

How non-additive are OH-Water Interactions?

Christopher Ing¹, Paulo Cabral do Couto² and Daniel M. Chipman²

¹ University of Waterloo, Department of Physics, Waterloo, ON, Canada

² University of Notre Dame, Radiation Laboratory, Notre Dame, IN, USA

The OH radical is known to play an important role as a powerful oxidant in biological and environmental systems. By virtue of its nonselectivity and high reactivity towards organic molecules, mainly through addition to unsaturated bonds or hydrogen abstraction reactions, high concentrations of the OH radical in living systems are known to result in damage to cell structure, including lipids and membranes, proteins and DNA, and ultimately, disease. For the same reason, it plays a key role in atmospheric chemistry, as the primary agent for the photooxidation of a wide range of atmospheric pollutants. As much of this chemistry takes place in bulk water as well as in or at the surface of cloud droplets, aerosols and small water complexes, hydrogen bonding has a significant impact on molecular properties, availability, and reactivity of the OH radical. Consequently, a detailed knowledge of OH-water interactions in such a wide range of hydrogen bonding environments is a fundamental prerequisite for a molecular level understanding of the chemical behavior of the OH radical. A relevant question is how different is OH-water hydrogen bonding from that of the corresponding neutral closed shell species: the water molecule.

The present work reports data for the many-body decomposition of the OH-water interaction energy in $\text{OH}(\text{H}_2\text{O})_{1-7}$ and $\text{H}_2\text{O}(\text{H}_2\text{O})_{1-7}$ clusters, where the many-body decomposition was truncated to the terms that involve the OH radical or the corresponding water molecule, in the same hydrogen bonding environment. Results show that the interaction energy and the magnitude of many-body interactions in single donor-single acceptor coordination patterns are similar for the OH radical and water. However, results for the single donor - double acceptor coordination pattern show a much different behavior: OH-water interactions are highly non additive. These results show that the magnitude of many-body OH-water interactions is strongly dependent on local coordination. Implications for the development of a classical intermolecular potential are discussed.