Predictive Electronic and Vibrational Many-Body Methods for Combustion Chemistry

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Electronic coupled-cluster (CC) theory and vibrational self-consistent field (VSCF) or configuration-interaction (VCI) theory were applied in a systematic way to accurately predict the anharmonic vibrational frequencies of molecules that were important in hydrocarbon combustion processes. CC with singles and doubles (CCSD), CCSD with second-order perturbation correction in the space of triples [CCSD(2)$_T$], and in the space of triples and quadruples [CCSD(2)$_{TQ}$] were combined with a variety of correlation-consistent basis sets to achieve the complete-correlation, complete-basis-set limit for the potential energy surfaces (PES). Two different representations of PES were used: fourth-order Taylor expansion and numerical energy values on a quadrature grid, both including up to three-mode coupling. Vibrational anharmonicity was taken into account by VSCF and VCI to any desired level as the latter is convergent to the exact result. The predicted and experimental (given in parenthesis) frequencies of HCN were 1506 (1501), 1561 (1565), and 2681 (2684) cm^{-1} and those of HCO were 1081 (1081), 1855 (1868), and 2421 (2434) cm^{-1}. This work was supported by the U.S. Department of Energy (Grant No. DE-FG02-04ER15621).