Anharmonic Vibrational Spectroscopy Calculations for Large Molecular Systems: Methods, Algorithms and Applications

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Abstract

Recent results on anharmonic vibrational spectroscopy calculations for large molecules are presented. Developments for new Vibrational Self-Consistent Field (VSCF) are discussed, with focus on: (1) The scaling of correlated VSCF algorithms with N, the number of vibrational modes; (2) the role of vibrational degeneracy effects in the spectra; and (3) applications of the algorithms for a range of experimental systems, as a tool for determination of molecular structure and of other properties. Successful applications to systems of biological relevance (peptides, sugars) and for atmospheric species (large hydrated ions) are mentioned.

As a detailed application, the Raman spectrum of the CH stretching band in the hydrocarbon dodecane (C_{10} H_{22}) is discussed. Comparison with experiment is made, and conclusions on the roles of anharmonicity and of vibrational degeneracy are presented.

Directions for future progress are suggested.