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The Coupling Between Electronic Structure, Geometric Structure, and Nonlinear Optical Properties in Conjugated Materials: The Case of Linear Polyenes

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The Coupling Between Electronic Structure, Geometric Structure, and Nonlinear Optical Properties in Conjugated Materials: The Case of Linear Polyenes

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This contribution deals with theoretical investigations of the electronic and optical properties of all-trans linear polyenes. The focus is on the geometry relaxation processes occurring in the first singlet, one-photon optically allowed excited state. Calculations are performed at various levels of sophistication, from a simple Su-Schrieffer-Heeger (Hückel-like) Hamiltonian up to Pariser-Parr-Pople single CI and Restricted Hartree-Fock ab initio Hamiltonians. It is found that explicit consideration of the electron-lattice coupling is essential in order to obtain a coherent evolution of the $1B_u$ state geometry relaxation, in going from short polyenes to long polyenes and polyacetylene. The relevance of our results in terms of the nonlinear optical properties of these compounds is pointed out.

1. INTRODUCTION

Since the discovery that polyacetylene can be made highly electrically conductive through doping with electron donors or acceptors,[1] extensive theoretical and experimental works have been devoted to this polymer. These have for example led recently to the synthesis of a new type of polyacetylene which exhibits conductivities after doping as high as that of copper.[2,3]

Most of the peculiar electrical, optical, and magnetic properties appearing upon doping of polyacetylene have been rationalized by invoking the formation of non-linear elementary excitations of soliton-type.[4,5] Solitons in all-trans polyacetylene are topological kinks that produce a reversal of the bond alternation pattern (see Figure 1). It takes about seven to ten bonds (i.e., 15 to 20 carbon atoms) for the

FIGURE 1 Reversal of the bond alternation pattern induced by the presence of a soliton along a polyacetylene chain (a neutral soliton, i.e. a radical defect, is illustrated here).

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bond alternation reversal to be complete. The presence of solitons on a polyacetylene chain also affects the polymer electronic structure: localized electronic states associated to solitons appear around midgap and thus produce novel subgap optical transitions that can be detected on doping.[5]

Following the pioneering work of Ducuing and co-workers,[6] it has been realized that conjugated polymers inherently possess very high nonlinear optical responses.[7,8] It has been recently pointed out that the influence of electron-lattice coupling and e.g. of the presence of nonlinear elementary excitations such as solitons could also be significant for the nonlinear optical properties.[9-13] In all-trans polyacetylene, photoexcitation across the gap into the $1B_u$ state produces electron-hole pairs that are found to decay very rapidly (in 10^{-13} sec.) into pairs of separated, positively and negatively charged, solitons.[14-16] Such an evolution is in agreement with the early theoretical predictions of Su and Schrieffer.[17] It is important to note that this process results in an efficient charge separation mechanism, a feature essential to provide large optical nonlinearities.[18] Furthermore, in the off-resonance regime, instantons (i.e., virtual soliton-antisoliton pairs)[19] have been suggested to yield enhanced optical nonlinearities with respect to a purely rigid lattice situation.[8-10]

In short polyenes, spectroscopic studies indicate that strong geometry relaxations also take place in the first B_u one-photon optically-allowed excited state.[20,21] These geometry relaxations are traditionally modeled theoretically using Bond Order/Bond Length (BOBL) relationships.[22] In this framework, the geometry relaxations follow exactly the wavefunction characteristics in the excited state. They are calculated to become smaller as the chain length increases and tend to be negligible for chains containing over 15–20 carbon atoms.[23,24] Such an evolution is, however, inconsistent with the situation appearing in very long chains, i.e., polyacetylene, where the first B_u state strongly relaxes to produce a pair of charged solitons, as mentioned above.[5,14,15]

Therefore, in this paper, we review the calculations we have performed in order to remove the inconsistency between the traditional understanding of the $1B_u$ relaxation process in short polyenes and the perception of the situation prevailing in all-trans polyacetylene and provide a coherent picture of the evolution between short and long polyenes. First, we investigate the relaxation process in the $1B_u$ excited state of polyene chains by means of the methodology of Su, Schrieffer, and Heeger,[4] as adapted by Brédas *et al.*[25] We make use of a Hückel Hamiltonian with bond-length dependent transfer integrals and σ-bond compressibility. We study chains ranging from 10 to 58 carbon atoms in order to understand the evolution of the relaxed geometry as a function of chain length. Second, calculations are

carried out at a much higher level of sophistication (combined Restricted Hartree-Fock ab initio/Pariser-Parr-Pople Configuration Interaction level) for three polyene molecules: hexatriene (C_6H_8), decapentaene ($C_{10}H_{12}$), and tetradecaheptaene ($C_{14}H_{16}$). We are in this way able to assess our results on a firmer ground.

2. SU-SCHRIEFFER-HEEGER HAMILTONIAN APPROACH

In order to be in a position, on the one hand, to examine the evolution in going from short to long polyenes and, on the other hand, to make a significant comparison to polyacetylene, we have chosen to work first at the Su-Schrieffer-Heeger Hamiltonian level. This corresponds to a Hückel technique with bond-length dependent transfer integrals and σ-bond compressibility.[4]

The parameters originally optimized for polyacetylene by Su, Schrieffer, and Heeger[4] are applied to polyene chains ranging in size from 10 to 58 carbon atoms.[11] These parameters lead to: (i) a degree of bond length alternation of 0.14 Å in the ground state (single bond equal to 1.47 Å and double bond equal to 1.33 Å), (ii) a (somewhat underestimated) bandgap of 1.4 eV in transpolyacetylene, and (iii) a creation energy of 0.92 eV for a pair of totally separated solitons.[11]

We search the configuration space to find the geometry providing the lowest $1B_u$ excited state total energy. Two types of situation are mostly investigated:

(i) We allow for geometries similar to those obtained with traditional BOBL relationships in the framework of Pariser-Parr-Pople (PPP) calculations including configuration interaction.[27] The amplitude and the extent of the relaxation are both optimized.

(ii) We look for geometries resulting in the formation of a soliton pair (two-soliton geometries). Both the distance between the solitons and the soliton widths are optimized.

The results corresponding to the two-soliton geometries are given in Table I for chains containing from 10 to 58 carbon atoms.

TABLE I

Evolution as a function of chain length n of: (i) the vertical excitation energy (in eV) to the first B_u excited state, E_{vert}; (ii) the corresponding relaxed excitation energy (in eV), E_{rel}; (iii) the relative total energy lowering (in %) due to the relaxation of the $1B_u$ excited state; (iv) the optimal soliton width, $2l$ (in number of sites); (v) the optimized site locations of the soliton defects, n_1 and n_2; and (vi) the HOMO-LUMO separation (in eV) in the relaxed geometry. The calculations are performed in the framework of the Su-Schrieffer-Heeger Hamiltonian [11].

n	E_{vert}	E_{rel}	%	$2l$	n_1,n_2	HOMO-LUMO
58	1.477	0.922	37.6	15	19,40	0.14
46	1.515	0.939	38.0	11	15,32	0.20
38	1.557	0.983	36.9	11	11,28	0.20
26	1.682	1.105	34.3	7	9,18	0.30
22	1.760	1.178	33.1	7	7,16	0.55
18	1.876	1.340	28.6	3	5,14	0.70
14	2.064	1.541	25.3	3	5,10	0.98
10	2.400	1.853	22.8	3	3,8	1.16

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In the longest polyene chain we investigated here (58 carbon atoms), results are identical to those obtained for the infinite polyacetylene chain.[4,25] The $1B_u$ excited-state geometry relaxes to form a pair of solitons (with a creation energy of 0.922 eV), which lowers the $1B_u$ excited state total energy by 38% relative to the vertical excitation energy. The solitons are calculated to be optimally located on sites 19 and 40, i.e., they are as distant from one another as from the chain ends. Each soliton is found to extend over about 15 carbons, as in trans-polyacetylene.[4]

As the chain length decreases, the total energy lowering due to the relaxation of the $1B_u$ excited state becomes smaller. However, even in the case of decapentaene, this energy lowering due to a soliton pair formation still amounts to 23% of the vertical transition energy.

Very importantly, the relaxed excitation energies obtained for excited-state geometries calculated on the basis of BOBL relationships are 0.2–0.3 eV larger than in the two-soliton formation situation. The major result of these Hückel-like calculations is thus to find that the relaxation effects in the $1B_u$ excited state of polyene molecules are qualitatively similar to those in trans-polyacetylene. *Even in the shortest chains considered here, the $1B_u$ excited state is found to relax optimally in such a way as to produce a pair of solitons*. In order to be accommodated in shorter chains, the solitons shrink in size: their width decreases from $2l = 15$ for trans-polyacetylene, to $2l = 11$ for chains containing between 30 and 50 carbon atoms, $2l = 7$ for chains between 20 and 30 carbon atoms, and $2l = 3$ in chains containing less than 20 carbons. In all cases, the solitons tend to be centered on locations separating them equally from one another and from the chain ends. The evolution between short and long polyene chains is thus found to be fully coherent.

It is important to stress that the two-soliton formation in the $1B_u$ excited state of decapentaene appears to agree better with experimental data than does the situation where the $1B_u$ excited state geometry is described in terms of BOBL relationships. In the former case, the average bond-length variations between the $1B_u$ excited state and the ground state are calculated to be 0.070 and 0.087 Å for the double and single bonds, respectively. In the latter case, the corresponding values are 0.043 and 0.047 Å.[24] These results are to be compared with the experimental estimates of Granville *et al.*[20] which provide average variations of 0.085 and 0.081 Å for double and single bonds, respectively. Furthermore, the relaxation energy experimentally measured in the $1B_u$ state of decapentaene (at 77 K) is on the order 0.8 eV.[20] Such a relaxation represents 20% of the vertical excitation energy.[20] Within the two-soliton configuration, the relaxation is calculated to be about 23% of the vertical transition energy, while it is only 10–12% in the BOBL-derived $1B_u$ excited state.[24]

The overall picture obtained within the simple Su-Schrieffer-Heeger Hamiltonian is that there exists a smooth evolution of the relaxation of the $1B_u$ exited-state geometry in going from short polyenes to polyacetylene. This evolution is consistent with the strong geometry relaxations experimentally observed in short polyenes (e.g. decapentaene) as well as polyacetylene. In all cases, the relaxation is such as to produce the formation of a soliton-antisoliton pair on the chain. Note that a relaxation tending to produce a two-soliton geometry is not unlike the ionic valence-bond pictures used to describe the $1B_u$ excited state.[26]

It is however important to address the question of the $1B_u$ excited-state relaxation using a more sophisticated theoretical approach, in particular taking explicitly into account the effects of electron-electron interactions and electron correlation. The calculations have therefore been extended on short polyenes, using a combined PPP Configuration Interaction and Hartree-Fock ab initio approach.

3. PPP-CI/RHF AB INITIO APPROACH

It is usually the case that PPP Hamiltonians are suitably parameterized to reproduce excited state transition energies. However, they do not provide reliable geometry optimizations in terms of total energy differences. On the other hand, if ab initio techniques (which can afford good total energy differences) can be used quite easily to optimize ground-state geometries, they soon prove to be too costly when applied to optimize excited-state geometries of systems containing over one hundred basis functions.

Therefore, we have seeked to combine these two techniques in order to be able to perform calculations on relatively large molecules and to assess more reliably the trends in the first B_u excited state geometry.[12] We have thus considered: (i) geometry optimizations at the Restricted Hartree-Fock (RHF) 3-21G split valence basis set level,[27] which allow for a correct sketch of the *ground-state potential energy curve*; and (ii) PPP Configuration Interaction (CI) calculations including single excitations from the ground-state reference framework and based on the various 3-21G optimized geometries. The PPP program and parameters we have used can be found in Reference 28. The parameters are chosen in such a way as to provide a degree of bond-length alternation in the ground state almost identical to that calculated at the RHF 3-21G level, see below. Although it does not predict a correct ordering of the excited states of polyene molecules, a single CI approach is known to describe adequately the first B_u excited state.[22,23,26] Combining the ground state total energies with the PPP vertical transition energies, leads to the *relative excited-state total energies* corresponding to various geometrical situations.

We have considered three linear polyene molecules: hexa-1,3,5-triene (C_6H_8), deca-1,3,5,7,9-pentaene ($C_{10}H_{12}$), and tetradeca-1,3,5,7,9,11,13-heptaene ($C_{14}H_{16}$). The RHF ab initio calculations are performed *in the ground state* for three different geometry situations[12]:

(i) In the first case, we carry out a full (i.e., all bond lengths and valence angles) 3-21G optimization of the ground state geometry assuming coplanar conformations.

(ii) In the second case, we consider the geometry corresponding to the relaxed $1B_u$ excited-state, obtained using BOBL relationships with the PPP Hamiltonian.[24] All bond angles are optimized at the ab initio 3-21G level, while the carbon-carbon bond lengths are kept at their PPP B_u-state values and the carbon-hydrogen bond lengths are set at their optimal ab initio ground-state values.

(iii) In the third case, we partly optimize the geometry corresponding to the formation of a pair of solitons, as obtained at the Hückel/SSH Hamiltonian level described previously. Here, we force the two carbon-carbon bonds surrounding the soliton centers to be of equal lengths. The values of these bond lengths and

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those of the bonds towards the ends of the molecules are optimized. The carbon-carbon bonds located between the solitons are chosen to be identical to the single and double bonds appearing in the 3-21G optimized ground-state geometry. All the bond angles are full optimized, while the carbon-hydrogen bonds are fixed at the ab initio ground-state optimal values.

In Table II, we present the ground-state geometries of hexatriene, decapentaene, and tetradecaheptaene, as optimized at the RHF ab initio 3-21G level. The decapentaene PPP values[24] are also indicated. The PPP values are obtained by using the following bond order (l_{pq})/bond length (R_{pq}, in Å) relationship: $R_{pq} = 1.51 - 0.19\, l_{pq}$

The evolution of the degree of bond-length alternation along the polyene chains obtained on the basis of BOBL relationships are depicted in Figure 2. It is clearly observed that in this framework the geometry relaxation in the first singlet B_u excited state strongly decreases with increasing chain length. In hexatriene, all bonds are significantly affected by the excitation; in the middle of the molecule, the sign of bond dimerization reverses. This is only slightly the case in decapentaene, where the two central bonds are almost equal and the bond alternation for the outer bonds reaches +0.09 Å. In tetradecaheptaene, however, the sign of the bond alternation remains positive all along the molecule, indicating no single bond-double bond character reversal. (Note that by convention, we consider the sign of the bond alternation to be positive when it is the same as in the ground state).

In Figure 3, we present the results obtained when considering the possibility of formation of a soliton-antisoliton pair as the $1B_u$ state relaxes. A comparison of Figures 2 and 3 illustrates that the two-soliton geometry leads to bond length modifications relative to the BOBL-derived geometries, which are smaller in the hexatriene case but much larger in the longer chains. We note that for hexatriene, it is actually rather misleading to speak in terms of the formation of a two-soliton configuration since the soliton and the antisoliton are localized on adjacent sites. Hexatriene is therefore too short a chain to provide for a complete bond alternation reversal in the middle of the molecule when considering a two-soliton configuration. Such a reversal, however, clearly occurs in decapentaene and tetradecaheptaene. In decapentaene, the average bond-length modification with respect to the optimal

TABLE II

Optimized RHF/3-21G carbon-carbon bond lengths (in Å) for the ground state of hexatriene, decapentaene, and tetradecaheptaene. The numbers between parentheses for decapentaene refer to the PPP Hamiltonian-optimized values [24]. The atoms are labeled starting from one end of the molecule.

	C_6H_8	$C_{10}H_{12}$	$C_{14}H_{16}$
R(C1-C2)	1.322	1.322 (1.325)	1.322
R(C2-C3)	1.462	1.461 (1.465)	1.461
R(C3-C4)	1.327	1.329 (1.330)	1.329
R(C4-C5)		1.456 (1.463)	1.455
R(C5-C6)		1.330 (1.332)	1.331
R(C6-C7)			1.454
R(C7-C8)			1.331

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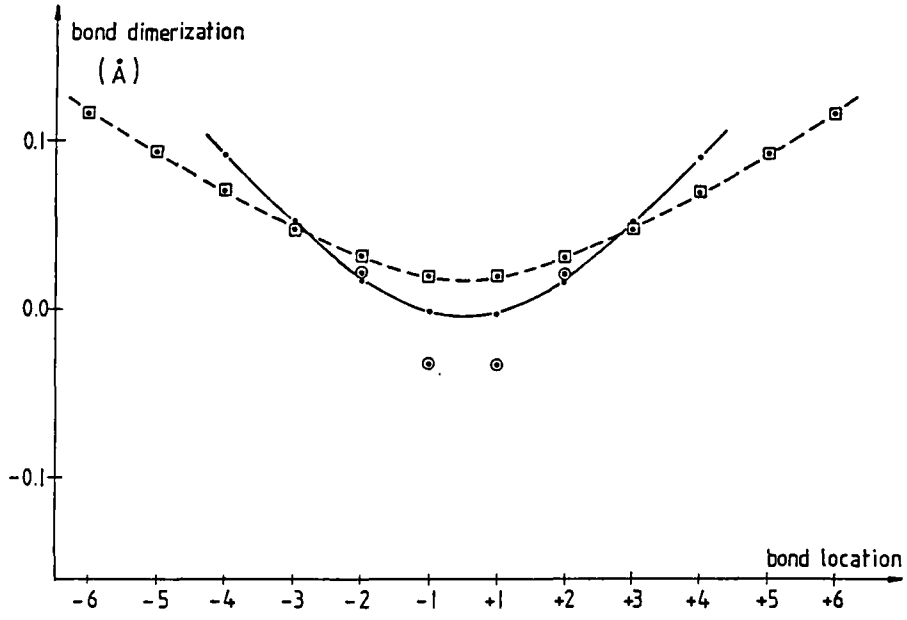

FIGURE 2 Illustration of the RHF ab initio evolution of the bond dimerization value (in Å) along the molecules of hexatriene (double circles), decapentaene (closed circles, solid line), and tetradecaheptaene (squares, dashed line), in the BOBL-derived relaxed geometry for the first B_u excited state. The sign of the dimerization is by convention taken to be positive if it is the same as in the ground state. The bonds are labeled starting from the central bond of the molecule (After Reference 12).

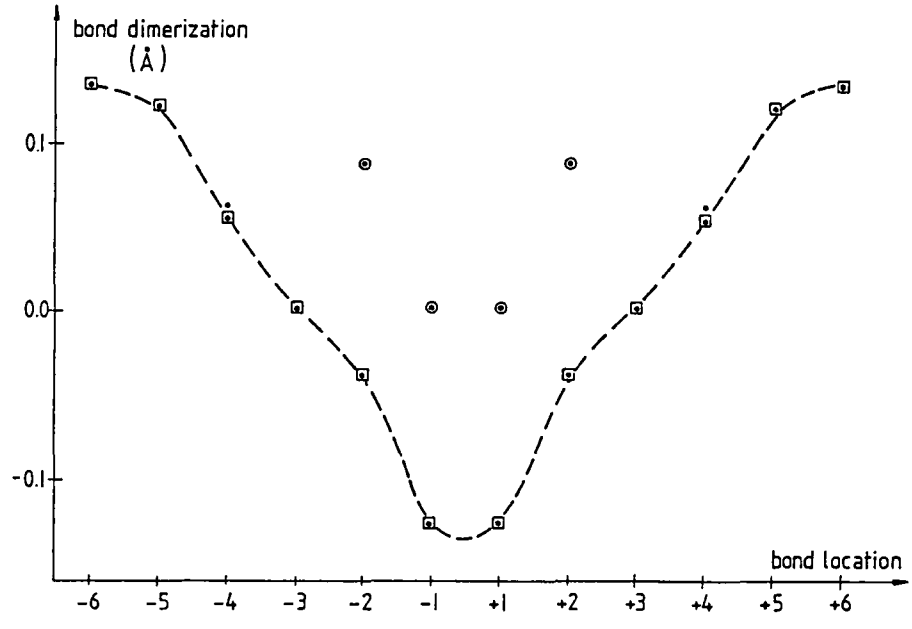

FIGURE 3 Illustration of the RHF ab initio evolution of the bond dimerization value (in Å) along the molecules of hexatriene (double circles), decapentaene (closed circles and dashed line), and tetradecaheptaene (squares, dashed line), in the two-soliton relaxed geometry for the first B_u excited state. The sign of the dimerization is by convention taken to be positive if it is the same as in the ground state. The bonds are labeled starting from the central bond of the molecule. (After Reference 12).

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ground-state geometry is 0.073 Å. We stress again that, relative to the 0.08 Å experimental estimate of Granville *et al.* for the relaxed B_u state,[20] this value is in much better agreement than that provided by BOBL relationships (on the order of 0.04 Å, i.e. twice smaller than the experimental value).

In Table III, we list for the three kinds of investigated geometries: (i) the relative total energies in the ground state, as obtained at the Hartree-Fock ab initio 3-21G level; (ii) the vertical transition energies to the first optically-allowed singlet B_u state, as calculated at the PPP-CI level; and (iii) the relative total energies in the $1B_u$ excited state, obtained by simply summing the first two terms.

What we need to compare for our purpose are the relative total energies in the excited state. For all three molecules, we find as expected that a strong relaxation takes place in the excited state, i.e. the geometry which is found to be optimal for the ground state does not constitute the optimal geometry in the B_u excited state. In hexatriene, the B_u relaxed geometry derived from BOBL relationships is significantly favored (by about 0.3 eV) over that corresponding to the two-soliton geometry. However, as discussed above, in the case of hexatriene, the BOBL configuration provides for a stronger geometry relaxation and a two-soliton configuration is not truly achieved. In decapentaene, the two-soliton geometry becomes very close in energy (within 0.05 eV) with respect to the BOBL geometry for the excited state. In both configurations, the relaxation relative to a vertical process is found to be on the order of 0.9 eV, a value in excellent agreement with the 0.84 eV value which is experimentally measured.[20] Importantly, in the case of tetradecaheptaene, the two-soliton geometry corresponds to the most stable situation for the excited-state, being about 0.07 eV lower in energy than the BOBL geometry. The gain in stability of the two-soliton configuration with respect to the BOBL configuration as chain length increases is fully consistent with the experimental observation on the photogeneration of soliton pairs in the first $1B_u$ excited state

TABLE III

Comparison of the energies involved in hexatriene, decapentaene, and tetradecaheptaene for the three geometry situations investigated in this work: (A) relative RHF ab initio total energies in the ground state(the fully optimized RHF ab initio 3-21G value being taken as reference); (B) PPP-CI vertical transition energies to the first singlet B_u state; (C) relative total energies in the first singlet B_u state (calculated by summing the first two terms). All energies are given in eV.

	A	B	C
hexatriene			
ab initio ground state	0.00	5.86	5.86
BOBL	0.63	4.14	4.77
two-soliton	0.27	4.83	5.10
decapentaene			
ab initio ground state	0.00	5.03	5.03
BOBL	0.51	3.56	4.07
two-soliton	1.19	2.93	4.12
tetradecaheptaene			
ab initio ground state	0.00	4.65	4.65
BOBL	0.43	3.37	3.80
two-soliton	1.08	2.65	3.73

of polyacetylene. In long chains, a BOBL-derived configuration would in contrast lead to negligible relaxation.

An interesting feature is uncovered when: (i) observing in Figures 2 and 3 the evolution in bond length alternation for decapentaene and tetradecaheptaene; and (ii) comparing it to the geometry relaxation process due to a photogenerated electron-hole pair in polyacetylene (see Figure 2a of Reference 19). From this observation, we suggest that the configuration given by BOBL relationships corresponds to the *early stage* of the process of electron-hole separation into a pair of solitons whereas the two-soliton configuration relates to the *final stage* of the separation process. This separation is actually induced through the explicit coupling of the electronic structure to the lattice, an ingredient which is absent from the BOBL approach where the geometry has to follow the wavefunction characteristics. It is worth pointing out that in the two-soliton configuration, the phase of the bond alternation pattern between the locations of the soliton and the antisoliton is *opposite* to that of the wavefunction bonding-antibonding pattern.

4. CONCLUSIONS

The results obtained from the combined RHF ab initio/PPP-CI approach thus confirm that in linear polyenes containing at least ten carbon atoms, the electron-lattice coupling plays a significant role in the relaxation of the first B_u excited state.

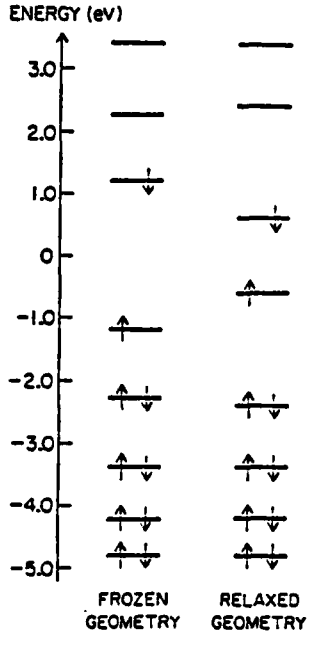

FIGURE 4 Evolution of the one-electron energy levels in the first B_u excited state of decapentaene, in going from the frozen ground-state geometry (left) to the relaxed excited state geometry (right). (After Reference 11).

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We stress that the fast relaxation of the $1B_u$ state related to the decay of a photoinduced electron-hole pair into a pair of charged solitons has been invoked to be an important factor in the large nonlinear optical response of polyacetylene.[8-10,19] Such a decay indeed provides major shifts in oscillator strengths and a very effective charge separation mechanism, which are essential to large hyperpolarizabilities.[6,7,18]

Our work thus suggests that going beyond frozen geometry models of the polarizabilities and hyperpolarizabilities by incorporating electron-lattice coupling could also prove to be essential to describe properly the optical nonlinearities in short and intermediate-sized polyenes,[29,30] as well as in other oligomers where electron-lattice coupling effects are known to be important (polypyrroles, polythiophenes, . . .).

We note that the two-soliton geometry relaxation leads to the appearance of new electronic states in the gap, see Figure 4.[11] This feature leads to important shifts in oscillator strengths. It would be therefore most interesting to carry out photoinduced absorption experiments in the subpicosecond regime. Such measurements indeed constitute an ideal means to probe the energies and fast time evolution of the new optical absorptions resulting from such a relaxation in linear polyenes.

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