Abstract Submitted
for the MAR10 Meeting of
The American Physical Society

***Ab initio* study of anharmonic vibrations for polymers** MURAT KECELI, SO HIRATA, University of Florida, KIYOSHI YAGI, University of Yamanashi, Japan — Energies of optically active $k = 0$ phonons in extended systems of one-dimensional periodicity (polyethylene) are computed by taking account of the anharmonicity in the potential energy surfaces (PES) and the resulting phonon-phonon couplings explicitly. The electronic part of the calculations is based on Gaussian-basis-set crystalline orbital theory at the coupled-cluster singles and doubles, second-order Møller–Plesset perturbation (MP2), and Hartree–Fock levels, providing one-, two-, and three-dimensional slices of the PES, respectively, which are in turn expanded in the fourth-order Taylor series of normal coordinates. For the vibrational part, we employ the vibrational self-consistent-field, vibrational MP2 and vibrational truncated configuration-interaction (VCI) methods within the Γ approximation that amounts to including only $k = 0$ phonons. It is shown that inclusion of both electron correlation and anharmonicity is essential in achieving good agreement between computed and observed frequencies of optical phonons in polyethylene. The VCI calculations also identify quantitatively the frequency separation and intensity ratio of the Fermi doublets in the vibrational spectrum of polyethylene.

Murat Keceli
University of Florida

Date submitted: 20 Nov 2009 Electronic form version 1.4