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Is Near-“Spectroscopic Accuracy” Possible for Heavy Atoms and Coupled Cluster Theory? An Investigation of the First Ionization Potentials of the Atoms Ga – Kr

Recent developments in *ab initio* coupled cluster theory and correlation energy consistent basis sets have ushered in an era of unprecedented accuracy when studying the spectroscopy and thermodynamics of molecules containing main group elements. These same developments have recently seen application to heavier inorganic or transition metal-containing species. The present work benchmarks conventional single reference coupled cluster theory (up to full configuration interaction for valence electron correlation and CCSDTQP for core-valence correlation) and explicitly correlated coupled cluster methods [CCSD(T)-F12] for the atomic ionization potentials of the six 4*p* elements (Ga – Kr), a property with experimental error bars no greater than a few cm^-1. When second-order spin orbit coupling effects are included, it is shown that accuracy approaching the experimental uncertainties (so-called “spectroscopic accuracy” where the *average* errors are within 1.0 cm^-1) is nearly obtained.