

Can Multi-Scale Modeling Accurately “Predict” Molecular Properties? An Illustrative Test for the $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ Reaction

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As the power of scientific computing continues to grow, detailed models for complex chemical-transport phenomena play a more significant role in the design process of advanced energy conversion devices (e.g. Ref. 1). As a result, there have been substantial research efforts devoted to the construction and further development of detailed chemical models for conventional and alternative fuels. However, given the enormity of temperature/pressure/bath-gas conditions of potential interest, kinetic models are often used at conditions far outside their validation set, where deficiencies in model performance are observed relatively often. A multi-scale approach to combustion model development has been recently proposed,² in which kinetic theory is directly incorporated as a means to ensure a physically meaningful kinetic model and provide reliable extrapolation to engine-relevant conditions. The modeling technique offers complete integration of information from a wide variety of sources – rate constant measurements, global combustion experiments, and *ab initio* theoretical kinetics calculations. The resulting kinetic model consists of a set of theoretical kinetics parameters (with constrained uncertainties), which can be related through kinetics calculations to rate constants (with propagated uncertainties), which can be related through physical models to combustion behavior (with propagated uncertainties). The validity of the approach, and the reliability of extrapolation to new conditions, relies on its ability to properly extract theoretical kinetics parameters from complex information.

In the present work, we evaluate the accuracy of the extracted molecular properties through comparison with high-level *ab initio* electronic structure calculations for the $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$ reaction. In the multi-scale modeling, molecular properties for the relevant reactions in H_2O_2 thermal decomposition are optimized against moderate-level *ab initio* electronic structure calculations using standard methods, rate constant measurements, and absorption measurements in shock-heated $\text{H}_2\text{O}_2/\text{Ar}$ mixtures. In the high-level *ab initio* electronic structure calculations, geometries were optimized at the CCSD(T)/cc-pVQZ level and corrections for higher order correlation, core-valence correlation, relativistic, spin-orbit, and diagonal Born-Oppenheimer effects were incorporated. Rovibrational properties of the ground and first excited state were also studied with multi-reference electronic structure methods. Preliminary comparisons between molecular properties from high-level theory and the confidence intervals from multi-scale modeling are promising. Implications for the underlying kinetic and physical models as well as applications to larger systems (where such high-level theory is intractable) are discussed.

References

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