

Title: "A machine learning model to classify dynamic processes in liquid water"

Manuscript number: JCP21-AR-01795

Authors: Jie Huang, Gang Huang, and Shibin Li

Referee report

This work studies hydrogen-bond (HB) rearrangement processes for a water dimer embedded in liquid water, using AIMD simulations (with the BLYP functional), and a machine learning analysis. There is an incredible number of papers on water dynamics in the literature with which to compare the more standard results. The authors calculate (among other things) water self diffusion and the number of hydrogen bonds, without any effort to compare with literature results. As far as I can see, comparison with the literature suggests that the present results are wrong. This may or may not be due to the machine learning algorithm introduced herein. Thus, I do not think the present results could be accepted for publication.

- 1) Figure 9 shows the average number of HBs as a function of T using two HB definitions. Both of these calculations yield way too small values as compared with BLYP results at room temperature, 3.44 HBs/molecule, see e.g., Lin *et al.*, J. Chem.Theory Comput. 8, 3902 (2012), Table 2 (1st line). Also, I wonder if the two definitions should lead to such disparate results as in Fig. 9.
- 2) The HB number in Fig. 9 is nearly independent of T in the range 280-360 K, slightly smaller at 280 compared to 360 K. In the literature, it decreases monotonically with increasing T (e.g., Han *et al.*, PHYSICAL REVIEW E 79, 041202 (2009), Fig. 1) quite in contrast to Fig. 9 here.
- 3) Figure 7A (blue bars) shows a quantity termed here “diffusion” that is supposedly proportional (or similar) to the water self-diffusion coefficient. From 280 to 340 K it increases here by a factor 2, and decreases upon further increase of T. This, also, is incorrect. Experimentally, it increases by ca. factor 5 in this range (<https://dtrx.de/od/diff/>), and continues to **increase** at higher temperatures. This agrees

nicely with classical MD simulations using the MB-pol potential energy function, Reddy *et al.*, The Journal of Chemical Physics 145, 194504 (2016), Fig. 11.

4) The present work “focus is on one specific dynamic process in bulk water: the donor-acceptor (DA) exchange” (p. 1). This was first observed in the gas-phase water dimer by Saykally and coworkers, who called it “interchange” or “interchange tunneling” [27]. Why change the name? Also, why “HH exchange” instead of Saykally’s “bifurcation tunneling”?

5) “As far as we know, the question of the ratio of DA exchange to other dynamic processes related to H-bonds has not been discussed” (p. 1). See, however, Samala & Agmon, ACS Omega 4, 22581–22590 (2019). In Fig. 3 there the onset of interchange events is at 40 K, while the onset of long range translational motion (“vaporization”) is at 140 K, meaning in the present nomenclature that “diffusion” is much slower than “DA exchange”. This is just **the opposite** of Fig. 7A here, where there are many more diffusion events as compared with DA exchanges. Is this due to the inaccuracies of the present calculations, differences between gas-phase and solution phase behavior, or between DFT/BLYP (here) and MB-pol (there)?

6) “The direct reason for the decrease in the number of DA exchange and diffusion processes at higher temperatures is that n_{HB} decreases with increasing temperature” (p. 5). Again, just the opposite: As these processes are governed by HB cleavage, they must become **faster** as n_{HB} decreases.

7) Simulating a gas-phase dimer at various temperatures should be easy as compared with the 64 water molecule simulation performed here, and then one could compare the “DA exchange” in solution and the gas-phase. In particular, one may determine what is the effect on the DA exchange rate of the additional HBs in which the dimer water molecules participate when embedded in liquid water.

8) MB-pol simulations for neat water (Reddy *et al.*, above) are faster and much more accurate than AIMD, so there is no reason for running AIMD in the present case.