

Dear Prof. Jungwirth,

Because of the depth and impact of the reviewer comments about our recently submitted manuscript, the authors have decided to completely re-run the simulations of SO₂ on water in order to bring the simulation parameters into line with the reviewer suggestions. This major reworking of the simulations and data resulted in major changes to the data presented, manuscript text, results and conclusions. We have put forth great effort to respond to each of the reviewer comments. Please find our enumerated responses below, matching to each numbered point of the original reviewer comments. We believe that with the changes to the work and the newly run simulations, the new manuscript is more accurate and in line with current simulation standards for aqueous systems. We hope you will further consider our manuscript for publication in the journal.

–Eric Shamay

Reviewer: 1

1,2,3. The authors have taken into consideration the entirety of all the reviewer suggestions regarding functional and basis sets, cutoffs, timesteps, and temperature that affect the simulations. The changes to the simulation parameters are reflected in the text, and meet the standards suggested in the reviews. All the simulations have been rerun, data has been re-analyzed, and the results are all presented from the new simulations.

4. The cold system temperature was set to 210K in the resimulated systems. This much larger separation of temperatures is more in line with the reviewer's concerns regarding temperature separation. Furthermore, included with this revised submission are plots of the temperature and the conserved quantity for each timestep for both low and high temperature systems. As is evident, the temperature increases until reaching the setpoint temperature soon after the start of the simulations. The plateau region of the temperature extends for the majority of the simulations. Lastly, it is clear that the separation of temperatures persists for the entire simulation time, confirming that the systems are representing temperatures that are distinct. The authors believe that this is evidence that the parameter set chosen for simulation of these small water systems are sufficient to recreate the expected temperature conditions, even when simulating in the NVE ensemble.

5. The temperature coupling constant was added to the text, and the typo was revised.

6. The text has been updated to reflect the correct equilibration period of 1 ps.

7. Both RDFs converge to 1.0 because of the normalization routine employed in the calculations. This is typical of RDF calculations - normalized to unity - and the authors prefer this normalization as it aids in comparison to the other RDFs published for similar systems (see Baer et al. cited in the text)

8. The inclusion of dispersion corrections were not explored for this simulation study. The goal of the project was to monitor specific bonding behaviors of SO₂ using previously established methods, not as a study of the results from various constraints or changes to simulation parameters. The authors believe that additional discussion on this topic would distract from the narrative presented.

Reviewer: 3

1. Because the re-simulated systems were done using B3LYP functional, the authors believe a benchmark

comparison is no longer necessary. Small cluster studies of SO_2 with several waters have been performed using high-accuracy basis and functionals previously, and we do not set out to reproduce that work here, but rather to build on it. The authors believe that the current work with the new simulation parameters achieves a level of accuracy suggested by the reviewers, but that lengthy discussion of this fact is not requisite in this particular simulation study.

2. After resimulating the systems the resulting relative populations of unbound SO_2 has changed. The more intuitive stronger binding of SO_2 at the cold temperature results from the higher accuracy of the functional and basis sets used in the new simulations. The new results are also more in line with the author’s experimental results from the previous publications cited in the text.

3. Several previous simulation studies have discussed the structure of water under similar simulated conditions. The focus of the work is on the structure of SO_2 and its behavior near a water cluster surface. Thus, the authors have made the conscious decision to avoid lengthy discussion of the surrounding water’s structure.

4. Reference to the Car-Parrinello method has been added to the text.

5. The new systems were simulated with a smaller number of water molecules and are referred to as a small water cluster. The effects of using few water are not discussed in detail as the number of waters used is representative of many small-cluster MD and DFT studies. The authors believe that the number of waters is in line with several previous studies of molecules bound to small water clusters, and further discussion is not warranted as part of the narrative being presented.

6. K-point integration was not used in the integration, as this was not addressed in similar previous studies. Also, the CP2K simulation package does not allow for this type of calculation. The authors do not believe this is detrimental to the accuracy of the calculations and further discussion is not pertinent to this study.

7. In the new simulations, the timestep has been reduced to 0.5 fs. The text has been updated to reflect this.

8. The authors thank the reviewer for pointing out this previous study using graph theoretical techniques (Oktay Sinanoglu J. Am. Chem. Soc., 1975, 97 (9), pp 23092320). That study pertains to synthetic or catalytic pathways of organic systems, but can be generalized to very convoluted and complicated reaction pathways leading to very intricate graphical networks. The systems investigated in that work are much more complicated, and the graphs are designed to convey a great deal more information than in the present text. In our work we wish to investigate only the transitions between different coordination or cyclic-hydrate states, and are not interested in multi-reactant processes. A citation to the work has been added to the text.