Modeling Water Cluster Anions

by

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A quantum Drude oscillator model was developed by our group to describe excess electrons interacting with water clusters[1]. This approach uses quantum Drude-oscillators to account for polarization and dispersion interactions between the excess electron and the water molecules. In the present work, the quantum Drude model, combined with a modified Thole-type water model[2] with point dipole polarizability, denoted DPP[3], is used to investigate the $(H_2O)_7^-$ cluster. Several low-energy isomers were characterized, and the finite-temperature properties of the cluster was investigated by means of parallel tempering Monte Carlo simulations[4].

Table of Contents

LIST OF TABLES

LIST OF FIGURES

PREFACE

I wish to thank my Thesis Committee, Profs. Ken Jordan, Peter Siska, and Lillian Chong for their insight while preparing for this exam. Also I thank Albert A. DeFusco, Thomas Sommerfeld, and all the other members of the Jordan group for their immeasurable help with my projects.

I. INTRODUCTION

For most of us, water is a taken-for-granted thing of our lives. Nevertheless, after more than a century of scientific study, water still holds many secrets. The wet electron, also called the hydrated electron — an extra electron added to water — has been widely studied because of its importance in radiation chemistry, electrochemistry and biology[5-9].

Most of what has been known about the wet electron involves bulk water — as opposed to clusters. $(H_2O)_n^-$ clusters have also received considerable attention from the experimental and theoretical communities[10-13]. New experimental work used sophisticated spectroscopic methods to analyze an extra electron attached to water clusters[10,14-16]. With computations providing the ability to interpret innovative laboratory studies, it is now possible to address question such as, what is the minimum size cluster for which the excess electron ''prefers'' interior binding rather than surface binding? How are the $(H_2O)_n^-$ ions formed in the various experimental studies? What is the origin of the magic numbers in the mass spectral distributions observed experimentally? What are the geometries of the $(H_2O)_n^-$?

Electron correlation contributions to the binding energies of the excess electron to water clusters have been found very important[17-19]. High level ab initio methods, such as coupled cluster theory with single, double, and noniterative triple substitutions $(CCSD(T))$[20], are so computationally expensive that they are applicable only to the $(H_2O)_n^-$ clusters with fewer than eight water monomers.

One-electron model potential approaches, on the other hand, can be applied to very

large clusters. Model potentials have been frequently applied to treat the interactions of an excess electron with water clusters and with bulk water[21-24]. However, none of these models include explicitly dispersion-like correlation contributions to the electron binding. This limitation can be potentially serious, since such interactions can significantly enhance electron binding[25].

Our group has developed a quantum Drude oscillator model to describe excess electrons interacting with water clusters[1]. This approach treats electron-water monomer polarization and dispersion[1,26]. The original Drude model was based on the Dang-Chang (DC) water model[27], but recently we have found that the DC model is considerably underpolarized[28,29] because it only includes one polarizable site on each water.

Albert DeFusco from our group has developed a new water model based on the TTM2 model of Xantheas[2], referred to as DPP[30] (DPP designates "distributed point polarizability"). It provides a more realistic treatment of polarization as it employs three polarizable sites. I used this new water model to carry out simulations of the $(H_2O)_7^-$.

II. METHODOLOGY

A. Drude Model for electron-molecule interactions

Our group introduced an one-electron model for describing the interaction between an excess electron and polar molecules[1,16,31]. This model, which employs quantum Drude oscillators to describe dispersion interactions, gives electron binding energies comparable to those from ab initio CCSD(T) calculations, while requiring orders of magnitude less CPU time.

In the Drude model, a fictitious harmonic oscillator is placed on each water, two charges, +q, and –q, coupled harmonically through a force constant k. The polarizability of a Drude oscillator is given by q^2/k, all in atomic unit, generally taken to correspond to the experimental polarizability of molecule of interest. If the Drude oscillators are treated quantum mechanically, a London-type expression is obtained for the dispersion interaction between the oscillators.
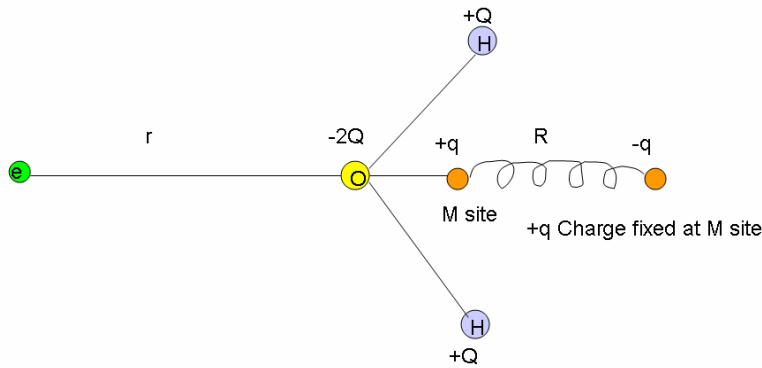

Figure 1. Drude model for describing the interaction between an excess electron and a neutral water molecule. Here the fixed +q charge associated with the oscillator is located at the M site of the water. The –q charge associated with the oscillator is separated from the +q charge by **R**.

The total model Hamiltonian for the system of an electron interacting with one or more Drude oscillators is

$$H_D = H_e + H_{osc} + V_{e,osc} \, ,$$

where H_e is the Hamiltonian of the extra electron, H_{osc} is the Hamiltonian of the collection of Drude oscillators, and $V_{e,osc}$ describes the interaction between the electron and the Drude oscillators. The Hamiltonian for the extra electron:

$$H_e = -\frac{\hbar^2}{2m_e}\nabla_e^{\;2} + V_{es} + V_{rep}$$

includes the electron kinetic energy operator and a pseudopotential that consists of an electrostatic part, V_{es}, and a short-range repulsion, V_{rep}, which is generated following the procedure of Schnitker and Rossky[32], except that we represent it in terms of Gaussians instead of Slater functions.

The Hamiltonian for the three dimensional Drude oscillator is

$$H_{osc} = -\frac{1}{2m_o}\nabla_o^2 + \frac{1}{2}k(X^2 + Y^2 + Z^2)$$

where $(X^2 + Y^2 + Z^2) = R^2$ and $\vec{R}$ is the vector in the Drude oscillator from the positive to the negative charge, the electron-oscillator coupling is:

$$V_{e,osc} = \sum_k q_D \frac{\vec{\mathbf{r}}_k \cdot \vec{\mathbf{R}}_k}{r_k^3} f(r_k)$$

where $\vec{r}_k$ is the vector from the electron to Drude oscillator k, and $f(r) = 1 - \exp(-br^2)$ is a damping function, introduced to cut off the unphysical short-range behavior, where b is a parameter.

B. Neutral Water Model

The water model used for describing the interactions between the neutral monomers, allows for electrostatic (charge-charge), polarization (charge-induced dipole), and Lennard-Jones type interactions (repulsion plus dispersion) between monomers. The neutral water model is also used for defining the electrostatic potential and induced dipoles experienced by the excess electron.

The DPP (distributed point polarizability) water model employs three, mutually

interacting, atom-centered point polarizable sites, which provide realistic treatment of polarization, with Thole-type damping[33] of the polarization and dispersion interactions. It also employs repulsive exponential interactions between the atoms of the various monomers and damped O-O dispersion interactions[34]. The experimental gas phase geometry of the water monomer is used in DPP water model, OM=0.25 Å, OH=0.9572 Å, HOH=104.52°.
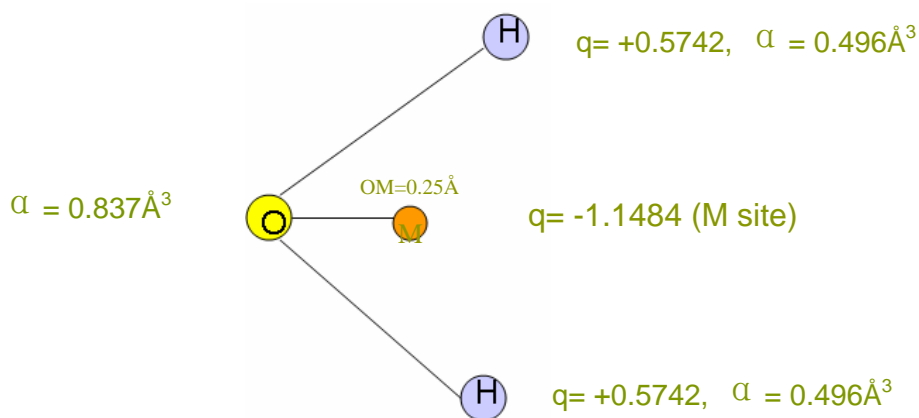

Figure 2. DPP water model, α is the polarizability of each polarizable site.

C.   Basis set and parameters.

The total basis set for the system of an electron interacting with n Drude oscillators consists of product of the form: $\left|\phi_\alpha \chi_l^{(1)}....\chi_m^{(n)}\right\rangle$, where ϕ_α is an electron orbital and χ_l^{j} is the lth energy state level associated with the jth oscillator.

After considerable experimentation, our group has derived basis set for the extra electron consisting of only six Gaussian functions per water monomer (one s function on each H atom and one sp set at the midpoint between the H atoms) combined with a 5s4p set of diffuse Gaussians located at the center of mass of each cluster. In order to minimize

the computational cost, we applied the "minimal" basis set, which consists of the ground state and the triply degenerate lowest excited state, each Drude oscillator. Test calculations show that this oscillator basis set is adequate for describing electron-water polarization and dispersion.

Concerning the parameters used in the Drude model, m_o is taken to be the mass of an electron, and q is taken to be 1 a.u.. q^2/k is set equal to the experimental polarizability of a water monomer[26].

D． *Ab initio* calculations

MP2 *ab initio* calculations with two different size basis sets were also carried out in order to compare with our Drude-model results. The B1 basis set is from Herbert and Head Gordon[19,35] and consists of the 6-31++G* basis set[36] augmented with two additional diffuse s-type functions (exponents 0.012 and 0.004) on the H atoms.

The larger basis set B2 is the aug-cc-pVDZ basis set plus a 4s3p (four of *s* type basis functions and three of *p* type basis functions) set of diffuse functions on the center of mass of the cluster. The exponents for the B2 basis set range from 0.015 to 0.00012 for the *s*-type functions and 0.012 to 0.00048 for the *p*-type functions. The *ab initio* calculations were carried out with the Gaussian03[37] computer program.

E. Parallel-tempering Monte Carlo Method

The PTMC method[4] was utilized for finite temperature simulations. In the PTMC simulations, we applied 12 temperatures for $(H_2O)_7^-$ cluster. At each temperature, most attempted moves used Metropolis sampling[38], and every 250 moves exchanges were

attempted between replicas at adjacent temperatures. The Metropolis moves involved displacements of only one water monomer at one time, where each displacement included both translation and rotation. Each simulation employed four million moves to equilibrate, followed by three million production moves. The maximal step sizes were chosen so that about 50% of the moves were accepted. To check convergence, the simulations for each water cluster were performed starting from at least two different isomers. Structures of the sampled configurations in the PTMC simulations were optimized by *quasi*-Newton method with numerical gradients.
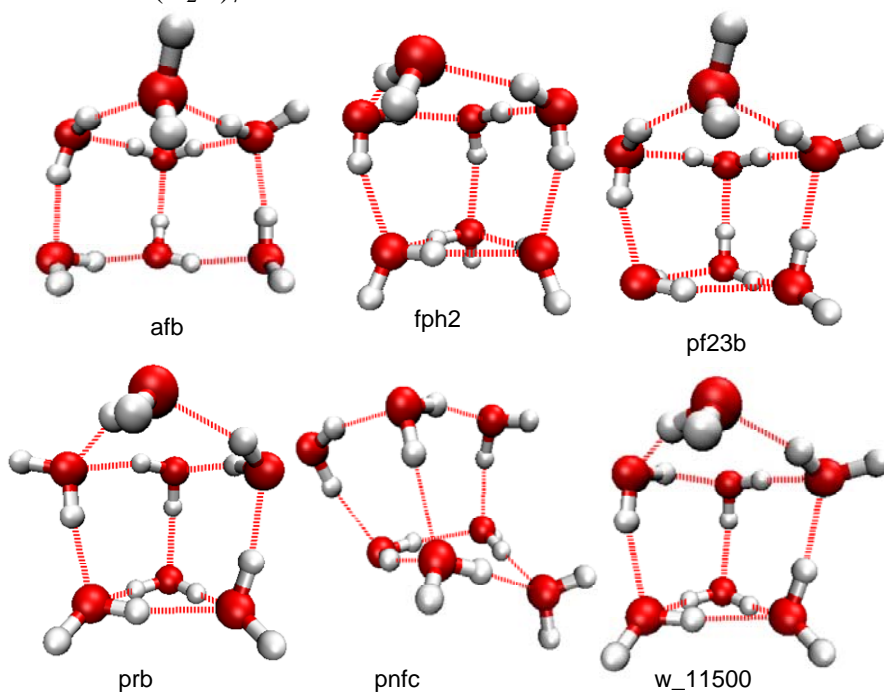
III. Results for $(H_2O)_7^-$

Figure 3. Structures of selected low-energy isomers of $(H_2O)_7^-$.

Isomer	μ (Debye)	total E(meV)	−EBE(meV)
afa	11.2	79.8	584
afa2	9.5	105	464
afb	11	74.6	575
pf23a	11.3	76.4	550
pf23b	11.3	65	552
pf24a	9.5	66.3	423
pf24b	8.9	112.1	409
pf25a	12.6	111	626
pf34a	8.9	66.4	399
pf34b	7.3	23.8	203
pnfa	9.1	61.2	437
pnfb	13.3	199.3	664
pnfc	15	241.1	749
pnfd	10.7	230.3	555
pra	5.9	69.7	131
prb	7.5	0	245
w-11500	7.5	2.8	251
w_83000	7.9	31.3	267
w_497000	6.6	39.3	184
w_463500	5.5	43.3	162
w_121500	7.1	21.2	234
w_489500	7.4	36.6	222
fph	9.7	83.5	378
fph2	10.2	64.1	448

TABLE I. Relative energies and electron binding energies of the $(H_2O)_7^-$ isomers depicted in Figure 3. The dipole moments, of the associated neutral clusters are also listed. All results have been obtained with the Drude-DPP model.

Isomer Prb was found to be the global minimum. The isomers with red names all have one AA water, which is a single water molecule with both of its hydrogen atoms pointing toward the excess electron; the blue ones do not have AA water. It can be seen from the total energies that isomers with an AA water are for the most part energetically less stable than isomers without an AA water, but that AA water helps bind the excess electron, which can been seen from the higher electron binding energies.
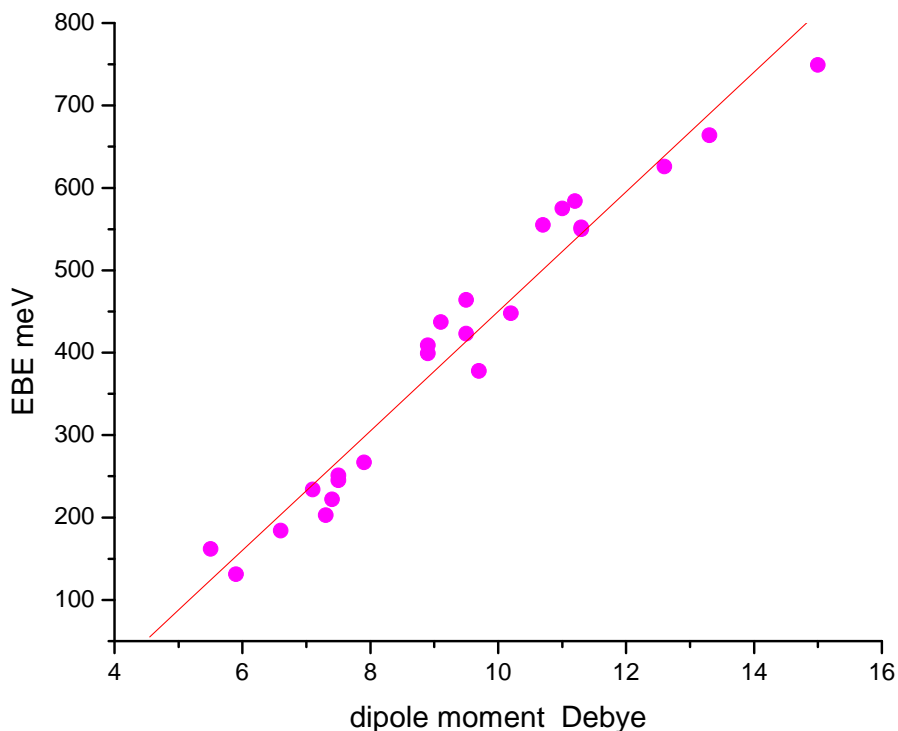
Figure 4. Electron binding energies of the selected isomers of $(H_2O)_7^-$ vs dipole moment.

As seen from Figure 4, the electron binding energy generally increases with dipole moment.

Figure 5 reports the electron binding energies of the selected isomers of $(H_2O)_7^-$ calculated using the calculated using the Drude/DPP, the MP2/B1 methods. The starting isomers for Drude/DPP optimization are the final geometries of MP2/B1 optimization. With the Drude model the total elapsed time for a single point calculation for $(H_2O)_7^-$ is about 0.12 sec on a 2.4 GHz AMD opteron processor, while the MP2/B1 single point calculation for the same isomer takes about 26 minutes cpu time.
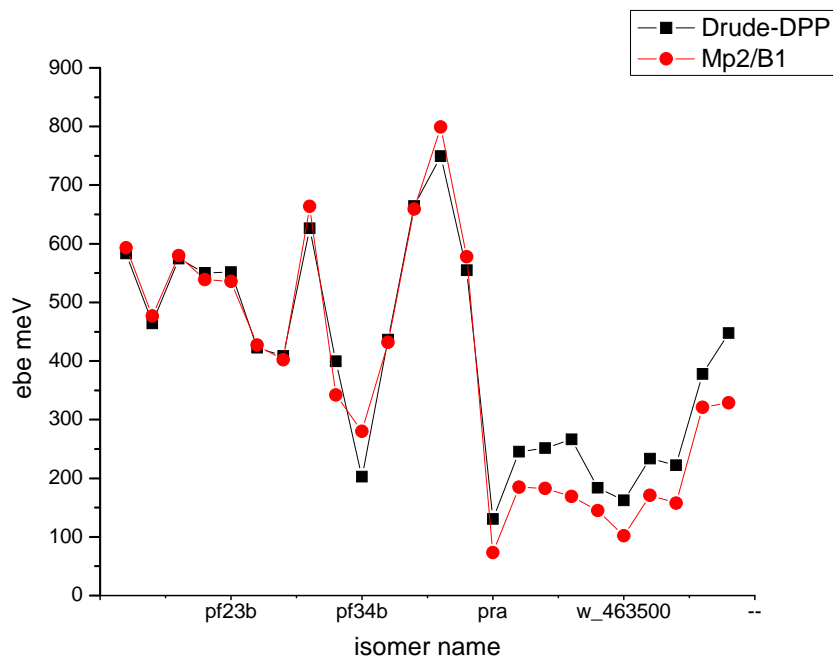
Figure 5. Electron binding energies of selected isomers of $(H_2O)_7^-$ calculated using the Drude /DPP and the MP2/B1 methods.

The MP2 procedure tends to underbind the excess electrons[1]，which maybe the reason for the lower MP2 electron binding energies of isomers to the right side of isomer Pra, including isomer Pra, as pictured in Figure 5.

Figure 6 reports the total energies of the selected isomers of $(H_2O)_7^-$ calculated using the calculated using the Drude/DPP, the MP2/B1 methods. The large difference between the energies of MP2/B1 and Drude/DPP energies for isomer Pf34b is due to geometry "collapse"; It can be seen from Figure 7 that new hydrogen bond formed during the Drude/DPP optimization progress.
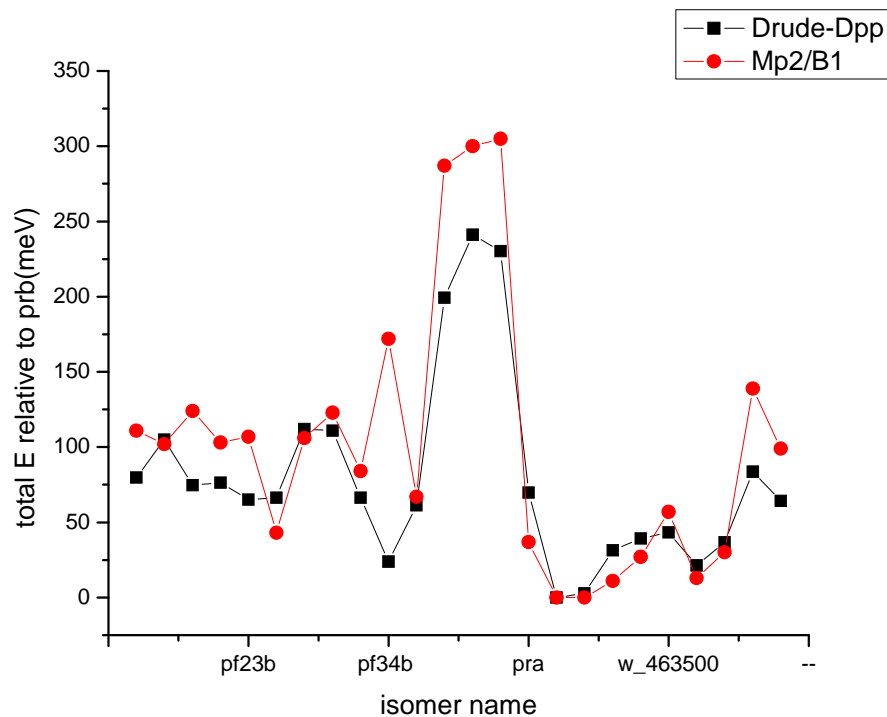
Figure 6. Total energies relative to prb of the selected isomers of $(H_2O)_7^-$ calculated using the Drude/DPP, and the MP2/B1 methods.
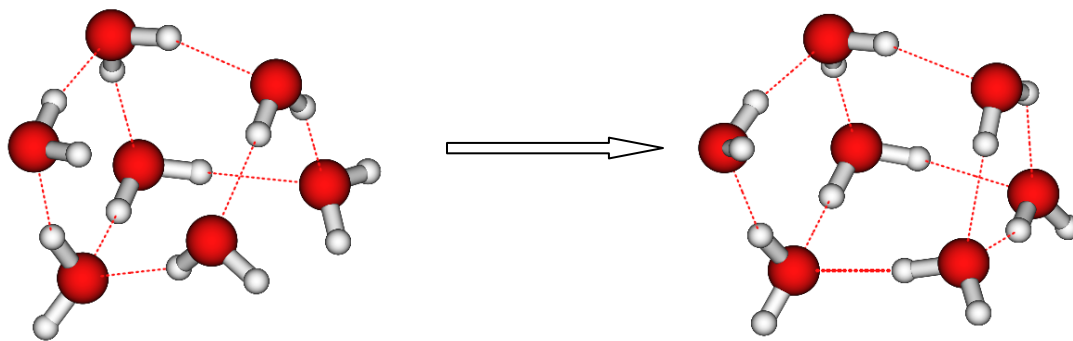

Figure 7. left: starting structure, right: ending structure of Pf34b for drude DPP optimization

We can see from Figures 5 and 6 that the Drude model predicts electron binding energies better than it predicts total energies, perhaps because the neutral water model applied in the Drude approach is rigid rather than flexible. Flexibility is important

because both the permanent and induced dipoles of the molecules change with distortions of the monomer geometry.
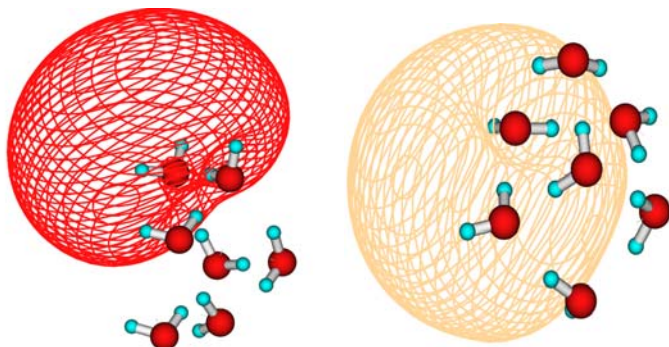

Figure 8. Distribution of the excess electron for isomers Afa and Prb. The pictures show iso-surfaces of the natural orbitals of the reduced CI density. The occupation numbers of these orbitals is 0.97. The iso-surfaces have been drawn at a value of 0.0141 bohr$^{-3/2}$ and contain roughly 70% of the electron density.

Figure 8 reports the density distribution of the excess electrons of isomers Afa and Prb, the excess electrons of all the other $(H_2O)_7^-$ isomers considered are also found to be surface bound，which is stabilized by the attractive potential provided by the AA waters.

CONCLUSION

The $(H_2O)_n^-$ (n≥7) cluster system is particularly challenging due to the large number of possible low energy isomers. A quantum drude model is used to enumerate the low energy isomers. This is accomplished by carrying out parallel tempering Monte Carlo simulations of the clusters and quenching sampled configurations to their inherent structures.

The DPP (distributed point polarizability) water model, coupled with a one electron model potential employing Drude oscillators to describe electron-molecule polarization and dispersion, is able to account in a near quantitative manner for the

binding of an excess electron to small water clusters. This Drude approach is much more computationally efficient than high level ab initio methods. Isomer Prb was found to be the global minimum of $(H_2O)_7^-$ clusters and in all the $(H_2O)_7^-$ isomers considered the excess electron is found to be surface bound. The low energy isomers are analyzed in the context of the experimental results.

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