A PROTOCOL FOR HIGH-ACCURACY THEORETICAL THERMOCHEMISTRY

BRADLEY WELCH, RICHARD DAWES, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*.

Theoretical studies of spectroscopy and reaction dynamics including the necessary development of potential energy surfaces rely on accurate thermochemical information. The Active Thermochemical Tables (ATcT) approach by Ruscic[1] incorporates data for a large number of chemical species from a variety of sources (both experimental and theoretical) and derives a self-consistent network capable of making extremely accurate estimates of quantities such as temperature dependent enthalpies of formation. The network provides rigorous uncertainties, and since the values don't rely on a single measurement or calculation, the provenance of each quantity is also obtained. To expand and improve the network it is desirable to have a reliable protocol such as the HEAT approach[2] for calculating accurate theoretical data.

Here we present and benchmark an approach based on explicitly-correlated coupled-cluster theory and vibrational perturbation theory (VPT2). Methyldioxy and Methyl Hydroperoxide are important and well-characterized species in combustion processes and begin the family of (ethyl-, propyl-based, etc) similar compounds (much less is known about the larger members). Accurate anharmonic frequencies are essential to accurately describe even the 0 K enthalpies of formation, but are especially important for finite temperature studies. Here we benchmark the spectroscopic and thermochemical accuracy of the approach, comparing with available data for the smallest systems, and comment on the outlook for larger systems that are less well-known and characterized.

[1]B. Ruscic, Active Thermochemical Tables (ATcT) values based on ver. 1.118 of the Thermochemical Network (2015); available at ATcT.anl.gov

[2]A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton. JCP 121, (2004): 11599.