# SPECTROSCOPIC ACCURACY IN QUANTUM CHEMISTRY: A BENCHMARK STUDY ON $Na_3$

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Modern techniques of quantum chemistry allow the prediction of molecular properties to good accuracy, provided the systems are small and their electronic structure is not too complex. For most users of common program packages, 'chemical' accuracy in the order of a few kJ/mol for relative energies between different geometries is sufficient. The demands of molecular spectroscopists are typically much more stringent, and often include a detailed topographical survey of multi-dimensional potential energy surfaces with an accuracy in the range of wavenumbers. In a benchmark study of current predictive capabilities we pick the slightly sophisticated, but conceptually simple and well studied case of the $Na_3$ ground state, and present a thorough investigation of the interplay between Jahn-Teller-, spin-orbit-, rovibrational- and hyperfine-interactions based only on ab initio calculations. The necessary parameters for the effective Hamiltonian are derived from the potential energy surface of the $1^2E'$ ground state and from spin density evaluations at selected geometries, without any fitting adjustments to experimental data. We compare our results to highly resolved microwave spectra.[a]

[a] L. H. Coudert, W. E. Ernst and O. Golonzka, J. Chem. Phys. 117, 7102–7116 (2002)