# Correlation, Anharmonic Treatments, and Basis Effects in comparing Computational IR Spectroscopy to Experimental Databases

Dr. Robert Molt Jr., Dr. Douglas Burns

We present a benchmark on the accuracy of computational IR spectroscopy results compared to experimental databases. We consider ~40 molecules with ~250 peaks in two distinct experimental databases (PNNL and NIST). We compare the relative merits in increasing sophistication of the correlation treatment (MBPT(2) to LCCD to CCSD to CCSD(T)) with harmonic oscillators vs. more crude KS-DFT treatments utilizing Baroni-style anharmonic perturbation treatments. After making minor modifications in the vibrational perturbation theory calculations to reject clearly divergent frequencies/intensities, KS-DFT with anharmonic perturbation theory can yield frequencies within $1.3 \pm 1.0\%$ ($\mu \pm 2\sigma$). This empirically divergence-vetted algorithm has considerably greater accuracy than either the standard KS-DFT perturbation anharmonic treatment or a CCSD(T) harmonic treatment. Regrettably, the intensities can be off by factors of two to four. We also examine the use of VSCF/MP2 anharmonic treatments, which have accuracy in frequency estimation of $1.1 \pm 0.5\%$ ($\mu \pm 2\sigma$); this stark reduction in the standard deviation ensures greater confidence in its utility. At this point, basis set effects are considered for VSCF/MP2 methods, as the increased accuracy delivered makes basis set effects no longer small compared to the errors intrinsic to the Hamiltonian/anharmonic treatments.