



Quantum mechanical calculations of electronic-conformational defects in phenylene vinylene oligomers

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We investigate the quasiparticle conformational defects (polarons, bipolarons and excitons) in the phenylene vinylene oligomers (PVOs). The most probable conformations are determined by means of the minimization of the total Hartree-Fock (HF) energy calculated at the 3-21G level. The Hartree-Fock calculations of the excited states are followed by the CI-Singles calculation. On the basis of these results the infra-red (IR) vibrational transitions are calculated. The theoretical transitions are compared with the IR vibrational spectrum of the poly(phenylene vinylene) (PPV). © 1998 Elsevier Science Ltd. All rights reserved

Introduction

The injection of charges into conjugated polymers involves several processes not appearing in inorganic semiconductors. The electron or hole added to a polymer chain can cause significant changes of the chain conformation. The alternation of the single and double bonds is reversed in the region of the added charge. Consequently, a new chain conformation occurs.

In the polymers containing phenylene rings in the main chain (including PPV), the conformations of the ground states and the conformations with the reversed single and double bonds are energetically non-equivalent. The energetically higher *quinoidal* conformation appears only in the region of the defect and is surrounded by the unchanged *aromatic* conformation of the ground state. This type of the quasiparticle defect is called *polaron*.¹

Two polarons can react by creating a singlet/triplet exciton or a bipolaron in accordance with the mutual orientations of their spins and their signs of the charges.¹

In the earlier theoretical works, conformational and electronic properties were investigated above all by means of empirical and semiempirical methods. A dynamical model based on the valence force field calculations was built to assign the observed Raman

(excitons) and open shell charged systems (polarons) may produce unreliable results.

For this reason, we investigate the above mentioned conformational defects (polarons, bipolarons and excitons) in the PVOs by means of *ab initio* methods. The molecules are assumed to be isolated. The most probable conformations are determined by means of the minimization of the total HF energy calculated at the 3-21G level. The HF calculations of the excited states are followed by the CI-Singles calculation. All conformational degrees of freedom (atomic coordinates) are optimized. The detailed description of the conformations of the PVOs consisting of up to 12 repeating units is presented in our previous work.⁵ We found that the extent of the polaron defect is about 4 repeating units and the extents of the exciton and bipolaron defects are about 6 repeating units.

In this paper, we investigate the IR vibrational spectra of the PVOs containing the above mentioned conformational defects. The theoretical results are compared with the experimental IR spectrum of PPV.

Infra-red vibrational spectra