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A theoretical study on TMAO hydration structure

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1. Introduction

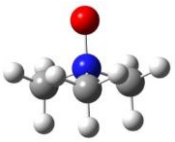

Figure 1.

The marine organisms hold osmolytes in intracellular fluid to adjust osmotic pressure and live in seawater. Trimethylamine oxide (TMAO; Figure 1) is well known as osmolyte. Here, we show the hydration structure of TMAO in aqueous solution and its high ability in capturing water molecules.

2. Computational methods

2-1. Ab initio MO method

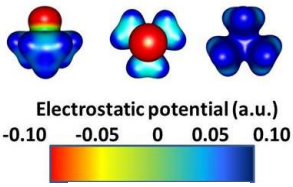

Figure 2.

We optimize the geometry of TMAO and the hydration complexes of TMAO with some water molecules at MP2/6-31G*. Gaussian09 is used for all ab initio MO calculations.

2-2. Monte Carlo (MC) calculation

We put 500 water molecules in cavity with a radius of 15.3 Å, such that the density is 1 g cm^{-3}. We use TIP3P potentials for water, and NPA charges for solute (TMAO). We perform MC calculations at 300K of 2×10^5 MC steps for the equilibration and then 4×10^7 steps for the analysis, from which we calculate oxygen and hydrogen number densities of water molecules around TMAO.

3. Results and Discussion

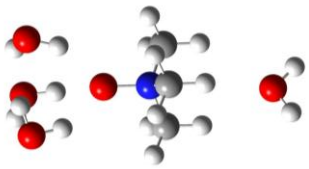

Figure 3.

3-1. Electrostatic potential map of TMAO is shown in Figure 2. Dipole moment of TMAO is calculated to be 4.92 Debye, which is much larger than that of a water molecule (2.24 Debye). One of the optimized structures of TMAO with 4 water molecules is shown in Figure 3. The hydration energy of this complex is -31.1 kcal/mol.

3-2. Oxygen number density (red) and hydrogen number density (white) of water molecules around TMAO are shown in Figure 4. We show the distribution where O number density of water molecules is larger than 0.09 atoms/$Å^3$, and H number density is larger than 0.12 atoms/$Å^3$. Note that the O number density of bulk water (1 g cm^{-3}) is uniform and 0.033 atoms/$Å^3$. It is noteworthy that the hydration structure of the TMAO cluster (Fig. 3) can be regarded as a representative of the hydration pattern of TMAO in aqueous solution (Fig. 4).

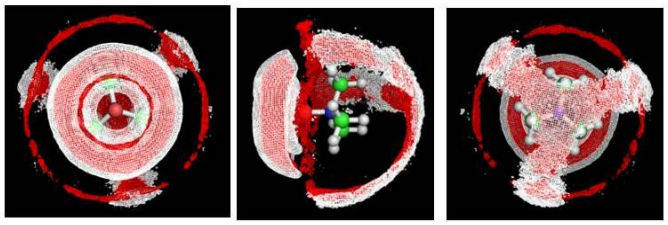

Figure 4.