

Coupled Cluster, Density Functional Theory or Experiment? A Benchmark Study of Diatomic Molecules Containing Transition Metals

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We present Coupled Cluster (CC) and Kohn–Sham Density Functional Theory (DFT) calculations of dissociation energies (D_e), equilibrium bond distances (R_e), and harmonic vibrational constants (ω_e) for 60 diatomic molecules containing 3d, 4d, and 5d transition metals and compare to experimental data. Ten density functionals were employed: M06, M06-2X, M06-L, PBE, PBE0, BP86, TPSS, B3LYP, B97, and BLYP. Single reference CC calculations were made with single and double excitations with a perturbative estimate for connected triples, CCSD(T), with valence only (frozen-core) and core-valence correlation. The convergence with respect to the one-particle basis sets and scalar relativistic effects were considered for DFT and CC calculations. For a subset of 25 molecules, we also performed a multireference analogue of CCSD(T), namely, the internally-contracted multireference CCSD(T) [icMRCCSD(T)] method. We found that CCSD(T) can provide accurate results, if used with a sufficiently large basis sets. Considering all 60 molecules, the best performing level of theory, using the experimental data as reference, is CCSD(T)(CV)/CBS+ Δ DK with mean absolute deviations (MAD) of 3.6 kcal mol⁻¹ for D_e , 0.009 Å for R_e , and 20 cm⁻¹ for ω_e . For D_e , the best performing functional is B97/aVQZ+ Δ DK with MAD of 3.9 kcal mol⁻¹, for R_e and ω_e , TPSS/aVQZ performs best with MADs of 0.011 Å and 23 cm⁻¹. The icMRCCSD(T) calculations show that the inclusion of a multireference treatment on top of the CCSD(T) calculations leads to corrections that range from 0.2 kcal mol⁻¹ to 18.1 kcal mol⁻¹. Even for these very expensive calculations, for some molecules, there are still large deviations between the dissociation energies computed with CC theory and the experimental data, which indicate that some experimental measurements may be inaccurate.