

Influence of Interchain Interactions on the Electronic Properties of Neutral and Charged Oligodiacetylenes Carrying Bulk Substituents

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We discuss the effect of the interchain interactions on the electronic properties of a “dimer”, named $(\text{CHD}_4)_2$, built from two molecules of a fully carbazolyl-substituted oligodiacetylene containing four repeating units. Each carbazolyl moiety is connected to its respective backbone through a methylene spacer, and the excitations of the neutral and doubly positively charged dimer are obtained using the CIS (configuration interaction including singles) and CEO (collective electronic oscillator) models. The separation distance between the backbones is fixed to a value that could possibly imply a very weak, if any, interchain interaction between the oligomers. In the charged dimer, where we have not been able to perform CEO calculations, it can be expected from previous results that the CIS method will behave satisfactorily. Contrary to the neutral case and surprisingly enough, the simulated photoinduced absorption (PA) spectra indicate a substituent-induced strong interaction between the oligomers, due to the very large amount of excess charge on the distorted oligomer which is spread over its carbazolyl moieties. Broadening of the lowest energy band due to the latter interaction improves the agreement between the theoretical and the experimental PA spectrum for the corresponding polymer. The through-space charge transfer directly connecting the charged with the neutral molecule could supply an efficient channel for charge transport in substituted polydiacetylenes.

1. Introduction

In a recent paper on isolated carbazolyl-substituted oligodiacetylenes,¹ hereafter referred to as paper I, we have applied for the first time the CEO quantum chemical approach (see below) to study the effect of a complete substitution with bulky carbazolyl groups on the electronic properties of conjugated polymers. Even in the presence of a methylene spacer, which interrupts the conjugation path between the backbone and carbazolyl moieties, a number of unexpected features have been predicted, showing the importance of explicitly considering substituents in interpreting spectroscopical features, such as the photoinduced absorption spectra of conjugated polymers of potential technological interest.^{2–5} In fact, the substituent effects in the systems studied are not negligible nor easily predictable, especially in the presence of an electronic excitation.¹ These results have prompted us to use the same direct approach to consider the effects of interchain interactions in neutral and charged clusters built from the same carbazolyl-substituted oligodiacetylenes that have been the object of our previous calculations. We earlier studied (ref 6, hereafter referred to as paper II) interchain effects in two types of clusters, each made of three unsubstituted $n = 15$ oligodiacetylenes, but in the light of the results obtained in paper I we expect that dealing explicitly with substituents can substantially modify the picture there obtained.

2. Calculations and Results

The electronic excitations have been computed using the Collective Electronic Oscillator (CEO) method, a TDHF-level

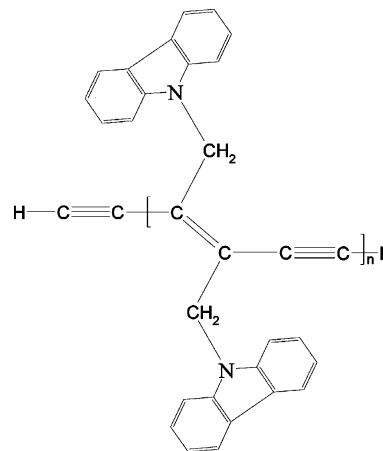


Figure 1. General formula of the CHD_n oligomers.

approach developed by Mukamel,⁷ and the well-known CIS (single-excitation configuration interaction) approximation, both based on a INDO–S Hamiltonian.⁸ Details of the CEO method are reported in the original papers⁹ and a very short account is given in paper I. We recall that in paper I we have studied two types of oligomers, in which the carbazolyl moieties were linked to the backbone either directly (CBD_n oligomers) or through a CH_2 spacer (CHD_n oligomers). Here we have studied only clusters of the latter (see Figure 1), because they have given the most interesting and unexpected results in paper I and because experimental data are available only for the corresponding polymers.

Although in paper I we considered oligomers up to $n = 6$, due to the presence of many large carbazolyl moieties, the present calculations refer to a system of two CHD_4 oligomers,

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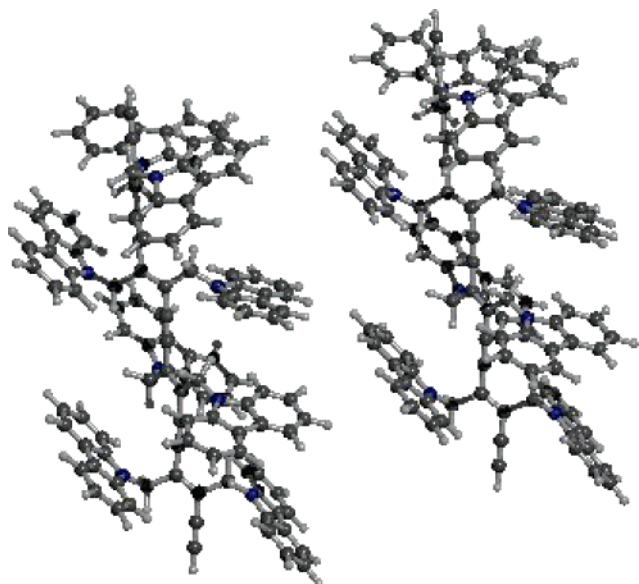


Figure 2. Sketch of the reciprocal positions of the two carbazoyl-oligodiacylenes in the dimer.

hereafter called the “dimer”. The Restricted Hartree–Fock (RHF) procedure used limits us to treat only singlet excitations in neutral or doubly charged systems. They are built by using the AM1¹⁰ geometries of the isolated oligomers, as they were obtained in paper I, and assembling two neutral oligomers or a neutral and a doubly positively charged one, for the neutral and the doubly positively charged dimer, respectively. No further optimization is performed here, the separation distance between the backbones being fixed to 15 Å (see Figure 2), which corresponds to a van der Waals contact between the surfaces of the oligomers. Under these conditions the minimal separation between two carbazoyl substituents belonging to different molecules results to be about 5 Å.

Between the two limiting cases considered in paper II, the present arrangement of the oligomers is somewhat reminiscent of structure a (the one corresponding to a minimum interaction), in which the backbones lay in the same plane and the distance between corresponding atoms on them was 4.5 Å. Here, however, the interbackbone distance is far larger, and there are very few atoms on the two molecules (belonging to a limited number of carbazoyl moieties) lying 5 Å apart. Accordingly, one could possibly expect the interchain interactions, if any, to be very weak in the present case.

We anticipate at this point that the considerable dimension of the whole system has caused serious computational problems (lack of convergence of the transition density matrix in the Liouville space) in the CEO calculation for the charged dimer, where only the CIS run (and not the CEO one) could be performed. It is therefore essential to assess, particularly in the charged case, the reliability of the CIS results against those given by the CEO approach, in which double, triple, and multiple excitations are also included in an implicit way.¹¹ To this end, in the following section we shall summarize the whole body of CIS and CEO results obtained by us for substituted and unsubstituted isolated oligomers, from which we infer that the CIS approach should behave satisfactorily in predicting the low-energy excitations of the charged dimer.

2.1. Single Chain. In paper II the CIS lowest transition energy for the $n = 15$ unsubstituted oligomer was found to be higher than the CEO one both in the neutral (2.67 vs 2.45 eV) and especially in the doubly charged case (0.80 vs 0.25 eV), an effect that we were not able to explain.⁶ In fact, the opposite occurs

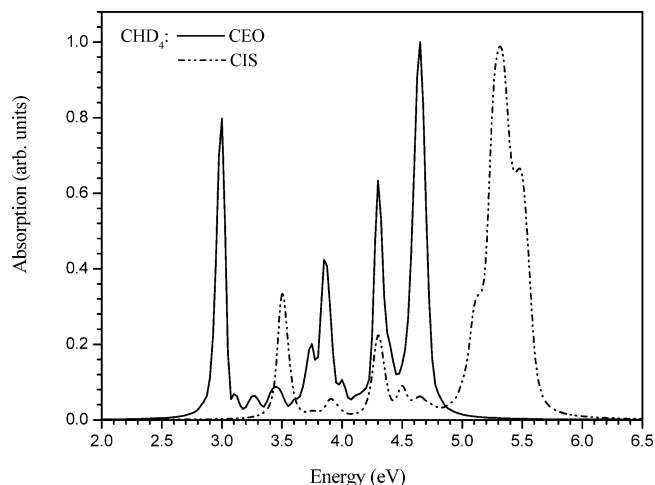


Figure 3. CEO (full line) and CIS (broken line) theoretical spectra of the neutral CHD_4 isolated oligomer.

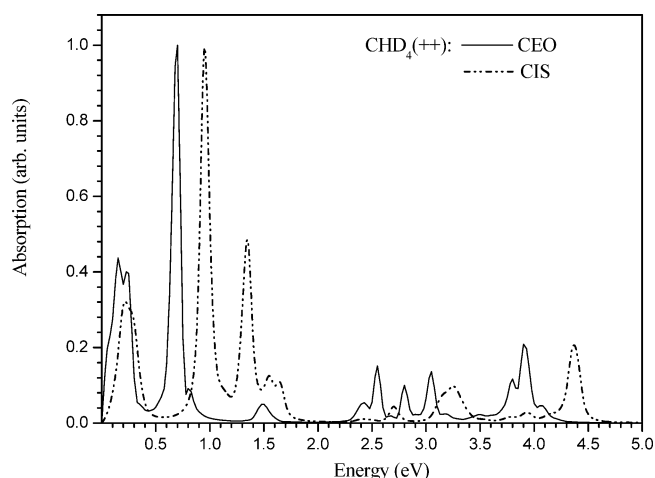


Figure 4. CEO (full line) and CIS (broken line) theoretical spectra of the doubly positively charged CHD_4 isolated oligomer.

for $n = 4$, the corresponding CIS (CEO) values being¹ 3.48 (2.84) eV (neutral) and 2.10 (1.95) eV (charged). The last result has been confirmed by an ab initio effectively correlated TDDF (time dependent density functional)/6-31G(d) value of 2.15 eV. While the n -trend of the neutral species appears to be reasonable, the behavior of the charged oligomers is not easily understood. In this respect, however, it may be recalled that the form of the charge-induced geometry relaxation changes dramatically with increasing chain size.¹² In the latter paper, the geometry results indicated that for $n \leq 11$ a bipolaron would be present, while for $n = 13$ and 15 the charged oligomer would instead contain two polarons, which in turn implied completely different CIS spectra. Such a relevant change, however, may reflect itself in a different way on the CEO results, as seems to be signaled by the extent of the weight of the HOMO→LUMO single excitation in the CIS and TDHF ab initio calculations we have performed as successful tests of the above results (see papers I and II). In fact, for $n = 4$ it is practically the same in the singly excited CIS wave function as it is in the TDHF one, while for $n = 15$ this excitation is dominant in the CIS case, but has lower weight for TDHF (see paper II).

Coming now to the substituted oligomer, the CEO¹ and CIS spectra for isolated neutral and doubly positively charged CHD_4 are displayed in Figures 3 and 4, respectively.

The CIS and CEO lowest energy transitions of CHD_4 relate to each other very likely as they did in the unsubstituted

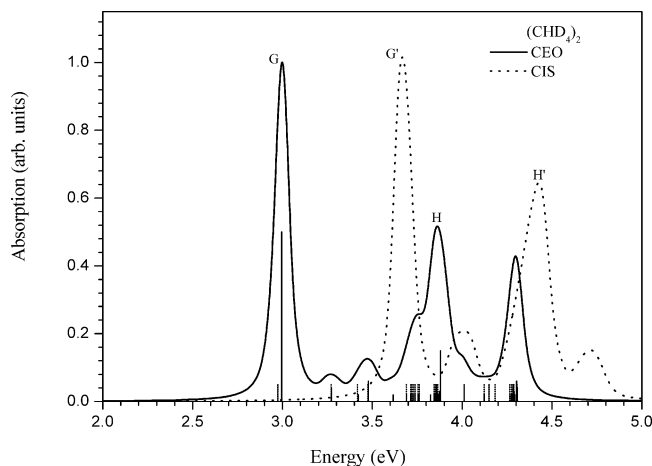


Figure 5. CEO (full line) and CIS (dotted line) theoretical spectra of neutral $(\text{CHD}_4)_2$. Sticks are proportional to the CEO oscillator strength of the transition. Dotted sticks refer to dark transitions.

oligomer, the excitation energies being 3.51 (2.99) eV (neutral) and 0.23 (0.21) eV (charged). In particular, in the charged case the CIS calculation is able to nicely reproduce the very small transition energy that is obtained at the CEO level. Good agreement in both transition energy and oscillator strength is found also for the next peak, which is the most intense in this spectrum. The importance of the above features is related to the fact that the carbazolyl-substituted charged oligomers with $n = 4-6$ show, despite their short length, a behavior that can be considered as nearly asymptotical, as was shown in paper I.

In conclusion, we believe that the above results allow us to be confident that the CIS approach will give an adequate picture of at least the low-energy transitions of the charged dimer.

2.2. Dimer Results. The number of CEO modes considered for the neutral dimer has been 60, while the active space for the CIS calculations was made of 70 occupied and 70 virtual π molecular orbitals (50 and 50 for the isolated molecule; see paper I). As could be expected, the electronic density in the ground state of the CHD_4 neutral dimer is strictly localized onto the individual molecules, as is also demonstrated by the calculation of the ZINDO electrostatic potential (ESP; see Figure 9 below). The computed spectra of the neutral dimer, obtained using the CEO and CIS approaches, are displayed in Figure 5.

The shape of the CEO spectrum is almost unchanged with respect to that of the single molecule. More specifically, despite

the large distance between the backbones, a small yet appreciable Coulomb interaction occurs, which splits each excitation of isolated CHD_4 into two transitions (one of which is dark) as could be predicted on the grounds of the excitonic theory.¹³ Similar considerations hold for the CIS spectrum, which, however, differs a bit more from the isolated-molecule counterpart, especially in its lowest energy peak (by about +0.15 eV in the latter case). This is most probably due to the high number of π molecular orbitals that have been left out of the active space in the CIS calculation for the dimer (30 occupied plus 30 virtual) due to practical reasons. This fact has the general consequence of slightly increasing the blue-shift of the CIS spectrum with respect to the CEO one, which was already found by us in the isolated oligomer. Nonetheless, the corresponding peaks in the two spectra are strictly similar in nature, as will be illustrated below for the two lowest energy, most intense maxima. In the CEO spectrum they are labeled (see Figure 5) G (at 2.99 eV) and H (at 3.88 eV), and the contour maps of the corresponding modes are depicted in logarithmic scale in Figure 6.

Despite the differences in the two modes, their common feature is the absence of any off-diagonal elements between the two molecules, i.e., of any interaction between them. The G and H excitations are simply the direct (in-phase) sums of the corresponding ones of the isolated CHD_4 oligomer. The corresponding peaks in the CIS spectrum are labeled G' (at 3.67 eV, corresponding to the isolated-molecule peak at 3.51 eV) and H' (at 4.43 eV, corresponding to the isolated-molecule peak at 4.32 eV). The G' wave function can be seen to be dominated by the $(\text{HOMO}-1) \rightarrow (\text{LUMO})$ configuration (with a coefficient of -0.666) and the $(\text{HOMO}) \rightarrow (\text{LUMO}+1)$ one (with a coefficient of 0.638), whereas some 70 configurations contribute to the H' wave function with non-negligible coefficients. Figure 7 shows a pictorial representation of the frontier molecular orbitals involved in the G' wave function.

The substituted and substituent orbitals in each configuration belong to the same oligomer, and moreover, in each case only the backbones play a role, similarly to what happens in the G CEO mode of Figure 6. No such representation is practical here for the many orbitals involved in H' , but even in this case it can be seen that the occupied and virtual orbitals involved in each component configuration are localized on the *same* oligomer, although now the carbazolyl moieties strongly contribute, just likely as depicted in the H CEO mode of Figure 6.

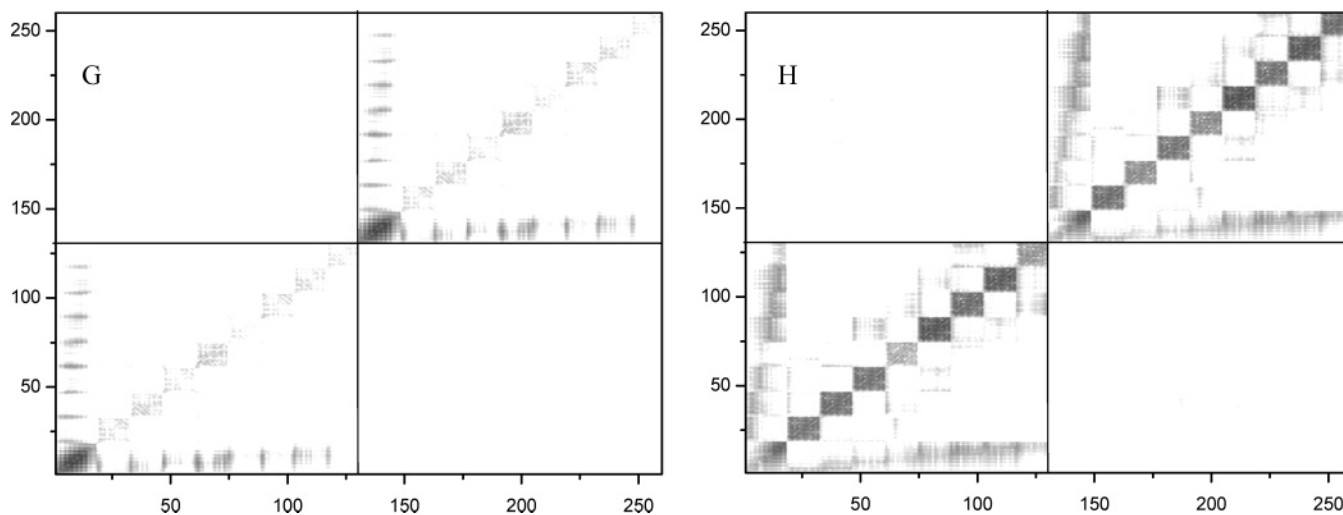


Figure 6. Contour maps (logarithmic scale) for the CEO modes corresponding to the G (2.99 eV) and H (3.88 eV) allowed neutral dimer transitions.

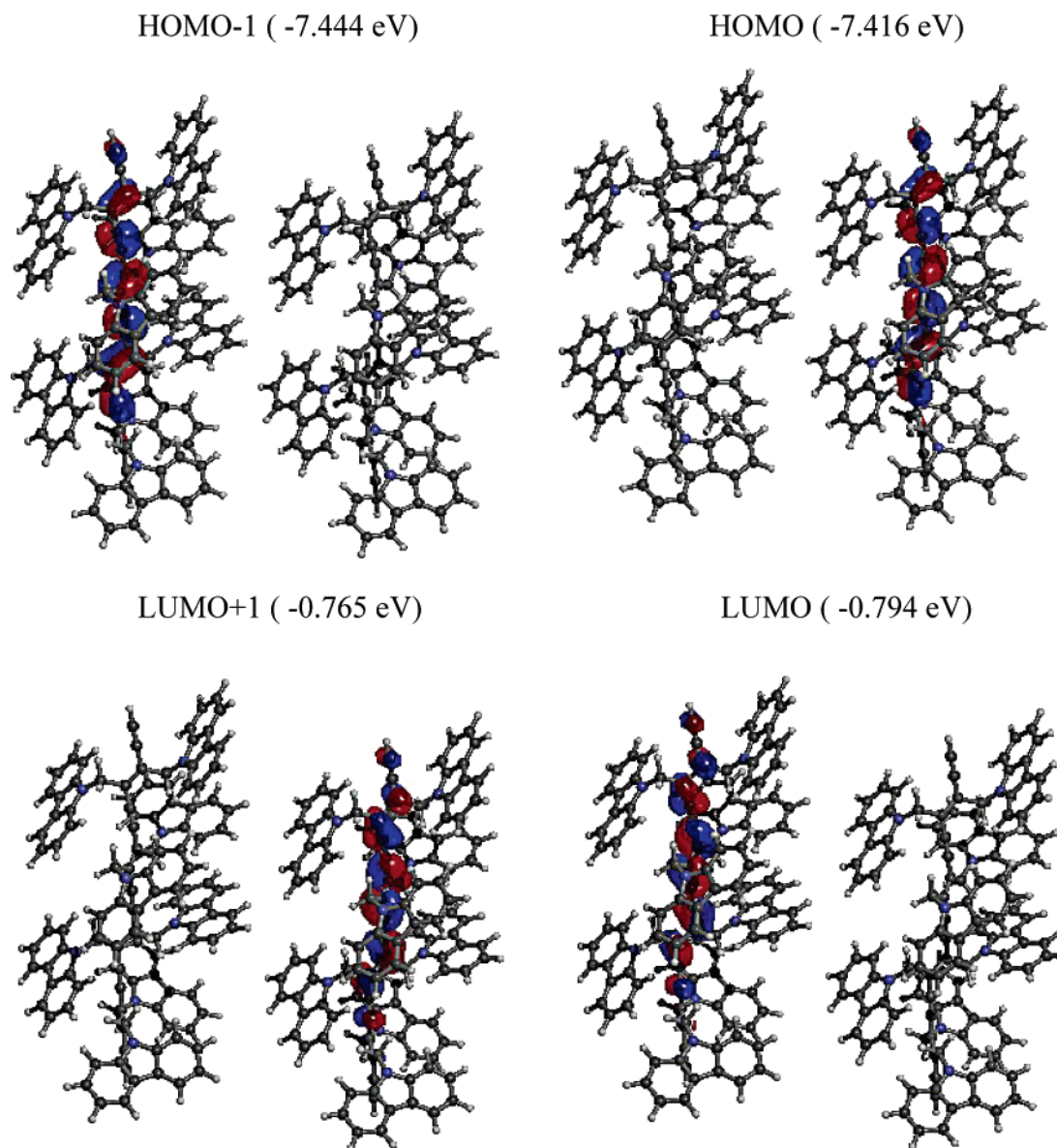


Figure 7. Sketch of the neutral dimer frontier MO's.

The CIS spectrum of the charged dimer is displayed in Figure 8, in which the corresponding spectra of the charged and of the neutral isolated oligomer are also reported for comparison.

In the region below 0.5 eV, the spectrum is strongly broadened with respect to that of the charged isolated oligomer, and new peaks appear, both allowed and dark, indicating the rise of a strong interaction between the two molecules, whose effect is apparent in Figure 9, in which the ESP isopotential surfaces (both corresponding to a common value of 0.10 au) of the charged and of the neutral dimer are compared.

As outlined above, the occurrence of such an interaction could not have been predicted without explicitly considering the *substituent* effect, in that it is only due to the very large amount (about 95%, see paper I) of the excess charge of the distorted oligomer, which is spread over its carbazolyl moieties. In fact, in the neutral dimer no similar effect appears, the spectra largely resembling those of the isolated molecule. In our opinion such a clear origin can almost rule out the possibility of calculation artifacts, although it would be desirable in this respect to have

a check at a very large interchain distance, which, however, has been proven impossible to date due to convergence difficulties.

The interaction reflects itself also in the form of the frontier molecular orbitals (Figure 10), which are no longer the mere combination of those of the separated oligomers.

Broadening of the lowest energy band due to the interaction leads to a further improved (see paper I) agreement between the theoretical spectrum and the experimental photoinduced absorption spectrum of polyDCHD (the polymer corresponding to CHD_n).¹⁴ The above band (named K') corresponds to the convolution of a number of allowed transitions in the energy range $0.16 \div 0.40$ eV, the most relevant ones being predicted at 0.16, 0.24, 0.26, 0.33, and 0.34 eV, respectively. They are two excited states carrying similar structures, where the dominant configuration is of the type $(\text{HOMO}-x) \rightarrow (\text{LUMO})$. A prototypical example of such states is that corresponding to an excitation energy of 0.16 eV, whose main (≥ 0.1) configuration coefficients, resulting in a global weight of 0.98, are collected in Table 1.

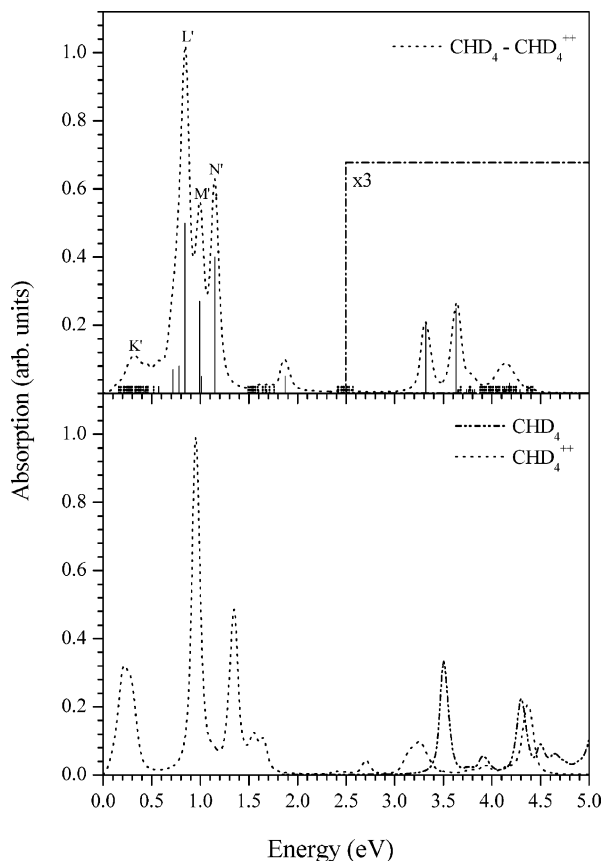


Figure 8. CIS theoretical spectrum of $\text{CHD}_4\text{-CHD}_4^{2+}$ (top). Sticks are proportional to the oscillator strength of the transition and are renormalized to 0.5. Dotted sticks refer to dark transitions. On the bottom the spectra of the isolated charged and neutral oligomer are reported for comparison on the same scale.

The configurations in Table 1 can be divided into two groups of nearly equal weight, namely the first configuration and the remainder. From Figure 10 it is seen that the (HOMO-1)→(LUMO) configuration describes a *through-space* charge transfer from the carbazolyl moieties of the charged oligomer to both backbones. The form of the subsequent occupied MO's in Table 1 resembles that of HOMO-2, which implies that the last six configurations describe a different type of through-space charge transfer, coming this time from the carbazolyl moieties of the

TABLE 1: Main Coefficients of the CIS Wave Function Describing the Excited State of $\text{CHD}_4\text{-CHD}_4^{2+}$ at 0.16 eV

single-excitation	CI coefficient
(HOMO-1) → (LUMO)	-0.705
(HOMO-9) → (LUMO)	0.522
(HOMO-3) → (LUMO)	0.371
(HOMO-8) → (LUMO)	0.160
(HOMO-4) → (LUMO)	-0.153
(HOMO-10) → (LUMO)	0.111
(HOMO-18) → (LUMO)	0.100

TABLE 2: Main Coefficients of the CIS Wave Functions Describing the L', M', and N' Excited States of $\text{CHD}_4\text{-CHD}_4^{2+}$ in Figure 8

single-excitation	CI coefficient
L'	
(HOMO) → (LUMO)	-0.615
(HOMO-33) → (LUMO)	-0.501
(HOMO-25) → (LUMO)	-0.389
(HOMO-35) → (LUMO)	0.242
(HOMO-34) → (LUMO)	-0.131
M'	
(HOMO-33) → (LUMO)	0.707
(HOMO) → (LUMO)	-0.434
(HOMO-37) → (LUMO)	0.397
N'	
(HOMO-37) → (LUMO)	-0.813
(HOMO) → (LUMO)	-0.426

neutral oligomer. It is worth noting that these two coexistent charge-transfer types (as well as those to be described below), which connect directly the charged with the neutral molecule, could supply an efficient channel for charge transport in bulk substituted materials.¹⁵

The peaks L' (at 0.84 eV), M' (at 0.99 eV), and N' (at 1.15 eV) are related to the most intense CIS peak of the isolated charged oligomer at 0.96 eV. Table 2 collects their main configuration coefficients, whose total weight is never less than 0.85.

The excitations are now highly delocalized on the two oligomers, as can be directly seen for the (HOMO)→(LUMO) configuration, which gives a substantial contribution especially to L'. It is for both these reasons that this peak becomes lower in energy with respect to its parent in the isolated oligomer.

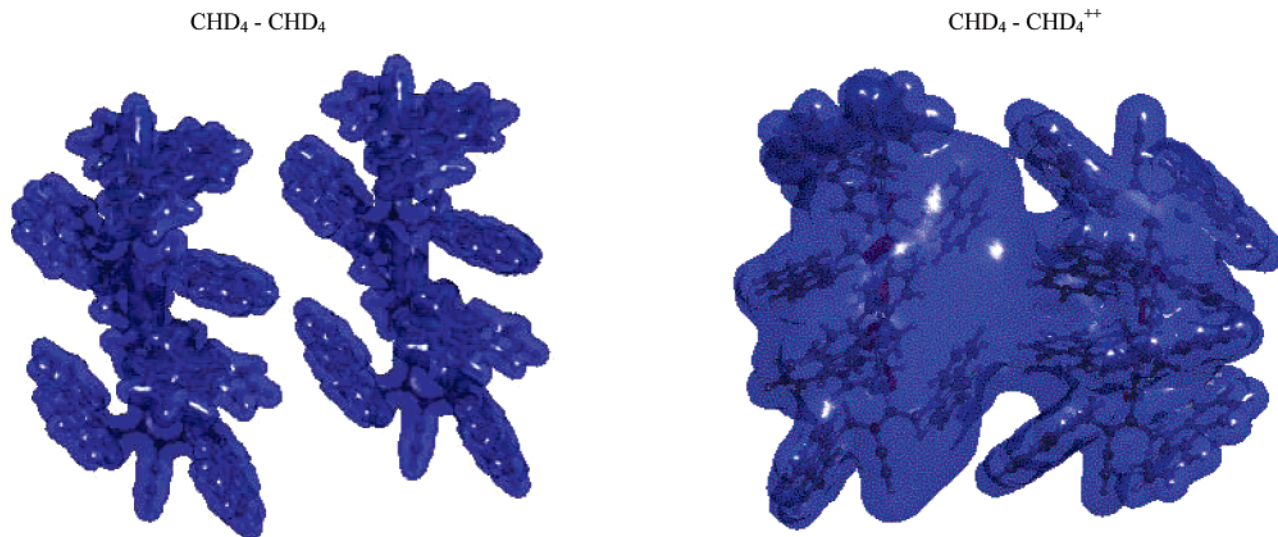


Figure 9. Ground-state electrostatic potential of the neutral (left) and doubly positively charged (right) CHD_4 dimer.

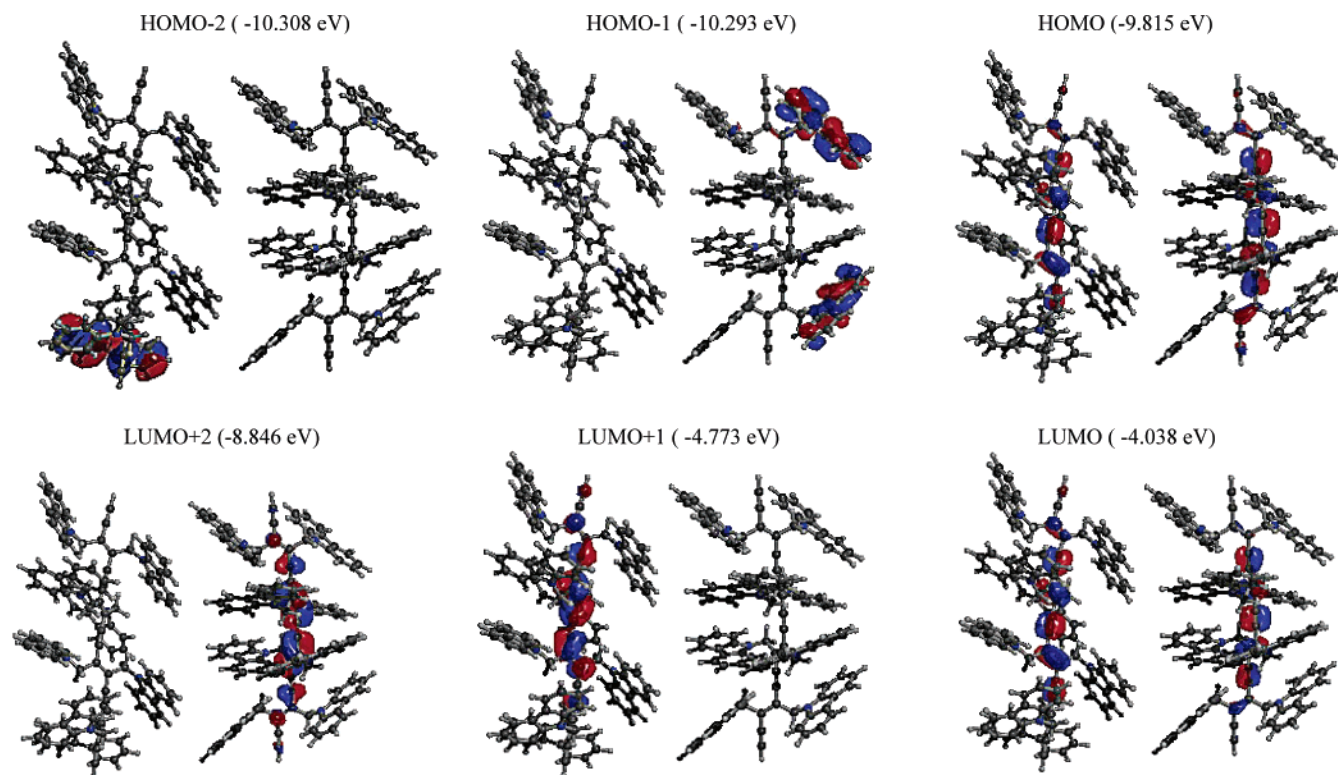


Figure 10. Sketch of the $\text{CHD}_4\text{--CHD}_4^{2+}$ frontier MO's.

The other occupied orbitals in Table 2, although similar in form to the HOMO, lie well deeper, which implies that peaks M' and N' behave similarly to L' but undergo a consequent blue shift.

3. Conclusions

The common practice (which has been used in the past also in our laboratory) of putting forward theoretical predictions on the basis of calculations that have been only performed on unsubstituted systems may be misleading and unreliable even as a first-approximation approach. In particular in our case the rise of a strong interaction between a charged and a neutral oligomer lying very far apart can only be traced back to the presence of substituents. Moreover, from our results it can be argued that the different shapes exhibited by the photoinduced absorption spectra of different polydiacetylenes, e.g. in the critical zone under 0.50 eV, could be possibly explained in terms of the role played by substituents. In any case, the intermolecular interaction has the effect of broadening the computed spectrum in this region (improving the agreement with experimental results) and of originating a through-space charge transfer between the charged and the neutral molecule that could supply an efficient channel for charge transport in bulk substituted polydiacetylenes.

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