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Theoretical investigation of the geometric and optical properties of neutral and charged oligophenylenes

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We have investigated the geometry and the nature of optically allowed transitions in neutral and charged phenylene-based oligomers by means of Hartree-Fock calculations. Geometry optimizations are performed using the semiempirical Austin Model 1 (AM1) method for oligomers containing from two ($2P$) to twelve ($12P$) benzene rings. The transition energies and related intensities of the optical-absorption spectra are calculated by means of the intermediate neglect of differential overlap Hamiltonian that is combined with a single configuration interaction technique in order to include electron correlation effects in the description of the excited states. The calculations show that two subgap absorption features appear in short oligomers carrying a single charge (polaron), whereas a single intense peak is observed in the presence of two charges (bipolaron). These results are consistent with a wide range of experimental and theoretical data obtained for various conjugated oligomers. Interestingly, the appearance of a second subgap feature is predicted in the spectra of long doubly oxidized chains as well as for chains supporting interacting bipolarons.
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I. INTRODUCTION

In recent years, the interest in organic conjugated materials has been steadily growing due to the wide range of possible applications, such as light-emitting diodes (LED's),[1] light-emitting electrochemical cells (LEC's),[2] or photodiodes.[3] Other technological applications such as organic transistors based on oligothiophenes have also been achieved.[4] Phenylene-based materials, such as poly(*p*-phenylene) (PPP), are widely used in light-emitting devices due to their high quantum efficiencies[5] and luminescence in the blue spectral range,[6] which allows for the fabrication of red-green-blue (RGB) full color displays via color conversion techniques.[7] The chemical or electrochemical doping of organic conjugated materials is also of high interest since (i) the physics of such processes, yielding localized charged distortions of the polymer backbone and high electrical conductivities,[8] is markedly different from that in inorganic semiconductors; and (ii) doping is of immediate importance for applications such as LEC's and electrochromic windows.

The study of *conjugated oligomers* is especially attractive since finite-size systems can be obtained with high purity and a well-defined chemical structure and conjugation length. The oligomer approach is thus convenient to investigate the fundamental electronic properties and nature of the excited states in neutral and doped conjugated materials.[9] Moreover, oligomers with a large number of repeat units often display properties very similar to those observed in the parent polymers, because limited conjugation lengths generally prevail in polymer samples as a result of the synthesis conditions.[9]

The main goal of the present work is to shed light on the modifications of the geometric and optical properties of PPP chains upon doping. To do so, we have considered phenylene-based oligomers and performed Hartree-Fock calculations coupled to a configuration-interaction (CI) technique[10] for the description of the excited states, in order to ensure an adequate treatment of the electron correlation effects. The calculated optical transitions of neutral and doped molecules compare very well to experimental data. The results show that several absorption features can be well characterized by one-electron pictures whereas others require the consideration of correlation effects that are lacking in standard band-structure techniques. The choice of isolated systems in our study is motivated by the fact that recent experimental results[11,12] have shown that the electronic structure of molecular crystals built up from conjugated oligomers is primarily based on the intrinsic properties of the molecular building blocks. This is further supported by the

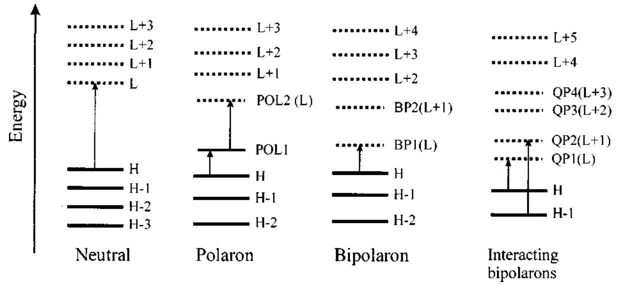

FIG. 1. Schematic diagram of the one-electron structure of neutral and singly, doubly, and quadruply positively charged oligophenylenes; bold lines represent singly or doubly occupied levels while the dashed lines refer to unoccupied orbitals. The lowest optical transitions provided within a single-particle representation are depicted with arrows. *H* and *L* denote the highest doubly occupied and lowest unoccupied molecular orbitals, respectively.

very good agreement between the calculated momentum-dependent excitation spectra of isolated oligomeric and polymeric *p*-phenylene chains and experimental data for solid-state samples.[13] We stress, however, that an explicit account of interchain interaction processes is required to allow for a detailed description of the absorption and luminescence characteristics of ordered materials.[14]

Important aspects concerning the properties of doped organic materials are the number and nature of subgap absorption peaks appearing upon the addition or removal of π electrons as well as the influence of geometry relaxation effects on the electronic structure of the chains.[15] A detailed knowledge of such properties is very helpful to isolate the optical signatures of charge carriers created in various processes initiated by light or redox agents. Calculations performed on short thiophene and phenylenevinylene oligomers[16,17] show the appearance of *two* strong subgap absorption features following the formation of polarons (radical ions in chemical terminology) and only a *single* intense maximum in bipolarons (di-ions). Interestingly, a second absorption feature is predicted for long, doubly charged chains and in systems in which interaction between bipolarons takes place along the backbone. A schematic diagram of the relative positions of the frontier levels, their evolution upon doping, and the nature of the most intense optical transitions provided by a single-particle representation are shown in Fig. 1. These features will be discussed in detail throughout the paper.

II. THEORETICAL METHODOLOGY

We have investigated *p*-phenylene oligomers containing from two to twelve repeat units (hereafter denoted *nP*, with *n* corresponding to the number of rings). The study of oligomers with a relatively large number of monomer units allows us to describe the actual extent of polarons and bipolarons without interferences from chain-end effects and also to deal with conjugation lengths close to those encountered in actual conjugated polymers.

The geometry of the neutral and charged oligomers is optimized with the semiempirical Hartree-Fock Austin model 1 (AM1) method, which provides good estimates of geometries and heats of formation for organic molecules in their ground state.[18] The AM1 approach also yields a reasonable description of torsion potential-energy curves when compared to those obtained by sophisticated *ab initio* calculations.[19,20] In the case of charged systems, the geometry optimizations are performed on isolated molecules, thus neglecting the possible effects of counterions whose impact on the geometry is expected to be weaker in solution than in the solid state. The effect of counterions on the structure of phenylene-based materials has been investigated in detail, for instance, in Refs. 21 and 22.

We have considered two oligomer conformations: (i) fully optimized molecules, in which a significant deviation from planarity is calculated (in good agreement with previous *ab initio* calculations performed on biphenyl[23] and terphenyl[22]) and (ii) planar conformations, for which the dihedral angles are set to zero and only the bond angles and bond lengths are optimized. The first situation corresponds to molecules in the gas phase and in solution, whereas a quasi-planar conformation is expected in the solid state as a result of packing effects.[24] The twisted molecules can actually display various conformations ranging from a chiral structure with all torsion angles having the same sign, to an alternating structure where the sign of the torsion angle changes when going from one ring to the next (so that every other ring is in the same plane). These conformations correspond to local minima in energy and show weak fluctuations in their other main geometric parameters. In the following, the results obtained with an alternating conformation are discussed. The neutral and doubly charged molecules are treated within the restricted Hartree-Fock formalism (RHF), whereas for the singly charged species a restricted open-shell Hartree-Fock (ROHF) approach is chosen. It is our experience that the latter better reproduces the localized nature of the geometry relaxations around the charge carriers than an unrestricted Hartree-Fock formalism (UHF).[25]

The transition energies and optical oscillator strengths are calculated on the basis of the semiempirical Hartree-Fock Intermediate neglect of differential overlap (INDO) method,[26] as parametrized by Zerner and co-workers,[27] with the Coulomb repulsion terms expressed via the Mataga-Nishimoto potential.[28] The electron correlation effects are included via a single configuration-interaction technique (SCI),[10] in which the excited states are described by a linear combination of Slater determinants generated by promoting one electron from an occupied to an unoccupied level. This INDO/SCI approach allows us to characterize the importance of correlation effects in various one-photon allowed excited states and is parametrized to reproduce the experimental linear absorption spectra of neutral organic molecules. If an excited state is dominated by a single Slater determinant, we can conclude that theoretical approaches based on a one-electron picture can provide a suitable description of the transition; in contrast, if there are several strongly interacting one-electron excitations with similar energies and the same symmetry, this gives rise to highly correlated states. In this context, we emphasize that the actual weights of the different configurations are to a certain extent influenced by the chosen parametrization. However, this does not prevent assessing qualitatively the single-particle versus highly correlated nature of the excited states from the CI expansion.

In order to maintain size consistency among the various systems (i.e., to keep a consistent level of correlation taken into account in our calculations independent of chain length), we have scaled the CI-active space according to the size of the molecules. For example, the description of the excited-state wave function of $2P$ (biphenyl) involves excitations from the 12 highest occupied to the 12 lowest unoccupied molecular orbitals, whereas for $10P$ and $12P$ we have included the 60 highest occupied and 60 lowest unoccupied levels.

In the case of charged systems, we stress that the INDO/SCI-simulated spectra presented here have been calculated for oxidized molecules. We are thus dealing with *p*-type doping processes associated with withdrawal of π electrons. The calculated optical spectra of positively and negatively charged PPP oligomers would actually be very similar if a full configuration-interaction (CI) (Ref. 29) calculation could be performed. However, within the SCI formalism, the final results critically depend on the nature of the one-electron structure provided by the Hartree-Fock self-consistent-field calculations used as an input to the CI process. Our experience is that the most reliable one-electron structure to be used as a starting point within the INDO/SCI approach is the one in which the defect levels coming from the valence band (i.e., the highest occupied molecular orbitals) can be treated as occupied levels whereas the defect levels emerging from the conduction band can be treated as unoccupied levels. Such a situation is not encountered in singly and doubly *n*-doped species, since in those cases the molecular orbitals originating from the conduction band and becoming the highest polaronic/bipolaronic levels are occupied. Artifacts are then experienced in the interaction of configurations. In contrast, calculations performed on positively charged molecules supporting a polaron do not suffer from such deficiencies; however, a reduced accuracy of the theoretical results has also to be expected with positive bipolarons for absorption features for which the lowest (empty) bipolaron level is involved in the CI expansion. Finally, we note that the reduction in the diffusive character of the electronic cloud in positively charged systems is *a priori* best adapted to a semi-empirical approach based on a minimal basis set. Despite the fact that calculations performed on negatively charged species suffer from several disadvantages, it is interesting to note that such calculations have yielded results which in most cases are in good qualitative agreement with those obtained for the positively charged species.

In order to get a better insight into the significance of correlation effects, we have compared the results obtained via the INDO/SCI approach to those afforded by valence effective Hamiltonian (VEH) calculations,[30] which are known to provide a reliable description of the one-electron structure of conjugated materials (band gap, ionization potential, and electron affinity). The VEH technique does not deal explicitly with electron-electron correlation effects and is parametrized to reproduce the energies of the occupied levels provided by *ab initio* calculations with molecular orbitals expanded in a double-zeta basis set.[30]

III. GEOMETRIC STRUCTURE

In neutral oligophenylenes, a strong aromatic structure is observed within the phenylene rings in both planar and twisted conformations, the latter corresponding to the global minimum in energy. The AM1 optimized inter-ring C-C bonds range between 1.461 and 1.464 Å (which is about 0.04 Å shorter than experimental results[24,31]), while the intra-ring bonds are calculated to be between 1.391 and 1.406 Å. The C-C bond lengths in the inner repeat units remain unchanged when increasing the number of benzene rings. The AM1-optimized geometry in the trimer $(3P)$ displayed in Fig. 2 is therefore representative of the whole series of oligophenylenes. The calculations do not show significant differences in bond lengths between the planar conformation and the twisted geometry. The bond angles between the *para* carbon atoms and their two intraring neighbors are estimated to 117° (instead of 120° for unsubstituted rings). The optimal torsion angle between rings is calculated to be about 40°. This is consistent with the results of both *ab initio* calculations[22,23,32] and x-ray-diffraction experiments on gaseous biphenyl.[33]

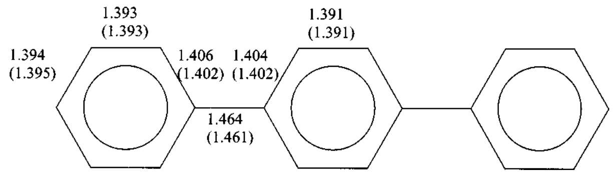

FIG. 2. AM1-optimized C-C bond lengths (in Å) of the PPP trimer in its planar conformation; the values obtained for the fully optimized (twisted) geometry are given in parentheses.

The doping process, corresponding to a chemical oxidation or reduction of the conjugated chains, leads to a significant modification of the geometric structure of the molecules. In the following, we discuss the effect of *p*-type doping and emphasize that very similar results are obtained in the case of *n*-type doping. In Fig. 3 the changes in C-C bond lengths upon single oxidation are shown for $6P$ in its fully optimized geometry. We note that slightly weaker modifications are obtained for a planar conformation (which in the case of singly charged molecules corresponds to a local minimum in energy). In the central rings we observe an evolution towards a semiquinoid structure with the central inter-ring bond reduced by 0.04 Å with respect to the neutral case. The geometry modifications in the outer rings are much weaker. On the basis of the AM1/ROHF calculations, we estimate the extent of the polaron to be close to four benzene rings. This value has to be regarded as an upper limit since interactions with counterions are neglected. These are expected especially in the solid state and lead to an increase in the confinement of the charged defects as pointed out, e.g., by Irle *et al.*[21] The evolution to a semiquinoid structure is also accompanied by a reduction in the calculated inter-ring twist angles of the central benzene rings, as illustrated in Fig. 3(b).

Doubly oxidized molecules display much larger geometry modifications than the singly charged moieties, in good agreement with previous calculations on charged oligo(phenylenevinylene)s[16] and oligo(thiophene)s.[17] The calculations indicate that for doubly charged molecules only $2P$ and $3P$ have a fully planar conformation corresponding to the global minimum in energy. In longer chains, the central rings adopt a strongly quinoid character and display very small torsion angles (see Fig. 4), while the outer rings adopt a geometry equivalent to that in neutral chains. Since very low inter-ring twist angles are observed in the conjugated segments mostly affected by the geometry relaxations, there

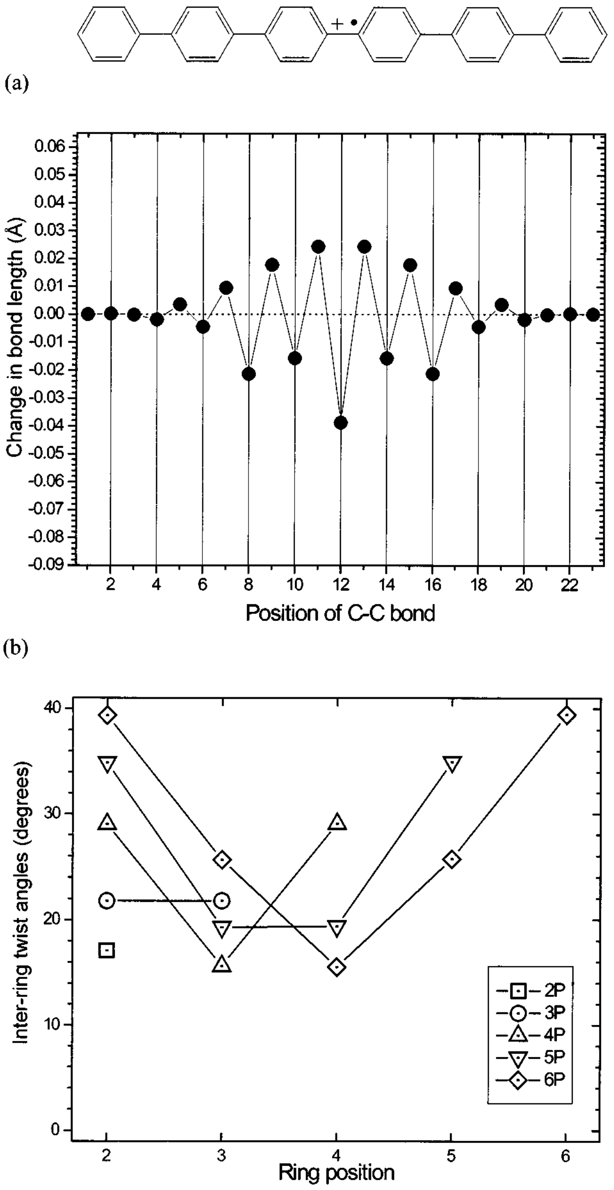

FIG. 3. (a) Changes in the AM1 calculated C-C bond lengths of 6*P* when going from the neutral state to the singly oxidized state in its fully optimized conformation; (b) AM1-optimized inter-ring twist angles in singly positive charged oligophenylenes containing from two to six benzene rings. (To ease comparison, the same scale as that in Figs. 4 and 5 is chosen.)

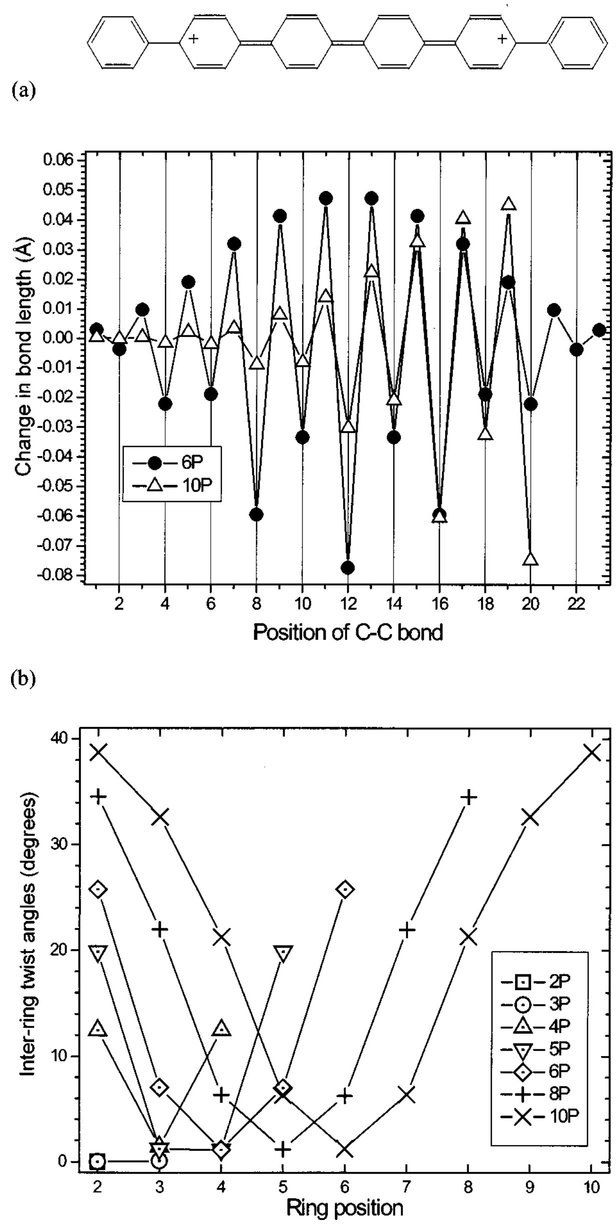

FIG. 4. (a) Changes in the AM1 calculated C-C bond lengths of 6*P* and 10*P* when going from the neutral state to the doubly oxidized state in its fully optimized conformation (only the geometry for half of the 10*P* molecule is shown); (b) AM1-optimized inter-ring twist angles in doubly positively charged oligophenylenes containing from two to ten repeat units.

are no significant differences in the C-C bond-length modifications between the planar and the fully optimized conformations. The distortion of the bond angle between a *para* carbon atom of the central ring and its two intraring neighbors is largest in doubly oxidized systems, giving a value close to 115°.

Due to the closed-shell nature of doubly oxidized molecules, we have been able to extend our calculations to rather long oligomers containing up to 12 rings. We can thus estimate, from both the changes in C-C bond lengths and inter-ring twist angles, that the extent of the geometry modifications induced by the formation of a bipolaron is of the order of six benzene rings. As expected, the extent of the geometry relaxations in bipolarons is wider than the upper limit estimated for polarons. Interestingly, the geometry modifications calculated for doubly oxidized 12*P* in a closed-shell configuration shift from the center to the two extremities of the molecule. This indicates that two polarons might become more stable than a bipolaron in long conjugated chains, as has been recently suggested by experimental measurements performed on doped oligothiophenes.[34] The present theoretical approach, however, is not appropriate to describe the properties of biradicals.

Ultraviolet photoelectron spectroscopy (UPS) experiments have recently shown that it is possible to add four charges to a single 6P molecule.[35] Accordingly, we have also investigated the properties of long oligophenylenes in the quadruply oxidized state, which can be regarded as a model for doped polymers supporting several bipolarons on a single

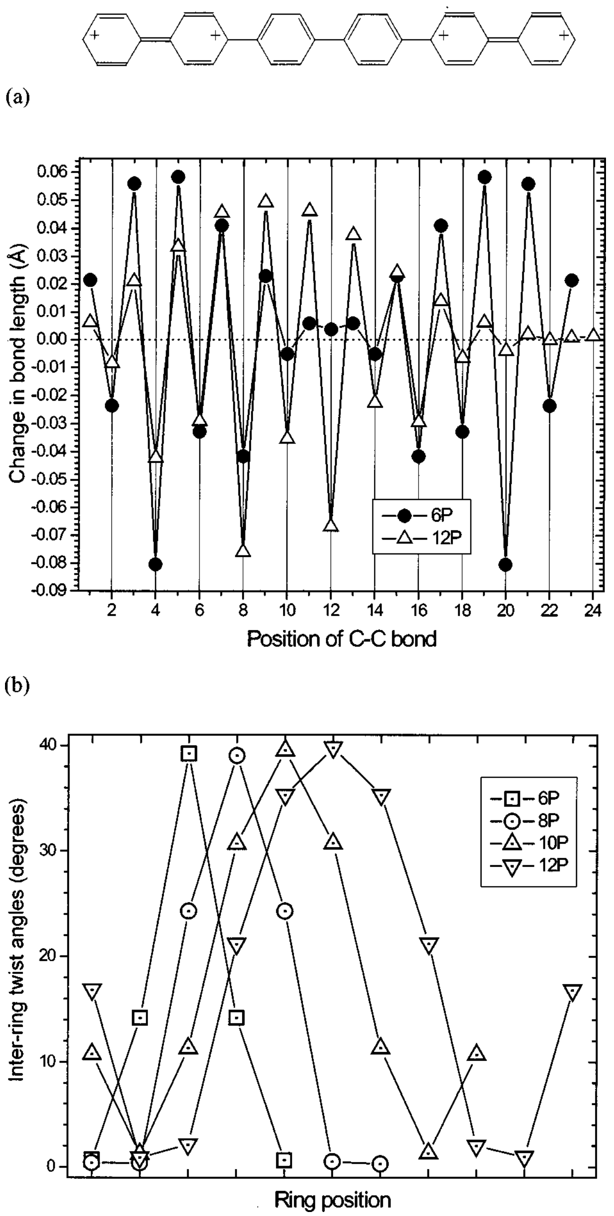

FIG. 5. (a) Changes in the AM1 calculated C-C bond length of 6*P* and 12*P* when going from the neutral state to the quadruply oxidized state in the fully optimized conformation (for 12*P* only half the molecule is shown); (b) AM1-optimized inter-ring twist angles in quadruply positively charged oligophenylenes containing from 6 to 12 benzene rings.

chain. (Note that the UPS experiments[35] have not found any indication of a doping level at which three additional charges reside on a single chain; this situation is therefore not included in our discussion.) The geometry modifications induced by the removal of four electrons from a single oligophenylene molecule containing between 6 and 12 rings are very different from those calculated for positive polarons and bipolarons. Instead of having the geometry relaxations located in the center of the molecule, the quadruply charged oligomers display their most significant deformations (i.e., an increase in the quinoid character and degree of planarity) at the two extremities of the chains (see Fig. 5). In the longest oligomers, no significant geometry modifications are calculated in the center of the molecule. The optimized geometries thus reflect the presence of two interacting bipolarons on a single chain.[36]

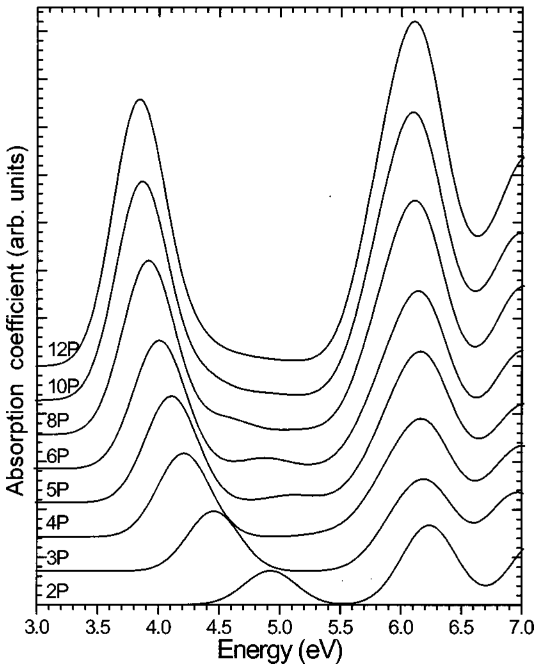

FIG. 6. INDO/SCI-simulated absorption spectra of neutral oligophenylenes, containing from 2 to 12 repeat units, in the fully optimized geometry.

IV. ELECTRONIC AND OPTICAL PROPERTIES

A. Neutral molecules

In Fig. 6 we present the INDO/SCI-simulated absorption spectra of the series of neutral oligophenylenes in the fully optimized conformation. The spectra have been obtained by a convolution of the calculated transition energies with 0.5 eV full width at half-maximum Gaussian functions. The first absorption feature is markedly shifted to lower energies with increasing chain length, in excellent agreement with corresponding experimental data; see Fig. 7.[37–39] The redshift pro-

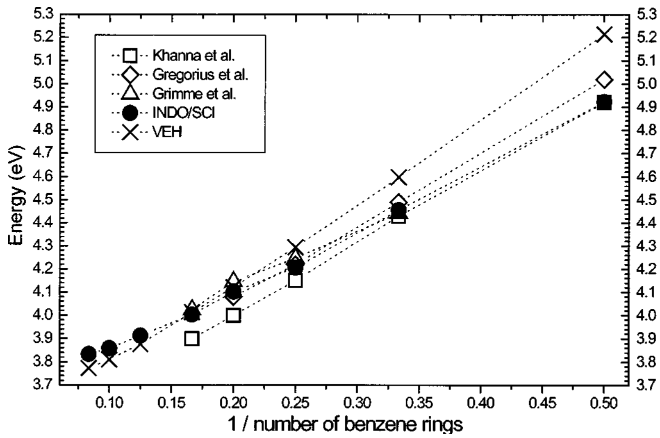

FIG. 7. Evolution of the energy of the first transition in neutral oligophenylenes as a function of inverse number of benzene rings; experimental data for unsubstituted (Refs. 37 and 38) and substituted PPP oligomers (Ref. 39) are compared to INDO/SCI and VEH results obtained on the basis of fully optimized geometries.

TABLE I. INDO/SCI transition energies, oscillator strengths, and main CI expansion coefficients of the lowest optically allowed excited state in neutral oligophenylenes containing from 2 to 12 repeat units (H and L refer to HOMO and LUMO, respectively).

Oligomer	Energy (eV)	Oscillator strength (arb. units)	Main CI expansion coefficients
$2P$	4.92	0.72	$0.98H\rightarrow L$
$3P$	4.46	1.24	$-0.97H\rightarrow L-0.20H-1\rightarrow L+2$
$4P$	4.21	1.73	$0.94H\rightarrow L-0.28H-1\rightarrow L+1$
$5P$	4.10	2.21	$-0.90H\rightarrow L+0.35H-1\rightarrow L+1$
$6P$	4.00	2.67	$-0.87H\rightarrow L-0.38H-1\rightarrow L+1+0.19H-2\rightarrow L+2$
$8P$	3.91	3.62	$0.80H\rightarrow L-0.43H-1\rightarrow L+1-0.27H-2\rightarrow L+2$
$10P$	3.86	4.55	$-0.75H\rightarrow L-0.45H-1\rightarrow L+1-0.31H-2\rightarrow L+2+0.20H-3\rightarrow L+3$
$12P$	3.83	5.49	$-0.70H\rightarrow L+0.46H-1\rightarrow L+1+0.33H-2\rightarrow L+2-0.24H-3\rightarrow L+3$

portional to the inverse number of repeat units obtained in our calculations has also been observed and predicted for other conjugated organic systems.[16,17,40] This can be explained by the delocalized nature of the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) wave functions, which are mostly involved in the description of the lowest excited state. At the scale of very long conjugated chains, such delocalized levels give rise to the formation of the broad valence and conduction bands, which dominate the low-energy absorption spectrum and the electronic properties of poly(para-phenylene).[41]

As pointed out before, the optical spectra calculated for molecules in their fully optimized conformations are expected to match very well experimental measurements in solution. In Fig. 7 we compare the transition energies of the lowest optical absorption calculated via the INDO/SCI and VEH approaches to experimental data obtained in solution. An excellent agreement between theory and experiment is observed. The suitability of a one-electron approach such as VEH to describe these transitions is explained by the fact that the lowest excited state at the CI level is dominated by the HOMO to LUMO transition, as shown in Table I.

As the chain length grows, the energy separation between the one-electron levels progressively decreases, introducing significant weight for the symmetry-allowed HOMO-1 to LUMO$+1$ transition in the CI description of the first excited state. Deviations between the spectra measured in solution and in solid state[42,6] originate from possible geometry modifications induced by packing effects and from the influence of interchain interactions on the electronic properties of the ground and excited states.[14] A discussion of the nature of the absorption spectra expected in the solid state as a function of the orientation of the chains relative to the direction of the incident light has been given by Niko *et al.*[43]

We now focus on the nature of the transitions in fully optimized $6P$, which is the most widely investigated and used PPP oligomer: The HOMO to LUMO transition at 4.00 eV (Fig. 6) is the dominant transition in $6P$ and is polarized in the direction of the molecular axis. The weak peak at 4.88 eV is described by a linear combination of three Slater determinants (involving HOMO→LUMO$+2$, HOMO-1→LUMO$+1$, and HOMO-2→LUMO excitations). The correlated nature of that state is explained by the very similar energies of these three transitions. Since this peak originates from transitions between delocalized levels, its polarization is also in the direction of the molecular axis. We also calculate several weak optically allowed and highly correlated features around 5.9 eV (not clearly resolved in Fig. 6 due to the Gaussian broadening), which are described by transitions from delocalized to localized orbitals and vice versa. (Note that localized level refers to a molecular orbital without significant electron density on the para-carbon atoms of the phenylene rings. It is thus localized within the rings). These transitions are polarized in a direction perpendicular to the molecular axis; for planar conformations, they are oriented in the plane formed by the benzene rings. The strong maximum at 6.18 eV is polarized in the direction of the chains axis and is characterized by several transitions between localized molecular orbitals. Our results are in agreement with those from the earlier tight-binding calculations of Rice and co-workers.[44] It is interesting to emphasize that the nature and the ordering of the optically allowed transitions are very reminiscent of those found in oligo(phenylene vinylene)s.[45–47]

B. Singly charged molecules

The INDO/SCI calculations indicate that the formation of polarons leads to the appearance of *two strong subgap absorption features* in the spectra of phenylene oligomers, as shown in Fig. 8. These results are fully consistent with the experimental data of Khanna *et al.*[37] and Gregorius *et al.*[39] as illustrated in Fig. 9. As is the case in oligo(phenylenevinylene)s[16] and oligo(thiophene)s,[17] the lowest transition is primarily described by an excitation between the HOMO and the lowest polaron level, while the second mainly corresponds to an excitation between the two polaron levels (see Table II, Fig. 1). Both transitions are polarized in the direction of the chain axis. As observed for the neutral molecules, measurements and calculations show the expected shift of the peak positions to lower energies as the chain size is increased. The redshift is also proportional to the inverse number of repeat units (see Fig. 9).

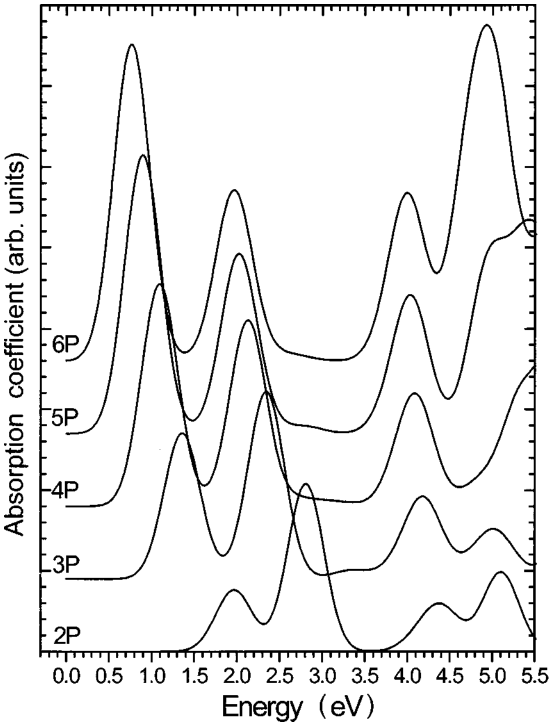

FIG. 8. INDO/SCI-simulated absorption spectra of singly positively charged oligophenylenes, containing from two to six repeat units, in the fully optimized geometry.

The energy of the first transition obtained with VEH agrees very well with the experimental data, whereas the VEH-calculated energies for the second absorption feature are systematically overestimated by about 1 eV. This discrepancy results from the more correlated nature of the second peak in singly charged phenylene oligomers (see Table II). This is supported by the fact that the transition energy between the two polaronic levels is calculated at the INDO one-electron level to be also about 1 eV larger than the value obtained after including the coupling to other single-particle transitions upon configuration interaction.

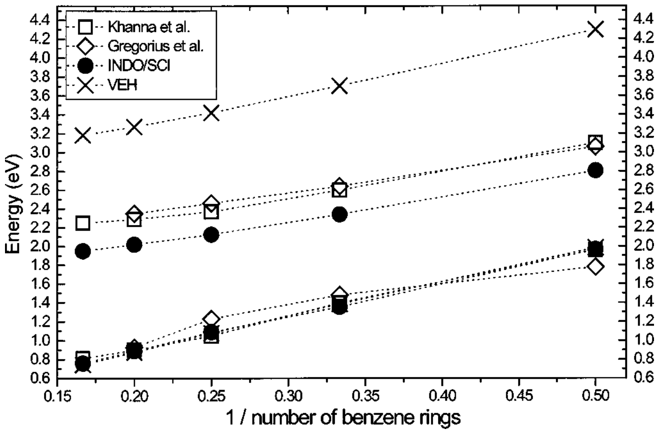

FIG. 9. Evolution of the lowest-energy transitions in singly charged systems as a function of inverse chain length. Experimental data for *n*-type doped unsubstituted (Ref. 37) and substituted oligomers (Ref. 39) are compared to INDO/SCI and VEH calculations performed for positively charged molecules in their fully optimized conformations.

The transition energies calculated for singly oxidized chains in a planar conformation do not show significant deviations from those obtained with the fully optimized geometry. This is related to the small inter-ring tilt angles calculated in the central part of the charged molecules, where the charge densities of the molecular orbitals involved in the transitions are the largest.

The transition from the HOMO to the upper polaron level has a vanishing oscillator strength, since in the D_{2h} group characterizing planar conformations, this excitation corresponds to a one-electron forbidden A_g transition between levels with b_{1u} symmetry. This situation does not change in weakly twisted conformations. The number of peaks might change when going from small to larger oligomers or at doping levels at which polaron-polaron interactions play a significant role, as discussed below for bipolarons. In that case, the appearance of new subgap maxima does not result from a violation of selection rules; the new peaks originate either from the emergence of highly correlated states gaining a significant optical coupling to the ground state or from a splitting of the polaronic/bipolaronic levels due to interactions among the charged species.

Above the two dominant subgap peaks, we calculate at the INDO/SCI level several highly correlated excited states optically coupled to the ground state in the low-energy region of singly doped oligophenylenes. For instance, in the case of $6P$ we obtain a relatively strong absorption feature at 4.02 eV. This peak is predominantly described by excitations involving localized states coupled to the transition between the two polaron levels. Since this absorption is located in the energy range of the HOMO to LUMO transition for the neutral molecule, the complete bleaching of the optical absorption at that energy cannot be a criterion for full doping, at least as far as the formation of polarons is concerned. We also calculate a feature at 4.71 eV that mainly originates from the HOMO to LUMO+1 and HOMO−1 to LUMO (upper polaron level) excitations (note that in the present terminology the HOMO in the singly charged system corresponds to the HOMO−1 in the neutral molecule—see Fig. 1). The shift of that peak (~0.17 eV) is very weak when compared to its original location in the neutral molecule at 4.88 eV. This indicates that the geometry relaxations induced by oxidation mostly affect the energetic positions of the HOMO and LUMO levels of the neutral molecule.

C. Doubly charged molecules

The INDO/SCI-simulated absorption spectra for doubly positively charged oligophenylenes are shown in Fig. 10. In oligomers up to $6P$, we observe a single strong subgap absorption feature, in agreement with previous calculations reported on short *p*-phenylenevinylene and thiophene oligomers.[16,17] The peak position monotonically shifts to lower energies with increasing chain length, as in the neutral and singly charged molecules. The agreement between the VEH calculations and the experimental data of Gregorius *et al.*[39] is very good, as shown in Fig. 11; the INDO/SCI calculations systematically lead to transition energies that are slightly overestimated, for the reasons emphasized in Sec. II. When comparing oligophenylenes in planar and fully optimized conformations, both VEH and INDO/SCI calculations

TABLE II. INDO/SCI transition energies, oscillator strengths, and main CI expansion coefficients of the lowest two optically allowed excited states in singly oxidized oligophenylenes containing from two to six repeat units. (H and L refer to the highest doubly occupied and lowest completely empty molecular orbital, respectively; POL1 and POL2 denote the two polaron levels with POL2 thus corresponding to L—see Fig. 1.)

Oligomer	Energy (eV)	Oscillator strength (arb. units)	Main CI expansion coefficients
$2P$-peak 1	1.97	0.15	$0.88H-2\rightarrow\text{POL1}-0.39\text{POL1}\rightarrow\text{POL2}(L)$
peak 2	2.81	0.42	$0.71\text{POL1}\rightarrow\text{POL2}(L)+0.38H-2\rightarrow\text{POL1}-0.23$ $H\rightarrow L+1+0.22H-1\rightarrow L+2$
$3P$-peak 1	1.36	0.37	$-0.91H\rightarrow\text{POL1}-0.23\text{POL1}\rightarrow\text{POL2}(L)$
peak 2	2.34	0.46	$0.78\text{POL1}\rightarrow\text{POL2}(L)+0.23H-3\rightarrow L+1-0.22$ $H\rightarrow\text{POL1}$
$4P$-peak 1	1.09	0.55	$0.93H\rightarrow\text{POL1}-0.18\text{H}-6\rightarrow\text{POL1}$
peak 2	2.13	0.46	$0.78\text{POL1}\rightarrow\text{POL2}(L)+0.19H\rightarrow L+1$
$5P$-peak 1	0.89	0.69	$-0.92H\rightarrow\text{POL1}+0.27H-6\rightarrow\text{POL1}$
peak 2	2.02	0.44	$0.77\text{POL1}\rightarrow\text{POL2}(L)+0.18H-3\rightarrow\text{POL2}(L)$ $-0.18H\rightarrow L+1$
$6P$-peak 1	0.76	0.78	$-0.91H\rightarrow\text{POL1}-0.34H-4\rightarrow\text{POL1}$
peak 2	1.95	0.39	$-0.73\text{POL1}\rightarrow\text{POL2}(L)+0.21H-1\rightarrow\text{POL2}(L)$

provide very similar transition energies for the lowest optical transition (the largest difference in the INDO/SCI results is 0.02 eV in $10P$). This behavior is easily rationalized by the fact that the formation of bipolarons induces an evolution towards a planar quinoidlike structure in the central part of the conjugated backbone.

The positions of the maxima for the doubly charged PPP oligomers reported by Khanna *et al.*[37] also display a shift to lower energies as the chain length increases; however, the actual positions of the absorption peaks do not match the data of Ref. 39 and are not reproduced by VEH or INDO/SCI calculations for positively or negatively charged bipolarons. This is possibly due to a strong pinning effect of the counterions for the specific dopants and solvents used in Ref. 37. The redshift of the peak positions as a function of chain length in Ref. 37 is indeed far weaker than both the calculated one and that observed in Ref. 39, thus indicating a reduced influence of the extent of conjugation (and hence a stronger localization of the bipolaron). Such a behavior has been theoretically predicted in the case of strong interactions between the charges located on a conjugated backbone and the counterions.[21] An alternative explanation to rationalize the data in Ref. 37 is the formation of complexes formed by two chains, with each of them supporting a polaron, i.e., π dimers[48] instead of bipolarons, at high doping concentra-

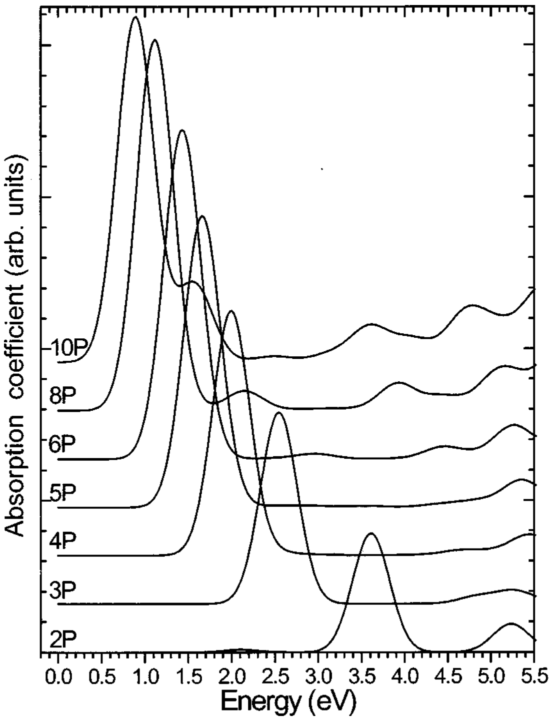

FIG. 10. INDO/SCI-simulated absorption spectra of doubly oxidized oligophenylenes, containing from two to ten phenylene rings, in their fully optimized geometry.

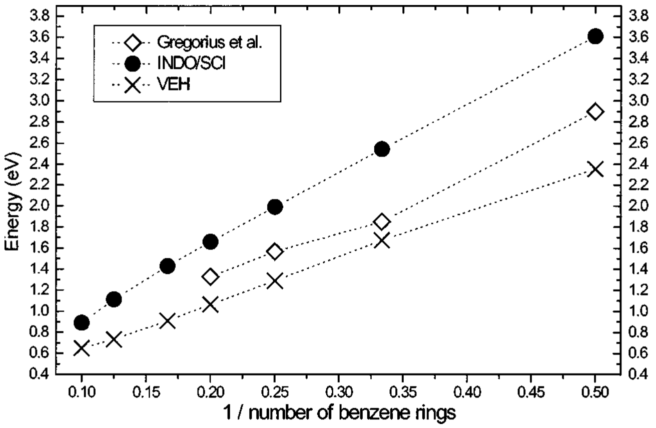

FIG. 11. Evolution of the lowest bipolaronic transition energy in doubly oxidized oligophenylenes as a function of inverse chain length. Experimental data for substituted PPP oligomers (Ref. 39) obtained upon n-type doping are compared to the INDO/SCI and VEH calculations performed on positively charged molecules in the fully optimized conformation.

TABLE III. INDO/SCI transition energies, oscillator strengths, and main CI expansion coefficients of the lowest excited states optically coupled to the ground state in doubly oxidized oligophenylenes containing from two to ten repeat units. [The LUMO (L) level here corresponds to the lower bipolaron level—see Fig. 1.]

Oligomer	Energy (eV)	Oscillator strength (arb. units)	Main CI expansion coefficients
$2P$	3.61	1.56	$-0.98H-2\rightarrow\mathrm{BP1}(L)$
$3P$	2.55	2.49	$-0.98H\rightarrow\mathrm{BP1}(L)$
$4P$	1.99	3.23	$0.97H\rightarrow\mathrm{BP1}(L)$
$5P$	1.66	3.84	$0.97H\rightarrow\mathrm{BP1}(L)+0.20H-1\rightarrow L+1$
$6P$	1.43	4.34	$-0.96H\rightarrow\mathrm{BP1}(L)-0.21H-1\rightarrow L+1$
$8P$-peak 1	1.12	4.88	$0.95H\rightarrow\mathrm{BP1}(L)-0.19H-1\rightarrow L+1$
$8P$-peak 2	2.14	0.26	$-0.93H-4\rightarrow\mathrm{BP1}(L)-0.18H\rightarrow\mathrm{BP1}(L)+0.18H-8\rightarrow\mathrm{BP1}(L)$
$10P$-peak 1	0.89	4.54	$-0.95H\rightarrow\mathrm{BP1}(L)-0.20H-2\rightarrow L$
$10P$-peak 2	1.57	1.03	$0.90H-2\rightarrow\mathrm{BP1}(L)+0.24H-8\rightarrow\mathrm{BP1}(L)-0.24H\rightarrow\mathrm{BP1}(L)$

tions. As pointed out earlier,[21] the relative stability of polarons versus bipolarons is expected to be strongly influenced by the nature and position of the counterions.

The first optical transition in doubly charged oligomers has a strong single-particle nature (see Table III) and is dominated by a transition from the HOMO to the lower bipolaron level (however, in doubly oxidized $2P$, since the highest two occupied levels are localized, the lowest-energy transition of this particular oligomer takes place between the HOMO−2 and the lower bipolaron level). In longer oligomers, a second subgap peak appears next to the first maximum and gains oscillator strength as the chain grows up. This spectral feature is weaker in molecules with a fully planar conformation. The energy and intensity of this absorption in films of polymers supporting isolated bipolarons will thus critically depend on the effective conjugation length as well as on the degree of planarity of the chains (driven by packing effects). A second subgap absorption feature in bipolarons is traditionally assigned to a transition from the HOMO to the higher bipolaron level.[49] As discussed already for polarons, a transition between these orbitals is one-photon forbidden due to selection rules. The second peak is actually dominated by a symmetry-allowed transition from a lower-lying molecular orbital (HOMO−4 in $8P$ and HOMO−2 in $10P$) to the lower bipolaron level (see Table III).[50]

D. Quadruply oxidized molecules

As shown in the discussion of the geometric structure of highly doped oligophenylenes, the removal of four electrons from a single molecule results in the formation of two interacting bipolarons. The corresponding absorption spectra are shown in Fig. 12 for fully optimized chains; similar results are obtained for the planar conformation. The generation of two interacting bipolarons on a single $6P$ molecule has been clearly identified in UPS measurements and supported by the results of VEH calculations.[35] Interaction between charged species might thus play a major role in determining the optical properties of polymer chains.

Upon quadruple oxidation, the highest two occupied molecular orbitals of the neutral molecule are depopulated, thus making the HOMO−2 level of the pristine molecule the HOMO of the charged system. The HOMO and HOMO−1 (LUMO and LUMO+1) levels of the neutral chain become the two lower (higher) bipolaronic levels, which are not degenerate due to the interaction between the two bipolarons. In all cases, the INDO/SCI-simulated absorption spectra show the appearance of two relatively strong subgap absorption peaks. The most intense peak is dominated by a transition from the HOMO level to the lowest bipolaronic level

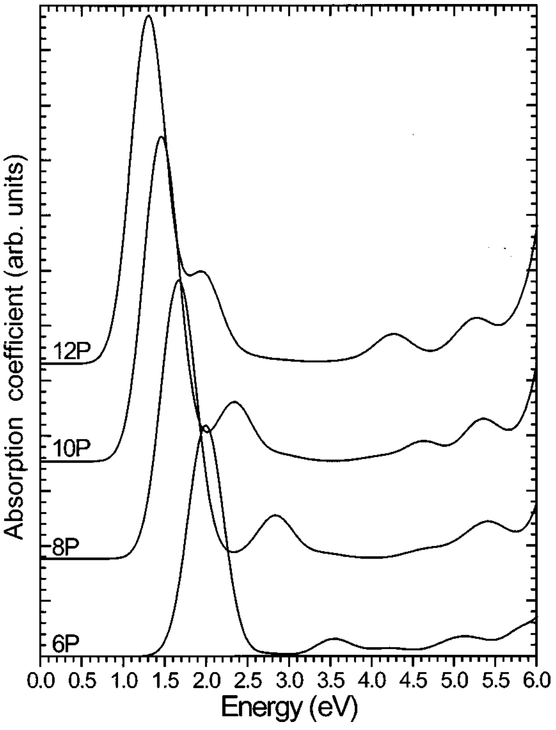

FIG. 12. INDO/SCI-simulated absorption spectra of quadruply oxidized oligophenylenes, containing from 6 to 12 rings, in the fully optimized conformation.

TABLE IV. INDO/SCI transition energies, oscillator strengths, and main CI expansion coefficients of the lowest two intense absorption peaks in quadruply positively charged oligophenylenes containing from 6 to 12 repeat units (see Fig. 1).

Oligomer	Energy (eV)	Oscillator strength (arb. units)	Main CI expansion coefficients
$6P$-peak 1	1.99	4.17	$0.91H\rightarrow\mathrm{QP1}(L)+0.36H-1\rightarrow\mathrm{QP2}(L+1)$
$6P$-peak 2	3.54	0.31	$-0.85H-1\rightarrow\mathrm{QP2}(L+1)+0.35H\rightarrow\mathrm{QP1}(L)$ $-0.33H-8\rightarrow L$
$8P$-peak 1	1.67	5.06	$0.87H\rightarrow\mathrm{QP1}(L)-0.43H-1\rightarrow\mathrm{QP2}(L+1)$
$8P$-peak 2	2.83	0.74	$-0.69H-1\rightarrow\mathrm{QP2}(L+1)+0.56H-3\rightarrow\mathrm{QP1}(L)$ $-0.39H\rightarrow\mathrm{QP1}(L)$
$10P$-peak 1	1.46	5.90	$0.82H\rightarrow\mathrm{QP1}(L)-0.48H-1\rightarrow\mathrm{QP2}(L+1)$
$10P$-peak 2	2.33	1.05	$-0.60H-2\rightarrow\mathrm{QP1}(L)-0.57H-1\rightarrow\mathrm{QP2}(L+1)$ $+0.45H\rightarrow\mathrm{QP1}(L)$
$12P$-peak 1	1.30	6.30	$0.79H\rightarrow\mathrm{QP1}(L)+0.51H-1\rightarrow\mathrm{QP2}(L+1)$ $+0.21H-2\rightarrow\mathrm{QP1}(L)$
$12P$-peak 2	1.96	1.62	$0.59H-2\rightarrow\mathrm{QP1}(L)-0.52H\rightarrow\mathrm{QP1}(L)+0.50$ $H-1\rightarrow\mathrm{QP2}(L+1)$

(QP1, see Fig. 1). The second peak in $6P$ and $8P$ is mainly described by the HOMO−1→LUMO+1(QP2) excitation, whereas in longer chains ($10P$ and $12P$) the HOMO−2→LUMO(QP1) and HOMO→LUMO(QP1) excitations start having significant weight in the CI expansion, thus increasing the correlated nature of the excited state. The transition energies, oscillator strengths, and main CI expansion coefficients are given in Table IV. It is interesting to note that transitions involving the highest two bipolaronic levels (LUMO+2 and LUMO+3 corresponding to QP3 and QP4) show up only in highly correlated states at energies above the band gap of the neutral molecules. The calculations also show that the energy difference between the two absorption maxima decreases with increasing chain length. It might thus be difficult to resolve the two features in the experimental spectra of polymers with a high effective conjugation length.

We note that VEH calculations also predict two strong absorption features, which are redshifted with respect to the results obtained via the INDO/SCI approach. These are described in all oligomers by transitions from the HOMO to the LUMO (QP1) and from the HOMO−1 to the LUMO+1 (QP2), respectively.

V. CONCLUSIONS

The geometry optimization at the AM1 level of neutral oligophenylenes yields a slightly quinoid character in the benzene rings and inter-ring twist angles on the order of 40°. Upon doping, the central part of the oligomer is strongly affected by geometry relaxations leading to an increase in the quinoid character of the rings and a strong reduction in the amplitude of the inter-ring twist angles. On the basis of the AM1 results and when neglecting the influence of counterions, we estimate an upper limit of four benzene rings for the extent of the geometry modifications induced by the formation of polarons and six rings for bipolarons. In quadruply charged oligomers, the geometry modifications are localized in a symmetric way at the two extremities of the chain and do not affect much the central part of the oligomer. This corresponds to the formation of two interacting bipolarons.

The transition energies calculated by means of the INDO/SCI approach compare very well to experimental data reported for neutral and doped oligophenylenes in solution. The lowest-energy absorption of neutral molecules and the subgap features of the charged species display a redshift with increasing chain length, which is proportional to the inverse number of benzene rings. We have shown that the formation of polarons in short oligomers leads to the appearance of two separate and intense subgap absorption peaks while a single feature appears in the presence of bipolarons, in agreement with previous calculations reported on oligo(phenylenevinylene)s[16] and oligo(thiophene)s.[17] In both cases the nature of the optical transitions is governed by selection rules imposed by molecular symmetry.

Investigations of longer oligomers such as $8P$, $10P$, and $12P$ in the doubly oxidized state reveal that correlated states involving transitions from lower-lying occupied orbitals can give rise to the appearance of a second subgap absorption peak. The assignment of the optical transitions in the spectra of doped conjugated chains containing a relatively high number of benzene rings thus becomes more complex than usually assumed. Furthermore, calculations performed on quadruply charged systems establish that the interaction between bipolarons also results in the appearance of a second subgap absorption feature. Further theoretical and experimental works carried out on well-defined oligomers are thus desirable to better understand the influence of the interaction between charged defects on the optical properties of conjugated organic macromolecules. The present calculations clearly demonstrate that the sole consideration of the number of subgap absorption peaks is not a good criterion to assess the nature of the charged species generated upon chemical doping or photoexcitations in long conjugated chains.

On the basis of our theoretical results, it is not straightforward to assign the second intense subgap feature observed in the spectra of highly doped conjugated polymers[51] to the optical signature of isolated or interacting bipolarons, as done traditionally. Indeed, we would expect a single subgap feature in the first case and a strong disproportion in the relative intensities of the two subgap peaks for the second; these features are not generally observed in the experimental spectra. A possible explanation to solve that discrepancy could be that polarons are stable at high doping rates and do not collapse to form bipolarons, as suggested in Ref. 34 and by recent measurements performed on doped oligothiophenes.[34] Moreover, polarons might interact, leading to the formation of π dimers that are also characterized by two strong subgap features.[48,34]

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