

# Anharmonic Vibrational Calculations for Polymers and a New Representation of Potential Energy Surfaces

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Anharmonic vibrational frequency calculations of polyacetylene and polyethylene are presented. The Hartree–Fock and second-order Møller–Plesset perturbation (MP2) theories with 6-31G\* basis set were used for the potential energy surface (PES) calculations of the polymers. The PESs were represented with either numerical energy values on a quadrature grid, or a cheaper alternative, a quartic force field (QFF), both including up to a two-mode coupling. Vibrational anharmonicity was taken into account by vibrational self-consistent field (VSCF) and second order perturbation (VMP2) theories and the mean absolute deviations (from the observed frequencies) of  $\sim 40 \text{ cm}^{-1}$  were obtained with the latter method.

A new hybrid representation of QFF and grid PESs has been proposed and shown to yield similar results to the expensive grid based method for small molecules where a direct comparison was possible. This representation was especially advantageous for the modes that have Morse-like potential energy curves which were poorly represented with QFF method.

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