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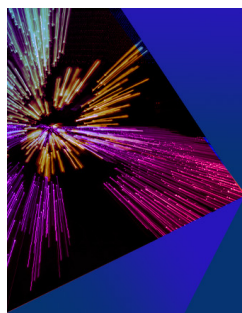
## Nature of the lowest excited states of neutral polyenyl radicals and polyene radical cations

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# Nature of the lowest excited states of neutral polyenyl radicals and polyene radical cations

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Due to the close relation of the polyenyl radicals  $C_{2n+1}H_{2n+3}^{\bullet}$  and polyene radical cations  $C_{2n}H_{2n+2}^{+\bullet}$  to the neutral linear polyenes, one may suspect their excited states to possess substantial double excitation character, similar to the famous  $S_1$  state of neutral polyenes and thus to be equally problematic for simple excited state theories. Using the recently developed unrestricted algebraic-diagrammatic construction scheme of second order perturbation theory and the equation-of-motion coupled-cluster method, the vertical excitation energies, their corresponding oscillator strengths, and the nature of the wave functions of the lowest excited electronic states of the radicals are calculated and analyzed in detail. For the polyenyl radicals two one-photon allowed states are found as  $D_1$  and  $D_4$  states, with two symmetry-forbidden  $D_2$  and  $D_3$  states in between, while in the polyene radical cations  $D_1$  and  $D_2$  are allowed and  $D_3$  is forbidden. The order of the states is conserved with increasing chain length. It is found that all low-lying excited states exhibit a significant but similar amount of doubly excited configuration in their wave functions of 15%–20%. Using extrapolation, predictions for the excitation energies of the five lowest excited states of the polyene radical cations are made for longer chain lengths. © 2009 American Institute of Physics. [doi:10.1063/1.3246350]

## I. INTRODUCTION

Neutral polyene chromophores play starring roles in biologically important photoprocesses and technical applications, and thus the study of their lowest electronic excited states has a long history in theory and experiment<sup>1–15</sup> starting in the early 1970s. In particular, linear all-*trans* polyenes  $C_{2n}H_{2n+2}$  serve as model systems for carotenoids which possess various functions in photobiology.<sup>16,17</sup> Today, they are well known to exhibit complicated electronic structures and most importantly an essentially doubly excited lowest  $S_1$  state with the same  $A_g$  symmetry as the electronic ground state posing substantial challenges to electronic structure theories.

Recently, radical cations of carotenoids have also attracted considerable attention. They have been observed in light-harvesting complexes of green plants and purple bacteria,<sup>18–22</sup> and they are supposed to play important roles in photoprotection.<sup>19,20</sup> Naturally, a detailed understanding of the underlying molecular mechanisms requires precise knowledge of the excited states of the carotenoid radicals or equally well of the corresponding linear polyene cations  $C_{2n}H_{2n+2}^{+\bullet}$  (Fig. 1). The latter also serves as important model systems for the study of conductivity of pure or doped polyacetylene.<sup>23,24</sup>

A second closely related class of radicals is the neutral polyenyl radicals  $C_{2n+1}H_{2n+3}^{\bullet}$  which exhibit an odd number of carbon atoms in contrast with the neutral closed-shell polyenes (Fig. 1). The polyenyl radicals are often employed as

model systems for electron transport in polyacetylene.<sup>25–27</sup>

Due to the close relation of the radical cations and the polyenyl radicals to the neutral polyenes, one may suspect also the former to possess complicated and highly correlated electronic structures requiring a high-level quantum chemical description of their excited states capturing the influence of doubly excited configurations.

Recently, the lowest vertical excited state of neutral all-*trans* linear polyenyl radicals has been studied using valence-bond (VB) theories,<sup>28,29</sup> however, only little is known about the other low-lying excited states. Therefore, we have studied the five lowest-lying electronic excited states of neutral polyenyl radicals  $C_{2n+1}H_{2n+3}^{\bullet}$  ( $n=2–7$ ) and polyene radical cations  $C_{2n}H_{2n+2}^{+\bullet}$  ( $n=2–7$ ) to gain insight into their excitation energies, oscillator strengths, and their electronic structure. For this objective, we employed the recently developed unrestricted algebraic-diagrammatic construction scheme of second order [UADC(2)],<sup>30</sup> which allows for a physically correct description of charge-transfer excited states as well as states with large double excitation character, when the so-called extended version of UADC(2) is employed.

The paper is organized as follows. In Sec. II, the details of our theoretical approach are outlined. The results of our investigations of the lowest excited states of neutral polyenyl radicals and polyene radical cations are presented in Secs. III A and III B. The paper concludes with a brief summary of the major results (Sec. IV).

## II. COMPUTATIONAL DETAILS

As first step in our study, geometry optimizations of the polyene radical cations and neutral polyenyl radicals have

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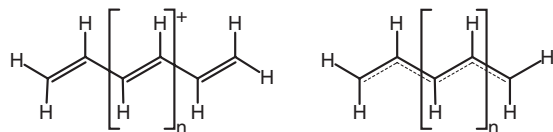


FIG. 1. Molecular structure of the polyene radical cations (left) and neutral polyenyl radicals (right).

been performed in their doublet electronic ground states at the level of unrestricted second order Møller–Plesset perturbation theory (UMP2) (Ref. 31) employing the standard 6-31G\* basis set. For our purposes, the small 6-31G\* basis set is sufficient for the geometry optimizations, since the geometrical parameters did not significantly change when larger basis sets were tested. Also, the detailed geometrical parameters of the investigated molecules are not the focus of this work.

MP2/6-31G\* optimized ground state geometries served as input for the calculation of the vertical excitation energies employing the UADC(2) (Ref. 30) and equation-of-motion unrestricted coupled cluster with singles and doubles (EOM-CCSD)<sup>32,33</sup> using the standard 6-31G\* basis set. A previous study of the basis set dependence of the excitation energies of the four lowest excited states of the pentadienyl radical and the hexatriene radical cation has shown that they are very stable with respect to basis set size.<sup>30</sup>

The unrestricted ADC scheme is a natural extension of restricted ADC<sup>34–37</sup> and can be conveniently derived via the intermediate state representation (ISR).<sup>30,38</sup> A detailed description of the ISR derivation of the UADC scheme has been presented in Ref. 30 and is only briefly reviewed here.

Eventually, the excitation energies are obtained by solving the secular equation

$$\mathbf{M}\mathbf{Y}_n = \Omega_n \mathbf{Y}_n, \quad (1)$$

where  $\mathbf{M}$  is the Hermitian ADC matrix,  $\Omega_n$  is the excitation energy of the  $n$ th state, and  $\mathbf{Y}_n$  its corresponding ADC vector. Here, the ADC matrix is a representation of the shifted electronic Hamiltonian ( $\hat{H} - E_0$ ) with  $E_0$  being the exact ground state energy in an orthogonal basis of intermediate states, the ISR basis,

$$\begin{aligned} \tilde{H}_{IJ} - E_0^N \delta_{IJ} &= \langle \tilde{\Psi}_I | \hat{H} - E_0^N | \tilde{\Psi}_J \rangle = \langle \Psi_0^N | \tilde{C}_I^\dagger [\hat{H}, \tilde{C}_J] | \Psi_0^N \rangle \\ &= M_{IJ}. \end{aligned} \quad (2)$$

The ISR basis is formally constructed from the exact ground state wave function by application of excitation operators and subsequent Gram–Schmidt orthogonalization of the resulting excitation classes.

The excitation energies of the excited states are thus obtained directly by diagonalization of the matrix  $\mathbf{M}$  without performing the corresponding ground state calculation. Transition dipole moments

$$T_n = \langle \Psi_n | \hat{\mu} | \Psi_0 \rangle, \quad (3)$$

where  $\hat{\mu}$  is the typical dipole operator, are given by

$$T_n = \mathbf{X}_n^\dagger \mathbf{F}(\mu) \quad (4)$$

as the scalar products of the eigenvectors  $\mathbf{X}_n$  with the so-called effective transition moments  $\mathbf{F}(\mu)$ . The corresponding oscillator strength is obtained according to the standard expression

$$f_n = \frac{2}{3} \Omega_n \langle T_n \rangle^2. \quad (5)$$

However, since the exact ground state wave function and energy are generally not known, one needs to resort to approximations to be applied within the ISR formalism. The choice of reference ground state finally determines the order of perturbation theory of the resulting ADC scheme: when the MP2 ground state wave function and energy are chosen, the strict ADC(2) scheme [ADC(2)-s] is obtained, for the MP3 ground state the ADC(3) scheme, and so on. In the extended ADC(2) scheme [ADC(2)-x], matrix elements from the ADC(3) scheme are included in the coupling block of the doubly excited configurations substantially improving the description of excited states with large double excitation character.

In general, ADC combines perturbation theory with configuration interaction (CI). It is size consistent like equation-of-motion and linear-response coupled-cluster (CC) methods; however, in addition the ADC matrix  $\mathbf{M}$  is Hermitian, i.e., only one set of eigenvectors exists in ADC, while two are present in the biorthogonal CC schemes.<sup>39</sup> Moreover, ADC is more compact than CI or CC. Compactness is defined as the size of the configuration space, which has to be taken into account for a consistent treatment of the ground and singly excited states through a particular order of perturbation theory. While CI methods generally require the full configuration space, i.e., for a consistent treatment of these primary states to say  $n$ th order of perturbation theory, one needs all  $n$ -tuply excited configurations. When the order of perturbation theory is even, say  $2m$ , both ADC and CC are identically compact and require a configuration space of  $m+1$ . For odd orders of perturbation theory,  $2m+1$ , ADC is slightly more compact with a configuration space size of also  $m+1$  compared with  $m+2$  for the CC methods. For a detailed comparison of ADC, CC, and CI the reader is referred to Refs. 36 and 40.

All ADC and EOM-CCSD calculations reported here have been performed with a development version of the QCHEM-3.0 quantum chemistry program package,<sup>41</sup> where we have implemented efficient restricted and unrestricted ADC(2)-s and ADC(2)-x programs for the computation of excitation energies and transition dipole moments of closed-shell and open-shell molecules.

### III. RESULTS AND DISCUSSION

#### A. Excited states of neutral polyenyl radicals

Let us first turn to the computation of the low-lying excited states of neutral all-*trans*-polyenyl radicals (right side of Fig. 1), which exhibit  $C_{2v}$  molecular symmetry. The electronic ground state of this class of radicals has either  $^2B_1$  or  $^2A_2$  symmetry depending on the number of carbon atoms: polyenyl radicals corresponding to the general formula

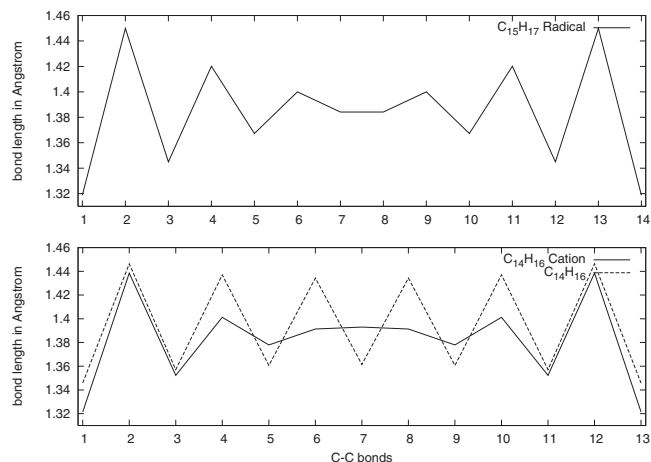


FIG. 2. Bond length alternation pattern of the conjugated single and double bonds in  $C_{15}H_{17}$ ,  $C_{14}H_{16}$ , and  $C_{14}H_{16}^+$  at the theoretical level of UMP2/6-31G<sup>\*</sup>.

$C_{4m+1}H_{4m+3}^{\bullet}$  ( $m=1,2,\dots$ ) have a  $^2B_1$  electronic ground state while it is  $^2A_2$  for those with general formula  $C_{4m+3}H_{4m+5}^{\bullet}$ . Since the irreducible representations of the excited states change accordingly, we will denote the energetically lowest states with  $1^2Y$ ,  $2^2X$ ,  $2^2Y$ , and so on in the following. Here  $X$  refers to the ground state irreducible representation  $B_1$  or  $A_2$  and  $Y$  to  $A_2$  or  $B_1$ , respectively.

The geometry optimization of the electronic ground state of the polyenyl radicals reveals the bond length alternation of the conjugated chain of the carbon double bonds. As can be seen for  $C_{15}H_{17}^{\bullet}$  as a representative example in the upper panel of Fig. 2, the lengths of the carbon-carbon bonds alternate at the ends of the polyenyl radical and in this area single and double bonds can be clearly distinguished. In the middle of the polyenyl radical, however, their lengths are equilibrated and individual single and double bond character can no longer be assigned. For comparison, in the neutral closed-shell polyene  $C_{14}H_{16}$  (lower panel of Fig. 2), the alternation pattern of single and double bonds is pronounced along the complete conjugated chain.

According to our calculations of the vertical excited states of the polyenyl radicals at UADC(2) and EOM-CCSD level of theory (Table I), the  $D_1$  state of the polyenyl radicals exhibits  $^2Y$  symmetry, i.e.,  $^2A_2$  or  $^2B_1$  depending on whether the electronic ground state is  $^2B_1$  or  $^2A_2$ , respectively. It has the largest contribution of an excitation, which at the molecular orbital level can be interpreted as an excitation of the  $\beta$ -electron occupying the highest (doubly) occupied molecular orbital (HOMO) to the singly occupied molecular orbital (SOMO) assuming that the SOMO is occupied by an  $\alpha$ -electron in the electronic ground state. This state also exhibits a small admixture of the excitation of the SOMO  $\alpha$ -electron into the lowest unoccupied molecular orbital (LUMO). We have decided to use the classification of the orbitals as doubly occupied, singly occupied, and unoccupied despite the fact that formally one orbital per electron is given in the unrestricted Hartree-Fock reference, with the  $\alpha$ -orbital possessing a different energy than the corresponding  $\beta$ -orbital. However, it is most intuitive to classify an orbital as doubly occupied, when for the occupied  $\alpha$ -orbital there

TABLE I. Computed vertical excitation energies (eV) of the five energetically lowest states of the polyenyl radicals  $C_{2n+1}H_{2n+3}^{\bullet}$  at the levels of UADC(2)-s, UADC(2)-x, as well as EOM-CCSD. The corresponding oscillator strengths are given in parentheses. For an explanation of the state symmetries  $X$  and  $Y$  see text. States labeled  $X$  exhibit the same symmetry as the ground state and are thus generally one photon forbidden.

$n$	UADC(2)-s	UADC(2)-x	EOM-CCSD
$D_1(1^2Y)$ : $HOMO_{\beta} \rightarrow SOMO_{\beta} (+SOMO_{\alpha} \rightarrow LUMO_{\alpha})$			
2	4.04(0.01)	2.36(0.00)	3.28(0.00)
3	3.69(0.01)	2.05(0.00)	2.95(0.00)
4	3.48(0.01)	1.87(0.00)	2.73(0.00)
5	3.35(0.01)	1.75(0.00)	2.59(0.00)
6	3.25(0.01)	1.66(0.00)	2.44(0.00) <sup>a</sup>
7	3.19(0.00)	1.60(0.00)	2.37(0.00) <sup>a</sup>
$D_2(2^2X)$ : $HOMO-1_{\beta} \rightarrow SOMO_{\beta} + SOMO_{\alpha} \rightarrow LUMO + 1_{\alpha}$			
2	5.37(0.00)	3.68(0.00)	4.70(0.00)
3	4.75(0.00)	3.18(0.00)	4.20(0.00)
4	4.33(0.00)	2.76(0.00)	3.76(0.00)
5	4.03(0.00)	2.46(0.00)	3.43(0.00)
6	3.80(0.00)	2.23(0.00)	3.16(0.00) <sup>a</sup>
7	3.65(0.00)	2.08(0.00)	2.96(0.00) <sup>a</sup>
$D_3(2^2Y)$ : $HOMO-2_{\beta} \rightarrow SOMO_{\beta} + HOMO-1_{\alpha} \rightarrow LUMO_{\alpha}$			
2			
3	5.81(0.00)	4.12(0.00)	5.17(0.01)
4	5.27(0.00)	3.72(0.00)	4.76(0.04)
5	4.84(0.01)	3.30(0.00)	4.33(0.00)
6	4.50(0.00)	2.95(0.00)	3.98(0.00) <sup>a</sup>
7	4.44 <sup>a</sup> (0.00)	2.79 <sup>a</sup> (0.00)	3.69(0.00) <sup>a</sup>
$D_4(3^2Y)$ : $SOMO_{\alpha} \rightarrow LUMO_{\alpha} (+HOMO_{\beta} \rightarrow SOMO_{\beta})$			
2	5.89(0.98)	5.13(0.82)	6.01(0.90)
3	5.17(1.36)	4.42(1.15)	5.28(1.36)
4	4.71(1.71)	3.96(1.42)	4.78(1.87)
5	4.40(2.00)	3.64(1.64)	4.33(2.29)
6	4.17(2.31)	3.42(1.86)	4.46(2.75) <sup>a</sup>
7	4.01(2.09)	3.26(2.81) <sup>a</sup>	4.25(3.20) <sup>a</sup>
$D_5(3^2X)$ : $SOMO_{\alpha}, HOMO_{\beta} \rightarrow LUMO_{\alpha}, SOMO_{\beta}$			
2	7.10(0.00)	4.64(0.00)	6.32(0.00)
3	6.53(0.00)	4.32(0.00)	5.91(0.00)
4	6.16(0.00)	4.12(0.00)	5.45(0.00)
5	5.81(0.00)	3.95(0.00)	5.11(0.00)
6	5.21(0.00)	4.01 <sup>a</sup> (0.00)	4.73(0.00) <sup>a</sup>
7	5.07 <sup>a</sup> (0.00)	3.63 <sup>a</sup> (0.00)	4.38(0.00) <sup>a</sup>

<sup>a</sup>Corresponding value of a calculation with the basis set 6-31G.

exists a corresponding, practically identical occupied  $\beta$ -orbital. The molecular orbitals are typical  $\pi\pi^*$  orbitals essentially identical to the ones of the neutral linear polyenes and the polyene radical cations, which are discussed below. The  $D_2$  state of the neutral polyenyl radicals has  $^2X$  symmetry, i.e., the same symmetry as the electronic ground state, and this state is best described by a linear combination of a  $\beta$ HOMO-1 to SOMO transition and an  $\alpha$ SOMO to LUMO + 1 excitation. The third lowest  $D_3$  state is a  $^2Y$  state best represented as a mixture of  $\beta$ HOMO-2 to SOMO and a  $\alpha$ HOMO-1 to LUMO transition with essentially single excitation character, while the wave function of the fourth lowest excited state  $D_4$  is composed of the same determinants as  $D_1$ ; however, in the  $D_4$  state, the  $\alpha$ SOMO to LUMO excitation is the most important contribution. The first excited state of the linear polyenyl radicals that exhibits substantial double excitation character of more than 50% is the  $D_5$  state with  $^2X$



TABLE II. Comparison of theoretical values for the vertical excitation energies (eV) of the energetically lowest  $D_1$  excited state ( $1^2Y$ ) of polyenyl radicals  $C_{2n+1}H_{2n+3}^\bullet$  ( $n=2-6$ ).

$n$	CASPT3 <sup>a</sup>	MRCI <sup>a</sup>	VBCISD <sup>a</sup>	ADC(2)-x
2	2.66	2.66	2.47	2.36
3	2.19	2.19	2.03	2.04
4	1.87	1.86	1.73	1.87
5 <sup>b</sup>	1.63	1.61	1.59	1.75
6 <sup>b</sup>			1.44	1.66

<sup>a</sup>Taken from Ref. 29.

<sup>b</sup>Results with split-valence basis set.

symmetry, which can in the molecular orbital picture best be described as a two-electron transition of a  $\beta$ -electron from the HOMO to the SOMO and of an  $\alpha$ -electron from the SOMO to the LUMO.

Let us now turn to the discussion of the obtained values for the vertical excitation energies of the polyenyl radicals  $C_{2n+1}H_{2n+3}^\bullet$  at the UADC(2)-s as well as UADC(2)-x and EOM-CCSD levels employing the standard 6-31G\* basis set unless otherwise mentioned. The computed excitation energies of the  $D_1$  to  $D_5$  states of the polyenyl radicals from all-*trans*-pentadienyl ( $n=2$ ) to all-*trans*-pentadecaheptenyl ( $n=7$ ) are compiled in Table I. The lowest excited  $D_1$  state ( $1^2Y$ ) of the  $C_9H_{11}^\bullet$  ( $n=4$  in Table I) radical, for example, exhibits an excitation energy of 3.48 eV at UADC(2)-s level and 1.87 eV at UADC(2)-x level of theory. The observed decrease in the excitation energy from the strict to the extended UADC(2) scheme indicates the importance of doubly excited configurations in the theoretical description of that state. Indeed, analysis of the corresponding ADC vector reveals an amount of 25% of doubly excited configurations. EOM-CCSD calculations give a value of 2.73 eV for this state of  $C_9H_{11}^\bullet$ , which is 0.75 eV lower than the UADC(2)-s value due to the better description of doubly excited states at formally first order of perturbation theory in EOM-CCSD. However, the value is also significantly higher (0.86 eV) than the UADC(2)-x value, which is probably due to a less balanced treatment of ground and excited state energies in EOM-CCSD. While the ground, singly, and doubly excited states are treated consistently in EOM-CCSD to third, second, and first order, they are described only to second, second, and first order within the ADC(2)-x scheme leading possibly to a more balanced treatment of the doubly excited states benefiting from a more favorable cancellation of errors.

Recently, the  $D_1$  state of the polyenyl radicals has been studied using theoretical approaches based on VB theory.<sup>28,29</sup> In particular, a newly developed VB CI approach has been employed,<sup>42-44</sup> and the obtained vertical excitation energies of the  $D_1$  state were compared with the results from high-level *ab initio* approaches such as multireference CI<sup>45,46</sup> and complete active space perturbation theory of third order (CASPT3).<sup>10,11</sup> For this study, the excited state calculations were carried out using an optimized geometry of the polyenyl radicals obtained at DFT/B3LYP/D95V level. The obtained values are compiled in Table II together with the ADC(2)-x values for the  $D_1$  excitation energies obtained in

this study. While for the shorter polyenyl radicals  $C_5H_7^\bullet$  and  $C_7H_9^\bullet$  the ADC(2)-x and valence-bond configuration interaction singles and doubles (VBCISD) values agree nicely with increasing chain lengths of the radicals, however, these two methods start to deviate slightly by up to 0.22 eV for  $C_{13}H_{15}^\bullet$ . For  $C_9H_{11}^\bullet$ , the excitation energy obtained at ADC(2)-x level agrees better with the values from multi-configurational configuration interaction (MRCI) and CASPT3. However, the excitation energies of the  $D_1$  state of  $C_{11}H_{13}^\bullet$  are practically identical at CASPT3, MRCI, and VBCI levels with values of 1.63, 1.61, and 1.59 eV, while the corresponding ADC(2)-x value is slightly larger with 1.75 eV.

In previous closed-shell applications it has been found<sup>47</sup> that excitation energies at EOM-CCSD or LR-CCSD level are of the same quality as those of the ADC(3) treatment, that is, clearly more accurate than the results at the ADC(2) level. The ADC(2)-x treatment certainly improves the description of the double excitations, but not necessarily that of the single excitations. However, ADC(2)-x results are most valuable as an indicator for the double excitation character of the respective excited states, but less destined for yielding a consistently accurate description of (singly) excited states. However, to conclusively evaluate the quality of the different approaches, more benchmark results for longer polyenyl radicals would be required or equally well experimental data for their  $D_1$  excitation energies in the gas phase.

For the  $D_2$  state ( $2^2X$ ) of the linear all-*trans*-polyenyl radicals a similar trend of the computed excitation energies is seen at ADC(2) and EOM-CCSD levels as for the  $D_1$  state. Doubly excited states are important, thus leading to a large difference in the excitation energies between strict and extended UADC(2) values.

While the third excited state  $D_3$  exhibits the same trend in the vertical excitation energies at the different levels of theory as the  $D_1$  and  $D_2$  states possessing about 25% of double excitation character, the  $D_4$  states, however, behave differently and are the most interesting regarding the configurations and energies with respect to the three applied theoretical methods. In fact, doubly excited configurations play only a minor role for the theoretical description of the  $D_4$  state. The ADC(2)-x vector reveals only 12% of doubly excited configurations leading to smaller differences between the excitation energies at UADC(2)-s and UADC(2)-x levels. Surprisingly, the excitation energies computed at EOM-CCSD are even higher than the ones obtained at UADC(2)-s level. This may also be an indication of the less balanced treatment of singly excited states and the ground state in EOM-CCSD. Here, they are treated consistently up to second and third orders of perturbation theory, respectively, while both are treated in second order consistently in ADC(2). For those states in which doubly excited configurations become important, the better theoretical treatment of doubly excited states in EOM-CCSD than in UADC(2)-s overcompensates the unbalanced treatment of the singles. However, this tentative explanation requires further thorough theoretical analysis. It is furthermore worth to note that the excitation energy of the  $D_5$  state decreases strongly by more than 2 eV for the shorter radicals when UADC(2)-x is employed as compared with UADC(2)-s and EOM-CCSD. This

is directly related with the large amount of doubly excited configurations in the ADC vector, which is better described at UADC(2)-x level at first order of perturbation theory than with UADC(2)-s at zeroth order.

Overall, the same trends in the excitation energies between the UADC(2) and EOM-CCSD methods are observed as in a previous analysis of medium-sized organic radicals.<sup>30</sup> The excitation energies computed at UADC(2)-s level seem to be generally higher than the ones obtained at UADC(2)-x level. The larger the amount of doubly excited configurations in the ADC(2)-x vector is, i.e., the more important doubly excited configurations are for the correct description of the excited states, the larger the difference in excitation energies at strict and extended UADC(2) level becomes. Unfortunately, experimental data for the excited states of the linear all-*trans*-polyenyl radicals are not available for comparison.

## B. Excited states of polyene radical cations

The polyene radical cations are more closely related with the polyenes than the polyenyl radicals are. In analogy to the polyenes, the polyene radical cations exhibit an even number of carbon atoms like their neutral counterparts; in fact, polyenes and polyene radicals differ only by one electron. Experimentally, radical cations of polyenes can thus be generated by chemical oxidation or by photoionization of polyenes. The radical cations of the polyenes exhibit  $C_{2h}$  molecular symmetry like their neutral parents. Similar to the polyenyl radicals the irreducible representation of the electronic ground state alternates with increasing number of double bonds. Polyene radical cations with an even number of double bonds possess an electronic ground state with  ${}^2B_g$  symmetry, while those with an odd number of conjugated double bonds have a  ${}^2A_u$  ground state. As for the polyenyl radicals, we will denote the ground state symmetry with  $X$  and the five lowest excited states with  $1\ {}^2Y$ ,  $2\ {}^2Y$ ,  $2\ {}^2X$ ,  $3\ {}^2X$ , and  $3\ {}^2Y$ , where  $Y$  refers to  $B_g$  or  $A_u$  in the case of a  $A_u$  or  $B_g$  ground state, respectively.

As first step, the ground state geometries of the linear all-*trans*-polyene radical cations  $C_{2n}H_{2n+2}^+$  ( $n=2-7$ ), i.e., of all-*trans*-butadiene ( $n=2$ ) to all-*trans*-tetradecaheptaene ( $n=7$ ), have been optimized at the theoretical level of UMP2/6-31G\*. Most interestingly, the conjugated carbon chain exhibits a bond length alternation pattern similar to the polyenyl radicals: at the ends of the chain the alternation pattern is pronounced and single and double bonds can easily be distinguished, while in the middle of the radical cation the carbon-carbon bond lengths equilibrate. As a representative example, the alternation pattern of  $C_{14}H_{16}^+$  is shown in Fig. 2. Comparison to the corresponding neutral polyene  $C_{14}H_{16}$  reveals that ionization does have a significant impact on the bond length alternation pattern of the conjugated chain, since it results in bond length equilibration in the middle of the conjugated chain.

Let us now turn to the investigation of the lowest excited states of the all-*trans*-polyene radical cations. Their vertical excited states have been computed at the UMP2/6-31G\* optimized equilibrium geometry of the respective electronic ground states. The results obtained at UADC(2) and EOM-

CCSD levels are compiled together with experimental and theoretical data from the literature in Table III. In analogy to the neutral polyenyl radicals described above, the energetically lowest  $D_1$  state of the polyene radical cations can also be characterized as transition of the  $\beta$ HOMO electron to the SOMO. The corresponding unrestricted molecular orbitals of the polyene radical cation  $C_{14}H_{16}^+$  are shown in Fig. 3 as a representative example together with the orbitals of its neutral parent polyene. In general, this state exhibits a small oscillator strength for all chain lengths. Comparison of its excitation energies at UADC(2)-s, UADC(2)-x, and EOM-CCSD levels reveals the same trends as found for the neutral polyenyl radicals: UADC(2)-s overestimates grossly by about 0.9 eV, EOM-CCSD less by only about 0.5 eV, and UADC(2)-x underestimates slightly by 0.3 eV. This can be explained with the significant amount of double excitation character in the UADC(2)-x vector, which exhibits about 25%. The second excited  $D_2$  state of the longer radical cations corresponds to the strongly dipole allowed  $\alpha$ SOMO to LUMO transition. For the second excited state doubly excited configurations are less relevant with at most 15% for the long radical cations. Therefore, the excitation energies computed at UADC(2) and EOM-CCSD levels show the same trend as the ones found for the  $D_3$  state of the polyenyl radicals. EOM-CCSD excitation energies are consistently larger than the ones at UADC(2)-s and UADC(2)-x and the difference between strict and extended UADC(2) with 0.7 eV is smaller than for the  $D_1$  state (1.2 eV). The  $D_3$  state of the longer radical cations is one photon forbidden due to its symmetry, and the major contribution to this state is the transition of the  $\beta$ HOMO-1 electron to the SOMO. For this state doubly excited configurations contribute as much as 25% to the UADC(2)-x vector pointing out their importance for a physically correct description of that state. This significant influence of double excitations leads to the trends in the excitation energies at UADC(2)-s, UADC(2)-x, and EOM-CCSD levels as already observed for the  $D_1$  state of the polyene radical cations. The state with the largest double excitation character of the five lowest states of the polyene radical cations is the  $D_4$  state with about 35% in the ADC vector. As a consequence, the excitation energy of that state drops stronger from UADC(2)-s to UADC(2)-x than the ones of the  $D_1$  to  $D_3$  states by about 2 eV for the shorter radical cations. Finally, the  $D_5$  state exhibits the typical trend as has been observed for the  $D_1$  and  $D_2$  states of the cation radicals.

In Table III also literature data stemming from high-level computations are reported for the shorter polyene radical cations from all-*trans*-butadiene to all-*trans*-decapentaene. These comprise data from calculations at semiempirical Pariser–Parr–Pople (PPP) level<sup>48</sup> at multireference Møller–Plesset (MRMP) perturbation theory level<sup>49</sup> and at the complete active space self-consistent field (CASSCF) level<sup>49,50</sup> including a second order perturbation correction (CASPT2).<sup>28,50</sup> In comparison to experimental gas-phase values for the vertical excited states of radical cations of all-*trans*-butadiene to decapentaene,<sup>51</sup> it is not surprising that high-level multireference methods such as MRMP2 and CASPT2 achieve the best agreement. These computationally demanding approaches are, however, not applicable to larger

TABLE III. Vertical excitation energies (eV) of the polyene radical cations  $C_{2n}H_{2n+2}^{+}$  computed at the theoretical level of UADC(2) and EOM-CCSD compared with theoretical and experimental data. The oscillator strengths are given in parentheses. For the definition of the state symmetries see text. States labeled  $X$  exhibit the same symmetry as the electronic ground state and are one photon forbidden.

$n$	UADC(2)-s	UADC(2)-x	PPP <sup>a</sup>	CASSCF <sup>b</sup>	MRMP <sup>b</sup>	CASPT2 <sup>c</sup>	EOM-CCSD	Expt. <sup>d</sup>
$D_1(1^2Y): \text{HOMO}_\beta \rightarrow \text{SOMO}_\beta$								
2	3.23(0.04)	1.91(0.02)		2.57	2.43	2.47	2.87(0.03)	2.32
3	2.81(0.03)	1.60(0.02)	1.81	2.11	1.98	1.98	2.54(0.03)	1.92
4	2.51(0.03)	1.37(0.01)	1.49	1.83	1.69	1.66	2.29(0.04)	1.67
5	2.29(0.02)	1.19(0.01)	1.26	1.61	1.43		2.12(0.04)	
6	2.12(0.02)	1.06(0.01)					1.97(0.05)	
7	1.98(0.09)	0.96(0.01)					1.89(0.05)	
$D_2(2^2Y): \text{SOMO}_\alpha \rightarrow \text{LUMO}_\alpha$								
2	4.70(0.64)	3.94(0.54)		5.07	4.16	4.23	4.75(0.55)	4.20
3	3.73(0.99)	3.00(0.80)	3.05	4.06	3.32	3.37	3.84(0.94)	3.27
4	3.13(1.30)	2.41(1.00)	2.55	3.43	2.88	2.86	3.28(1.34)	2.77
5	2.70(1.57)	2.00(1.15)	2.19	2.89	2.46		2.86(1.72)	
6	2.40(1.73)	1.70(1.23)					2.55(2.07)	
7	2.17(1.77)	1.46(1.56)					2.30(2.39)	
$D_3(2^2X): \text{HOMO-1}_\beta \rightarrow \text{SOMO}_\beta$								
2								
3	4.25(0.00)	2.97(0.00)	3.15	3.57	3.36		3.94(0.00)	
4	3.75(0.00)	2.52(0.00)	2.71	3.22	3.01	2.88	3.54(0.00)	2.97
5	3.37(0.00)	2.17(0.00)	2.33	2.87	2.61		3.21(0.00)	
6	3.06(0.00)	1.90(0.00)					2.95(0.00)	
7	2.80(0.00)	1.69(0.00)					2.74(0.00)	
$D_4(3^2X): \text{HOMO}_\alpha \rightarrow \text{LUMO}_\alpha + \text{HOMO-1}_\beta \rightarrow \text{SOMO}_\beta$								
2	5.90(0.00)	3.71(0.00)					5.49(0.00)	
3	5.30(0.00)	3.44(0.00)					5.20(0.00)	
4	4.67(0.00)	3.13(0.00)					4.78(0.00)	
5	4.15(0.00)	2.87(0.00)					4.44(0.00)	
6	3.72(0.00)	2.64(0.00)					4.13(0.00)	
7	3.37(0.00)	2.41(0.00)					3.86(0.00)	
$D_5(3^2Y): \text{HOMO-2}_\beta \rightarrow \text{SOMO}_\beta$								
2								
3	5.08(0.00)	4.14(0.00)					5.03(0.00)	
4	4.89(0.00)	3.66(0.00)					4.61(0.00)	
5	4.44(0.00)	3.24(0.00)					4.24(0.00)	
6	4.07(0.00)	2.89(0.00)					3.90(0.00)	
7	3.77(0.01)	2.58(0.02)					3.61(0.00)	

<sup>a</sup>Reference 48. Semiempirical Pariser–Parr–Pople calculations.

<sup>b</sup>Reference 49. Complete active space SCF and multireference Møller–Plesset calculations.

<sup>c</sup>Reference 50. Complete active space with perturbation theory of second order calculations.

<sup>d</sup>Reference 51. Electron absorption spectra in gas phase.

polyenes due to the steep scaling of their computational cost. UADC(2)-s, CASSCF, and EOM-CCSD overestimate the experimental data by 0.2–0.5 eV, while UADC(2)-x consistently underestimates the vertical excitation energies by approximately 0.3 eV.

Finally, let us compare the vertical excited states of the all-*trans*-polyenyl radicals and polyene radical cations with those of the parent neutral linear polyenes.<sup>15</sup> In general, the excitation energies of the lowest excited states of the radicals are lower than those of the neutrals, which owes to two major effects. On one hand the gap between the occupied and virtual orbitals decreases upon ionization of the neutral polyenes to create the polyene radical cations due to the stronger effective electrostatic attraction between the electrons and the nuclei in the cations as compared with the neutrals. On the other hand, the  $\beta$ HOMO to SOMO transition, which has

a low energy, is one photon allowed for symmetry reasons and is possible only for the radicals. In both classes of radicals this transition constitutes the major contribution to the  $D_1$  state, and its admixture to the strongly allowed state ( $D_3$  of the neutral polyenyls and  $D_2$  of the radical cations) leads also to a decrease in its excitation energy compared with the well-known optically allowed  $S_2$  state of neutral all-*trans*-polyenes.<sup>15</sup> This is particularly apparent in the comparison of the radical cations to the neutral closed-shell polyenes. The  $2^2X$  state of the radicals exhibiting the same symmetry as the ground state is related to the dark  $2^1A_g^- S_1$  state of the neutral polyenes. However, different from the neutral polyenes where more than 70% of doubly excited configurations, in particular HOMO<sup>2</sup> to LUMO<sup>2</sup>, contribute to the  $S_1$  state, only about 25% is important for the  $2^2X$  state of the radicals. Since the amount of doubly excited configuration is

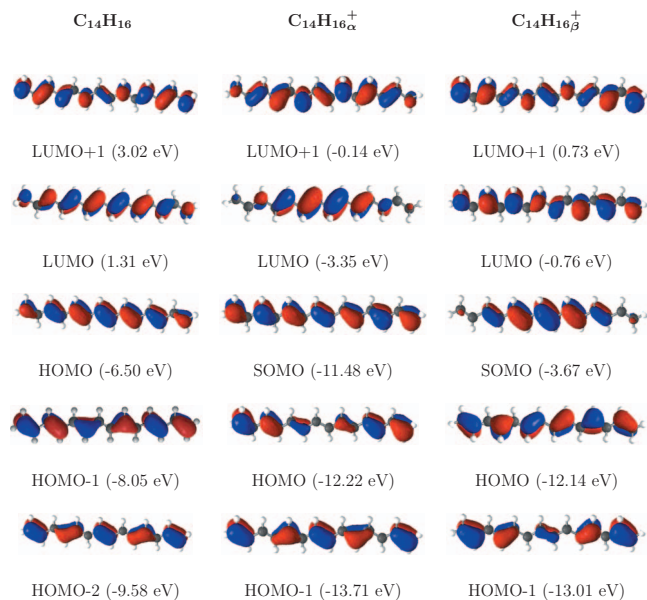


FIG. 3. Doubly occupied and virtual orbitals of neutral  $C_{14}H_{16}$  (left column) and the occupied and virtual  $\alpha$ - and  $\beta$ -orbitals of  $C_{14}H_{16}^+$  (middle and right columns).

about the same for all low-lying excited states of the radicals, one can in general expect theories taking only singly excited configurations into account to yield reasonable relative energies and the correct ordering of the lowest excited states of the polyene-related radicals due to fortuitous cancellation of errors. This can already be seen in our UADC(2)-s results for these radicals.

As already mentioned in Sec. I polyene radical cations serve as important model systems also for carotenoid radical cations. However, carotenoids do usually possess longer conjugated carbon double bond chains with 10–13 double bonds, which is computationally still out of reach for the employed theoretical methods. Therefore, we extrapolated the vertical excitation energies as obtained at ADC(2)-x level of the five lowest states of the polyene radical cations to longer chain lengths using a particle-in-a-box fitting model. The employed fitting function is thus given as

$$E(n) = \frac{a}{L(n)^2 - b} + c, \quad (6)$$

where  $L(n)$  corresponds to the length of the polyene radical cation, which can be well approximated by a linear function of the number of carbon atoms as  $L(n) = 2.41n - 1.152$ . The parameters  $a$ ,  $b$ , and  $c$  are then least squares fitted to the calculated vertical excitation energies and the obtained parameters are given in Table IV. It is worthwhile to note that the parameter  $c$  corresponds to the vertical excitation energy of the corresponding state at infinite chain lengths. According to the model, the lowest excited  $D_1$  state of  $1^2Y$  symmetry is supposed to have an excitation energy of only 0.66 eV at infinite chain length at UADC(2)-x level of theory. Interestingly, the bright  $2^2Y$  and the forbidden  $2^2X$  states exhibit the same asymptotic limit of their excitation energies of 0.90 eV. The  $D_4$  ( $3^2Y$ ) and  $D_5$  ( $3^2X$ ) states approach excitation energies of 1.46 and 1.23 eV, respectively, for an infinitely long chain length. The extrapolation error for the

TABLE IV. Fitted parameters for the particle-in-a-box model of the vertical excited states of the five lowest excited states of the polyene radical cations.

State	$a$	$b$	$c$
$1^2Y$	97	-64.0	0.66
$2^2Y$	268	-93.0	0.90
$2^2X$	173	-43.6	0.90
$3^2Y$	395	-162.1	1.46
$3^2X$	535	-147.3	1.23

parameters is moderate with a maximum error for the parameters  $a$  of 11% and  $b$  of 12.5% for the  $3^2Y$  state and only 1.25% for  $c$  for the  $3^2Y$  state. Note that in particular the physically meaningful fitting parameter  $c$  exhibits a very small fitting error. Taking the error of UADC(2)-x into account, i.e., an underestimation of the vertical excitation energies of the carotenoid radical cations of about 0.2–0.3 eV, one may predict an asymptotic excitation energy for the  $D_1$  state of 0.8–0.9 eV.

The graphical representation of the dependence of the excitation energies of the five lowest states on the number of double bonds of the polyene radical cations is shown in Fig. 4. As can be easily seen, no crossings between the three lowest excited states occur when the carbon chain length is extended. As described above, the  $2^2Y$  and  $2^2X$  states approach the same asymptotic excitation energy but do not cross. However, our fitting model predicts one crossing between the  $3^2Y$  and  $3^2X$  states to occur at approximately ten double bonds. Since the  $3^2X$  is symmetry forbidden and thus not directly accessible via one-photon excitation, it will be very difficult to observe that change in state ordering experimentally.

#### IV. SUMMARY AND CONCLUSIONS

The lowest-lying excited states of polyenyl radicals and polyene radical cations have been studied with strict and extended UADC(2) as well as with EOM-CCSD. According to our calculations on the neutral polyenyl radicals, a strongly

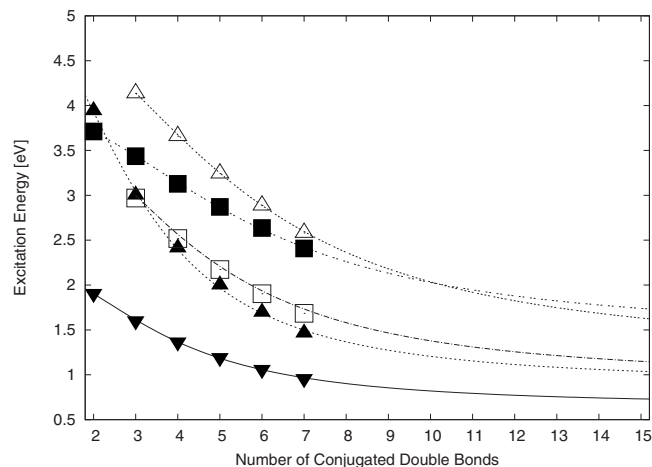


FIG. 4. Extrapolation of the vertical excitation energies obtained at UADC(2)-x/6-31G level of theory for the five lowest excited states of linear polyenyl radical cations to long chain lengths ( $\nabla$   $1^2Y$ ,  $\blacktriangle$   $2^2Y$ ,  $\square$   $2^2X$ ,  $\blacksquare$   $3^2Y$ ,  $\triangle$   $3^2X$ ).



optically allowed state is found as the fourth lowest  $D_4$  state and two new forbidden  $D_2$  and  $D_3$  states could be identified to be lower in energy. In the polyene radical cations, on the other hand, the  $D_2$  state exhibits large oscillator strength and the  $D_3$  and  $D_4$  states are symmetry forbidden. For both classes of radicals the  $D_1$  state exhibits a small oscillator strength and corresponds essentially to an excitation of the  $\beta$ HOMO-electron into the SOMO. Extrapolation of the vertical excitation energies of the polyene radical cations to longer chain lengths revealed no change in the order of the three lowest states. However, while the  $D_1$  state approaches an asymptotic excitation energy of 0.66 eV, the  $D_2$  and  $D_3$  have the same asymptotic limit of 0.90 eV according to our model at UADC(2)-x level of theory.

In general, the UADC(2)-x calculations of the excited states of the polyenyl radicals and polyene radical cations reveal that the amount of doubly excited configuration in their corresponding ADC vectors is very similar with about 15%–25%, i.e., their double excitation character is much smaller than the one of the famous  $S_1$  state of neutral closed-shell polyenes exhibiting up to 70% doubly excited configurations. Therefore one can expect theories such as ADC(2)-s and CC2 treating doubly excited states only in zeroth order of perturbation theory or even more approximate linear-response time-dependent density functional theory methods to yield reasonable relative excitation energies and electronic spectra. However, for the quantitatively correct description of individual excited state properties, the correct treatment of doubly excited configurations will be probably indispensable also for the radicals. However, this remains to be conclusively demonstrated and is subject of ongoing research.

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