

# Electronic Structure of Thienylene Vinylene Oligomers: Singlet Excited States, Triplet Excited States, Cations, and Dications

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This paper describes a quantum chemical study of the electronic structure of thienylene vinylene oligomers ranging in size from two thienylene rings (2TV) to 12TV. The geometries of the TV oligomers in the ground state, the lowest triplet state, and the singly and doubly oxidized states were optimized using density functional theory calculations. The electronic absorption spectra were obtained from configuration interaction calculations with an INDO/s reference wave function. Comparison with experimental data shows that the agreement is satisfactory, except for the triplet–triplet absorption spectra. For closed shell systems (ground state and doubly occupied state), the spectra were also calculated by time dependent density functional theory (TDDFT). TDDFT considerably underestimates the neutral singlet–singlet excitation energies for longer chains. The nature of the excited states for the TV radical cations was found to be more similar to that of thiophenes than to that of phenylene vinylenes, indicating that the sulfur atom has a marked influence on the  $\pi$ -electron system. For the (singlet) absorption spectra of doubly oxidized TVs, the results from TDDFT calculations are surprisingly good; they are also good for long chains. TDDFT calculations for doubly charged TVs also confirm the existence of a second, weak absorption band as has been found experimentally.

## 1. Introduction

Conjugated polymers and oligomers are being studied extensively for possible applications in plastic (opto-) electronic devices, such as field effect transistors, light emitting diodes, and photovoltaic cells.<sup>1–3</sup> Conjugated polymers are wide band gap semiconductors that can become conducting by oxidative or reductive doping. The optoelectronic properties of conjugated polymers combined with the low cost and processability from common organic solvents make them attractive materials for application in the devices mentioned above. The application of these materials relies critically on their ability to transport charge. Therefore, a detailed knowledge of the nature of charge carriers in these materials is of obvious importance. Important information on the properties of charged species in conjugated molecules can be obtained experimentally from electronic absorption spectra of doped conjugated oligomers<sup>4</sup> or from vibrational spectroscopy.<sup>5</sup> Electronic absorption spectra of singly charged conjugated oligomers generally exhibit two transitions below the absorption maximum of the neutral parent compound, which can be explained by the formation of a polaron in a one-electron band-structure model (see below).<sup>6</sup> The appearance of

two subgap absorption maxima has been shown for several conjugated oligomers, including thiophenes and phenylene vinylenes (PVs). However, it has also been shown, both theoretically and experimentally, that for longer PVs and for PVs bearing alkoxy side chains a third subgap transition can appear that is not explained in the polaron band model.<sup>4,7</sup>

Electronic spectra of doubly charged conjugated oligomers are generally characterized by a single strong subgap transition; however, there are also indications (e.g., for oligothiophenes) that a second, weak subgap absorption feature is present.<sup>8</sup>

Quantum chemical electronic structure calculations can be of great value to aid in the understanding of the electronic properties of (charged) conjugated oligomers. Comparison of calculated electronic spectra with experimentally obtained spectra can be useful in assigning the different absorption features to specific electronic transitions. It is also possible to directly obtain information that is very difficult to extract from experiments, such as direct information on geometric deformations induced by charge carriers. Electronic structure calculations have been performed for a variety of conjugated oligomers.<sup>4,6,9,10</sup> Materials for which such calculations have been performed include phenylene vinylenes (PVs)<sup>4,6</sup> and oligothiophenes.<sup>10</sup> For thienylene vinylenes (TV),<sup>11–13</sup> compounds that are related to both PVs and thiophenes, the electronic structure calculations performed are limited to the optical properties of neutral molecules.<sup>14</sup> TVs have received a considerable amount of attention recently because of their low oxidation potential and their relatively low band gap.<sup>12</sup> The dependence of the nTV absorption energy on the chain length suggests that the effective

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conjugation length in these materials is significantly larger than in, for example, thiophenes and PVs.<sup>13</sup> This makes TVs attractive for application in photovoltaic devices<sup>15</sup> and as the active material in field effect transistors for plastic electronics.<sup>16,17</sup>

The aim of this paper is to provide a theoretical background for the interpretation of optical absorption spectra of neutral, singly, and doubly charged TVs. Electronic absorption spectra were calculated for the neutral ground state, the lowest triplet state, and the singly and doubly charged states. The focus is more on the nature of the excited states than on the magnitude of the transition energies.

## 2. Computational Details

The geometries of the thienylene vinylene oligomers studied in this work were optimized using the Amsterdam Density Functional program (ADF).<sup>18,19</sup> The geometry optimizations were performed using the Local Density Approximation (LDA) with the exchange and correlation functionals based on the parametrization of the electron gas data given by Vosko, Wilk, and Nusair (VWN).<sup>20</sup> Generalized Gradient Approximation (GGA) corrections by Becke (exchange) and Perdew (correlation) were included.<sup>21,22</sup> All geometry optimizations were performed using a basis set of double- $\zeta$  quality including polarization functions (DZP, basis set III in ADF) consisting of Slater-type functions. Test calculations for short oligomers showed that there are no significant changes in geometry if a larger basis set is used. For the singly charged oligomers, the restricted open shell method was used to avoid artifacts due to spin contamination. The geometries were restricted to either  $C_{2h}$  or  $C_{2v}$  symmetry depending on the number of repeat units. For the triplet state, the unrestricted open shell method was used.

The electronic absorption spectra of the closed shell systems (neutral and doubly charged TVs) were calculated using the semiempirical intermediate neglect of differential overlap (INDO)<sup>23–26</sup> method combined with a singly excited configuration interaction (CIS) calculation for the excited states. A Restricted Hartree–Fock (RHF) calculation was performed for the ground state. The Coulomb repulsion terms were described using the Mataga–Nishimoto parameters,<sup>27</sup> which have been especially developed for spectroscopic calculations. This parametrization of the INDO Hamiltonian is usually called INDO/s.<sup>26</sup> The single determinant RHF wave function was used as the reference determinant in a CIS calculation for the excited state, in which excitation from the highest 30 occupied orbitals into the lowest 30 unoccupied orbitals was included. This was found to be sufficient for convergence of the lowest allowed (most intense) electronic transition. Alternatively, the electronic spectra of closed shell TVs was calculated using the time dependent density functional theory (TDDFT) method<sup>28</sup> as implemented in ADF. For these calculations, a basis set of triple- $\zeta$  quality with polarization functions (TZP) was used. It should be noted that the description of response properties using conventional exchange correlation functionals is troubled by the local description of electron–electron interaction, leading to underestimates of excitation energies for systems with delocalized  $\pi$ -electron systems.<sup>29,30</sup>

For open shell systems (singly charged and triplet state), the spectra were calculated only by the INDO/s-CIS method using a restricted open shell Hartree–Fock (ROHF) wave function as the reference determinant. Presently, it is not possible to calculate electronic spectra for open shell systems with ADF. It was shown recently that the combination of a geometry optimized using DFT and an INDO/s-CIS calculation of the

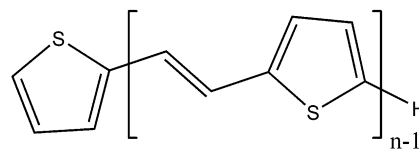


Figure 1. Structure of  $n$ TV oligomers.

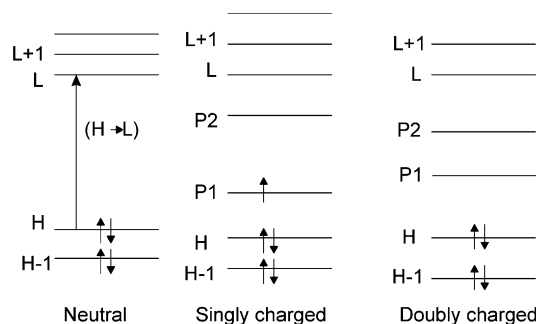


Figure 2. Single determinant energy levels and their nomenclature in neutral, singly charged, and doubly charged PV oligomers.

electronic spectrum gives good results for the optical absorption spectrum of radical cations of phenylene vinylene oligomers.<sup>4</sup> For neutral molecules, it is well known that INDO/s-CIS gives reliable predictions of optical absorption spectra.<sup>26</sup>

No counterions have been taken into account in the present calculations. Comparison with experiments in which counterions are present is justified, however, since it is expected that the counterions are sufficiently screened by the solvent to not have an effect on the trend in the transition energies obtained. Solvent effects may also influence the transition energy; however, it is expected that inclusion of solvent effects leads to a uniform change in the transition energies rather than a change in the trends observed.

## 3. Results and Discussion

The electronic absorption spectra of  $n$ TV with  $n$  varying from 2 to 12 were calculated for the ground state, the lowest triplet state, and singly and doubly oxidized states, using the methodology described in the preceding section (the structure of  $n$ TV oligomers is shown in Figure 1). The electronic transitions are described in detail below, in terms of the configuration state functions (CSF) that contribute to the excited state to which the excitation takes place. The nomenclature of the one-electron levels is indicated in Figure 2 for neutral, singly charged, and doubly charged oligomers. For the neutral systems, the abbreviations are straightforward; the highest occupied molecular orbital (HOMO) is called H and the lowest unoccupied molecular orbital (LUMO) is indicated as L. For the charged systems, the nomenclature originating from a one-electron band model with a charged defect is adopted.<sup>31</sup> Although this description based on a band model is not directly applicable to oligomers of finite length, the nomenclature derived from it is generally used in the literature and will therefore also be adopted here.

In the band model the introduction of a charge leads to the formation of two localized states inside the band gap, the so-called polaron levels, P1 and P2. In a singly charged system, P1 is singly occupied while P2 is empty, whereas both levels are empty in a doubly charged system (bipolaron). Note that according to this nomenclature the level indicated as L is actually the second empty level for singly charged molecules

**TABLE 1: Electronic Absorption Spectra of Neutral Thienylene Vinylene Oligomers Calculated by INDO/s-CIS<sup>a</sup>**

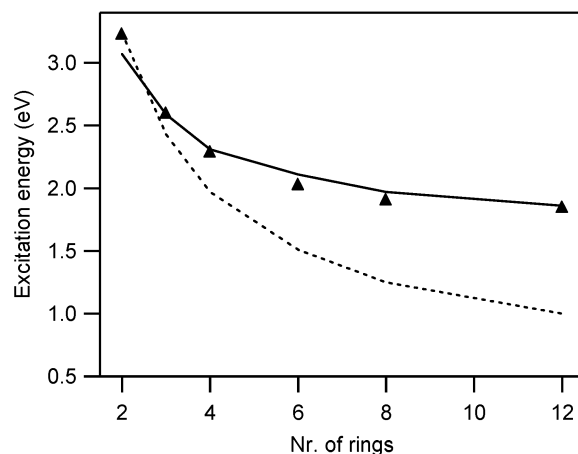
compound	$\Delta E$ (exp.)	$\Delta E$ (calc.)	$f$	main CI expansion coefficients
2TV	3.23 <sup>b</sup>	3.07	1.06	0.96(H $\rightarrow$ L)
		4.92	0.06	0.39(H - 2 $\rightarrow$ L) + 0.8 (H $\rightarrow$ L + 2)
		5.29	0.01	-0.41(H - 1 $\rightarrow$ L + 4) + 0.89(H $\rightarrow$ L + 6)
		5.42	0.47	-0.66(H - 2 $\rightarrow$ L) + 0.38 (H - 1 $\rightarrow$ L) + 0.33(H $\rightarrow$ L + 2) - 0.41(H $\rightarrow$ L + 5)
3TV	2.60 <sup>b</sup>	2.59	1.49	0.96(H $\rightarrow$ L)
		3.61	0.30	0.92(H $\rightarrow$ L + 2)
		3.83	0.14	0.92(H - 1 $\rightarrow$ L)
		2.31	2.20	0.94(H $\rightarrow$ L)
4TV	2.29 <sup>b</sup>	3.78	0.32	0.84 (H $\rightarrow$ L + 2)
		4.06	0.58	0.96(H - 2 $\rightarrow$ L) + 0.54(H - 1 $\rightarrow$ L + 1)
		2.11	3.28	0.87(H $\rightarrow$ L) + 0.40(H - 1 $\rightarrow$ L + 1)
		3.20	0.35	0.36(H - 2 $\rightarrow$ L) + 0.50(H - 1 $\rightarrow$ L + 1) 0.68(H $\rightarrow$ L + 2)
6TV	2.03 <sup>b</sup>	3.47	0.02	-0.32(H - 3 $\rightarrow$ L + 1) - 0.67(H - 2 $\rightarrow$ L) + 0.40(H $\rightarrow$ L + 3)
		3.98	0.43	0.42(H - 1 $\rightarrow$ L + 3) + 0.69(H $\rightarrow$ L + 4)
		1.97	4.33	0.80(H $\rightarrow$ L) + 0.45(H - 1 $\rightarrow$ L + 1)
		2.78	0.42	0.47(H - 2 $\rightarrow$ L) + 0.46(H - 1 $\rightarrow$ L + 1) + 0.57(H $\rightarrow$ L + 2)
8TV	1.91 <sup>b</sup>	3.53	0.18	0.32(H - 2 $\rightarrow$ L + 2) - 0.45(H - 1 $\rightarrow$ L + 3) + 0.63(H $\rightarrow$ L + 4)
		3.74	0.07	0.45(H - 3 $\rightarrow$ L + 1) - 0.59(H - 4 $\rightarrow$ L)
		1.86	6.42	0.69(H $\rightarrow$ L) - 0.48(H - 1 $\rightarrow$ L + 1) - 0.33(H - 2 $\rightarrow$ L + 2)
		2.35	0.52	0.48(H - 2 $\rightarrow$ L) + 0.38(H - 1 $\rightarrow$ L + 1) + 0.52(H $\rightarrow$ L + 2)
12TV	1.85 <sup>b</sup>	2.90	0.31	-0.34(H - 4 $\rightarrow$ L) + 0.38(H - 2 $\rightarrow$ L + 2) - 0.38(H - 1 $\rightarrow$ L + 3) + 0.46(H $\rightarrow$ L + 4)

<sup>a</sup> Transition energy (in eV), oscillator strength ( $f$ ), and main CI expansion coefficients for the first three allowed transitions are given. <sup>b</sup> Experimental data obtained from Apperloo et al.<sup>15</sup>

and the third empty level for doubly charged ones. The subgap absorption features are due to excitations involving the P1 and P2 levels.

An additional process that can occur on ionization of TV oligomers in solution is the formation of  $\pi$ -dimers. In this process, two radical monocation TVs form a complex that has no net spin, as indicated by ESR experiments. The formation of such  $\pi$ -dimers has been observed for certain TVs, depending on the side chains.<sup>32</sup> Formation of  $\pi$ -dimers is outside the scope of the present work.

**3.1. Singlet Excited Etates of Thienylene Vinylenes.** In Table 1, the calculated electronic transitions for TV oligomers of increasing length are listed. The INDO/s-CIS calculated transition energies for the lowest four allowed transitions are given together with their oscillator strength and the main CI expansion coefficients. In all TVs, the lowest transition is the most strongly allowed one, with oscillator strengths that are roughly proportional to the number of repeat units in the chains. The higher allowed transitions have oscillator strengths that are an order of magnitude or more lower than that for the lowest transition. The calculated excitation energies for the lowest transition are compared to experimental data by Apperloo et al.<sup>15</sup> in Table 1 and Figure 3. The experimental transition energies correspond to the low energy vibronic transition at low temperature; this is the most intense vibronic transition in the experimental spectra for 6TV, 8TV, and 12TV at 90 K. The agreement between the calculated and experimental excitation energies is excellent, as is evident from Figure 3. It should be noted that the good agreement may be somewhat fortuitous, since the calculations were performed on isolated molecules, whereas the experimental data were obtained in (frozen) solution. Moreover, the comparison is somewhat hampered by the absence of substituents in the calculation, whereas in the experimental data all thienyl rings are substituted with two alkyl chains. There are some experimental data for the absorption maxima of unsubstituted TVs;<sup>33</sup> however, these measurements were performed in a different solvent (DMF vs dichloromethane), which makes direct comparison somewhat difficult. It is, however, clear that the introduction of alkyl chains leads to a general lowering of the excitation energy without altering

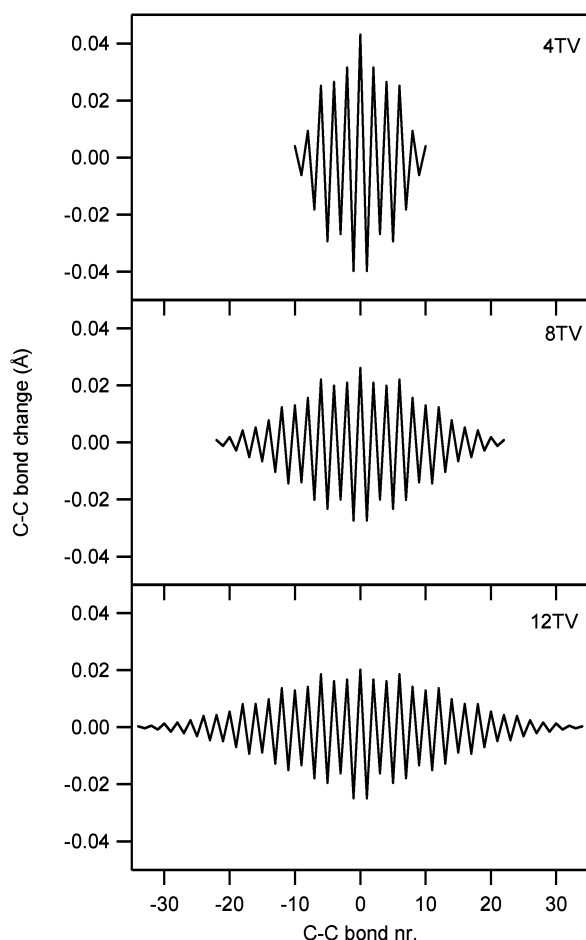


**Figure 3.** Comparison of calculated and experimental lowest optical transition for TV oligomers. Triangles: experimental data by Apperloo et al.;<sup>15</sup> full line: INDO/s-CIS calculations; dotted line: TDDFT calculations.

the trend as a function of chain length, as also noted by Apperloo et al.,<sup>32</sup> who studied TVs containing with different alkyl substituents.

The nature of the lowest excited state can be examined by considering the main CI expansion coefficients obtained from the CIS calculations. The lowest transition is in all cases dominated by a configuration in which an electron is excited from the highest occupied molecular orbital (H) to the lowest unoccupied molecular orbital (L); this configuration is indicated as (H  $\rightarrow$  L) in Table 1. For TVs up to 4TV, the transition is almost entirely due to (H  $\rightarrow$  L). For longer oligomers, other configurations, especially (H - 1  $\rightarrow$  L + 1), start contributing significantly. The second transition is mainly due to (H  $\rightarrow$  L + 2) in all TVs.

Electronic absorption spectra for closed shell systems can also be calculated by the TDDFT method. Such calculations have been performed for the TV oligomers, and the transition energies are compared to results from INDO/s-CIS calculations and experimental data in Figure 3. For 2TV and 3TV, the correspondence between the TDDFT results and the experimental data is excellent; however, for longer TVs the excitation energy



**Figure 4.** Changes in bond length upon transition to the  $T_1$  state.

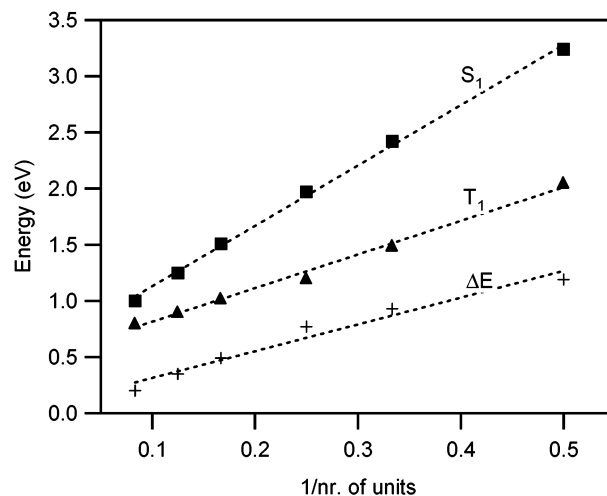
is considerably underestimated. The discrepancy increases with increasing chain length. For 12TV, the experimental excitation energy is more than twice as large as the TDDFT value. This underestimation of excitation energies for large conjugated molecules has been observed previously.<sup>29,34</sup> It is attributed to the short-sightedness of traditional exchange correlation (XC) functionals, which depend only on the local density and are insensitive to polarization charges induced at the extremes of large molecules by an external (oscillating) electric field.<sup>30,35,36</sup> The inadequacy of these XC functionals is also revealed in the large overestimation of ground and excited state polarizabilities.<sup>35,37</sup> It was shown recently by Van Faassen et al.<sup>30,38</sup> that the problem of large overestimations of ground state polarizabilities can be solved by introducing so-called current density functionals that also depend on the local *current* density rather than on the density alone. It is expected that these functionals will also give a better description of excitation energies for large conjugated systems; however, these functionals have not yet been implemented for use in TDDFT calculations of electronic absorption spectra.

**3.2. Triplet Excited States of Thienylene Vinylenes.** The geometry of a conjugated molecule in the lowest triplet state ( $T_1$ ) is, in general, different from its geometry in the ground state. The geometry changes are primarily observed in the bond length changes along the carbon backbone of the chain. In Figure 4, the calculated changes in the C–C bond lengths along the TV oligomers upon excitation from the ground state to the lowest triplet state for 4TV, 8TV, and 12TV are shown. It is evident from this figure that the length of the (formally) double bonds increases somewhat, whereas the single bonds become

**TABLE 2: Triplet Excited States of Thienylene Vinylene Oligomers<sup>a,b</sup>**

compound	TDDFT		INDO/s-CIS		exp.
	$T_1$ (vert.)	$T_1$ (rel.)	$T_n \leftarrow T_1$	$f$	$T_n \leftarrow T_1$
2TV	2.05	1.70 (1.52 <sup>c</sup> )	3.60	1.37	—
3TV	1.49	1.24 (1.32 <sup>c</sup> )	3.34	1.62	2.28 <sup>c</sup>
4TV	1.20	1.01 (1.23 <sup>c</sup> )	3.04	2.34	1.94 <sup>c</sup>
6TV	1.02	0.83 (1.14 <sup>c</sup> )	2.38	3.38	1.63 <sup>c</sup>
8TV	0.90	0.72 (1.10 <sup>c</sup> )	2.20	4.19	1.50 <sup>c</sup>
12TV	0.80	0.65 (1.06 <sup>c</sup> )	1.91	5.59	1.42 <sup>c</sup>

<sup>a</sup> Energy of triplet state with respect to the ground state (vertical and relaxed) obtained from DFT calculations, and in parentheses the experimental values. <sup>b</sup> Also shown are the  $T_n \leftarrow T_1$  transition energy and oscillator strength ( $f$ ) obtained from INDO/s-CIS calculations. <sup>c</sup> Experimental results obtained from Apperloo et al.<sup>15</sup>



**Figure 5.**  $S_1$  and  $T_1$  energy and the  $S_1 - T_1$  difference calculated by TDDFT plotted against the inverse chain length.

shorter; that is, a so-called quinoidlike structure is formed. The largest changes occur in the center of the oligomer, while the changes toward the chain ends are very small, especially for 12TV. It should be noted that the spatial extent of the geometry deformations is not constant; the deformations continue to extend over the entire chain when the length increases, at least up to 12TV. The magnitude of the bond length changes decreases when the chain becomes longer, from close to 0.04 Å for 4TV to 0.02 Å for 12TV.

In Table 2, the energy of the lowest triplet state with respect to the ground state as obtained from TDDFT calculations is given. The vertical value represents the triplet energy obtained using the ground state geometry. The vertical  $T_1$  energy is plotted in Figure 5 as a function of the inverse chain length, together with the  $S_1$  energy from TDDFT calculations and the energy difference between  $S_1$  and  $T_1$ . The decrease in the transition energy of  $T_1$  with increasing chain length is slower than for  $S_1$ , which is indicative of a more localized nature of the triplet exciton.<sup>39</sup> The energy difference between  $S_1$  and  $T_1$  is a measure of the exchange energy, a parameter of interest for the efficiency of electroluminescence from organic materials.<sup>40</sup> This calculated energy difference is seen to decrease from 1.2 eV for 2TV to 0.2 eV for 12TV, see Figure 5. The very low exchange energy for 12TV does not correspond to recent experimental data by Köhler et al.,<sup>39</sup> who showed that the exchange energy converges to around 0.7 eV for a variety of conjugated polymers. It was shown by the same authors that the  $S_1 - T_1$  difference converges to around 1 eV if calculated by the INDO/s-CIS methods.<sup>39</sup> The difference is attributed to the large underestimate of the  $S_1$  energy by TDDFT. It also



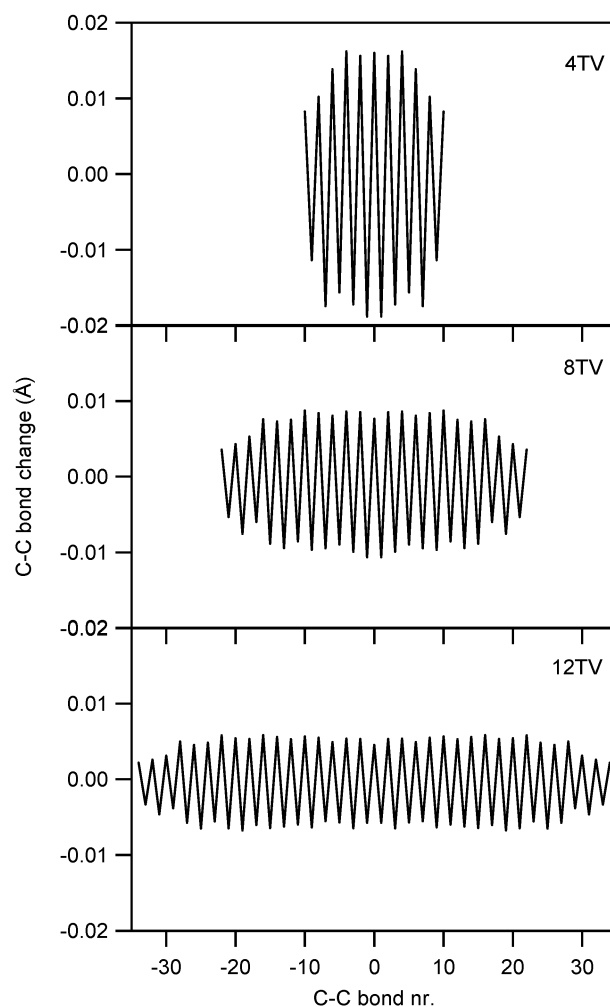
implies that the description of chain length dependence of the  $T_1$  transition energy is better than that for the  $S_1$  energy, since the energy difference between them decreases too fast.

The relaxed  $T_1$  energy was obtained from a TDDFT calculation using the geometry optimized for the triplet state and adding the change in the ground state energy caused by the deformation of the geometry. The energy difference between the vertical and relaxed  $T_1$  states is the energy drop when the molecule relaxes from the ground state geometry to the most stable geometry for the triplet. This energy difference decreases upon lengthening of the TV chain, which is consistent with the decrease in the absolute changes in C–C bond lengths in Figure 4. The calculated relaxed  $T_1$  energy can be compared with the experimental  $T_1$  energies estimated by Apperloo et al.,<sup>15</sup> these values are also given in Table 2. The experimental  $T_1$  energy of 1.52 eV for 2TV is somewhat lower than the calculated value of 1.70 eV. The calculated energy decreases upon lengthening of the chain to 0.65 eV for 12TV, which is lower than the experimental value (1.06 eV). Although the calculated  $T_1$  energies decrease somewhat more rapidly with increasing chain length, as compared to the experimental data, the correspondence is found to be satisfactory, particularly in view of the assumptions made in the estimates of the experimental values.

Experimentally, the triplet–triplet absorption spectra of TVs (and of conjugated molecules in general) are dominated by a single strong absorption feature.<sup>15</sup> The electronic absorption spectra for the lowest triplet state ( $T_1$ ) were calculated using the INDO/s-CIS methodology with the geometry obtained from DFT calculations. The calculated spectrum exhibits a single strong transition. The excitation energies for this transition are compared to experimental data in Table 2. The calculated values are considerably higher than the experimentally observed excitation energies. The difference between the calculated and experimental values decreases from close to 1 eV for 2TV to approximately 0.5 eV for 12TV. This better agreement for longer chains is attributed to an effective increase in the size of the basis set. The rather poor agreement between the calculated values and the experimental data is somewhat surprising in view of the excellent agreement obtained for the singlet absorption spectra. A similar large overestimation of the triplet–triplet absorption energy has been found by Beljonne et al.,<sup>41,42</sup> both for oligophenylenevinylenes and for oligothiophenes using the same reference Hamiltonian (INDO/s) but combined with more sophisticated multireference configuration interaction (MRCI) calculations of the excitation energies. It should be kept in mind that the lowest singlet excited state involves mainly the lowest unoccupied molecular orbital, whereas in the case of the  $T_n \leftarrow T_1$  transition higher lying orbitals are also involved. The description of such higher lying diffuse orbitals is usually rather poor when a minimal basis set is used that does not contain polarization functions.

The absorption is in all TVs due to a mixture of two determinants: one in which an electron is excited from the highest doubly occupied orbital to the lowest singly occupied orbital in  $T_1$  and one in which the electron in the highest singly occupied orbital in  $T_1$  is transferred to the lowest unoccupied orbital.

**3.3. Singly Charged Thienylene Vinylenes.** Abstraction of an electron from a conjugated chain leads to deformations of the molecular structure similar to structural changes upon transition to the lowest triplet state as discussed above. Again, these deformations are most notably observed in the carbon–carbon bonds along the conjugated backbone. The changes in the C–C bond length upon removal of an electron were



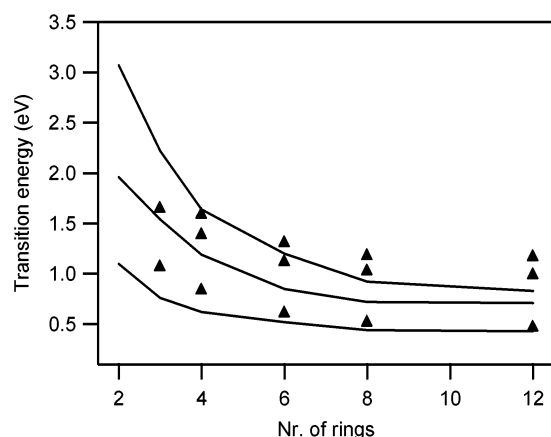
**Figure 6.** Changes in C–C bond length upon removal of an electron from thienylene vinylene oligomers.

calculated by comparing the bond lengths in the optimized geometries of neutral and singly oxidized TVs. These bond length changes are shown in Figure 6 for 4TV, 8TV, and 12TV. The spatial extent of the geometry deformations can be considered as a measure of the “size” of the charge carrier. The C–C bond length changes are largest for the shortest TV considered in Figure 6. For 4TV, changes close to 0.02 Å were obtained. If the chain length is increased, the bond length changes gradually become smaller and, more importantly, the geometry deformations remain evenly spread over the entire chain. This is similar to the results recently obtained from DFT geometry optimizations of phenylene vinylene (PV)<sup>4</sup> and thiophene oligomers,<sup>43,44</sup> where the geometry deformations were also found to extend evenly over the length of the chain. It should be noted that results obtained from Hartree–Fock (HF) geometry optimizations are very different for both thiophenes<sup>10</sup> and PVs.<sup>6</sup> In HF calculations, the geometry deformations are always found to be localized over a limited part of the conjugated chain, typically about five repeat units leading to the formation of a self-localized polaron. Outside of these five units, the geometry is virtually unchanged. It has not yet been unanimously established which of the two methods (HF or DFT) give the most realistic description of the geometry deformations. For thiophene oligomers, calculations at the MP2 level seem to indicate that the delocalization in DFT is an artifact; however, it was also shown that the MP2 geometry deformation for a singly charged oligothiophene is more delocalized than the HF

**TABLE 3: Electronic Absorption Spectra of Radical Cations of Thienylene Vinylene Oligomers Calculated by INDO/s-CIS<sup>a</sup>**

compound		$\Delta E$ (exp.) <sup>b</sup>	$\Delta E$ (calc.)	$f$	main CI expansion coefficients
2TV	RC1	-	1.10	0.02	0.46(H $\rightarrow$ P1) - 0.77(P1 $\rightarrow$ P2)
	RC2	-	1.96	0.63	0.79(H $\rightarrow$ P1) + 0.45(P1 $\rightarrow$ P2)
	RC3	-	3.07	0.03	-0.63(H - 2 $\rightarrow$ P1) + 0.44(P2 $\rightarrow$ L + 1)
3TV	RC1	1.08	0.76	0.01	-0.45(H $\rightarrow$ P1) + 0.68(P1 $\rightarrow$ P2)
	RC2	1.66	1.54	0.86	0.67(H $\rightarrow$ P1) + 0.57(P1 $\rightarrow$ P2)
	RC3	-	2.22	0.12	0.47(H $\rightarrow$ P1) - 0.47(P2 $\rightarrow$ L + 1)
4TV	RC1	0.85	0.62	0.01	0.47(H $\rightarrow$ P1) + 0.66(P1 $\rightarrow$ P2)
	RC2	1.40	1.19	1.13	-0.67(H $\rightarrow$ P1) + 0.55(P1 $\rightarrow$ P2)
	RC3	1.60	1.64	0.08	-0.38(P1 $\rightarrow$ P2) + 0.42(H - 2 $\rightarrow$ P1) - 0.39(P1 $\rightarrow$ L + 1)
6TV	RC1	0.62	0.52	0.04	-0.57(H $\rightarrow$ P1) - 0.49(P1 $\rightarrow$ P2)
	RC2	1.13	0.85	1.48	-0.57(H $\rightarrow$ P1) + 0.61(P1 $\rightarrow$ P2)
	RC3	1.32	1.20	0.01	-0.32(P1 $\rightarrow$ P2) - 0.37(H - 2 $\rightarrow$ P1) + 0.35(P2 $\rightarrow$ L + 1)
8TV	RC1	0.53	0.44	0.13	-0.54(H $\rightarrow$ P1) - 0.38(P1 $\rightarrow$ P2)
	RC2	1.04	0.72	1.57	0.47(H $\rightarrow$ P1) - 0.59(P1 $\rightarrow$ P2) - 0.32(H $\rightarrow$ L)
	RC3	1.19	0.92	0.01	-0.39(P1 $\rightarrow$ P2)
12TV	RC1	0.46	0.43	0.50	-0.51(H - 2 $\rightarrow$ P1) - 0.42(H $\rightarrow$ P1)
	RC2	1.00	0.71	0.81	No single component > 0.1
	RC3	1.18	0.83	1.11	-0.64(P1 $\rightarrow$ P2)

<sup>a</sup> Transition energies (in eV), oscillator strength ( $f$ ), and main CI expansion coefficients for the first three allowed transitions are given. <sup>b</sup> Experimental results obtained from Apperloo et al.<sup>15</sup>



**Figure 7.** Comparison of calculated optical absorption spectrum of thienylene vinylene radical cations with experimental data. Triangles: experimental data by Apperloo et al.;<sup>15</sup> full lines: INDO/s-CIS.

geometry deformation.<sup>45,46</sup> To resolve this issue, more experimental data on long oligomers and calculations using other methods (e.g., MP2 calculations) are called for.

The optical absorption spectra of singly charged TVs were calculated by INDO/s-CIS using the DFT geometry as discussed in Section 2. In Table 3, the excitation energy, oscillator strength, and main CI coefficients for the lowest three allowed transitions are given. All three calculated bands gradually shift to lower energy with increasing chain length, which is consistent with an increasing spatial extent of the charge. The lowest energy band (RC1) exhibits a low oscillator strength for short oligomers but becomes more intense for longer chains. The RC2 band is more intense and the RC3 band is again rather weak for all but the longest TV (12TV). In Figure 7, the calculated transitions are compared to experimental data by Apperloo et al.,<sup>15</sup> who measured the optical absorption spectra of doped thienylene vinylenes oligomers in solution. These experimental data are included in Table 3. For the RC1 band, the correspondence with the experimental transition energy is reasonable for all chain lengths. For RC2, the transition energy is somewhat underestimated, especially for the longer chains. The calculated RC3 values are close to the experimental values listed as RC3 in Table 3. It should be noted, however, that the experimental RC3 transition energies were actually attributed to a vibronic progression of the RC2 band. Given the rather low calculated

oscillator strength, it is very well possible that the RC3 electronic transition is below this, the RC2 (0-1) band, and therefore is not observed in the experimental spectrum.

The nature of the subgap absorption features can be examined by looking at the main CI coefficients. It becomes clear from examining the CI coefficients that the transitions in TVs are not dominated by only a single determinant. For the TVs up to 4TV, the largest contribution to the RC1 transition is from the configuration in which the electron in the P1 level is excited to the P2 level (P1  $\rightarrow$  P2); however, the (H  $\rightarrow$  P1) contribution is also rather large. For longer TVs, (H  $\rightarrow$  P1) becomes the most important contribution. For the RC2 transition, the situation is reversed; for short chains, (H  $\rightarrow$  P1) is the dominant contribution but for oligomers longer than TV4 (P1  $\rightarrow$  P2) has the largest coefficient. For 12TV, the situation is even more complicated, since in this case no single configuration with a coefficient larger than 0.1 was found.

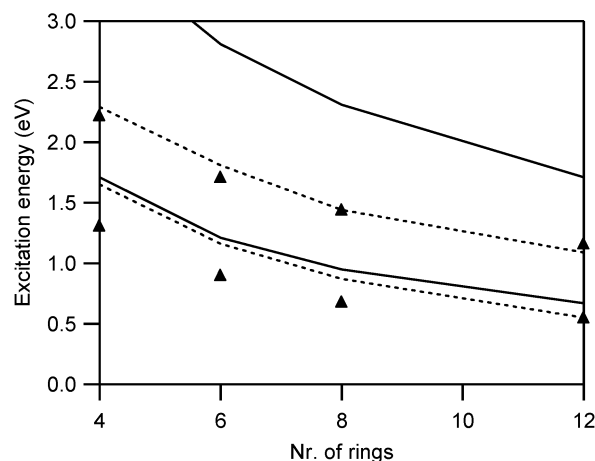
Comparison of the CI coefficients to previous INDO/s-CIS calculations for phenylenevinylene (PV)<sup>4,6</sup> and for thiophene oligomers<sup>10</sup> shows that the nature of the excited state is more similar to that for thiophenes than it is to the excited states in phenylenevinlenes. In thiophenes, the RC1 band was also found to consist mainly of the (P1  $\rightarrow$  P2) configuration, whereas in the case of PVs the RC1 band consists mainly of (H  $\rightarrow$  P1) character. For the RC2 band, the situation is also reversed with respect to the PVs. The RC2 band in thiophenes and TVs is characterized mainly by the (H  $\rightarrow$  P1) configuration, whereas in PVs the RC2 transition is mainly due to (P1  $\rightarrow$  P2). The reversal of the nature of the excited states indicates that orbitals on the sulfur atom contribute to a considerable extent to the  $\pi$ -electron system.

**3.4. Doubly Charged Thienylene Vinylenes.** For doubly charged thienylene vinylene oligomers, similar geometry deformations are found as for singly charged TVs: the single bonds become shorter while the length of the double bonds increases. The distribution of the geometry deformations along the conjugated chain was also similar to the situation for the singly charged TVs: a fully delocalized geometry deformation was found. The only difference is in the absolute magnitude of the C-C bond length changes. For the singly charged 12TV, bond length changes up to  $\sim 0.007$  Å were found, as shown in Figure 6. For doubly charged 12TV, C-C bond changes up to 0.013 Å are obtained, which can easily be understood because the change in charge on the oligomer is larger. It should again

**TABLE 4: Calculated (TDDFT and INDO/s-CIS) Electronic Absorption Spectra for Dications of Thienylene Vinylene Oligomers<sup>a</sup>**

compound		exp. <sup>b</sup>	TDDFT		INDO/s-CIS		main CI expansion coefficients
		$\Delta E$	$\Delta E$	$f$	$\Delta E$	$f$	
4TV	DC1	1.21	1.66	2.23	1.71	3.05	0.93(H $\rightarrow$ P1)
	DC2	2.22	2.29	0.25	3.62	0.32	-0.48(H - 2 $\rightarrow$ P1) - 0.65(H - 1 $\rightarrow$ P2) - 0.36(H $\rightarrow$ L)
6TV	DC1	0.90	1.16	3.64	1.21	4.16	0.89(H $\rightarrow$ P1) - 0.37(H - 1 $\rightarrow$ P2)
	DC2	1.71	1.81	0.28	2.81	0.25	-0.71(H - 2 $\rightarrow$ P1) + 0.50(H - 1 $\rightarrow$ P2)
8TV	DC1	0.68	0.87	4.33	0.95	4.92	-0.85(H $\rightarrow$ P1) - 0.40(H - 1 $\rightarrow$ P2)
	DC2	1.44	1.44	1.03	2.31	0.18	-0.69(H - 2 $\rightarrow$ P1) - 0.43(H - 1 $\rightarrow$ P2)
12TV	DC1	0.55	0.55	4.89	0.67	5.78	0.71(H $\rightarrow$ P1) + 0.35(H - 1 $\rightarrow$ P2) - 0.38(H - 2 $\rightarrow$ P1)
	DC2	1.16	1.09	2.50	1.71	0.26	-0.67(H - 2 $\rightarrow$ P1) - 0.33(H - 1 $\rightarrow$ P2)

<sup>a</sup> Main CI expansion coefficients for the first two allowed transitions obtained from INDO/s-CIS calculations are also given. <sup>b</sup> Experimental results obtained from Köhler and Beljonne.<sup>39</sup>



**Figure 8.** Comparison of calculated optical absorption spectra with experimental data for doubly charged thienylene vinylene oligomers. Triangles: experimental data by Apperloo et al.;<sup>32</sup> full lines: INDO/s-CIS; dotted lines: TDDFT.

be noted that it has not been unanimously established whether the delocalized geometry deformation in DFT is an artifact of the method or a real physical phenomenon.<sup>46</sup>

The electronic absorption spectra of (closed shell) doubly charged 4TV, 6TV, 8TV, and 12TV were calculated by INDO/s-CIS and by TDDFT. The results from both methods are compared to experimental data from Apperloo et al.<sup>32</sup> in Table 4 and Figure 8. From the INDO/s-CIS calculations, one strongly allowed transition, DC1, is found. The calculated excitation energy is reasonable compared to the experimental data for all chain lengths. The experimental data show a second subgap absorption feature. A second allowed transition is found in the INDO/s-CIS calculation, but at an energy that is even higher than the transition energy for the neutral compound. The DC1 absorption is almost exclusively due to the transition from the doubly occupied HOMO level to the unoccupied P1 level (H  $\rightarrow$  P1), although other contributions start mixing in for longer chains. The second transition (DC2) that is found is due to a combination of (H - 2  $\rightarrow$  P1) and (H - 1  $\rightarrow$  P2).

From the TDDFT calculation, two subgap absorption features are obtained: a strongly allowed low energy band, DC1, and a much weaker second band, DC2, at higher energy. Comparison of the TDDFT absorption energies with the experimental data and the INDO/s-CIS calculations shows that the DC1 band is close to both of these for all chain lengths. The calculated energy for the DC2 band also agrees very well with the experimental excitation energy. The much better correspondence for the RC2 energy, as compared to the INDO/s-CIS calculations, is probably due to the use of a much larger basis set that describes the higher lying orbitals involved in the RC2 transition better. The good

correspondence between the TDDFT calculations and the experimental spectra is surprising, especially for the longer oligomers, since the charge is fully delocalized over the whole chain. For the neutral spectra, a large underestimation of the excitation energy was found from TDDFT calculations on long conjugated oligomers as discussed above.

#### 4. Summary and Conclusions

The electronic structure of thienylene vinylene (TV) oligomers was studied using a combination of density functional theory and semiempirical INDO/s calculations. The singlet-singlet absorption spectrum of neutral TVs was shown to be dominated by a strong absorption mainly due to the HOMO-LUMO transition. The agreement between the calculated (INDO/s-CIS) and experimental  $S_1 \leftarrow S_0$  excitation energies was found to be excellent. Calculation of the singlet-singlet absorption spectra by time dependent density functional theory (TDDFT) using the gradient corrected Becke-Perdew functional leads to considerable underestimates of the excitation energy for long chains.

Calculations of the triplet-triplet absorption spectra using the INDO/s-CIS method show that the  $T_1$  spectrum is dominated by a single strong absorption peak. The correspondence between the calculated excitation energy and the experimental data is rather poor in this case. This is attributed to the use of a small basis set in the semiempirical calculations.

The geometry deformations that occur when one or two electrons are removed from the TV oligomers were found to be evenly spread along the conjugated chain. The absolute magnitude of the geometry deformations also decreases with increasing chain length. This indicates that at the DFT level no self-localized polaron (or bipolaron) is formed. This is significantly different from calculations at the Hartree-Fock level. The DFT geometries should be considered with some care since there are indications that DFT overestimates the delocalization of charge.<sup>45</sup>

The electronic absorption spectra of singly charged TV oligomers were calculated using the INDO/s-CIS method and the results were found to be in reasonable agreement with experimental data. It was found that the nature of the excited states of singly charged TVs is more similar to that found previously for thiophene oligomers than to that found for phenylenevinylene oligomers. This indicates that the sulfur orbitals influence the  $\pi$ -electron systems to a considerable extent.

For doubly charged TV oligomers, INDO/s-CIS predicts only a single absorption feature below the lowest absorption peak of the neutral parent compound, whereas a weak second band has been observed experimentally. A second allowed transition is obtained from INDO/s-CIS calculations; however, it is with

an excitation energy that is even higher than that of the neutral transition. Using the TDDFT method, the existence of a second, weak, subgap absorption band is confirmed and the excitation energies are in excellent agreement with experiment, even for the longest TV chains. The latter is somewhat surprising since in the case of the absorption spectra for the neutral TV the energy for the lowest singlet–singlet absorption was considerably underestimated for the longer chains.

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