Path integral simulation for H/D isotope effect in protonated/deuterated aqueous solution

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Water dissolves various substances, and many important chemical reactions occur in aqueous solution. The behavior of proton (H^+) in aqueous solution is also important in biochemical reactions and proton transfer in living organisms. On the other hand, the behavior of deuteron (D^+) in heavy water (D_2O), an isotope of water, has been still unclear, yet. In this study, thus, we have applied the *on-the-fly* path integral molecular dynamics (PIMD) simulation, which can include both the nuclear quantum effect and thermal effect, with PBE density functional. To elucidate the isotope effects of H^+/D^+ behavior in aqueous solution, we calculated the systems of H^+ in light water solvent and D^+ in heavy water one. We found the large isotope effect at around Eigen H_3O^+/D_3O^+ region. First, the structures with Zundel $H_5O_2^+$, $H_7O_3^+$, and $H_9O_4^+$ was confirmed at the system of H^+ in light water solvent, while such structures are less at that of D^+ in heavy water. We also found the H/D isotope effect at the radial distribution function of O-O distances.