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The π → π* excited states of long linear polyenes studied by the CASCI-MRMP method

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Abstract

Multireference Møller–Plesset perturbation theory with complete active space configuration interaction (CASCI-MRMP) is applied to the study of the valence π → π* excited states of all-*trans* linear polyenes $C_{2n}H_{2n+2}$ (n = 3–14). Our focus was to determine the nature of the four lowest-lying singlet excited states, $2^1A_g^-$, $1^1B_u^+$, $1^1B_u^-$ and $3^1A_g^-$ and their ordering. The ionic $1^1B_u^+$ state is the lowest optically allowed excited state, while the covalent $2^1A_g^-$, $1^1B_u^-$ and $3^1A_g^-$ states are the optically forbidden states. Theory predicts that the $1^1B_u^-$ state becomes lower than the $1^1B_u^+$ state at $n \geqslant 7$ and that the $3^1A_g^-$ state also becomes lower than the $1^1B_u^+$ state at $n \geqslant 11$.

1. Introduction

There is a long and rich history of experimental and theoretical investigations on the nature of linear polyene electronic structures [1]. There are many reasons for this, including the historical importance of these systems in the development of molecular orbital theory, the fundamental importance of *cis–trans* photoisomerization and organic conducting polymers, and the fact that polyene chromophores play starring roles in biologically important photoprocesses. In 1970s, the experimental and theoretical findings [2–4] have suggested that the polyene electronic structure is more complicated and more interesting than was previously thought.

The nature and ordering of the low-lying excited states of shorter polyenes up to decapentaene are now well known [5,6]. Particular attention has been paid to the two lowest-lying π → π* singlet excited states, $1^1B_u^+$ and $2^1A_g^-$. The $1^1B_u^+$ state is a singly excited state, with an ionic nature originating from the HOMO → LUMO one-electron transition, while the covalent $2^1A_g^-$ state is the doubly excited state, which comes mainly from the $(\mathrm{HOMO})^2 \rightarrow (\mathrm{LUMO})^2$ transition. For butadiene, the $1^1B_u^+$ state is slightly lower than the doubly excited $2^1A_g^-$ state at the ground-state equilibrium geometry. For hexatriene, the two states are virtually degenerate, and the $2^1A_g^-$ state becomes the lowest excited singlet state at the ground-state geometry for longer polyenes than hexatriene.

However, little is known about the higher excited states, and the relative ordering of low-lying excited states for longer polyenes [7–16] is still an open question. Recently, Sashima et al. [10,12] detected the $1^1B_u^-$ state between the $2^1A_g^-$ state and the $1^1B_u^+$ state in all-*trans*-carotenoids (n = 9–11) by resonance-Raman excitation profiles (RREPs). Fujii et al. [13,14] also observed the $1^1B_u^-$ fluorescence spectra of all-*trans*-carotenoids (n = 11–13). Very recently, Furuichi et al. [16] identified the $3^1A_g^-$ state in all-*trans*-catrotenoids (n = 10–13) by measurements of RREPs and predicted the state ordering of $2^1A_g^- < 1^1B_u^- < 3^1A_g^- < 1^1B_u^+$ for n = 11–13. The

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assignments of these newly-detected states were based on the extrapolation of the multireference single and double excitation configuration interaction with Pariser–Parr–Pople model Hamiltonian (PPP-MRD-CI) calculations [17] for shorter polyenes ($n = 2$–8), and this extrapolation was predicted by the Hubbard and PPP models in finite polyenes [18].

It is a challenge to carry out highly accurate ab initio calculations of longer polyenes. In the present Letter, we apply multireference Møller–Plesset (MRMP) method to the study of the valence $\pi \rightarrow \pi^*$ excited states of all-*trans* linear polyenes $C_{2n}H_{2n+2}$ ($n = 3$–14). Our focus is to determine the nature of the four lowest-lying singlet excited states, $2^1A_g^-$, $1^1B_u^+$, $1^1B_u^-$ and $3^1A_g^-$, and their ordering.

In a previous paper [5], we studied the valence $\pi \rightarrow \pi^*$ excited states of shorter linear polyenes using the MRMP method based on complete active space self-consistent field (CASSCF) functions [19–24]. MRMP with pairing properties has proved to be of great value in understanding and predicting the experimental data of alternant hydrocarbons [5,25]. However, for longer polyenes, the CASSCF functions are not necessarily a best choice, since the SCF procedure sometimes gives improper orbitals unless we could include *all* the π orbitals as active orbitals. Recently, we proposed MRMP using complete active space configuration interaction reference functions (CASCI-MRMP) [26,27] rather than the CASSCF functions, and demonstrated that CASCI-MRMP is comparable in accuracy to MRMP based on the CASSCF reference functions. Thus, we employ CASCI-MRMP to compute the energies of the states throughout the present Letter.

2. Computational details

The excitation energies of linear polyenes with $n = 3$–14 were computed using CASCI-MRMP. The molecules were assumed to have C_{2h} symmetry and lie on the *xz*-plane. Thus the *y*-axis becomes the C_2 axis. To calculate the vertical excitation energies, we used the ground-state equilibrium geometries optimized at the MP2 level. Dunning's correlation consistent polarized valence double zeta (cc-pVDZ) basis sets [28] were used for all calculations.

A reference CASCI wave function was obtained by partitioning the SCF orbitals, and optimizing the expansion coefficients of all configurations generated by all the possible arrangements of the active electrons among the active orbitals. The 10 valence π electrons were treated as active electrons and distributed among the five bonding π and five anti-bonding π* orbitals. We also calculated shorter polyenes. For hexatriene and octatetraene, all π electrons were treated as active electrons and distributed among all valence bonding π and anti-bonding π* orbitals.

The effect of the σ electrons is included through the perturbation calculations performed with MRMP. MRMP was applied to each individual state.

3. Results and discussion

The main configurations in CASCI wave functions are given in Table 1. As discussed previously [25], polyenes are alternant hydrocarbons and the pairing properties are satisfied at the CASSCF level. Table 1 shows that the pairing properties are satisfied even at the CASCI level. These one-electron symmetry properties were first utilized by Pariser [29] who distinguished the states as so-called '*plus*' and '*minus*' ones. The valence π orbitals of alternant polyenes, which are normally filled in the ground-state configuration, are designated by 1, 2, ..., and those which are not filled by 1′, 2′, ... The occupied orbitals are numbered from the highest one down and

Table 1
Main configurations in CASCI wave functions of polyenes

State	Orbital picture	Number of double bonds											
		3	4	5	6	7	8	9	10	11	12	13	14
$1^1A_g^-$	$\ldots(2)^2(1)^2$	0.95	0.93	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.91	0.92	0.92
$2^1A_g^-$	$(1)^2 \rightarrow (1')^2$	0.57	0.56	0.55	0.56	0.56	0.55	0.55	0.54	0.54	0.53	0.52	0.52
	$2 \rightarrow 1'$	0.44	0.40	0.37	0.36	0.35	0.34	0.34	0.34	0.33	0.34	0.34	0.34
	$1 \rightarrow 2'$	−0.40	−0.36	−0.34	−0.33	−0.33	−0.32	−0.32	−0.32	−0.32	−0.32	−0.32	−0.32
	$1,2 \rightarrow 1',2'$	0.29	0.30	0.30	0.33	0.34	0.34	0.35	0.35	0.36	0.36	0.36	0.37
$3^1A_g^-$	$(2)^2 \rightarrow (1')^2$	0.34	0.30	0.32	0.29	0.28	0.20	0.19	0.17	0.32	0.32	0.32	0.32
	$(1)^2 \rightarrow (2')^2$	0.29	0.39	0.28	0.26	0.26	0.18	0.18	0.16	0.29	0.30	0.30	0.29
	$1,3 \rightarrow (1')^2$	−0.27	−0.26	−0.26	−0.26	−0.26	−0.35	−0.36	−0.36	−0.10	−0.09	−0.09	−0.08
	$(1)^2 \rightarrow 1',3'$	0.27	0.24	0.23	0.25	0.26	0.25	0.31	0.32	0.10	0.09	0.08	0.08
	$3 \rightarrow 2'$	0.29	0.10	0.24	0.22	0.23	0.11	0.13	0.12	0.21	0.21	0.22	0.22
	$2 \rightarrow 3'$	−0.32	−0.26	−0.23	−0.21	−0.18	−0.19	−0.16	−0.14	−0.20	−0.21	−0.21	−0.21
$1^1B_u^+$	$1 \rightarrow 1'$	0.92	0.93	0.92	0.92	0.91	0.90	0.90	0.89	0.89	0.88	0.88	0.87
$1^1B_u^-$	$3 \rightarrow 1'$	0.45	0.44	0.41	0.40	0.40	0.39	0.39	0.39	0.38	0.38	0.38	0.39
	$1 \rightarrow 3'$	−0.47	−0.38	−0.35	−0.35	−0.35	−0.35	−0.34	−0.34	−0.34	−0.35	−0.35	−0.35
	$1,2 \rightarrow (1')^2$	0.36	0.37	0.39	0.42	0.42	0.43	0.42	0.42	0.42	0.41	0.40	0.40
	$(1)^2 \rightarrow 1',2'$	−0.33	−0.38	−0.38	−0.38	−0.40	−0.40	−0.40	−0.40	−0.40	−0.39	−0.39	−0.39

the unoccupied orbitals from the lowest one up. The orbitals i and i' are called a conjugated pair. The energy of the configuration obtained by exciting an electron from the orbital i to the orbital j' is equal to that obtained by excitation from j to i' due to the pairing property. The linear combinations of these two degenerate configurations generate the *minus* and *plus* states. In our definition [25], the *minus* state is a covalent state while the *plus* state is an ionic state both for singlet and triplet states, which stems from the character of the states in a valence bond (VB) description. More details were discussed in our previous papers [5].

The *plus* states do not interact with the *minus* states, and the ground state behaves like a *minus* state. Excited configurations of the type of $i \rightarrow i'$ behave like *plus* states for singlet states and *minus* states for triplet states. Doubly excited configurations of the type of $(i)^2 \rightarrow (j')^2$ behave like *minus* states and are predicted to interact with the singly excited $^1A_g^-$ states. The dipole transition moment between any two *plus* states or between any two *minus* states is zero.

The general rules mentioned above are satisfied in the Hückel and PPP Hamiltonians but could possibly serve as valuable tools for the qualitative interpretation of the excited states calculated with the sophisticated ab initio methods of alternant hydrocarbons.

From the pairing properties, the ground state is the covalent state, $1^1A_g^-$. The $1^1B_u^+$ state is a singly excited state with an ionic nature, originating from the $1 \rightarrow 1'$ one-electron transition, and the covalent $2^1A_g^-$ state is the doubly excited state which comes mainly from the $(1)^2 \rightarrow (1')^2$ transition. The $3^1A_g^-$ state is a covalent state and has a heavily multiconfigurational character. The state comes from the doubly excitations of $(1)^2 \rightarrow (2')^2$, $(2)^2 \rightarrow (1')^2$ but includes a large fraction of single and doubly excited configurations of $2 \rightarrow 3'$, $3 \rightarrow 2'$ and $1,3 \rightarrow (1')^2$, $(1)^2 \rightarrow 1',3'$. The $1^1B_u^-$ state is a covalent state originating from a mixture of one- and two-electron transitions, $3 \rightarrow 1'$, $1 \rightarrow 3'$ and $1,2 \rightarrow (1')^2$, $(1)^2 \rightarrow 1',2'$.

We have also proposed a complete active space valence bond (CASVB) [30,31] method. A CASVB wave function can be obtained simply by transforming a canonical CASSCF function, and is readily interpreted in terms of the well-known classical VB resonance structures. The nature of the low-lying electronic states of polyenes can easily be understood from the CASVB description: Fig. 1.

The above VB structures suggest that the vertical excitation energies to the covalent excited states, $2^1A_g^-$, $3^1A_g^-$ and $1^1B_u^-$ will approach constant values. However, the ionic excited state $1^1B_u^+$ is quite different in nature from the covalent states, and will approach a different limiting energy. Vertical singlet $\pi \rightarrow \pi^*$ excitation energies of polyenes with the corresponding number of double bonds are shown in Table 2. The state ordering of $2^1A_g^- < 1^1B_u^+ < 1^1B_u^- < 3^1A_g^-$ is satisfied for $n = 3$–6. However, for tetradecaheptaene ($n = 7$), the $1^1B_u^-$ state becomes lower than the $1^1B_u^+$ state, and the ordering $2^1A_g^- < 1^1B_u^- < 1^1B_u^+ < 3^1A_g^-$ holds for $n = 7$–10. For docosaundecaene ($n = 11$), CASCI-MRMP suffered from the intruder state problem for the calculation of the $3^1A_g^-$ state. By using the intruder state avoidance (ISA) method [32], we successfully estimated the excitation energies of the $3^1A_g^-$ state and found that the $3^1A_g^-$ state is slightly lower than the $1^1B_u^+$ state. The state ordering for $n = 11$–14 is $2^1A_g^- < 1^1B_u^- < 3^1A_g^- < 1^1B_u^+$.

Since our focus is on the ordering of the low-lying excited states of the long polyenes, detailed comparison between experimental and calculated values is not done in this Letter. We show a few numbers, however, to

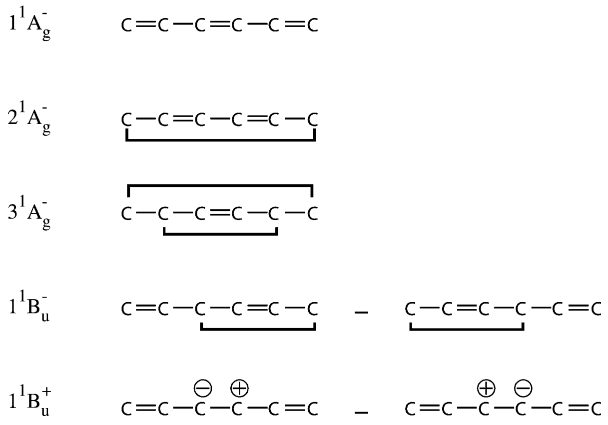

Fig. 1. The valence-bond resonance structures of the ground state and the low-lying excited states of hexatriene: calculated by CASVB method.

Table 2

Calculated vertical excitation energies (eV) of low-lying polyene singlet states by CASCI-MRMP

State	Number of double bonds											
	3	4	5	6	7	8	9	10	11	12	13	14
$2^1A_g^-$	5.10	4.26	3.68	3.19	2.80	2.50	2.25	2.04	1.86	1.70	1.56	1.43
$3^1A_g^-$	8.25	7.02	6.06	5.12	4.47	3.99	3.46	3.11	2.82[a]	2.45	2.25	2.05
$1^1B_u^+$	5.25	4.57	4.17	3.87	3.60	3.38	3.18	3.00	2.84	2.69	2.56	2.43
$1^1B_u^-$	6.06	5.30	4.68	3.98	3.53	3.10	2.79	2.51	2.27	2.05	1.86	1.69

[a] Corrected by intruder state avoidance calculation.

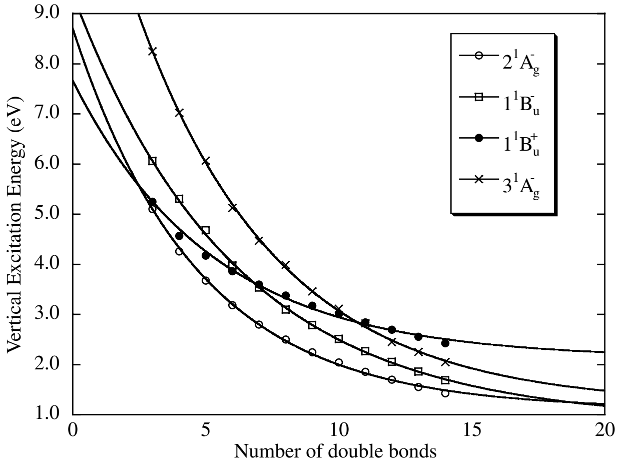

Fig. 2. The exponential fittings for the vertical excitation energies from the CASCI-MRMP results.

illustrate accuracy of our calculations. Let us take the $2^1A_g^-$ and $1^1B_u^+$ states of decapentaene ($n = 5$), for instance. The vertical excitation energies of the CASCI-MRMP and the experiment [33] were 3.68 and 3.48 eV for $2^1A_g^-$, and 4.17 and 4.02 eV for $1^1B_u^+$, respectively. For the longer polyenes, we cannot do direct comparison due to the structural differences in the compounds between the calculations and experiments [9–16].

The Hubbard and PPP models calculations [18] of the excitation energies for polyenes predicts the dependence of the state energies on the number of conjugated double bonds n as a linear function of $1/(2n + 1)$. The slopes of the linear functions were often used for the assignments of the excited states in the experiments. In our case, however, calculated vertical excitation energies do not follow a simple linear dependence on $1/(2n + 1)$. Thus we fitted the energies to an exponential function

$$E_n = E_\infty + (E_{n_0} - E_\infty)\exp[-a(n - n_0)] \quad \text{(for fixed } n_0\text{)},$$

suggested by Meier et al. [34]. The fittings for each state are showed in Fig. 2 by the solid lines (note $n_0 = 3$ in this case). The asymptotic excitation energies of the $1^1B_u^+$, $3^1A_g^-$, $2^1A_g^-$ and $1^1B_u^-$ states are 2.12, 1.20, 1.11 and 0.86 eV, respectively. The ionic state clearly converged to the higher excitation energy in the infinite n limit than the covalent states did. In other words, we can say all the covalent states $2^1A_g^-$, $1^1B_u^-$ and $3^1A_g^-$ cross the ionic $1^1B_u^+$ state at finite n.

4. Summary

CASCI-MRMP is applied to the study of the valence $\pi \rightarrow \pi^*$ excited states of all-*trans* linear polyenes $C_{2n}H_{2n+2}$ ($n = 3$–14). Theory predicts that the $1^1B_u^-$ state becomes lower than the $1^1B_u^+$ state at $n \geqslant 7$ and that the $3^1A_g^-$ state also becomes lower than the $1^1B_u^+$ state at $n \geqslant 11$. Extrapolation by an exponential function for the excitation energies were carried out to predict the state-ordering of longer polyenes. The excitation energy of the ionic $1^1B_u^+$ state at the infinite n limit is clearly higher than those of the covalent excited states. Thus all the covalent $2^1A_g^-$, $1^1B_u^-$ and $3^1A_g^-$ states cross the ionic $1^1B_u^+$ state at finite n.

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