Ensembles of Water-Halide Clusters

Brian Nguyen and Luke Nambi Mohanam

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Abstract

Cluster models of water-halide solutions have been widely studied and have well-defined chemical composition. Often, certain ions have higher concentration closer to the surface at the air-water interface. In this report, a computational study of chloride-water clusters is investigated by determining local minima of a chloride cluster with 3 water, and comparing to experimental spectra. Two local minima structures were determined with the difference of an additional hydrogen bond between water molecules. It is seen that the additional hydrogen bond led to a higher overall energy suggesting that there is some steric strain from forming the additional hydrogen bond.

1   Introduction

At the troposphere of the atmosphere, a complex combination of gaseous, aqueous, and surface processes are present that involves a wide variety of compounds[1]. The understanding of these complex reactions requires learning the aqueous solvation properties of ions in water clusters. In particular, there are evidence that active inorganic chlorine compounds in the marine boundary layer.[2] A molecular description of this process is of interest for atmospheric chemistry.

Photon electron spectroscopy (PES) has been previously used to study the anionic solvation in water clusters ranging from 1 to 60 water atoms[3]. These studies have provided better understanding of the solvation phenomena in bulk solutions. However, a molecular and structural description of the anionic solvation remains to be studied. We set out to explore the effects of a chloride ion surrounded by three water molecules and to understand the structural basis for the solvation of halogens. The ab initio molecular dynamic (AIMD) simulations of $[Cl(H_2O)_3]^-$ were performed and compared to previous PES experiments of halogen atoms solvated in water clusters.

2   Methods

2.1   Statement of the Models

The Born-Oppenheimer approximation is used, separating the electronic and nuclear degrees of freedom. Hence electrons are in energy eigenstates at each time step, and the nuclei are treated as classical point charges with a verlet-leapfrog algorithm. This creates a potential energy surface that the nuclei propagate on. With this nuclei propagation started with random nuclei velocities with a total nuclei temperature, the potential energy surface is explored for local minima. Each minima was treated as a quantum harmonic potential to obtain zero-point energies of this harmonic motion, to obtain more accurate energies of these minima.

Subsequently a statistical mechanics treatment of the vibrational motion with the same quantum harmonic oscillator, the rotational motion with a quantum rigid rotor, and treating the translational motion classically, ignoring electronic contributions to the partition function, allows for the computation of the enthalpy and entropy at finite temperatures. This also allows for an estimation of the chemical potential at finite temperature.

The vertical energy of removing one electron from the cluster is estimated as the energy difference of the potential energy surfaces when removing one electron, at the local minima geometry, including the zero point energy before the electron is removed. In the absence of self interaction error this is simply the energy of the highest occupied molecular orbital minus the zero point energy. Due to self-interaction error the electronic energy is converged again after the removal of an electron.

2.2   Computational Details

All calculations were performed with TURBOMOLE 7.2.1.[4] Free molecular dynamics were performed with the methods described above, starting from an optimized geometry with maximum hydrogen bonding. The PBE0 functional was used with the def2-SVP basis set. Initial random nuclear velocities were set to give an initial temperature of 3000 K. A time step of 1 fs was used for a total of 215 time steps. While 5 low energy images from the molecular dynamics were selected for geometry optimization, only two images produced unique minimum energy geometries. The scripts and subroutines called to set up and run the calculation include define, mdprep, jobex, and freeh.

3   Results

From the AIMD trajectory of approximately 2 ps, 5 chloride water clusters were selected within 4.40 kcal/mol difference. Additional geometry refinement to the 5 structures yielded only 2 unique conformations as seen in Fig 1. The difference between the structures is the hydrogen network prevalent within the water cluster. However, it appears that the more stable conformation is the hydrogen bonded to the chloride ion. This can be seen by
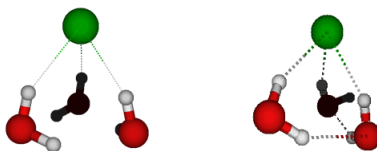
Figure 1: These are geometry optimized chloride water clusters from AIMD simulations using TPSS-D3/def2-TZVP. Conformation 1 is on the left and conformation 2 is on the right which will be referenced on the tables.

the conformation 1 having a higher free energy and minimum energy, which include zero vibrational energy, than conformation 2 indicated in Tables 1 and 2.

Table 1: These are reported chemical potential and free energy of the chloride water cluster conformations.

Conformation	Temperature(K)	Chemical Potential(kJ/mol)	Free Energy(kJ/mol)
1	0.00	—	197.50
	298.15	112.07	
2	0.00	—	193.65
	298.15	103.99	

Table 2: These are repoted energy, enthalpy, and entropy of the cholride water cluster conformations.

Conformation	Temperature(K)	Energy(kJ/mol)	Enthalpy(kJ/mol)	Entropy(kJ/mol)
1	0.00	197.50	197.50	—
	298.15	219.43	221.91	0.36841
2	0.00	193.65	193.65	—
	298.15	217.58	220.06	0.38929

The detachment energies of comformation 1 and 2 are 115.0 kcal/mol and 114.9 kcal/mol, respectively. In comparison to the PES experiments, the reported detachment energy is approximately 126.8 kcal/mol which is approximately 11 kcal/mol difference from the computed detachement energies of the structures[3]. In addition, from Fig **??** the computed vibrational spectrum of comformation 2 appears to match more closely to experimental IR spectra than conformation 1. The computed band positions of conformation 2 are 3355, 3584, and 3679 wavenumbers which correspond fairly close to the experimental IR spectra of 3310, 3354, 3391, 3585, and 3600 wavenumbers[5]. Only two additional bands were experimental observed that were not predicted by the computation.
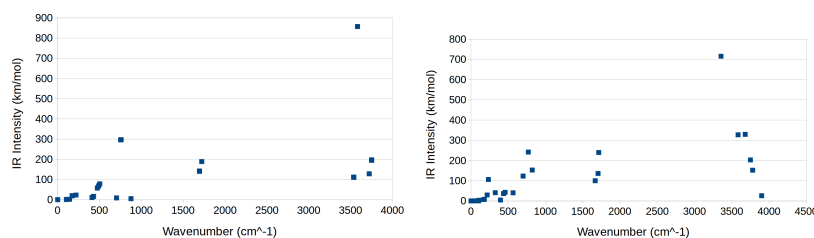
Figure 2: The computed IR spectrum of conformation 1 (Left) and conformation 2 (Right).

4   Conclusions

In conclusion, two structures were found to be local minimas of the chloride water clusters and only one structure appears to fairly match the experimentally determined IR spectrum. The only structural difference between the two conformations is the appearance of the hydrogen network within the water cluster. This suggested a competition between hydrogen bond networking and the solvation of the chloride ion. Meanwhile, the overall energy of conformation 1 is lower than conformation 2 suggesting that conformation 1 is potentially the global minima. However, this contrasts the experimental results which are in better agreement with conformation 2. Further sampling may be needed to investigate the potential energy surface of the chloride water clusters.

References

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