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Polaron formation and symmetry breaking

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In a molecular semiconductor, a charged molecule experiences a lattice relaxation which reorganizes it into a cation or an anion-radical. This species is not, in general, a polaron. By using calculations of the geometry and the electronic structure both ab initio and at the semi-empirical levels, we have explored the conditions of polaron formation in a molecular model system: oligophenylene–vinylenes, PVs of increasing sizes. The symmetry breaking occurs at sizes larger than five monomers for the anion and six monomers for the cation. The driving force for this process is primarily the charge–lattice coupling through the stretching mode at 1600 cm^{-1}.

1. Introduction

Very early in the development of conducting polymers, Su, Schrieffer and Heeger introduced the concept of the self-trapped carrier, arising as a consequence of the strong electron–lattice coupling in these systems. This idea provided a series of coherent and powerful explanations of the optical, vibrational and electronic properties of doped polymers [1]. More recently a few clear and reproducible experiments have provided evidence for the existence of polarons even in the absence of doping counterions:

(1) Transient excited state absorption in the spectral region spanning the infrared active, vibrational active (IRAV) modes, (7–9 μm) in poly(paraphenylene–vinylene)-PPV and poly(2-methoxy, 5-(2-ethyl-hexyloxy) paraphenylene–vinylene)-MEH–PPV reveal polaron formation within 100 fs (to 3 ps) after photoexcitation [2,3].

(2) The optical spectroscopy of the field induced charge in a polymer transistor based on regio regular poly(3-hexylthiophene)-P3HT also demonstrates the polaronic character of the carrier [4].

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(3) The electron nuclear double resonance (ENDOR) signal in undoped PPV is also attributed to polarons [5,6].

One of the important aspects of self-trapping is symmetry breaking. This effect is particularly clear in the IRAV experiment which detects a forbidden infrared mode due to a local loss of symmetry. The polaron formation on a chain of conjugated polymer is a non-linear process which breaks the symmetry. Empirical hamiltonians, like Holstein's [7] or Su, Schrieffer and Heeger's [1] are built on purpose to introduce such a non-linearity into the Schrödinger's equation, and provoke the occurrence of a bifurcation [8].

The problem is more complicated when other computational approaches are used which go beyond empirical, non-linear hamiltonians. Several first principle calculations of the spectra of charged oligomers have been published concerning oligophenylene–vinylenes (PVs) [9,10] and oligothiophenes [11–14]. The density functional calculations (DFT) performed on oligomers containing 1–9 monomers exhibit no features characteristic of a formation of self-localized states either in PVs [10] or PTs [12,13] while semi-empirical calculations [9,11], Hartree–Fock [13] and hybrid DFT methods [14] yielded the formation of well-defined polarons either in PVs or PTs. In this Letter, we have explored polaron formation in PVs of increasing sizes at both the semi-empirical (AM1) and DFT levels. We show that the difficulties of pure DFT methods to account for the existence of a well-defined polaron are not only related to the tendency of the pure DFT calculations to overestimate the delocalization of a charge on a conjugated chain [10,14], but also to the tendency of this method to underestimate the electron–phonon coupling. Our study also emphasizes the role of the symmetry breaking in the polaron formation, by showing a sudden increase in the relaxation (or the reorganization) energy of the radical at a given size. We have finally achieved a mapping of the quantum-chemistry results on an Holstein's hamiltonian [7] with parameters that we have determined completely and consistently in the case of PVs. They provide the non-linear description of the electronic states which is useful in calculations of the charge transport through assemblies of oligomers or polymer chains. Other first principle calculations concerning the exciton formation in organic conjugated oligomers are of some interest for the present work although they do not deal with charged molecules and radicals [15,16].

2. Computational methods

Two different methods were used and their results compared. In the first approach, the electronic system was described within the DFT on the local density approximation (LDA) level. Norm-conserving pseudopotentials [17] were used along with plane wave expansions of the electron orbitals with a kinetic energy cutoff at 40 Ry. The molecules were placed in supercells large enough to ensure negligible interaction between neighboring molecules while the atomic relaxation at $T = 0$ was obtained through the standard Car–Parinello molecular dynamics scheme [18].

In the second method, both the electronic structure and the vibration spectra were determined through semi-empirical calculations based on the neglect of diatomic differential overlap (NDDO) type of approximation [19] with the Austin's Model 1 (AM1) parametrization scheme [20]. The anions, the cations and the neutral molecules were fully optimized separately within both the unrestricted and the restricted Hartree–Fock framework including a small amount of configuration interaction, namely, a [2,2] active space (two electrons distributed over two molecular orbitals).

3. The existence of the polaron

The first part of the calculation was a study of 2 PV, 4 PV, 6 PV, 8 PV and 10 PV molecular ions charged with an electron or a hole (Fig. 1). We first tried to detect directly a tendency of the charge to self-localized. For this purpose, we compared the ground state geometries of the ions to those of the neutral molecules. Fig. 2 shows the deviation of the bond lengths of the 8 PV anion with respect to the corresponding neutral molecule. Each bond length has been numbered according to the conjugation path shown in Fig. 1. The strongest de-

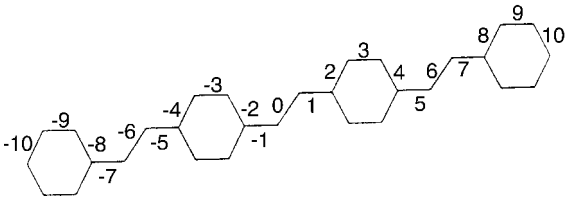

Fig. 1. Schematic representation of the oligomer 4 PV, showing how the different bonds have been numbered along the conjugation path. The origin is on the central bond (see Figs. 2 and 3).

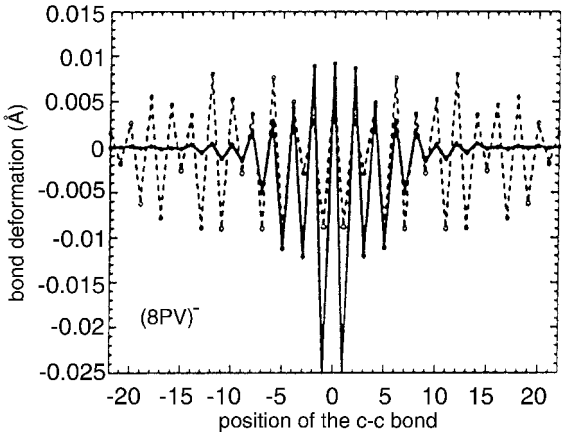

Fig. 2. Deformation of the C–C bond along the skeleton of the charged oligomer $(8\ PV)^-$. The continuous line is the result of the semi-empirical AM1 calculation while the dashed line refers to the ab initio DFT calculation.

formations are seen on the vinyl bridges that link the phenyl rings together. However, in the DFT calculations, the amplitude of deformation is uniform on the bridges over the entire molecule. Obviously, the DFT polaron is broader than the oligomer size, while the semi-empirical calculation gives a well-defined polaron with a total width $2L \sim 3$ monomers. The results are similar for the cation. These results are in perfect agreement with the works of [9] and [10].

In optimizing the geometries, we explored, with particular care, the role of ethylene rotations with respect to the phenyl rings. These originate from the repulsion between two hydrogen atoms, one sitting on the phenyl ring and the other on the ethylene. The relative distance between the two is 2.04 Å in the planar configuration (while the Van der Waals radius of each is 1.2 Å). As in the calculations of [21], we observed a very flat potential for torsions between +20° and −20°. A total energy change of 32 meV was calculated for 20°, compatible with the experimental ring torsion diffraction study in PPV [22], where the equilibrium torsional angle was found to vary from 7° to 13° as the temperature varies from 300 to 600 K. We shall see further on, that such low-energy values give a totally negligible contribution to the polaron formation.

The relaxation energy of the charged oligomer represents the gain in energy of the molecular ion when the geometry is relaxed from the neutral to the ionic configuration. When a polaron can be clearly identified, this energy contribution coincides with the formation energy of the polaron. In Fig. 3, this is shown both for the cation and the anion as a function of the number of phenyl rings from 2 to 10. At large oligomer sizes, a polaron with a formation energy of 0.3 eV can be clearly identified both for the cation and the anion.

Obviously, at equilibrium, the polaron is centered on the central double bond of the symmetrical oligomer. However, the other local energy minima, obtained by shifting the polaron by one or two vinylene double bonds, are quite close. Indeed, the relaxation energies obtained at the center and at the second nearest vinylene double

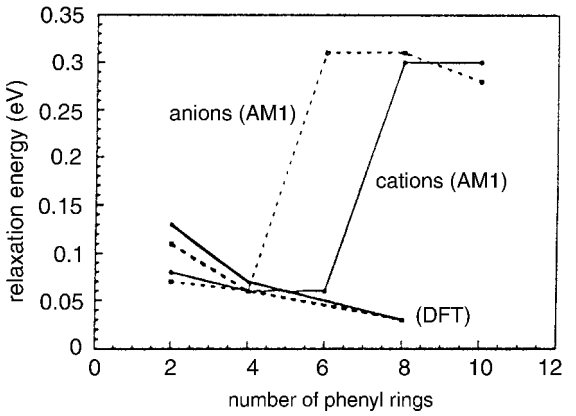

Fig. 3. Relaxation energies of the molecular ions from the neutral geometry to the ionic one as a function of the size of the oligomer; as the charge increases, anions relax first to the polaron configuration at size 6. Above size 8, oligomers recover the electron–hole symmetry observed in stilbene.

bond differ by only 4.7 meV in the case of the anion and 8.3 meV in the case of the cation. Thus when an appropriate substituant is attached on the phenyl ring at the extremity of the chain, the center of the equilibrium polaron can be easily displaced. For example, an OCH_3 substitution achieved on the *para* position of the terminal ring of 8 PV displaces the equilibrium center of the polaron of two monomers, without changing its extension.

A perfect understanding of the nature of the intrinsic polaron requires knowledge of the molecular deformations (phonons) that are involved in its formation. Raman spectroscopy gives some hints that help in this task: First, recent experiments have shown in *n*- (as well as in *p*-) doped PPV that the vibrational modes that feel the presence of an extra charge the most are in the 1300–1600 cm^{-1} range [23,24]. Second, it has been noted that in pristine as well as in doped oligomer solids, the frequencies of these modes are only slightly dependent on the length of the oligomer [23,25]. It is reasonable therefore to consider studying the vibrational properties of the smallest PPV oligomer, stilbene, with the hope of extracting some important numerical values driving polaron formation.

Consequently, the phonon spectrum for neutral stilbene was computed using the DFT results and compared to the experimental spectrum of [25]. The determination of the normal modes of the vibrational spectrum was based on the standard diagonalization procedure of the dynamical matrix of the system. Using this method was the average difference between the two spectra was less than 3%. The Raman mode which shows the stronger shift upon charging the stilbene molecule with a hole or with an electron is almost a pure stretching of the central bond of the vinylene group with a vibration frequency of 1627 cm^{-1}. (The semi-empirical calculation gives 1597 cm^{-1}.) Two other modes at 1265 and 1560 cm^{-1} are significantly less active.

4. Consistent parameters for an Holstein hamiltonian

The vinylene chain has been identified as the main deformable molecular unit driving polaron formation. It is a real chance in PVs, that this pertinent deformation can be accurately described with only a stretching parameter u as in the simple version of the Holstein model. It was thus possible to calculate the stiffness K and the electron–phonon coupling constant γ determining formation. Because these quantities are essentially local, this was done for the case of stilbene first. In the ranges of stretching considered ($u < 0.05$ Å), the total energy is parabolic with the deformation u. The values of K in both models and for both ions were deduced from this total energy E through the relation $E = (1/2)Ku^2$. The value of the phonon coupling constant γ was deduced from the energy variations with u of the singly occupied molecular orbitals (SOMO) of the molecular ions. In the semi-empirical calculations, the SOMO levels were directly accessible while in the DFT calculation, the many-body molecular problem had to be mapped onto a set of one-electron Schrödinger equations known as Kohn and Sham's.

In the range of deformations from −0.06 to +0.06 Å the electron lattice coupling is indeed linear for all species and models ($E_{\mathrm{SOMO}} = \gamma u$). The local parameters for polaron formation are reported in Table 1. The linear electron–phonon coupling constant γ in stilbene is of the same order of magnitude for all species and models with values varying from 1.3 to 2.8 eV/Å. However, the values obtained from the AM1 model were always larger than those from the DFT approach, and we were not surprised that the latter did not produce the same polaron as the former.

We also wanted to check the variation of the local coupling constants with the size of the oligomer. For this purpose we considered, the case of the 8 PV and 10 PV anions within the AM1 frame where a fully relaxed polaron is indeed observed. We found that the electron–phonon coupling constant deduced from the SOMO variation upon stretching was significantly larger in 8 PV and 10 PV ($\gamma = 3.7$ and 3.9 eV/Å) than in 2 PV (2.6 eV/Å). The stiffness $K = 46$ eV/Å^2 per vinylene unit is comparable to the other values in Table 1.

If we attribute to this precise SOMO level the total electron lattice coupling driving the polaron formation, we get, in the spirit of the Holstein model [7] a relaxation energy $\gamma^2/2KL \simeq 0.1$ eV which is three times too low with respect to the

Table 1
Local parameters (stiffness K and electron–phonon coupling constant γ) determining the polaron in PPV

Type of calculation	Neutral or charged state	γ (eV/Å)	K (eV/Å^2)	$u_{max} = \gamma/K$ (Å)
DFT stilbene	Neutral HOMO	2.15	41.0	0.05
	Cation SOMO	1.64	39.3	0.04
	Neutral LUMO	2.10	41.0	0.05
	Anion SOMO	1.26	39.3	0.04
Semi-empirical AM1 stilbene	Neutral HOMO	2.76	67.4	0.04
	Cation SOMO	2.92	55.4	0.05
	Neutral LUMO	2.13	67.4	0.03
	Anion SOMO	2.61	58.2	0.04
Semi-empirical 8 PV	Anion SOMO	3.7	46	0.08
Semi-empirical 10 PV	Anion SOMO	3.9	52	0.08

These parameters are relative to the stretching mode at $\sim$1600 cm^{-1}. In the case of stilbene the coupling constant γ has been determined both for the HOMO and LUMO of the neutral molecule and for the SOMOs of the molecular ions. The ratio γ/K is an estimation of the maximum deformation of the chain due to the polaron. The eight lines on the top of the table are related to stilbene, while the last ones concern the oligomers 8 PV and 10 PV, where a polaron is clearly visible (see Fig. 2).

'measured' value of 0.31 eV. The rest of the contribution comes from the numerous electrons in the 'valence band' which are also coupled to the stretching field. We found, in the AM1 calculation, that each one of the 62 π-electrons of 8 PV contributes on the average a $\gamma' = 0.05$ eV/Å to γ. Thus the total contribution to the relaxation energy can be roughly estimated by $(\gamma + 62\gamma')^2/2KL \cong 0.35$ eV.

5. Conclusions

The polaron in PPV is basically intrinsic; it results from a symmetry breaking in the electron density distribution at oligomer sizes larger than three monomers for the anion-radical and four monomers for the cation-radical; its formation energy is large (0.3 eV) and compatible with experiments. Correlatively the polaron is rather small ($2L \sim 3$ monomers), but can glide easily along the polymer segment at room temperature. The driving force for polaron formation is primarily the charge–lattice coupling through the stretching mode at 1600 cm^{-1}. The hole–polaron and the electron–polaron have similar formation energies and a similar width. The librations of the phenyl rings with respect to the ethylene groups were considered by different authors [26] as a possible driving force for polaron formation. We have always found here that the vibrations corresponding to these torsional modes correspond to wave numbers between 60 and 250 cm^{-1}. This is too low to enter into competition with the 1600 cm^{-1} stretching mode for polaron construction, but these low-frequency modes can easily play an important role in polaron motion either along the chain or from chain to chain.

The intrinsic character of the polaronic ground state does not mean that disorder has no influence: a model has been developed by one of us (MNB) to understand the interplay between electron–lattice coupling and disorder in polaron formation [27].

The mapping of the polaron to an Holstein model [7] (or a Su, Schrieffer and Heeger model [1]) is always useful for transport models, especially in PPV [28]. We have demonstrated here that this mapping is possible with the following set of parameters: transfer integral from monomer to monomer, $t = 0.5$ eV [20], electron–phonon linear lattice coupling $\gamma \sim 8$ eV/Å and lattice stiffness $K = 50$ eV/Å^2. This effective γ already contains the contribution of valence electrons to the energy relaxation due to an extra-charge.

The existence of an oligomer size threshold for polaron formation can also be demonstrated within the Holstein model. A work is in progress on these lines [29]. Our first results show that this

threshold varies approximately like $g^{-1/2}$ where $g = \gamma^2/(2Kt)$ is the dimensionless, vibrational coupling constant.

Although electron interactions and correlations are far from being negligible in PPV, the mapping of the actual hamiltonian with a one-electron model is finally possible as in many other conjugated polymers, provided that a linear effective electron–phonon coupling term γ is added to the effective tight binding model. This is just a sign that it is possible to confirm the crude picture of the hole as well as the electron polaron as a piece of quinoïd structure within a conjugated chain.

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