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

P Toman, a L Skála* and J Pospíšil, b * Charles University, Faculty of Mathematics and Physics, Department of
Chemical Physics and Optics, Ke Karlovu 3, 121 16 Praha 2, Czech Republic; b* Charles University, Faculty of
Mathematics and Physics, Department of Polymer Physics, V Holešovičkách 2, 180 00 Praha 8, Czech Republic

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 sev-
eral processes not appearing in inorganic semiconductors. The
electron or hole added to a polymer chain can cause significant
changes of the chain conformation. The alteration 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.2

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 pro-
duce unreliable results.

For this reason, we investigate the above mentioned con-
formational 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.3
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