is an exponentially decaying short-range function. To more correctly describe hydrogen-bonding interactions, Elstner<sup>46</sup> added a damping factor to the  $S_{\alpha\beta}$  term in the  $\gamma_{\alpha\beta}$  function for atomic pairs involving hydrogen atoms

$$\gamma_{\alpha\text{H}} = \frac{1}{R_{\alpha\text{H}}} - S_{\alpha\text{H}} \exp\left[-\left(\frac{U_\alpha + U_{\text{H}}}{2}\right)^\xi R_{\alpha\text{H}}^2\right] \quad (3)$$

where  $U_\alpha$  is the atomic Hubbard parameter that is related to the chemical hardness of atom  $\alpha$ .<sup>60</sup> The parameter,  $\xi$ , in the damping function was adjusted by fitting G3B3<sup>61</sup> energies for small hydrogen-bonded clusters and MP2/G3large<sup>62</sup> energies for

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**Figure 1.** Interaction energies of the protonated water dimer as a function of the shared proton OH distance for fixed OO distances of (a) 2.432, (b) 2.540, and (c) 2.600 Å. Results obtained with the SCC-DFTB+D, SCC-DFTB+D[HB+third], and MP2/aug-cc-pVDZ methods are indicated by green dotted, red dash-dotted, and blue solid lines, respectively.

large complexes. The SCC-DFTB+D[HB+third] method includes this hydrogen bonding modification as well as third-order corrections of the form

$$E^{\text{3rd}} = \frac{1}{6} \sum_{\alpha} \eta_{\alpha\alpha\alpha} (\Delta q_{\alpha})^3 \quad (4)$$

where  $\eta_{\alpha\alpha\alpha}$  is related to the charge derivative of the atomic Hubbard parameter,  $U_{\alpha}$ . A more detailed description can be found in refs 38 and 45.

Whether a protonated water cluster is Zundel-like or Eigen-like depends on the solvation environment of the excess proton in the cluster.<sup>1,2</sup> Thus it is instructive to evaluate the performance of the SCC-DFTB methods at describing the potential energy of an excess proton located between two water monomers. To accomplish this, the geometry of  $\text{H}_3\text{O}_2^+$  was first optimized at the MP2/aug-cc-pVDZ level,<sup>63</sup> giving an OO distance of 2.432 Å. The OO distance was then fixed at this value and the shared proton was displaced along the line joining the two O atoms, keeping all other degrees of freedom fixed. At each geometry the energy was calculated using both SCC-DFTB+D methods as well as at the MP2 level of theory. Analogous potentials were calculated for OO distances of 2.54 and 2.60 Å. The resulting potential energy curves are depicted in Figure 1, from which it

is seen that both SCC-DFTB+D approaches are biased toward Zundel structures especially for short OO distances, with the bias being less for the SCC-DFTB+D[HB+third] procedure.

Before applying the SCC-DFTB methods to the  $\text{H}^+(\text{H}_2\text{O})_{21}$  and  $\text{H}^+(\text{H}_2\text{O})_{22}$  clusters, we first assess their performance for  $\text{H}^+(\text{H}_2\text{O})_6$ , which has been investigated previously at the MP2/aug-cc-pVTZ<sup>63</sup> level as well as using several different implementations of the MSEVB method.<sup>31,33,37</sup> Table 1 reports for various theoretical methods the formation energies of the eleven isomers examined previously in ref 33. (The formation energies are obtained by subtracting the energy of the cluster from the sum of the energies of  $\text{H}_3\text{O}^+$  and five  $\text{H}_2\text{O}$  molecules.) Using the MP2 results as the reference, it is seen that the SCC-DFTB+D and SCC-DFTB+D[HB+third] methods underestimate the magnitudes of the formation energies by about 20 and 6 kcal/mol, respectively. The two SCC-DFTB approaches are more successful at predicting the relative energies than the formation energies of the various isomers. At the MP2 level, isomers V and VI, which are essentially isoenergetic, are the most stable isomers. Using isomer VI as the reference, and again comparing to the MP2 results, the rmsd in the relative energies are 2.3, 1.7, 1.0, 1.2, and 0.6 kcal/mol for the MSEVB1,<sup>31</sup> MSEVB3,<sup>37</sup> MSEVB4P,<sup>33</sup> SCC-DFTB+D, and SCC-DFTB+D[HB+third] methods, respectively. (MSEVB1 is an early version of the MSEVB method, while MSEVB3 and MSEVB4P were introduced in 2008.) Thus, for the relative energies of this test system, the SCC-DFTB+D method is comparable in performance to the MSEVB3 and MSEVB4P methods, while the SCC-DFTB+D[HB+third] method performs significantly better.

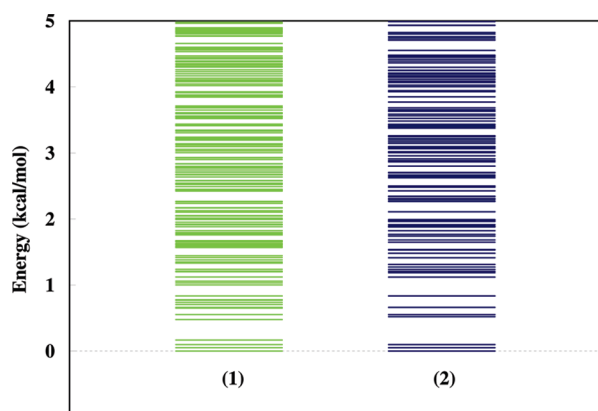
In Table 1 the clusters are also characterized as to their Eigen/Zundel nature, established using an OO distance criterion (Zundel,  $R_{\text{OO}} < 2.46$  Å; Eigen,  $R_{\text{OO}} > 2.49$  Å; intermediate,  $2.46 < R_{\text{OO}} < 2.49$  Å). From the table it is seen that both the original SCC-DFTB+D and SCC-DFTB+D[HB+third] methods are biased toward Zundel structures.

**Basin Hopping Monte Carlo Calculations.** The basin-hopping Monte Carlo method uses Monte Carlo walks combined with gradient-based optimizations to locate local potential energy minima.<sup>32,47–57</sup> At each move, the structure is optimized to the local minimum in its “basin”, and acceptance of moves is based on the energies of the minima. As a result, barriers are effectively removed, making this an efficient approach for searching for low-energy minima. In the present study a modified version of the limited-memory quasi-Newton routine (LBFGS)<sup>64</sup> by Nocedal is employed for the minimizations, and the Monte Carlo moves involve both translations and rotations of the  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$  species. It was found that alternating blocks of 100 pure translational and 500 pure rotational moves at a reduced temperature of 2.0 kJ/mol, with a target acceptance ratio of 0.4, worked reasonably well. A similar strategy was employed by James and Wales in their applications of the basin hopping algorithm.<sup>32</sup> At each Monte Carlo step, the number of molecules to be moved was chosen at random. Monte Carlo moves that generated OO distances less than 3 bohr (1.59 Å) were rejected, and moves involving Zundel-like species [ $\text{H}_3\text{O}_2^+$ ] were not attempted. For the  $\text{H}^+(\text{H}_2\text{O})_{21}$  and  $\text{H}^+(\text{H}_2\text{O})_{22}$  clusters, ten basin hopping Monte Carlo runs of 15 000 steps each were carried out. For the  $\text{H}^+(\text{H}_2\text{O})_{21}$  cluster, one run used as the initial geometry the lowest energy structure reported in ref 3, and the other nine runs were started from randomly generated structures. For  $\text{H}^+(\text{H}_2\text{O})_{22}$ , the initial structures for all ten runs were chosen at random.

**TABLE 1: Formation Energies (kcal/mol) of the Eleven Isomers of  $\text{H}^+(\text{H}_2\text{O})_6^a$** 

isomer	MP2 <sup>b</sup>		MSEVB1	MSEVB3	MSEVB4P	SCC-DFTB+D <sup>b</sup>		SCC-DFTB+D[HB+third] <sup>b</sup>	
I	−105.33	(E)	−101.51	−106.56	−104.41	−84.97	(E)	−98.53	(E)
II	−105.22	(E)	−101.51	−106.56	−104.59	−84.97	(E)	−98.53	(E)
III	−105.71	(E)	−101.51	−106.51	−104.59	−84.97	(E)	−99.48	(E)
IV	−105.02	(E)	−101.34	−105.45	−105.55	−85.48	(Z)	−98.62	(E)
V	−105.80	(E)	−103.29	−106.89	−104.48	−85.31	(E)	−99.31	(E)
VI	−105.80	(E-Z)	−104.83	−108.83	−105.77	−86.51	(Z)	−99.39	(Z)
VII	−105.49	(E)	−103.12	−107.32	−104.41	−86.08	(Z)	−99.25	(E)
VIII	−105.24	(E-Z)	−104.12	−107.70	−106.26	−87.06	(Z)	−99.51	(Z)
IX	−104.05	(Z)	−105.46	−109.18	−106.15	−87.58	(Z)	−99.28	(Z)
X	−104.41	(E)	−104.27	−107.48	−103.48	−85.29	(E)	−97.87	(E)
XI	−101.79	(Z)	−97.41	−102.55	−101.86	−81.97	(Z)	−96.21	(Z)
rmsd	0.0		2.3	1.7	1.0	1.2		0.6	

<sup>a</sup> The MP2 and MSEVB results are from ref 33. The MP2 results were obtained using single-point calculations with the aug-cc-pVTZ basis set<sup>63</sup> at the MP2/aug-cc-pVDZ<sup>63</sup> optimized geometries. <sup>b</sup> The MP2 and SCC-DFTB structures are characterized as Eigen (E), Zundel (Z), or intermediate (E-Z).

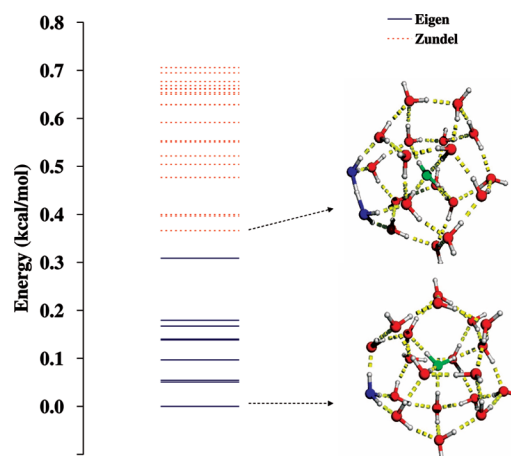


**Figure 2.** Distribution of potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  found using the basin hopping Monte Carlo procedure with the SCC-DFTB+D method starting from (1) the global minimum and (2) a randomly generated structure.

## Results

**Low-Energy Minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$ .** Figure 2 reports the relative energies of the low-lying local minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  found using basin-hopping Monte Carlo calculations with the SCC-DFTB+D method starting from the lowest energy structure reported in ref 3 as well as from a randomly generated structure. The differences in the distributions of local minima obtained using the two initial structures reflects the need to run longer basin-hopping simulations when dealing with such a complex potential energy surface. However, since the goal of this paper is to assess the performance of SCC-DFTB methods for describing such clusters, rather than to locate all of the low-energy minima, these calculations will suffice for present purposes. Figure 3 presents a blowup of the energy level diagram up to 0.7 kcal/mol (merging the results from the ten optimization runs). The nine lowest energy local minima are Eigen-like with ten five-membered rings on the surface and with nine free OH (AAD) groups (A indicates acceptor and D, donor). This is the type of structure identified as the global minimum isomer in ab initio and DFT calculations.<sup>3–7</sup>

Starting at about 0.36 kcal/mol above the global minimum, there is high density of Zundel-like structures, some of which are derived from the water dodecahedron, with all rings on the surface being five-membered, and the others having one four-membered and one six-membered ring in addition to the five-membered rings on the surface (see Figure 3). A subset of the low-lying Zundel structures identified in the SCC-DFT+D calculations were reoptimized at the Becke3LYP/6-31+G(d)



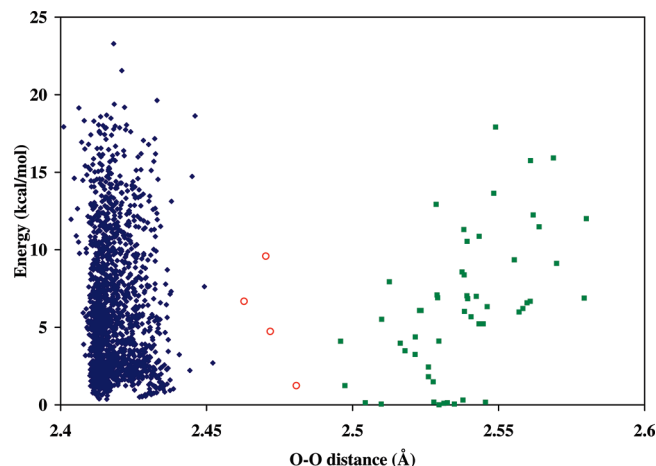
**Figure 3.** Low-lying potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  determined using basin hopping Monte Carlo optimization with the SCC-DFTB+D method.

level<sup>58</sup> and found to collapse back to Eigen-like structures, consistent with the SCC-DFTB+D method having a bias toward Zundel-like species. (Although the B3LYP method is not as reliable as the MP2 method for calculating the relative energies of different isomers, it appears to be adequate for establishing the Eigen vs Zundel character of the ions.)

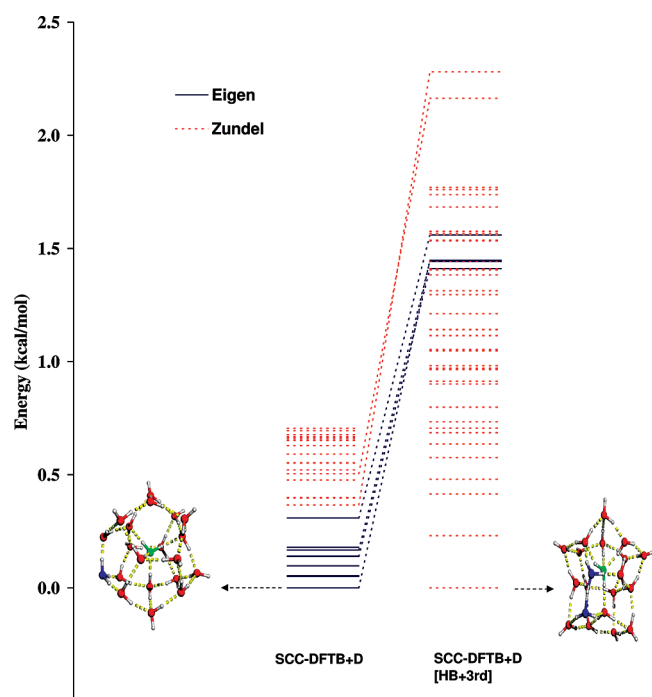
Additional insight into the occurrence of Zundel and Eigen structures in the SCC-DFTB+D calculations is provided by examination of Figure 4, which reports the OO distances of the 1714 potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  located in the basin hopping Monte Carlo optimizations. A total of 1657 of these minima have OO distances of 2.40–2.46 Å, which we characterize as Zundel-like, and 53 minima have OO distances ranging from 2.49 to about 2.58 Å, which we attribute to Eigen-like structures. The four remaining minima have OO distances between 2.46 and 2.49 Å and can be viewed as intermediate between Zundel and Eigen.

For  $\text{H}^+(\text{H}_2\text{O})_{21}$  the bias toward Zundel structures is even more pronounced in the SCC-DFTB+D[HB+third] approach, as can be seen from Figure 5, which reports the energies and structures of the low-lying minima obtained with the original and modified SCC-DFTB+D methods. With the SCC-DFTB+D[HB+third] method, all low-lying local minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  are Zundel-like. Moreover, the low-energy minima obtained with this method have structures very different from those found with SCC-DFTB+D, DFT, or MP2 optimizations.

We have also applied the two SCC-DFTB+D methods to selected isomers of the neutral  $(\text{H}_2\text{O})_{21}$  cluster, and find that



**Figure 4.** OO distances of 1714 potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  determined using basin hopping Monte Carlo optimization with the SCC-DFTB+D method. The Zundel-like structures (OO distances of 2.4–2.46 Å) are denoted by dark-blue diamonds, and the Eigen-like structures (OO distances of 2.49–2.58 Å) are indicated by green squares. The intermediate structures are indicated with open red circles.



**Figure 5.** Low-energy local minima of  $\text{H}^+(\text{H}_2\text{O})_{21}$  determined using basin hopping Monte Carlo optimization with the SCC-DFTB+D and SCC-DFTB+D[HB+third] methods.

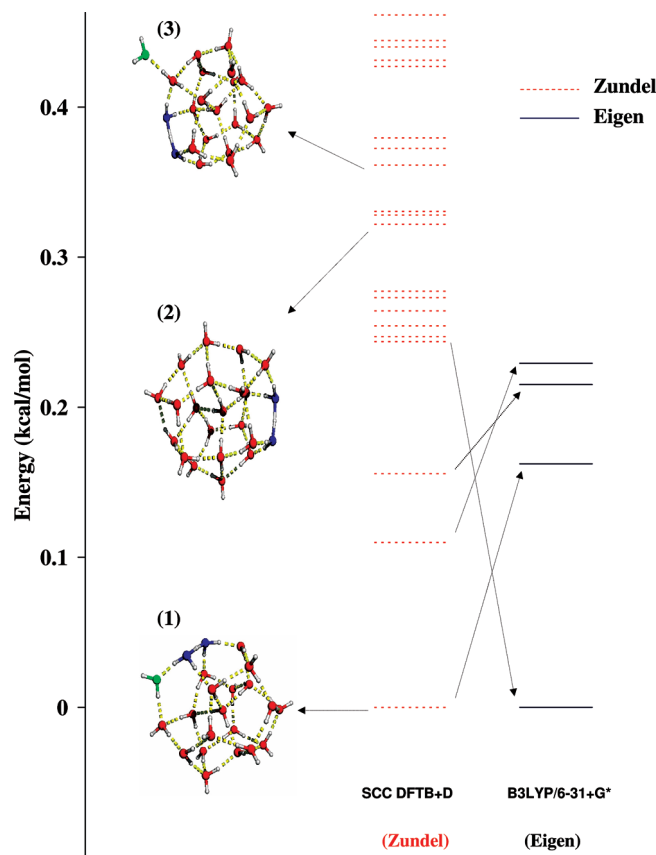
the uncorrected SCC-DFTB+D method gives relative energies closer to the results of RIMP2<sup>65</sup> calculations. However, even for the uncorrected SCC-DFTB+D method the relative energies differ by as much as 6 kcal/mol from the RIMP2 results, indicating that much of the deficiency of the SCC-DFTB+D method in describing the protonated water clusters, in fact, derives from errors in describing the interactions between the neutral water molecules.

**Low-Energy Minima of  $\text{H}^+(\text{H}_2\text{O})_{22}$ .** Although our tests on  $\text{H}^+(\text{H}_2\text{O})_6$  showed that for this system the SCC-DFTB+D[HB+third] method significantly outperforms the SCC-DFTB+D method, the results presented in the previous section indicate that the opposite is true for  $\text{H}^+(\text{H}_2\text{O})_{21}$ . We expect that the better performance of the SCC-DFTB+D method carries over to other large  $\text{H}^+(\text{H}_2\text{O})_n$  clusters. To show that this is indeed

**TABLE 2: Energies (kcal/mol) of 13 Isomers of  $\text{H}^+(\text{H}_2\text{O})_{22}$  Relative to That of Isomer A<sup>a</sup>**

isomer	RIMP2 <sup>b</sup>	SCC-DFTB+D	SCC-DFTB+D[HB+third]
A	0.00 (E)	0.00 (Z)	0.00 (Z)
B	9.53 (E)	9.86 (Z)	8.26 (E)
C	2.94 (E)	1.18 (Z)	2.29 (Z)
D	7.49 (E)	2.28 (Z)	0.69 (Z)
E	6.56 (E)	4.96 (Z)	2.23 (Z)
F	5.38 (E)	3.83 (Z)	4.03 (Z)
G	9.81 (E)	7.72 (Z)	7.22 (Z)
H	2.72 (E)	1.85 (E)	−0.70 (E)
I	2.45 (E)	1.91 (Z)	−0.90 (E)
J	0.57 (E)	1.53 (E)	1.23 (E)
K	12.06 (E)	10.38 (Z)	8.65 (E)
L	3.45 (E)	4.49 (Z)	3.38 (Z)
M	6.87 (E)	4.32 (Z)	4.60 (Z)
rmsd <sup>c</sup>	0.0	2.0	3.0

<sup>a</sup> The Eigen- and Zundel-like structures are denoted by (E) and (Z), respectively. <sup>b</sup> The RIMP2<sup>65</sup> results are from single-point calculations with the aug-cc-pVTZ basis set using B3LYP/6-31+G(D)<sup>58</sup> optimized geometries. <sup>c</sup> rmsd given relative to the RIMP2 energies.



**Figure 6.** Low-lying potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{22}$  determined using basin hopping Monte Carlo optimization with the SCC-DFTB+D method. The four lowest energy Zundel structures found with the SCC-DFTB+D method were reoptimized with the B3LYP method and found to collapse to Eigen structures.

the case, we compare the results of the two SCC-DFTB approaches to those of RIMP2 calculations for the 13 isomers of the  $\text{H}^+(\text{H}_2\text{O})_{22}$  cluster characterized in an earlier study from our group.<sup>33</sup> Table 2 reports the relative energies of these isomers obtained using the various theoretical methods. Compared to the results from the RIMP2 calculations, the SCC-DFTB+D method has a rmsd error of 2 kcal/mol in the relative energies, whereas the SCC-DFTB+D[HB+third] method has a rmsd error in the relative energies of 3.0 kcal/mol.



In light of the results discussed above, we consider only the SC-DFTB+D method in our application of the basin-hopping Monte Carlo procedure to  $\text{H}^+(\text{H}_2\text{O})_{22}$ . Figure 6 reports the energies of the low-lying potential energy minima of  $\text{H}^+(\text{H}_2\text{O})_{22}$  located with the basin-hopping optimizations. All low-energy structures are Zundel-like and can be separated into three classes. One class (1), which includes the lowest-energy structure, has ten dangling OH groups, nine of which are associated with AAD monomers and one of which is associated with a AD monomer (highlighted in green in Figure 6). The second class of isomers (2), has nine free OH groups all of which are AAD. The third, higher energy, class of isomers (3) all have a dangling acceptor  $\text{H}_2\text{O}$  molecule bound by a single H-bond to the remainder of the cluster. The four lowest energy structures have two six-membered rings and ten five-membered rings on the surface. When reoptimized using the Becke3LYP method, these four species convert to Eigen-like structures. We note also that although the SCC-DFTB+D method gives a energy gap of about 0.25 kcal/mol between the lowest energy type 1 and type 2 isomers, the energy separation between these two types of isomers is 2.8 kcal/mol at the RIMP2/aug-cc-pVDZ level.

## Conclusions

In this work two versions of the SCC-DFTB+D method were applied to the  $\text{H}^+(\text{H}_2\text{O})_6$ ,  $\text{H}^+(\text{H}_2\text{O})_{21}$ , and  $\text{H}^+(\text{H}_2\text{O})_{22}$  clusters. The SCC-DFTB+D[HB+third] method, which includes H-bonding and third-order corrections, performs better for the  $\text{H}^+(\text{H}_2\text{O})_6$  cluster. However, for the  $\text{H}^+(\text{H}_2\text{O})_{21}$  and  $\text{H}^+(\text{H}_2\text{O})_{22}$  clusters, the SCC-DFTB+D method without these corrections is more successful at reproducing the RIMP2 values of the relative energies of different isomers, although there are sizable errors with both SCC-DFTB+D methods. Much of the error in the relative energies calculated using the SCC-DFTB+D method derives from deficiencies in this approach for describing the neutral water networks. In spite of these limitations, the SCC-DFTB+D method is a viable method for identifying low-energy isomers for subsequent calculations with more-expense electronic structure methods such as RIMP2.

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