COMPOSITE APPROACHES FOR AB INITIO SPECTROSCOPY: THE CCN, CCSb, AND HNNO RADICALS

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Over the last several years, composite methods have found great utility in the area of accurate ab initio thermochemistry. Utilizing highly correlated wavefunction-based methods such as CCSD(T) in conjunction with basis set extrapolations and corrections due to relativistic effects, core electron correlation, etc., accuracies approaching 1 kJ/mol have been possible in some cases. In the present work a similar methodology, including the use of explicitly correlated F12 methods and the inclusion of spin-orbit coupling, has been employed for the near-equilibrium potential energy surfaces of the $^2\Pi$ ground states of CCN and CCSb. A detailed analysis of the anharmonic vibrational spectra calculated from these surfaces and the Renner-Teller effect in these molecules will be discussed. The vibrational spectrum of the HNNO radical is found to be a challenging case for ab initio methods due to strong higher level electron correlation effects.[a]

[a] K. A. Peterson and J. S. Francisco *J. Chem. Phys.* **134**, 084308 (2011).