EQUILIBRIUM MOLECULAR STRUCTURES : HOW GOOD ARE COMPOSITE SCHEMES?

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Molecular structures help determine spectroscopic parameters that allow molecular identification and reveal qualitative information about bonding, energetics and other things. Today, the most satisfactory method for determining very high-accuracy structures is a mixed experimental-theoretical approach that uses ground state rotational constant data from microwave and/or high-res vibrational spectroscopy and vibrational corrections obtained from quantum-chemical calculations (r_e^{SE}). Here we consider two different ab initio composite schemes for obtaining equilibrium structures (energy scheme vs geometry scheme) and compare them to the semi-experimental equilibrium structure. The comparison is performed for a test set of ten molecules which includes ome diatomics, linear triatomics and a few polyatomics. The ab initio calculations were performed using three levels of composite chemical recipes. The results showed that as the overall rigor of calculation is increased, the semi-experimental and the ab initio numbers agree with each other within the desirable level of accuracy (< 0.0003 $\mathring{A}$) for all molecules in the test set. The composite recipe based on correcting the PES (energy scheme) and the one dependent on correcting the geometry directly (geometry scheme) also show excellent agreement with each other.