

Aqueous Solvation of the Chloride Ion Revisited with Density Functional Theory: Impact of Correlation and Exchange Approximations

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Below we have plotted some relevant structural and dynamic measures of the H_2O molecules in the ab-initio molecular dynamics simulations of $\text{Cl}^--(\text{H}_2\text{O})_{63}$. This includes the O-O and O-H radial distribution functions, the O-O-O angular distribution function (ADF), and the vibrational density of states of the H atoms.

H-bonds are defined between H_2O molecules and Cl^- using the Cl-O RDF shown in the main manuscript and the Cl-O-H ADF shown in Figure 4. The cutoffs for the Cl-O and Cl-H distances when computing the ADF are chosen such that only the nearest neighbors are included. A similar procedure is followed when computing the O-O-H ADF shown in Figure 3, such that only the nearest neighbors are included. Figure 3 thus shows the distributions of O-O-H angles used to determine the existence of a H-bond, where one sees a sharp peak small angles associated with H-bonded H_2O molecules. Note that the Cl-O-H ADF in Figure 4 has a very similar shape to the O-O-H ADF in Figure 3, and both show a sharp peak at small angles which goes to zero at roughly 30° . H-bonds between H_2O and Cl^- are therefore defined by a O-Cl distance less than 3.80 \AA and a Cl-O-H angle less than 30° .

Note of the infrared adsorption coefficient of H_2O $\alpha(\omega)$ in Figure 5. We don't see the same behavior in $\alpha(\omega)$ for H_2O as for Cl^- , as the intensity of the spectrum does not on the functional as strongly as the Cl^- anion.

References

- [1] F. J. Harris. On the use of windows for harmonic analysis with the discrete Fourier transform. *Proceedings of the IEEE*, 66(1):51–83, January 1978.

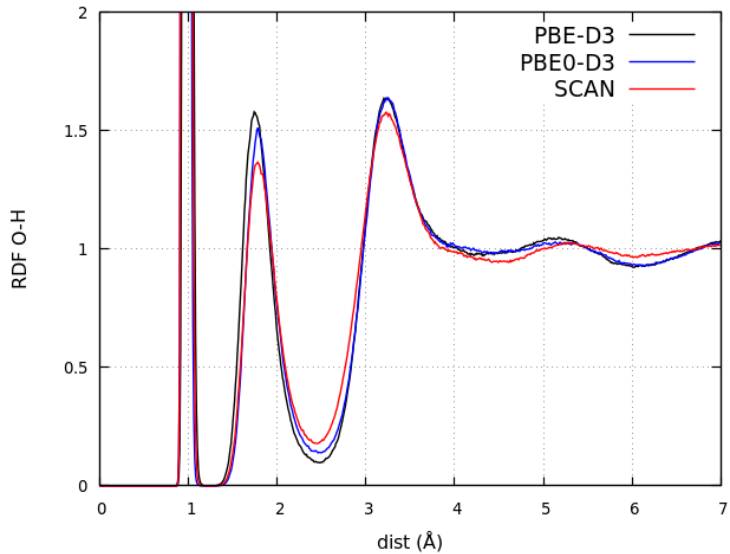


Figure 1: The O-H radial distribution function for each simulation.

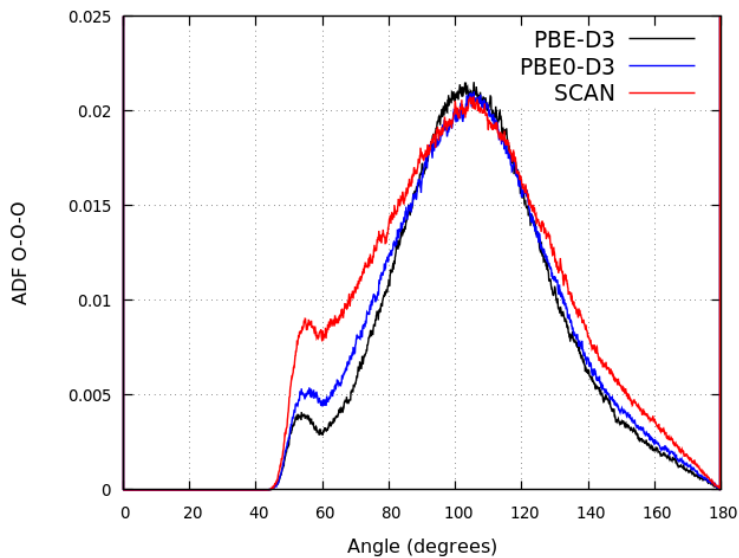


Figure 2: The O-O-O angular distribution function for each simulation for all O atoms within the first minimum of the O-O RDF (3.35 Å).

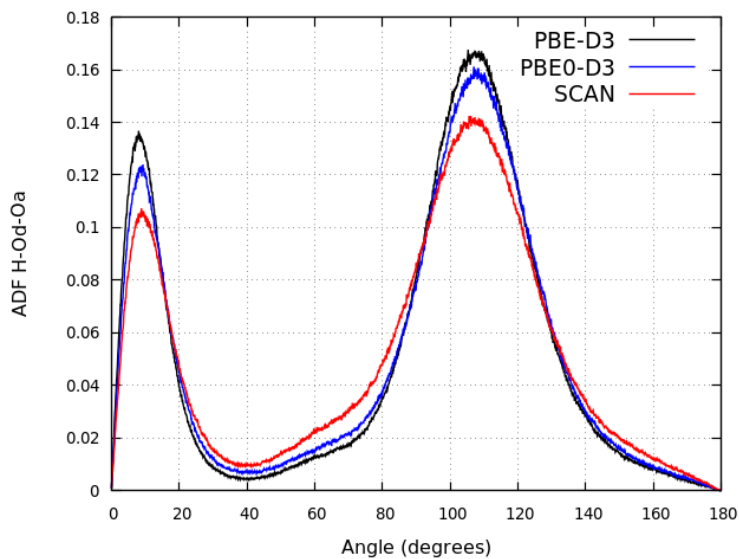


Figure 3: The O-O-H angular distribution function for each simulation, where we use a cutoff of 3.35 Å for the O-O distance and a cutoff of 1.2 Å for the O-H distance.

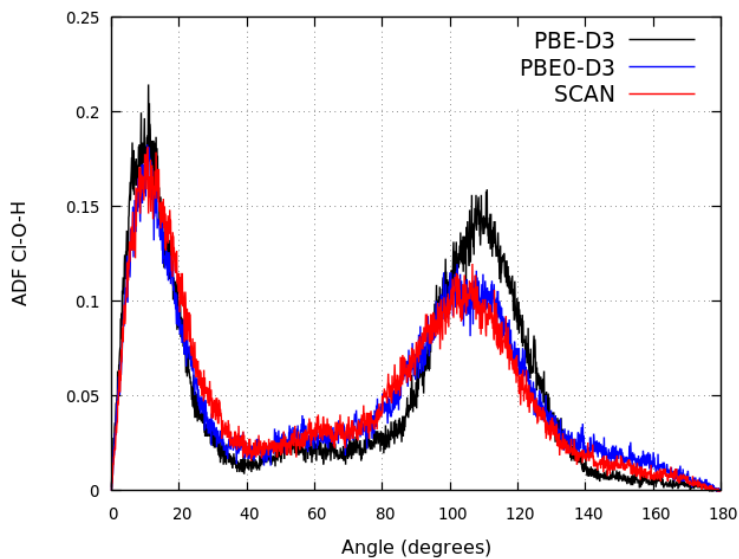


Figure 4: The Cl-O-H angular distribution function for each simulation, where we use a cutoff of 3.75 Å for the O-Cl distance and a cutoff of 1.2 Å for the O-H distance.

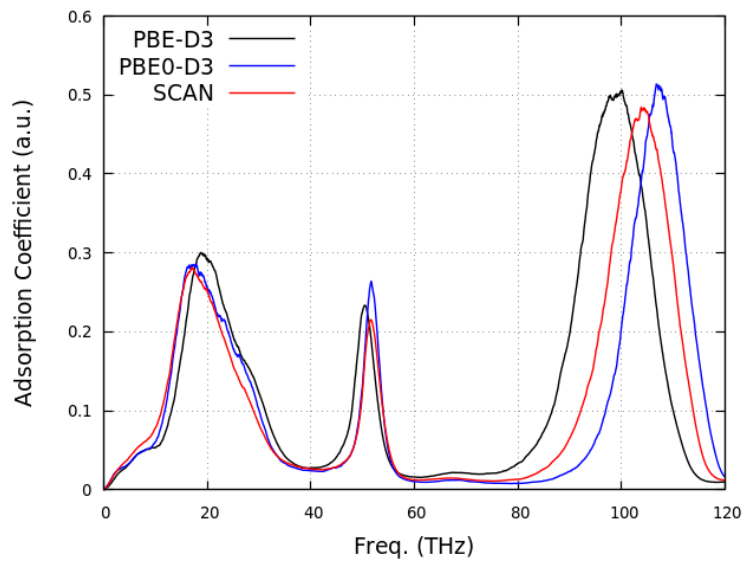


Figure 5: The infrared adsorption coefficient per unit length computed from the dipole moment of the H_2O molecules. The spectrum has been windowed using the Blackmann-Harris function[1] and smoothed with a Gaussian with a width of 75.0 fs.