Dear Editor:

Enclosed please find the manuscript "Staying Hydrated: The Molecular Journey of Gaseous Sulfur Dioxide to a Water Surface" by Eric S. Shamay and Geraldine L. Richmond, submitted for consideration for publication in *The Journal of Physical Chemistry C.*

The scientific community's understanding of the behavior of simple, inorganic gases at an aqueous interface is currently sparse as such systems have remained largely unexplored. Great advances have been made in studying gases at air-water interfaces over the last few years, however much can still be learned in the study of the binding geometries and specific interactions that occur with the water surface. Computational analysis of molecular dynamics simulations is well suited for the study of narrow interfacial regions due to its ability to address microscopic environments and to probe the origins of specific phenomena that are otherwise impossible through current experimental techniques.

In this study we have shown that sulfur dioxide gas molecules affect the structure and hydrogen bonding of water at the air-liquid interface through adsorption and binding with the water surface. We augment recent computational and experimental sum frequency spectroscopic studies by our group, and strengthen the conclusions of those works while also building a more complete microscopic picture of the interfacial region. The binding behavior of sulfur dioxide to the interfacial water, and the resultant hydrate species are quite complex. We find a specific adsorption pathway for gaseous sulfur dioxide onto a water surface via ab initio molecular dynamics simulations at two environmentally relevant temperatures. Our analysis reveals the bonding patterns of sulfur dioxide, lifetimes, and transitions of the various bonding coordinations, and we take a unique look at cyclically bonded hydrate species that form at the interface. Our work will be of interest to the readership of *The Journal of Physical Chemistry C* because it contributes significantly to our understanding of how the subtle interplay between water and an adjacent gas uniquely alters the interfacial region and molecular geometries, orientations, and hydrate species within the air-liquid interface, a subject that has implications in many important processes such as gas adsorption and transport into aqueous systems.

I am the corresponding author and may be contacted at the above address, by e-mail (richmond@uoregon.edu), telephone (541-346-4635), or fax (541-346-5859). All authors have seen and approved the submission of this manuscript, and we look forward to the results of the review.

Thank you for your consideration.

Sincerely, Geraldine Richmond

Richard M. and Patricia H. Noyes Professor