Vibrational Zero-Point Energies and Their Uncertainties

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Molecular energetics is increasingly derived from ab initio electronic structure calculations instead of experimental measurements. For quantitative applications, and for incorporation into databases, theoretical results require associated uncertainties, i.e., error-bars. In collaboration with Dr. Raghu N. Kacker, we are developing procedures for determining the uncertainties associated with theoretical predictions. Such work is only possible when benchmark experimental values are available for representative systems. In the present paper we are evaluating experimentally-derived zero-point energies in order to produce such a collection of benchmark values, along with their associated uncertainties. A number of issues have arisen, ranging from spectroscopic details for individual molecules to the definition of "experimental zero-point energy."