A benchmark study of molecular structure by gas-phase electron diffraction (GED) and microwave spectroscopy (MW) methods and coupled-cluster computations

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Molecular structures determined by MW (r_0) and GED (r_g) methods have different physical meaning. For correct comparison of the experimental data for maleic anhydride [1] (Fig.), uracil [2] and other molecules, they have been converted to an equilibrium structures taking into account rovibrational corrections calculated with high-level *ab initio* anharmonic force constants. Accurately determined semi-experimental equilibrium structures (r_e^{se}) have been used to check the quality of *ab initio* calculations up to CCSD(T) level. The coupled cluster calculations for middle-size molecules have been carried out in the "frozen core" or "all electron correlated" approximation using triple zeta basis sets. Extrapolation of the results to the higher basis sets or to complete basis set has been performed at the MP2 level. Remarkable agreement between the semi-experimental equilibrium structure r_e^{se} and the "best *ab initio*" one (within experimental uncertainties) points to high accuracy of both experiment and theory.

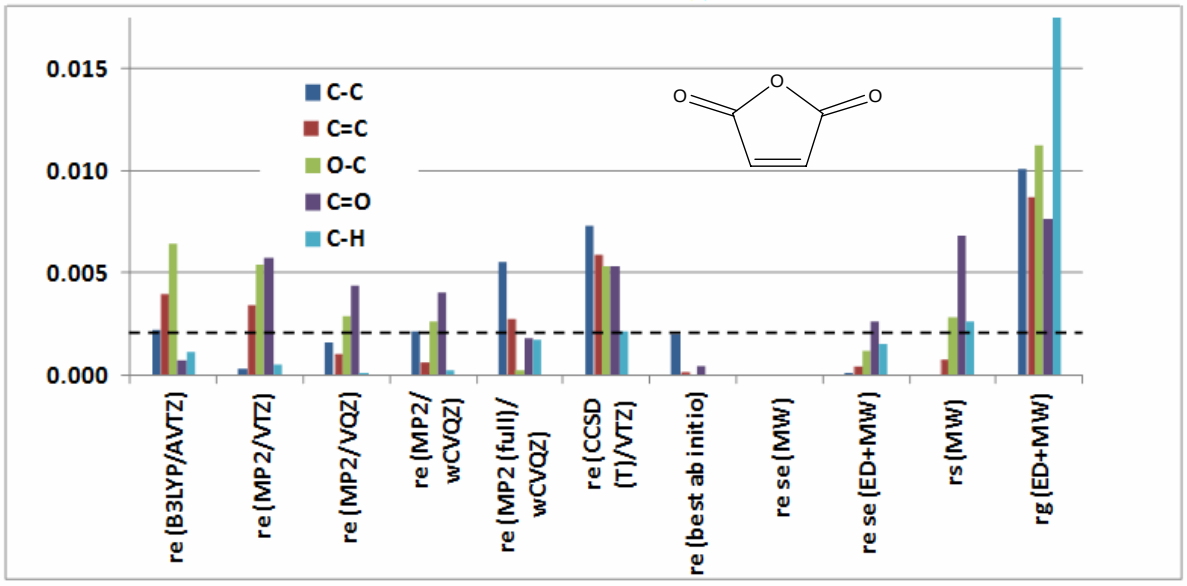

Fig.: Histogram of absolute deviations of theoretical and experimental bond lengths from r_e^{se}(MW) values (in Å) for maleic anhydride molecule.

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[1] N. Vogt, J. Demaison, H. D. Rudolph, *Struct. Chem.* **2011**, *22*, 337.
[2] N. Vogt, L.S. Khaikin, O. E. Grikina, A. N. Rykov, *J. Mol. Struct.* **2013**, in press.