A NEW STANDARD OF AGREEMENT OF SEMI-EXPERIMENTAL EQUILIBRIUM (r_e^{SE}) AND COMPUTED EQUILIBRIUM (r_e) STRUCTURES

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Recently, the CCSD(T) equilibrium (r_e) structures and the Semi-Experimental Equilibrium (r_e^{SE}) structures of several small molecules (hydrazoic acid, benzene, pyridazine, pyrimidine, thiophene, thiazole, etc.) demonstrated a new standard of agreement between theory and experiment (typically 0.001 Å for bond distances and 0.04° for bond angles). In each of these examples, all or nearly all of the computed parameters fell within the 2σ statistical uncertainties of their corresponding experimental values. This agreement is typically possible by obtaining an r_e^{SE} structure based upon many isotopologues beyond single-isotopic substitution from many hundreds or thousands of transitions for each isotopologue. The resulting rotational constants are corrected using CCSD(T) calculations for the impact of the vibration-rotation interaction and for the electron-mass distribution. Additionally, we have found that such close agreement requires an r_e structure calculated at the CCSD(T)/cc-pCV5Z level further corrected to account for an incomplete basis set, untreated correlation, and relativistic effects. This talk will feature examples to demonstrate the agreement possible, current best practices, and the tools used to analyze these structures. Outstanding questions and future investigations will be discussed.