

Exploring Water Clusters

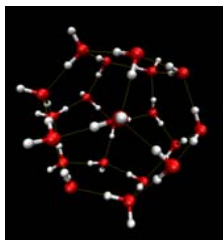
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Introduction

Water clusters are finite collections of water molecules containing from two to hundreds of molecules

• Water clusters are important in atmospheric chemistry and play a major role in transport processes in biological systems.

• The Jordan group has studied neutral water clusters using a combination of quantum chemical calculations and classical simulations.



An isomer of the neutral (H₂O)_n species water studied by Tsai and Jordan

• A sophisticated model potential, the Distributed Point Polarizable model (DPP), based on electronic structure calculations on small neutral water clusters has been developed in the group.



An isomer of the neutral (H₂O)_n species water studied using the DPP model.

• Currently we are investigating the excess electrons and protons in water clusters.

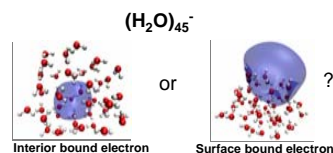
Hydrated Electron Systems

Motivation

• Excess electrons in water gives rise to the hydrated electron species (e_{aq}⁻).

• e_{aq}⁻ is involved in electron transfer reaction in biological systems, electrochemical reactions, and in radiation chemistry of water

• A topic of hot debate among both theorists and experimentalists is the location of the excess electron in water clusters.



• A strategy to treat these systems has been developed in our group. It combines:

- The DPP water model.
- A local polarization model, based on the Quantum Drude oscillator method, to treat the electron-water interaction.

Local Polarization Model

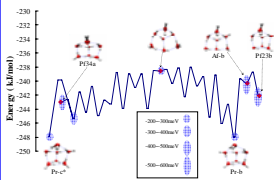
The Hamiltonian for the interaction between the excess electron and the water molecules is defined as follows:

$$H = H^e + H^{osc} + V^{e,osc}$$

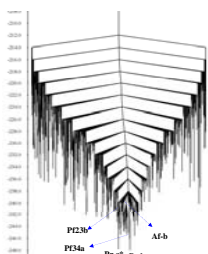
$$H = \left(-\frac{1}{2} \nabla_e^2 - \sum_i \frac{Q_i}{r_i} + V_{rep} \right) + \sum_j \left(-\frac{\alpha_D}{2r_j^4} f^2(r) \right) + \left(\sum_k q_{Dk} \frac{r \cdot R}{r^3} f(r) \right)$$

- Interaction of electron with point charges on water molecules
- Short-range repulsion between electron and each water monomer
- Polarization of water monomer by the excess electron
- Interaction of the electron with induced dipoles on the water molecules.

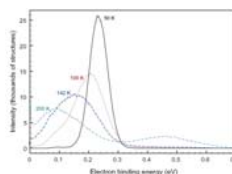
• Recently gradients for the model were implemented allowing for the use of Molecular Dynamics to study such systems. They also permit the exploration of the topology of the potential energy surfaces.



Isomers of the (H₂O)_n system



Disconnectivity diagrams of the water cluster anions (512 minima and 1067 TSs)



Electron Binding energy from Parallel Tempering Monte Carlo simulations

Future Work

• Extend the method developed for the hydrated electron system to treat excess electrons in non-aqueous solvents, for example in methanol.

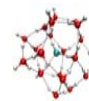
Protonated Water Clusters

Why study protonated water systems ?

• Protonated water clusters play an important role in atmospheric processes (e.g. ion chemistry in the lower atmosphere, nucleation etc.)

• Experiments on H⁺(H₂O)_n clusters reveal magic numbers and interesting trends in the IR spectra.

• Proton transport in aqueous systems important in biology (e.g., proton channels).

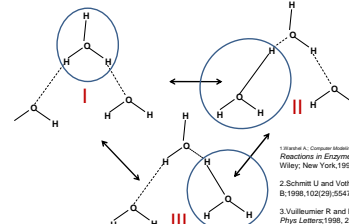


<http://www.sccc.uconn.edu/research/CI/CIwater/CIwater.html>

MSEVB model

The Multistate Empirical Valence Bond (MSEVB) model of Voth and coworkers delocalizes the proton over a number of water molecules.

Example : In the case of the protonated trimer, there are 3 valence bond states I, II and III.



1. Voth A. Current Chemistry of Chemical Reactions in Enzymes and Solution; Wiley: New York, 1991
2. Schmitt V and Voth G. J Phys Chem B: 1998, 102(29):5547
3. Vulliamier R and Borgis D. Chem Phys Letters: 1998, 284, 71
4. Branzato G and Tuckerman M E.J. Chem Phys: 2005, 122(2):224507

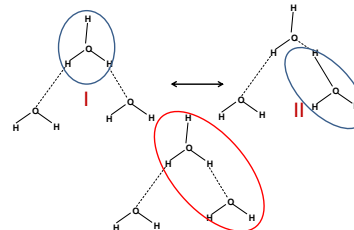
Hamiltonian for the MSEVB model (based on the model of Voth et al)

Diagonal terms : $H_{ii} = V_{intra}^{H_2O} + \sum_{i=1}^N V_{intra}^{H_3O^+} + \sum_{i,j} V_{inter}^{H_2O} + \sum_{i=1}^N V_{H_2O}^{H_3O^+}$

- $V_{intra}^{H_2O}$ → Intramolecular term for the ith water monomer
- $V_{intra}^{H_3O^+}$ → Intramolecular term for the hydronium species
- $V_{H_2O}^{H_3O^+}$ → Interaction between the hydronium species and the ith water molecule
- $V_{inter}^{H_2O}$ → Intermolecular interaction between the ith and jth water molecules

Off-diagonal terms : $H_{ij} = V_{connect} f(v_{ij}) \cdot g(q) + V_{ij} f(v_{ij}) \cdot g(q)$

V_{ij} → Modelling using Coulombic interactions between the Zundel species (formed from states i and j) and the remaining water molecules

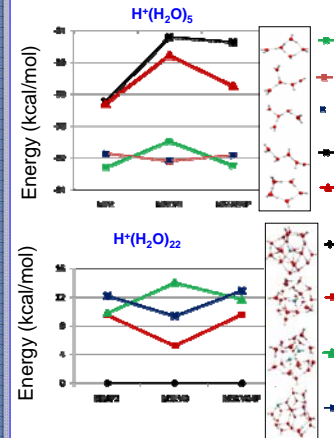


TIP4P has been shown to be superior to the TIP3P water potential in describing neutral water clusters.

• We replaced the TIP3P model (MSEVB) with the TIP4P water model (MSEVB4P)

• The MSEVB4P model was re-parameterized to fit the energies and geometries of H₅O₂⁺, H₇O₃⁺ and 2 isomers of H₉O₄⁺.

• We used the MSEVB4P model to study H⁺(H₂O)_n with n=5, 6 and 22. The MSEVB4P model shows considerable improvement over the original MSEVB model !



Future Directions

• Although the MSEVB4P model shows substantial improvement over the MSEVB1 model and a modest improvement over MSEVB3, the errors in the relative energies between isomers are still substantial.

• We are now working to extend these studies by using a polarizable water model.

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