

## MODEL CHEMISTRY RECOMMENDATIONS FOR HARMONIC FREQUENCY CALCULATIONS: A BENCHMARK STUDY

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While harmonic frequency calculations are widespread across chemistry<sup>1</sup>, sparse benchmarking is available to guide users on appropriate model chemistry recommendations (i.e., a method and basis set pair). Instead, studies exploring the dependence of harmonic frequencies on model chemistry have focused on producing multiplicative scaling factors to match the calculated harmonic frequencies to experimental fundamental frequencies<sup>2</sup>.

Along with the scaling factor, it is often common to calculate the root-mean-squared error (RMSE) between the scaled harmonic and experimental fundamental frequencies, and use this value as metric of model chemistry performance. We recently compiled a set of over 1,400 scaling factors<sup>3</sup> spanning hundreds of methods and basis sets, thus allowing approximate comparisons between different model chemistries<sup>2</sup>. However, initial recommendations from this analysis can only be preliminary, as the differences in the benchmark databases used means that the RMSE metrics cannot be fairly compared across different publications.

Here, we introduce a new benchmark database for vibrational frequency calculations (VIBFREQ1292) containing 1,292 experimental fundamental frequencies and CCSD(T)-F12c/cc-pVDZ-F12 harmonic frequencies for 141 molecules. Assuming that our ab initio calculations reduce model chemistry error to a minimum, and noting the importance of using frequency-range-specific scaling factors, our analysis shows that the intrinsic error between the scaled harmonic and experimental frequencies usually lies below  $15\text{ cm}^{-1}$ .

Thus, using VIBFREQ1292 as our reference set, we have rigorously assessed the performance of over 300 general-purpose model chemistry choices for harmonic frequency calculations. Model chemistry recommendations, as well as expected computational errors will be presented in this talk.

1. Scott, A.; Radon, L., *J. Phys. Chem.* 1996, 41, 16502-16513.
2. Zapata Trujillo, J. C.; McKemmish, L. K., *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2021, e1584.
3. Zapata Trujillo, J. C.; McKemmish, L. K., *Harvard Dataverse*, V1, 2021, <https://doi.org/10.7910/DVN/SQK6YU>.