AB INITIO CALCULATIONS OF EXCITED VIBRATIONAL STATES FROM QUARTIC POTENTIAL ENERGY SURFACES

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Spectroscopy of excited vibrational states is complicated by the existence of anharmonicities and resonances. The purpose of this project is to identify these effects theoretically in order to assist in the assignment of spectra. High-accuracy computations of quartic molecular potential energy surfaces (PES's) were completed for H_2O, HFCO, $SCCl_2$, HCO, and their deuterated analogs. Harmonic frequencies (ω_i), anharmonicities (x_{ij}), and resonance constants (k) were extracted from the PES, and excited vibrational levels were predicted from the spectroscopic constants. The theoretical values will be assessed by comparing predicted to observed vibrational energy levels and by comparing predicted to fitted spectroscopic constants. Trade-offs between basis set size and accuracy will be discussed.