MULTIREFERENCE BOND LENGTHS OF SMALL MOLECULES: COMPARISON TO SINGLE-REFERENCE METHODS AND EXPERIMENT

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Using multi-reference methods and basis set extrapolations, we calculated the equilibrium bond lengths of 20 small molecules used in previous systematic studies of bond lengths computed using single-reference methods. We compare our computed bond lengths with those from the single-reference methods and with empirical equilibrium bond lengths. We find that the valence correlation from generalized valence bond MCSCF calculations improves the accuracy of the bond lengths relative to SCF. The MCSCF bonds tend to be too long compared to experiment, while the SCF bonds tend to be too short. Adding correlation in the form of singles and doubles CI to the MCSCF wave function produces bond lengths that agree well with empirically-derived and CCSD(T) bond lengths.