Theoretical Study of the $\pi \rightarrow \pi^*$ Excited States of Linear Polyenes: The Energy Gap Between $1^1B_u^+$ and $2^1A_g^-$ States and Their Character

KENICHI NAKAYAMA, HARUYUKI NAKANO, KIMIHIKO HIRAO

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan 113

ABSTRACT: Multireference perturbation theory with complete active space self-consistent field (CASSCF) reference functions is applied to the study of the valence $\pi \rightarrow \pi^*$ excited states of 1,3-butadiene, 1,3,5-hexatriene, 1,3,5,7-octatetraene, and 1,3,5,7,9-decapentaene. Our focus was put on determining the nature of the two lowest-lying singlet excited states, $1^1B_u^+$ and $2^1A_g^-$, and their ordering. The $1^1B_u^+$ state is a singly excited state with an ionic nature originating from the HOMO $\rightarrow$ LUMO one-electron transition while the covalent $2^1A_g^-$ state is the doubly excited state which comes mainly from the $(HOMO)^2 \rightarrow (LUMO)^2$ transition. The active-space and basis-set effects are taken into account to estimate the excitation energies of larger polyenes. For butadiene, the $1^1B_u^+$ state is calculated to be slightly lower by 0.1 eV than the doubly excited $2^1A_g^-$ state at the ground-state equilibrium geometry. For hexatriene, our calculations predict the two states to be virtually degenerate. Octatetraene is the first polyene for which we predict that the $2^1A_g^-$ state is the lowest excited singlet state at the ground-state geometry. The present theory also indicates that the $2^1A_g^-$ state lies clearly below the $1^1B_u^+$ state in decapentaene with the energy gap of 0.4 eV. The 0−0 transition and the emission energies are also calculated using the planar C_{2h} relaxed excited-state geometries. The covalent $2^1A_g^-$ state is much more sensitive to the geometry variation than is the ionic $1^1B_u^+$ state, which places the $2^1A_g^-$ state significantly below the $1^1B_u^+$ state at the relaxed geometry. © 1998 John Wiley & Sons, Inc. Int J Quant Chem **66**: 157−175, 1998

Key words: MRMP; multireference-based perturbation theory; excited states; polyenes; excited-state energy gaps

Introduction

Polyene chemistry is very old but still very new chemistry. The study of the electronic structure and spectroscopy of linear polyenes has a long history [1]. There are many reasons for this, including the historical importance of these systems in the development of molecular orbital (MO) 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, such as vision and energy production.

The electronic structure of the polyenes was thought to be rather simple and well understood in the framework of approximate MO models as written in the freshman textbook. The nature of the lowest-lying excited singlet state was assumed to be the dipole-allowed $1^1B_u^+$ state, originating from HOMO → LUMO one-electron transition. In 1972, Hudson and Kohler [2] observed that α, ω-diphenyl-1,3,5,7-octatetraene has a dipole-forbidden state below the above-mentioned strongly allowed $1^1B_u^+$ by a careful analysis of the mixed crystal absorption spectra. In an accompanying publication, Schulten and Karplus [3] provided a theoretical rationalization of this finding and concluded that the new lowest singlet excited state is a doubly excited $2^1A_g^-$ state, which is poorly described without extensive CI. Hudson and Kohler [4] further recognized that this ordering of electronic states, $2^1A_g^-$ below $1^1B_u^+$, must be a general feature of the polyene electronic structure. Since then, extensive literature has reported on this subject. The reversed ordering is supported by theory, mostly by semiempirical methods [5−7] and by various experiments [8−16], including the comparison between the first absorption and the first fluorescence bands. Much evidence has been presented to show that the level ordering, $2^1A_g^-$ below $1^1B_u^+$, is generally the case, except in butadiene and hexatriene. Experimental evidence is more difficult to obtain in butadiene and hexatriene since they emit no detectable fluorescence [17]. Considerable effort has been made to search for the low-lying $2^1A_g^-$ state in these two molecules without relying on fluorescence, by electron-impact [18−20], multiphoton ionization [21, 22], and thermal blooming [22, 23], finding no sign of the existence of the $2^1A_g^-$ state below $1^1B_u^+$. It is thus very likely that the level ordering in butadiene and hexatriene is different from that in octatetraene and the larger homologs.

Since the size of the most conjugated polyenes is far too large for rigorous ab initio treatment, a number of semiempirical methods are used to obtain an approximate quantum mechanical description of large π-electron systems. Ab initio computations for small polyenes [24−42], on the other hand, not only yield an understanding of electronic structures, but these calculations are also important for testing semiempirical theories that are used for larger polyenes. The semiempirical theory found that the doubly excited $2^1A_g^-$ is significantly below $1^1B_u^+$ for almost all linear polyenes [5−7]. But ab initio calculations for small polyenes did not reproduce the ordering of the doubly excited $2^1A_g^-$ below $1^1B_u^+$ [24−30]. This discrepancy is now well understood [39, 41]. The parameters in such semiempirical schemes are optimized to treat the dipole-allowed HOMO → LUMO transition. As will be discussed later, the ionic states such as the $^1B_u^+$ state require extensive treatment of $\sigma-\pi$ correlation, the dynamic $\sigma-\pi$ polarization effect. In a semiempirical π electron model, this means that the choice of π-electron parameters must compensate for the neglect of σ-electron effects. However, for the covalent states such as the $2^1A_g^-$ state, use of the same parametrization overestimates the $\sigma-\pi$ correlation and *artificially* lowers the covalent states, leading to the ordering of electronic states, $2^1A_g^-$ below $1^1B_u^+$, in all the linear polyenes. The relative success of the past semiempirical treatments is due mainly to the approximate inclusion of the dynamic $\sigma-\pi$ polarization effect.

In the previous study, a multireference Møller−Plesset (MRMP) theory [43] was applied to the study of the valence $\pi \to \pi^*$ excited states of polyacenes such as benzene and naphthalene [44]. The excited states of polyacenes are classified into the covalent *minus* states and ionic *plus* states with the use of the alternancy symmetry. The covalent *minus* states and ionic *plus* states exhibit different behavior as far as the electron correlation is concerned. In particular, π ionic configurations strongly polarize the σ space. These effects are taken into account by the second-order perturbation treatment in MRMP. The dynamic $\sigma-\pi$ polarization effects on covalent excited states are usually the same as in the covalent ground state. The excitation energies of ionic *plus* states are overestimated considerably at the CASSCF [45] level and the introduction of dynamic $\sigma-\pi$ polarization ef-

fects through the second-order perturbation reduces the excitation energies drastically. The ionic *plus* states are dominated by the single excitations but covalent *minus* states include a large fraction of doubly excited configurations. The theory satisfactorily described the ordering of low-lying valence $\pi \to \pi^*$ excited states. The overall accuracy is surprisingly high. The MRMP approach with the pairing properties has proved to be of great value in understanding and predicting experimental data of the alternant hydrocarbons.

This article describes the electronic structure of the ground and low-lying valence $\pi \to \pi^*$ excited states of linear polyenes: *trans*-1,3-butadiene, *trans*,*trans*-1,3,5-hexatriene, all-*trans*-1,3,5,7-octatetraene, and all-*trans*-1,3,5,7,9-decapentaene (hereafter called butadiene, hexatriene, octatetraene, and decapentaene, respectively). We have addressed in this article the problem of the energy gap between the two lowest excited states and their character.

In the second section, we summarized the computational details. Vertical excitation energies are discussed in the third section. The basis-set effect and the active-space effect on the transition energies are examined carefully in butadiene. Based on these, we apply an extrapolation method to estimate the excitation energies of larger polyenes. The calculated 0–0 and emission energies (fluorescence maximum) of polyenes are presented in the fourth section. The excited-state geometries are relaxed within the C_{2h} symmetry. The change of the carbon–carbon bond lengths in excited states is also discussed. A summary is given in the final section.

Computational Details

The molecules are taken to have C_{2h} symmetry and chosen to lie in the *xz*-plane; thus, the *y*-axis is the C_2 axis. For the calculation of the vertical excitation energies, we use the ground-state equilibrium geometries taken from the experiment [46–49]. For decapentaene, there are no data available and we optimize the geometry at the CASSCF level. For the calculation of nonvertical excitation energies, we also use the geometries of the ground and the excited $1^1B_u^+$ and 2^1A_g states optimized with CASSCF.

The basis sets used for carbon and hydrogen are taken from Dunning's correlation consistent basis sets [50]. In the previous study, we examined the effect of the polarization functions of hydrogen in benzene and found that polarization functions on hydrogen have little effect on the valence $\pi \to \pi^*$ excitation energies and the oscillator strengths [44]. In the present study of polyenes, three kinds of basis sets are used: $[3s2p1d/2s]$, $[4s3p2d/3s2p]$, and $[5s4p3d/3s2p]$. The f and g polarization and Rydberg functions are not included in the present treatment. We shall refer to these three basis sets as DZp, TZ2p, and QZ3p, respectively.

We first carry out the state-averaged CASSCF calculations [45]. The active space should include all valence π orbitals in conjugated systems. All π electrons are treated as active electrons and distributed among all valence bonding π and antibonding π^* orbitals. To study the effect of the enlargement of the active space on the excitation energies, we also used the extended active space for butadiene and hexatriene, where all π electrons are distributed among extended π orbitals, i.e., the active space is doubled in each symmetry and the same set of calculations is performed. In this article, we use the abbreviation (n, m) to define the active electrons and active orbitals. n is the number of active π electrons, and m, the number of active π orbitals. The (n, n) is referred to as a single active space, and $(n, 2n)$, as a double active space.

The effect of the σ electrons is included through the perturbation treatment. Perturbation calculations are performed with MRMP. MRMP is applied to each individual state. Oscillator strengths are calculated by using transition moments computed at the CASSCF level and the MRMP transition energies.

Vertical $\pi \to \pi^*$ Excitation Energies of Polyenes

Vertical singlet and triplet $\pi \to \pi^*$ excitation energies of polyenes are summarized in Tables I and II. The main configurations in CASSCF wave functions calculated with DZ$p/(n, n)$ are given in Table III.

As discussed previously [44], polyenes are alternant hydrocarbons and the pairing properties are satisfied even at the CASSCF level. These one-electron symmetry properties were first utilized by Pariser [65] who distinguished the states as so-called ''*plus*'' and ''*minus*'' ones. Let the valence π

TABLE I
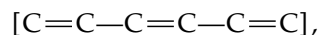**Calculated vertical excitation energies (eV) of low-lying polyene singlet states.**

Polyenes	Method	CASSCF	MRMP	MRMP (corrected)	Oscillator strength	Exptl.
Ethene						
$1^1B_{2u}^+$	QZ3p / (2, 4)	9.30	8.01	—	0.494	≈ 8.0[a]
Butadiene						
$2^1A_g^-$	QZ3p / (4, 8)	6.67	6.31	—	Forbidden	?
$1^1B_u^+$	QZ3p / (4, 8)	7.73	6.21	—	0.803	6.25,[b] 5.92[c]
Hexatriene						
$2^1A_g^-$	DZp / (6, 12)	5.64	5.34	5.09	Forbidden	
$1^1B_u^+$	DZp / (6, 12)	7.06	5.37	5.10	1.082	4.93,[d] 4.95,[d] 5.13[e]
$1^1B_u^-$	DZp / (6, 12)	6.63	6.31	—	0.0069	
Octatetraene						
$2^1A_g^-$	DZp / (8, 12)	5.16	4.72	4.47	Forbidden	
$1^1B_u^+$	DZp / (8, 12)	6.62	4.81	4.66	1.382	4.41[f]
$1^1B_u^-$	DZp / (8, 12)	6.25	5.76	—	0.0067	
$1^1A_g^+$	DZp / (8, 12)	7.03	6.40	—	Forbidden	
Decapentaene						
$2^1A_g^-$	DZp / (10, 10)	4.32	3.95	3.65	Forbidden	3.48[g]
$1^1B_u^+$	DZp / (10, 10)	6.37	3.97	4.05	1.396	4.02[g]
$1^1B_u^-$	DZp / (10, 10)	5.40	4.91	—	0.0000	
$1^1A_g^+$	DZp / (10, 10)	8.33	5.32	—	Forbidden	
$3^1A_g^-$	DZp / (10, 10)	6.24	5.64	—	Forbidden	

[a] Estimated vertical excitation energy.
[b] [51].
[c] [19, 20, 52–56].
[d] [57, 58].
[e] [18, 53a].
[f] [59, 60].
[g] [14].

orbitals of alternant polyenes, which are normally filled in the ground-state configuration, be designated by $1, 2, \ldots$, and those which are not filled by $1', 2', \ldots$. The occupied orbitals are numbered from the highest one down and 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 π orbital i to the j' is equal to that obtained by excitation from j to i' due to the pairing property. The linear combinations of the two degenerate configurations generate the *minus* $(-)$ and *plus* $(+)$ states. In our definition [44], 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.

Recently, we proposed a complete active-space valence-bond (CASVB) method [66]. A CASVB wave function can be obtained simply by transforming a canonical CASSCF function and readily

interpreted in terms of the well-known classical VB resonance structures. For example, the ground state of hexatriene is mainly composed of the covalent Kekule-like structure:

$$[C=C—C=C—C=C],$$

while the $2^1A_g^-$ state is expressed predominantly by the Dewar-like structure:

$$\left[C—C=C—C=C—C \right].$$
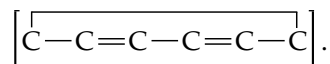
The $1^1B_u^+$ state is expressed as a mixture of a large number of ionic structures. The leading terms are the singly and doubly polar structures of
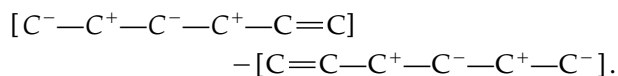
$$[C=C—C^-—C^+—C=C]$$
$$-[C=C—C^+—C^-—C=C]$$

and

$$[C^-—C^+—C^-—C^+—C=C]$$
$$-[C=C—C^+—C^-—C^+—C^-].$$
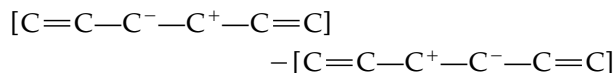
TABLE II
Calculated vertical excitation energies (eV) of low-lying polyene triplet states.

Polyenes	Method	CASSCF	MRMP	MRMP (corrected)	Oscillator strength[a]	Exptl.
Ethene						
$1^3B_{2u}^-$	QZ3p / (2, 4)	4.24	4.36	—	—	4.36[b]
Butadiene						
$1^3B_u^-$	QZ3p / (4, 8)	3.28	3.20	—	—	3.22[c]
$1^3A_g^-$	QZ3p / (4, 8)	4.96	4.87	—	0.000005	4.91[c]
Hexatriene						
$1^3B_u^-$	DZp / (6, 12)	2.74	2.60	2.40	—	2.61,[d] 2.58[e]
$1^3A_g^-$	DZp / (6, 12)	4.35	4.24	4.15	0.00021	4.11,[d] 4.07[d]
$2^3B_u^-$	DZp / (6, 12)	5.26	5.20	—	Forbidden	
Octatetraene						
$1^3B_u^-$	DZp / (8, 12)	2.59	2.37	2.20	—	2.10[f]
$1^3A_g^-$	DZp / (8, 12)	3.74	3.61	3.55	0.00034	3.55[f]
$2^3B_u^-$	DZp / (8, 12)	4.84	4.71	—	Forbidden	
$2^3A_g^-$	DZp / (8, 12)	5.61	5.43	—	0.000017	
Decapentaene						
$1^3B_u^-$	DZp / (10, 10)	2.21	1.95	1.89	—	
$1^3A_g^-$	DZp / (10, 10)	3.24	3.02	2.98	0.0002	
$2^3B_u^-$	DZp / (10, 10)	4.24	4.07	—	Forbidden	
$2^3A_g^-$	DZp / (10, 10)	5.05	4.86	—	0.0001	
$3^3B_u^-$	DZp / (10, 10)	5.38	4.97	—	Forbidden	
$1^3A_g^+$	DZp / (10, 10)	7.99	5.19	—	1.0799	

[a] The oscillator strength for the transition from the lowest $1^3B_u^-$ state to higher triplet state.
[b] [61, 62].
[c] [52].
[d] [18, 53a].
[e] [63].
[f] [64].

TABLE III
Main configurations in CASSCF wave functions of polyenes.

State	Transitions	Ethene	Butadiene	Hexatriene	Octatetraene	Decapentaene
$1^1A_g^-$	(Ground state)					
	...$(3)^2(2)^2(1)^2$	0.978	0.955	0.919	0.894	0.859
$1^1B_u^+$						
	$1 \to 1'$	0.996	0.967	0.936	0.913	0.887
$2^1A_g^-$						
	$1 \to 2'$		0.482	0.425	0.394	0.370
	$2 \to 1'$		−0.503	−0.470	−0.434	−0.403
	$(1)^2 \to (1')^2$		−0.548	0.563	−0.560	0.544
$1^3B_u^-$						
	$1 \to 1'$	1.000	0.928	0.900	0.848	0.811
$1^3A_g^-$						
	$1 \to 2'$		0.482	0.425	0.394	0.370
	$2 \to 1'$		−0.503	−0.470	−0.434	−0.403

The nature of the two lowest excited states of polyenes can easily be understood from the CASVB description.

The *plus* states do not interact with the *minus* states. The ground state behaves like a *minus* state. The excited configurations of the type of $i \rightarrow i'$ behave like *plus* states for singlet-spin states and *minus* states for triplet-spin states. The 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 a valuable tool for the qualitative interpretation of the excited states calculated with the sophisticated ab initio methods of alternant hydrocarbons.

BASIS-SET AND ACTIVE-SPACE EFFECTS ON THE VERTICAL EXCITATION ENERGIES

To examine the adequacy of the basis set and the active space for the description of electronic structure of polyenes, several preliminary calculations were performed on butadiene. Table IV summarizes the MRMP results on the two lowest triplet, $1^3B_u^-$ and $1^3A_g^-$, and two excited singlet, $1^1B_u^+$ and $2^1A_g^-$, states.

The highest level of the present theory [QZ3p basis and $(n, 2n)$ active space] predicts the $1^3B_u^-$ and $1^3A_g^-$ states to have excitation energies of 3.20 and 4.87 eV, respectively. The agreement of the results with the experimental values of 3.22 and 4.91 eV [52] is almost complete. The present theory places the energy of the $1^1B_u^+$ state at 6.21 eV above the ground state or 0.4 eV below the experimental value of 6.25 eV [51]. No definitive experimental data are known on the hidden $2^1A_g^-$ state because the state is probably reached by a nonvertical transition. The same level of theory also yields very accurate results for ethene. MRMP with QZ3p/(2, 4) predicts that the singlet excited state appears at 8.01 eV (experimental estimate is 8.0–8.2 eV [29–31]) and the triplet one at 4.36 eV (experimental values are 4.36 [61] and 4.32 [62] eV) for ethene. The same level of theory is sufficient to be able to predict the transition energy of the low-lying excited states of polyenes.

Table IV shows that the basis-set effect on the transition energy is rather significant, particularly for singlet states. The transition energies decrease with increasing the quality of a basis set, indicating that the description of excited states needs a more flexible basis set than that used for the ground state. The DZp basis is clearly insufficient for quantitative accuracy on the transition energy. Both $1^3B_u^-$ and $1^3A_g^-$ excitation energies decrease by 0.3–0.9 eV in proceeding from DZp to TZ2p

TABLE IV

Basis-set and active-space effects on the vertical excitation energies (eV) of butadiene.

State	Active space	Basis set			Exptl.
		DZp	TZ2p	QZ3p	
Singlet					
$1^1B_u^+$	(4, 4)	6.13	5.81	5.69	
	(4, 8)	6.48	6.26	6.21	6.25,[a] 5.92[b–d]
$2^1A_g^-$	(4, 4)	6.61	6.41	6.32	
	(4, 8)	6.56	6.37	6.31	
Triplet					
$1^3B_u^-$	(4, 4)	3.24	3.18	3.18	
	(4, 8)	3.29	3.20	3.20	3.22[e]
$1^3A_g^-$	(4, 4)	5.05	4.92	4.90	
	(4, 8)	5.07	4.91	4.87	4.91[e]

[a] [51].
[b] [52].
[c] [53].
[d] [19, 20, 54 –56].
[e] [52].

but do not change significantly with QZ3p. TZ2p appears to be nearly complete for describing the triplet excitation energies but it is still poor for singlet excited states. A precise description requires the basis set of QZ3p quality.

The enlargement of the active space has a significant effect on the transition to the ionic *plus* states although it has a minor effect on the covalent *minus* states. The CASSCF with π-only active orbitals computes the ionic excited states higher in energy than the experiment. A proper description of the ionic states requires explicit inclusion of $\sigma-\pi$ correlation effects and that, without these, the valencelike component is strongly biased against. The ionic $1^1B_u^+$ energy is considerably underestimated by MRMP with the single active space. It is also seen from Table IV that the balance between the basis set (one-electron function) and the active space (many-electron function) is important.

EXTRAPOLATION METHOD

It is possible to treat smaller polyenes accurately using MRMP with a large basis set and a double active space, but the same level of theory cannot be applied at present to larger polyenes. As shown above, the excitation energies, particularly singlet excitation energies, are rather sensitive to the basis set and the active space employed. Table III shows that the CASSCF description of both $1^1B_u^+$ and $2^1A_g^-$ states is entirely analogous from butadiene to decapentaene. The $1^1B_u^+$ state comes mainly from the HOMO $\to$ LUMO ($1 \to 1'$) excitation. The $2^1A_g^-$ state is a mixture of the singly excited configurations of $1 \to 2'$ and its conjugate and the doubly excited configurations of $(HOMO)^2 \to (LUMO)^2$. In the description of CASVB [57], these low-lying excited states are expressed in terms of the local excitations, singlet and triplet single excitations in ethene units, and their couplings. The $2^1A_g^-$ state, e.g., is described by configurations involving two simultaneous triplet single excitations in ethene units coupled to form an overall singlet state. Thus, its excitation energy is roughly determined to be about twice of the lowest triplet excitation to the $1^3B_u^-$ state [37]. In a CASVB description, the $1^1B_u^+$ state is represented by a number of ionic configurations, composed of the ionic structure of ethene units. Thus, the excitation in polyenes is a combination of the local excitations that occurred in ethene units. These considerations suggest that similar errors should be engendered in calculations of other polyenes.

Thus, an energy extrapolation procedure is used to estimate the low-lying excited states of larger polyenes, i.e., excitation energies calculated at a lower level of theory are extrapolated to ones at a higher level of theory equivalent to MRMP with QZ3$p/(n, 2n)$.

We treat the basis-set effect and active-space effect separately. The validity of the extrapolation method is assessed on hexatriene and octatetraene. First, two low-lying singlet excited states of hexatriene are calculated with DZ$p/(6, 6)$. The $1^1B_u^+$ and $2^1A_g^-$ excitation energies at this level of theory are 5.02 and 5.35 eV, respectively. Then, we add the active-space effects on the ionic and covalent states estimated in butadiene separately. The corrected excitation energies are 5.37 eV for $1^1B_u^+$ and 5.31 eV for $2^1A_g^-$. The real MRMP excitation energies computed with DZ$p/(6, 12)$ are 5.37 eV for $1^1B_u^+$ and 5.34 eV for $2^1A_g^-$. The extrapolation procedure works very well for the active-space effect. The extrapolation procedure also achieves a good convergence on octatetraene.

The basis-set deficiency is also recovered using the similar additive correction procedure. The basis-set effect from DZp to TZ2p with a single active space is estimated to be -0.32 ($= 5.81-6.13$) eV for the $1^1B_u^+$ state. The corresponding effect for the $2^1A_g^-$ state is -0.20 eV. These effects are added to the MRMP values calculated with DZ$p/(6, 6)$. Then, we obtain the corrected excitation energies of 4.70 eV for the $1^1B_u^+$ state. The real value with TZ2$p/(6, 6)$ is 4.77 eV. For the $2^1A_g^-$ state, the corrected value of 5.15 eV is compared with the real value of 5.21 eV. Even though the correction slightly tends to lower a given state's energy, the extrapolation is still acceptable and well within the expected accuracy.

Note that the basis-set effect on $1^1B_u^-$ and $2^1A_g^-$ excitation energies shows a very similar convergence pattern if the same active space is used. Thus, the basis-set effect is rather insensitive to the ordering of $1^1B_u^-$ and $2^1A_g^-$ states.

trans-1,3-BUTADIENE

Table V is the summary of the calculated results on butadiene. The lowest singlet excited state is computed to be the $1^1B_u^+$ state. The $1^1B_u^+$ state is well described by a singly excited $\pi \to \pi^*$ configuration of $1 \to 1'$. MRMP predicts that it appears at 6.21 eV above the ground state. The oscillator strength for the transition is computed to be 0.803. The old experimental value is 0.4 [58]. Our excita-

TABLE V
trans-1,3-Butadiene vertical excitation energies (eV); comparison with previous accurate calculations.[a]

State	CI4[b]	SACCI[c]	H[vd]	MRCI[e]	CASPT2[f]	MRMP	Exptl.
$1^3B_u^-$	—	3.48	3.23	3.18	3.20	3.20	3.22[g]
$1^3A_g^-$	—	5.15	4.83	4.90	4.89	4.87	4.91[g]
$1^1B_u^+$	6.23	6.39	6.14	6.48	6.23	6.21	6.25,[g] 5.92[h–j]
	(0.508)				(0.686)	(0.803)	(0.4[k])
$2^1A_g^-$	6.67	7.00	6.19	6.53	6.27	6.31	?

[a]Oscillator strengths are given in parentheses.
[b][33, 34].
[c][30].
[d][35].
[e][36].
[f][32].
[g][51].
[h][52].
[i][53].
[j][19, 20, 54 –56].
[k][67].

tion energy agrees well with the previous accurate calculations. Graham and Freed [35] placed the $1^1B_u^+$ state at 6.19 eV. The best MRSDCI results by Cave and Davidson [33, 34] predicted the $1^1B_u^+$ state to have an excitation energy of approximately 6.2 eV with the oscillator strength of 0.508. CASPT2 [32], which is similar to our MRMP, gave the excitation energy of 6.23 eV. Thus, all the recent accurate theoretical values are nearly converging to about 6.2 eV. The dominant feature in the optical and electron impact spectra is a broad intense band stretching from 5.7 to 6.3 eV [20], having four peaks with the intensity maximum at 5.92 eV. This feature has been assigned as the lowest $\pi \rightarrow \pi^*$ excitation to a state of $1^1B_u^+$ symmetry. In a recent experiment, McDiarmid [51] placed the $1^1B_u^+$ state at 6.25 eV, which is close to the theoretical estimate.

MRMP predicts the $2^1A_g^-$ state to lie at 6.31 eV above the ground state or at 0.10 eV above the $1^1B_u^+$ state. The $2^1A_g^-$ is a covalent state and has a multiconfigurational character. The state contains significant contributions of the singly excited configurations of $1 \rightarrow 2'$ and $2 \rightarrow 1'$ and the doubly excited configuration of $(HOMO)^2 \rightarrow (LUMO)^2$.

The ordering, the $1^1B_u^+$ below the $2^1A_g^-$, is reproduced by almost all the previous accurate calculations. However, the $1^1B_u^+ - 2^1A_g^-$ energy gap varies in the range of 0.04–0.62 eV. The SACCI $2^1A_g^-$ excitation energy of 7.05 [30] is probably too high. Cave and Davidson [33, 34] placed the $2^1A_g^-$ state

at 6.77 eV, and Graham and Freed [35], at 6.16 eV. A recent CASPT2 study [32] gave the excitation energy of 6.27 eV, which is very close to the present value. Although the lack of the complete convergence of the basis set prevents us from making a precise energy gap of these two states, the $1^1B_u^+$ state is definitely slightly lower than the $2^1A_g^-$ state at the ground-state equilibrium geometry. This is consistent with experiment in that multiphoton [21] and electron-impact [18, 52, 53] studies do not show evidence for the existence of the $2^1A_g^-$ state below the $1^1B_u^+$ state in butadiene.

We obtained excellent agreement with the experimental data for the transitions to the triplet states, $1^3B_u^-$ and $1^3A_g^-$. Both states are described well by singly excited configurations. The $1^3B_u^-$ state originates from $1 \rightarrow 1'$ and the $1^3A_g^-$ state from $1 \rightarrow 2'$ and its conjugate, which have nearly the same weight with a different sign in the CASSCF wave function. Both states are covalent in nature. The MRMP excitation energies are 3.20 and 4.87 eV, respectively, which are in the experimental range of 3.2–3.3 eV for the $1^3B_u^-$ and 4.8–4.93 eV for $1^3A_g^-$.

trans−trans-1,3,5-HEXATRIENE

Hexatriene has been extensively studied experimentally because of its relationship to the vitamin D_2−steroid system. The $1^1A_g^- \rightarrow 2^1A_g^-$ transition is predicted to occur in the immediate vicinity of the $1^1A_g^- \rightarrow 1^1B_u^+$ excitation, whose first band has a

peak at 4.93 or 4.95 eV [18, 57–60]. Post et al. [68] found a slight indication of the presence of the $2^1A_g^-$ state at a 4.4 eV energy loss. However, a more extensive high-sensitivity investigation at higher resolution failed to confirm that such a state exists in the range of 4.2–4.6 eV [18, 57, 69]. Parker et al. [70] observed a two-photon-allowed transition at 6.2 eV in the multiphoton ionization spectrum, but subsequently showed the Rydberg nature from the polarization properties [71]. Electron impact has brought no significant information about the $2^1A_g^-$ state of hexatriene thus far. A two-photon absorption study [72] indicated the presence of a two-photon-allowed band near an intense dipole-allowed transition in liquid hexatriene. The cross section is most reasonably assigned to the transition to the $2^1A_g^-$ state, but the level ordering of $2^1A_g^-$ and $1^1B_u^+$ is not established with certainty. The location of the doubly excited state relative to the optically allowed $1^1B_u^+$ state is still an open question.

Calculated results are shown in Table VI. MRMP with (6, 12) places the $2^1A_g^-$ state slightly below the $1^1B_u^+$ state. The MRMP excitation energies are 5.37 eV for $1^1B_u^+$ and 5.34 eV for $2^1A_g^-$. The corrected excitation energies to the $2^1A_g^-$ and $1^1B_u^+$ states are 5.09 and 5.10 eV, respectively. The present theory predicts that two lowest states are virtually degenerate in hexatriene.

The most striking points to note are the ordering of the two lowest excited states and their energy gap. It is seen from the corrected values that the doubly excited $2^1A_g^-$ state always lies below the $1^1B_u^+$ state although the energy splitting

is rather small, less than 0.06 eV. The present theory predicts that the $1^1B_u^+$ state occurs at 5.10–5.17 eV. The optical absorption intensity maximum for this state is at 4.93 eV [57–60]. However, the computed excitation energy is in quite good agreement with the electron-impact intensity maximum of 5.13 eV [63]. For the $2^1A_g^-$ state, there is no significant information. The relative position of the one-photon ($1^1A_g^- \to 1^1B_u^+$) and two-photon ($1^1A_g^- \to 2^1A_g^-$) bands and their spectral features are generally similar to those of isotachisterol with a triene chromophore equivalent to *trans*-hexatriene, which were obtained by Pierce et al. [73] in an absorption and two-photon absorption excitation study. They concluded that the $2^1A_g^-$ state is slightly (~ 0.06 eV) lower than the $1^1B_u^+$ state in isotachisterol from the spectral contour analysis. A similar conclusion was also obtained by Andrews and Hudson [74] for cholesta-4,6,8(14)-triene having the *cis*-hexatriene chromophore from the gap between the absorption and the fluorescence. These experiments are consistent with the present calculations.

The present study provides a significantly different picture of the low-lying singlet valence states of hexatriene from past theoretical results. Table VI includes a GVB-CI study of Nascimento and Goddard [37], a quadruple CI of Cave and Davidson [39], and a CASPT2 of Serrano-Andres et al. [32] for comparison. All previous calculations except GVB-CI indicated the presence of the $1^1A_g^- \to 2^1A_g^-$ transition above the $1^1A_g^- \to 1^1B_u^+$ transition. GVB-CI excitation energies are 5.62 eV for $2^1A_g^-$ and 6.56 eV for $1^1B_u^+$. Both were calculated consid-

TABLE VI
trans,trans-1,3,5-Hexatriene vertical excitation energies (eV); comparison with previous accurate calculations.[a]

State	GVB-CI[b]	CI(Q) / CI6[c]	CASPT2[d]	MRMP[e]	MRMP[e] (corrected)	Exptl.
$1^3B_u^-$	2.71	2.84	2.55	2.60	2.40	2.61,[f] 2.58[g]
$1^3A_g^-$	4.32	—	4.12	4.24	4.15	4.11,[f] 4.07[f]
$1^1B_u^+$	6.56	5.14 (1.24)	5.01 (0.85)	5.37 (1.08)	5.10	4.93,[h] 4.95,[f] 5.13[f]
$2^1A_g^-$	5.62	5.74	5.19	5.34	5.09	?

[a] Oscillator strengths are given in parentheses.
[b] [37].
[c] [39].
[d] [32].
[e] MRMP results with ($3s2p1d / 2s$) / (6, 12).
[f] [18, 53a].
[g] [63].
[h] [57, 58].

erably higher than the observed dipole-allowed transition. The CI6 excitation energy to the $1^1B_u^+$ state is 5.14 eV, which is close to our value of 5.10 eV. However, Cave and Davidson estimated the vertical transition energy for $2^1A_g^-$ to be in the range of 5.5–5.8 eV based on an empirical correction. The overall CASPT2 results are close to the present estimate but CASPT2 also predicts the ordering of the doubly excited $2^1A_g^-$ state above the singly excited $1^1B_u^+$ state at the ground-state geometry.

For the low-lying triplet states, the present theory yields satisfactory results. The $1^3B_u^-$ state is predicted to be located at 2.60 eV above the ground state. The lowest-energy loss feature is reported as a singlet → triplet transition, which peaks at 2.61 eV [18]. MRMP result agrees well with the experiment but this agreement could be fortuitous. The extrapolated excitation energy for the $1^3B_u^-$ state is 2.40 eV, which has somewhat larger error than expected. The second lowest excited state is the $1^3A_g^-$ state. The MRMP excitation energy of 4.24 eV is corrected to 4.15 eV, which is in good agreement with the electron-impact intensity maximum of 4.11 eV [18].

ALL-*trans*-1,3,5,7-OCTATETRAENE

The spectroscopy of octatetraene was studied in the gas phase, in solution, and in solids. The lowest optically allowed state occurs at 4.41 eV in the gas phase [12, 59, 64, 75]. It is found that the spectrum in solution is rather sensitive to the solvent dielectric constant [12, 14]. This state is assigned as a valence $1^1B_u^+$ state of ionic nature. An

interesting feature of the $1B_u^+$ band is its sharpness. The diffuse character of the $1B_u^+$ band seen in the shorter polyenes has been lost. This suggests the possibility of geometric distortions leading to radiationless decays to lower-lying states [11, 16]. In solution and solids, the lowest singlet transition has been identified as occurring to a state of the same symmetry as the ground state. However, the gas-phase fluorescence spectrum [12] shows no Stokes shift relative to the absorption spectrum and no evidence for a low-lying $2^1A_g^-$ state was obtained in electron-energy-loss spectra in the gas phase. Yet, the gas-phase fluorescence lifetime is still much longer than one expects for an allowed transition returning to the ground state.

We used the DZp basis and (8, 12) active spaces for octatetraene. The results are presented in Table VII with previous ab initio calculations. MRMP places the $2^1A_g^-$ state below the $1^1B_u^+$ state by 0.1 eV. The transition to the $1^1B_u^+$ state is computed to be 4.81 eV while that to the $2^1A_g^-$ state is 4.72 eV. The corrected excitation energy to the $2^1A_g^-$ state is estimated to be 4.47 eV, and that to the $1^1B_u^+$ state, 4.66 eV. The extrapolated results show that the $2^1A_g^-$ state lies below the $1^1B_u^+$ state by about 0.2 eV.

The quadruple (Q) CI by Cave and Davidson [41] yields the excitation energy to the $1^1B_u^+$ state of 4.76 eV, which is close to our MRMP value of 4.81 eV. However, QCI yields a considerably larger excitation energy (5.21 eV) for the transition to the $2^1A_g^-$ state. Said et al. [40] found the vertical excitation energy for the $2^1A_g^-$ state to be 4.88 eV, using an effective Hamiltonian method (EHM). CASPT2 calculations by Serrano-Andres et al. [42]

TABLE VII

All-*trans*-1,3,5,7-octatetraene vertical excitation energies (eV); comparison with previous accurate calculations.[a]

State	EHM[b]	CI(Q)[c]	CASPT2[d]	MRMP[e]	MRMP[e] (corrected)	Exptl.
$1^3B_u^-$	2.07	2.45	2.17	2.37	2.20	2.10[f]
$1^3A_g^-$	—	—	3.39	3.61	3.55	3.55[f]
$1^1B_u^+$	—	4.76	4.42 (1.83)	4.81 (1.08)	4.66	4.41[g]
$2^1A_g^-$	4.88	5.21	4.38	4.72	4.47	

[a]Oscillator strengths are given in parentheses.
[b][40].
[c][41].
[d][42].
[e]MRMP results with $(3s2p1d/2s)(8, 12)$.
[f][64].
[g][59, 60].

placed the lowest singlet excited state at 4.38 eV having the $2^1A_g^-$ symmetry. The state ordering is same as ours but their energy splitting between $2^1A_g^-$ and $1^1B_u^+$ is only 0.04 eV, which is much smaller than ours.

The lowest triplet state is computed to be $1^3B_u^-$ state, which lies at 2.37 eV above the ground state by MRMP with $(8, 12)$ active space. The excitation energy is corrected to be 2.20 eV. The experimental evidence locates the lowest vertical absorption at 2.10 eV. The error is only 0.1 eV. MRMP predicts that the second triplet excited state is the $1^3A_g^-$ state and the transition occurs at 3.61 eV. The excitation energy is corrected to be 3.55 eV by taking into account of the basis-set and active-space effects. Allan et al. [64] reported a second band with an intensity maximum at 3.55 eV. They assigned the band to the transition to the second $^3B_u^-$ state. But the present calculation suggests the peak at 3.55 eV originated from the transition to the $1^3A_g^-$ state.

ALL-*trans*-1,3,5,7,9-DECAPENTAENE

The absorption, emission, and excitation spectra of decapentaene were measured by D'Amico et al. [14]. Spectra exhibit the characteristic gap between the origin of the strongly allowed absorption and the origin of fluorescence. The transition to the $1^1B_u^+$ state is found at 4.02 eV. The $2^1A_g^-$ state is estimated to lie at 3.48 eV from the fluorescence spectrum, assuming mirror symmetry between absorption and emission. The estimation is based on the assumption that the ground- and excited-state potentials are similar. It is known, however, that there are qualitative differences between the ground- and the $2^1A_g^-$-state potentials. Thus, it should be noted that an estimate of the vertical excitation energy based on mirror symmetry could have a considerable error.

The geometry of the ground state of decapentaene is optimized at the CASSCF level with DZp/(10, 10). MRMP results along with the previous calculations are summarized in Table VIII. The lowest excited state is computed to have the same symmetry as the ground state. The excitation to the $2^1A_g^-$ state is calculated to be 3.95 eV. The second valence excited state is identified as the $1^1B_u^+$ state. The state is predicted to locate at 3.97 eV slightly above the $2^1A_g^-$ state with a strong intensity of 1.40. Starting from these values, we obtained the corrected excitation energies of 3.65 eV for $2^1A_g^-$ and 4.05 eV for $1^1B_u^+$. The extrapola-

TABLE VIII
All-*trans*-1,3,5,7,9-decapentaene vertical excitation energies (eV).[a]

State	EHM[b]	MRMP[c]	MRMP[c] (corrected)	Exptl.
$1^3B_u^-$	1.85	1.95	1.89	
$1^3A_g^-$	—	3.02	2.98	
$1^1B_u^+$	—	3.97	4.05	4.02[d]
		(1.40)		
$2^1A_g^-$	4.19	3.95	3.65	3.48[d]

[a] Oscillator strengths are given in parentheses.
[b] [40].
[c] MRMP results with $(3s2p1d/2s)(10, 10)$.
[d] [14].

tion enhances the energy splitting between two states. The corrected $1^1B_u^+$ excitation energy of 4.05 eV is in good agreement with the directly observed value of 4.02 eV [14]. The extrapolation predicts the $2^1A_g^-$ state lies at 3.65 eV while the experimental estimate is 3.48 eV [14]. Said et al. [40] reported that the vertical excitation energy for the $2^1A_g^-$ state is 4.19 eV, which is too large compared to the present calculations.

The lowest triplet $1^3B_u^-$ state is predicted to lie at 1.95 eV with MRMP. The corrected value is 1.89 eV. Said et al. [40] predicted the transition energy to be 1.85 eV, which is very close to the present result. The second lowest triplet state is the $1^3A_g^-$ state, which is predicted to appear at 3.02 eV (MRMP) and 2.98 eV (corrected).

THE ENERGY GAP BETWEEN $1^1B_u^+$ AND $2^1A_g^-$ STATES

Emphasis is placed here on the low-lying $2^1A_g^-$ and $1^1B_u^+$ states. Since the two states are quite different in character, it is rather difficult to describe both states in a balanced way. The $1^1B_u^+$ state is ionic and represented well by singly excited configurations while the $2^1A_g^-$ state is covalent in nature and a mixture of doubly and singly excited configurations.

The corrected excitation energies of the low-lying $2^1A_g^-$ and $1^1B_u^+$ states with a number of carbon chains are shown in Figure 1. For butadiene, the $1^1B_u^+$ state is slightly lower by 0.1 eV than the doubly excited $2^1A_g^-$ state at the ground-state equilibrium geometry. For hexatriene, our calculations predict the two states to be virtually degenerate. The energy splitting between two states is
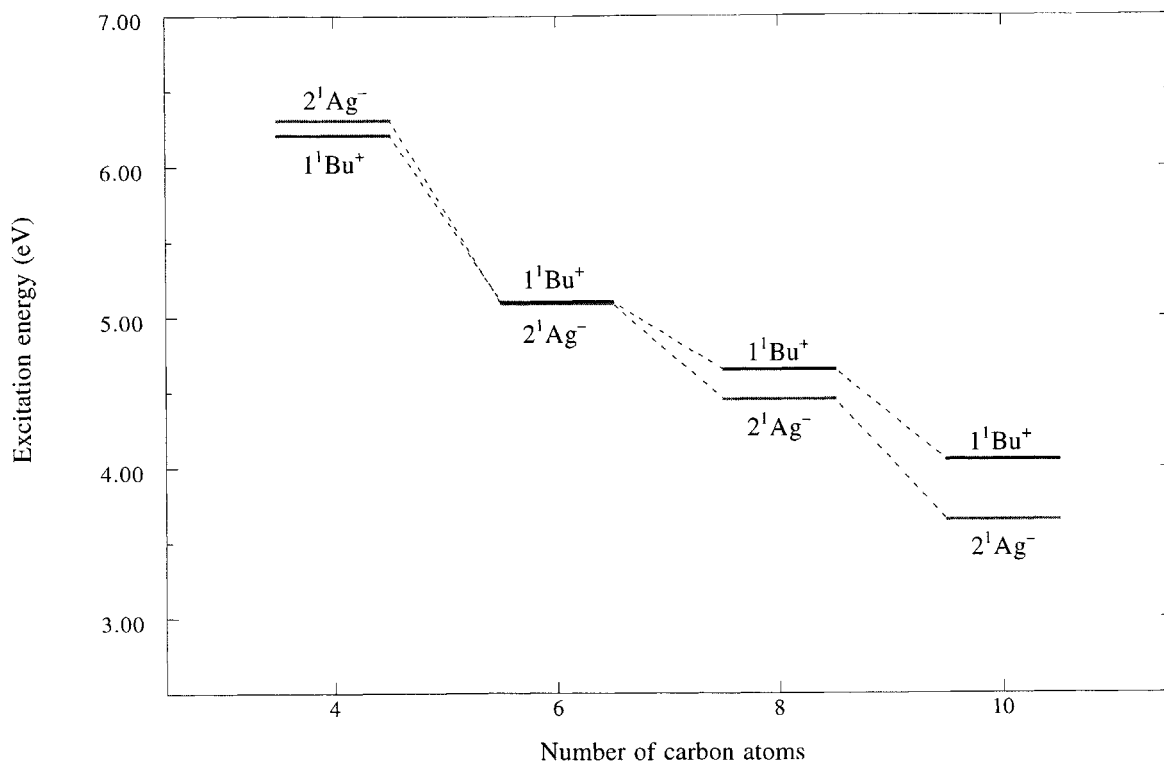
FIGURE 1. Vertical excitation energies to the two lowest polyene singlet states. MRMP results are corrected by taking into account the basis-set and active-space effects for hexatriene and larger polyenes.

estimated to be less than 0.06 eV. Octatetraene is the first polyene for which we predict that the $2^1A_g^-$ state is the lowest excited singlet state at the ground-state geometry. The present theory also predicts that the $2^1A_g^-$ state lies clearly below the $1^1B_u^+$ state in decapentaene with the energy splitting of 0.4 eV. The uncorrected MRMP excitation energies listed in Table I also lead to the similar overall conclusion as to the energy gap between the $1^1B_u^+$ and $2^1A_g^-$ states.

The low-lying triplet states, $1^3B_u^-$ and $1^3A_g^-$, are both covalent in nature and both are described well by singly excited configurations. Thus, the present prediction is very accurate and in good agreement with the known experiment.

Nonvertical $\pi \rightarrow \pi^*$ Excitation Energies of Polyenes

In this section, we discuss the nonvertical excitation energies, the 0–0, and emission (an estimated fluorescence intensity maximum based on a vertical transition from the excited state to the ground state) excitation energies for $1^1B_u^+$ and $2^1A_g^-$ states of polyenes. To estimate the nonvertical transition energies, we calculated the ground- and excited-state equilibrium geometries. Geometry optimization for butadiene was performed at the CASSCF level with TZ2p/(4, 4) while for larger polyenes we used DZp/(n, n). The $\sigma-\pi$ polarization effect is not included at the CASSCF level. Thus, the optimized geometry of the ionic $1^1B_u^+$ state may have some error. However, the $1^1B_u^+$ state is less sensitive to the geometry variations compared to the covalent $2^1A_g^-$ state as will be discussed later. The molecular symmetry is assumed to be C_{2h} and therefore planar. There is some evidence to believe that these polyenes in excited states are planar. On the other hand, other studies indicate that the excited states may be twisted about a terminal C—C bond. Whether the excited states are twisted or not is not clear but it is of interest to examine the energetic effects of significant changes in the bond lengths in excited states. In these calculations, zero-point corrections are not included.

EQUILIBRIUM GEOMETRIES OF THE GROUND AND EXCITED STATES OF POLYENES

The most interesting results on the polyene structure are the values of the carbon–carbon bond lengths. The differences between the ground-state and excited-state bond angles and C—H bond lengths are quite small due to the small steric hindrance and we focused on the change of C—C bond lengths. Table IX summarizes the change of the C—C bond lengths with the carbon chains.

Let us first discuss the optimized geometries of the ground state. Calculated results show that there is clear alternation of the C—C bond lengths in these polyenes. Although additional information of larger polyenes is necessary, it is seen from the calculated data that increasing the carbon chains decreases the mean single-bond length and increases the mean double-bond length. The terminal C_1—C_2 double bond becomes longer and the C_2—C_3 single bond becomes shorter with the increase of the chains although the change is small.

The present results on butadiene are in good agreement with experiment determined by electron diffraction [48]. The C—C bond lengths agree well with the experimental values but the C—H bond lengths are computed somewhat too short. A significant lengthening of the central double bond of hexatriene was observed relative to the terminal double bonds [48]. The central double bond is elongated to 1.367 Å, which is 0.03 Å longer than the terminal double bond. This is not supported by the present calculations. The central double bond is certainly longer than the terminal double bond but the difference is computed to be only 0.007 Å. The terminal double-bond length is computed to be 1.338 Å, which is very close to the value of 1.333 Å for ethene. The octatetraene structure was determined by X-ray spectroscopy [49]. Our results for octatetraene are very close to the previous calculations done by Serrano-Andres et al. [42] optimized at the CASSCF with an atomic natural orbital basis. The X-ray value of 1.327 Å for the C_3—C_4 double bond is obviously too short, as suggested by Serrano-Andres et al. Our predicted bond length is 1.351 Å. Also, the X-ray C—H bond distances varies significantly in the range of 0.93–1.17 Å. However, our C—H bond lengths are

TABLE IX

Calculated C—C bond lengths (Å) of the ground and excited $2^1A_g^-$ and $1^1B_u^+$ states at their relaxed geometries.[a]

	C_1————	C_2————	C_3————	C_4————	C_5—	C_6
$1^1A_g^-$ (ground state)						
Ethene	1.334 (1.339)[b,c]					
Butadiene	1.335 (1.343)[d]	1.463 (1.467)[d]				
Hexatriene	1.338 (1.337)[d]	1.469 (1.457)[d]	1.345 (1.367)[d]			
Octatetraene	1.345 (1.336)[e]	1.457 (1.451)[e]	1.351 (1.327)[e]	1.451 (1.451)[e]		
Decapentaene	1.346	1.454	1.351	1.450	1.352	
$2^1A_g^-$						
Butadiene	1.425	1.411				
Hexatriene	1.445	1.383	1.427			
Octatetraene	1.432	1.369	1.432	1.390		
Decapentaene	1.407	1.375	1.434	1.385	1.415	
$1^1B_u^+$						
Ethene	1.446					
Butadiene	1.405	1.379				
Hexatriene	1.395	1.397	1.423			
Octatetraene	1.379	1.413	1.401	1.395		
Decapentaene	1.369	1.430	1.406	1.406	1.425	

[a] Values in parentheses are experimental C—C bond lengths.
[b] [46].
[c] [47].
[d] [48].
[e] [76].

almost constant (1.09 Å). There is no available experimental data for decapentaene. The clear bond alternation is found in the C—C bond lengths while the C—H bond lengths remain almost constant around 1.08 Å.

The $2^1A_g^-$ state includes a large contribution from the doubly excited configurations of $(HOMO)^2 \rightarrow (LUMO)^2$. Thus, it is expected that the inversion between single and double bonds will occur upon excitation to this state. Table IX shows clearly that the bond length of the double bonds in the $2^1A_g^-$ excited state increases while the single bonds decrease. This tendency becomes more apparent with the increase of the carbon chains. The C—C bonds of the ground state and the $2^1A_g^-$ state differ significantly. Thus, it is understandable that the vertical $2^1A_g^-$ excitation energies are rather sensitive to the ground-state geometry used. Previous studies of the $2^1A_g^-$ state of octatetraene by Aoyagi et al. [77] show the same tendencies in the bond lengths. Our results for octatetraene are very close to the previous calculations done by Serrano-Andres et al. [42]. It is seen that the C_3—C_4 bond, the second double bond from the terminal in the ground state, becomes very loose in the excited states. For example, the C_3—C_4 distance in decapentaene is 0.027 Å longer than the terminal C_1—C_2 distance. This point is of particular interest because of its relevance to the photoisomerization reactions. The $2^1A_g^-$ state may be an intermediate in the visual process, which involves the photoisomerization of 11-*cis*-retinal.

The one-electron HOMO → LUMO transition gives rise to the ionic $1^1B_u^+$ state. Simple theory suggests that the bond alternation will disappear in the $1^1B_u^+$ state. This is confirmed in the present calculations. The longer polyenes clearly indicate this tendency of no bond alternation. Particularly, the C—C bond lengths near the center of the chains approach 1.4 Å, the mean value of the single- and double-bond lengths. However, the terminal C—C bond becomes shorter with increase of the carbon chains, i.e., the terminal bond increases a double-bond character with the increase of the carbon chains. On the other hand, the second C—C bond from the terminal becomes looser with the increase of the carbon chains and shows the character of a single bond. The C—C bond lengths change rather dramatically in butadiene upon excitation to this state. As far as butadiene, the $1^1B_u^+$ state shows inverse bond alternation and the $2^1A_g^-$ state shows no bond alternation. The excitation again has a minor effect on the C—H bond lengths and bond angles. The C—H bond lengths in the ionic $1^1B_u^+$ state are found to be slightly longer than those in the covalent $2^1A_g^-$ state.

BASIS-SET AND ACTIVE-SPACE EFFECTS ON THE NONVERTICAL EXCITATION ENERGIES

Table X gives basis-set and active-space effects on the adiabatic and emission excitation energies in butadiene. The basis-set effect on the nonvertical $1^1B_u^+$ excitation energy is also significant as in the case of the vertical excitation energy. However, the basis-set effect leads to little change on the transition to the covalent *minus* states in a relaxed geometry. This is quite different from the vertical transition. As shown above, there are large bond distance changes in the carbon backbone in the $2^1A_g^-$ state. This indicates that it requires greater flexibility to describe the $2^1A_g^-$ states at the ground-state geometry. If the geometry is relaxed, the one-electron function converges more rapidly as in the cases of other covalent states. The active-space effect is found also significant on the transition to the ionic $1^1B_u^+$ state. This effect is rather

TABLE X _____

Basis-set and active-space effects on the 0−0 excitation energies (eV) of butadiene.

State	Active space	Basis set			Exptl.
		DZp	TZ2p	QZ3p	
$1^1B_u^+$	(4, 4)	5.61	5.53	5.38	
	(4, 8)	5.97	5.95	5.93	5.73,[a] 5.92−6.02[b]
$2^1A_g^-$	(4, 4)	5.45	5.49	5.50	
	(4, 8)	5.39	5.49	5.49	

[a] [1].
[b] [52a].

common to all the ionic states in any circumstance. The active-space effect has little effect on the non-vertical transition of the covalent $2^1A_g^-$ states. The basis-set and active-space effects are important particularly for excited states, but not for the ground state. Thus, a very similar trend is observed for both 0–0 and emission excitations. These effects are also taken into account to estimate the nonvertical excitation energies of larger polyenes.

THE 0–0 AND EMISSION EXCITATION ENERGIES FOR POLYENES

The singlet 0–0 and emission excitation energies for polyenes are given in Tables XI and XII. The corrected values are also listed. There is a significant change in the excitation energies compared to the vertical excitation energies. Although the ground $1^1A_g^-$ state is somewhat less sensitive to geometry changes in proceeding from the ground-state geometry to the relaxed geometries of the excited state, the excited states decrease in energy considerably at the corresponding relaxed geometry. The $2^1A_g^-$ state is more sensitive to the geometry change than to the $1^1B_u^+$ state. The C—C bond

lengths change more significantly in the $2^1A_g^-$ state than those in the $1^1B_u^+$ state. This is the main reason why the energy of the $2^1A_g^-$ state drops considerably in proceeding to its relaxed geometry. It is partly due to the nature of the two states, the covalent $2^1A_g^-$ state and the ionic $1^1B_u^+$ state. The ionic states are less sensitive to the geometry changes compared to the covalent states.

The MRMP with $QZ3p/(2,4)$ yields the $1^1B_u^+$ 0–0 and emission excitation energies of ethene to be 7.42 and 7.16 eV, respectively. The vertical excitation energy is 8.01 eV at the same level of theory. Thus, the geometry relaxation has a considerable effect on the excitation energy. Although the ground state increases in energy only by 0.18 eV in going from the ground-state equilibrium geometry to the $1^1B_u^+$ relaxed geometry, the excited-state energy decreases by 0.67 eV in proceeding to its relaxed geometry. It is now established that the observed intense and broad band with a maximum at 7.66 eV [78] corresponds to the transition to a somewhat twisted molecule [80].

The present theory predicts that the $1^1B_u^+$ 0–0 transition energy for butadiene is 5.93 eV, in reasonable agreement with the experimental 5.73 eV

TABLE XI
The $2^1A_g^-$ and $1^1B_u^+$ 0–0 transition energies (eV) of polyenes.

Polyenes	Method	CASSCF	MRMP	MRMP (corrected)	Exptl.
Ethene					
$1^1B_{2u}^+$	$QZ3p/(2,4)$	8.95	7.42	—	7.66[a]
Butadiene					
$2^1A_g^-$	$QZ3p/(4,8)$	5.74	5.49	—	?
$1^1B_u^+$	$QZ3p/(4,8)$	7.48	5.93	—	5.73,[b] 5.92–6.02[c]
Hexatriene					
$2^1A_g^-$	$DZp/(6,12)$	4.35	4.07	4.17	
$1^1B_u^+$	$DZp/(6,12)$	6.68	4.88	4.84	4.93[b]
Octatetraene					
$2^1A_g^-$	$DZp/(8,8)$	3.63	3.45	3.50	3.59,[b,d] 3.54[e]
$1^1B_u^+$	$DZp/(8,8)$	6.43	4.02	4.34	4.38, 4.41[f]
Decapentaene					
$2^1A_g^-$	$DZp/(10,10)$	3.26	2.94	2.99	3.10[b,d]
$1^1B_u^+$	$DZp/(10,10)$	6.12	3.56	3.88	3.98,[d] 4.02[b]

[a][78].
[b][1].
[c][52a].
[d][14].
[e][13].
[f][12, 15].

TABLE XII
The $2^1A_g^-$ and $1^1B_u^+$ emission energies (eV) of polyenes.

Polyenes	Method	CASSCF	MRMP	MRMP (corrected)	Exptl.
Ethene					
$1^1B_{2u}^+$	QZ3p / (2, 4)	8.59	7.16	—	
Butadiene					
$2^1A_g^-$	QZ3p / (4, 8)	5.30	5.13	—	
$1^1B_u^+$	QZ3p / (4, 8)	7.04	5.58	—	
Hexatriene					
$2^1A_g^-$	DZp / (6, 6)	3.72	3.71	3.62	
$2^1A_g^-$	DZp / (6, 12)	3.73	3.69	3.65	
$1^1B_u^+$	DZp / (6, 6)	6.80	4.45	4.59	
$1^1B_u^+$	DZp / (6, 12)	6.40	4.81	4.59	
Octatetraene					
$2^1A_g^-$	DZp / (8, 8)	2.91	2.89	2.80	~ 3.1[a]
$1^1B_u^+$	DZp / (8, 8)	6.26	3.94	3.80	4.20[b]
Decapentaene					
$2^1A_g^-$	DZp / (10, 10)	2.50	2.46	2.37	
$1^1B_u^+$	DZp / (10, 10)	5.85	3.52	3.38	

[a] [79].
[b] Optical spectroscopy in solution [12].

[1]. The $2^1A_g^-$ 0–0 transition energy is estimated to be 5.44 eV. The vertical transition energies are 6.21 eV for $1^1B_u^+$ and 6.31 eV for $2^1A_g^-$. Thus, the $2^1A_g^-$ state is much more sensitive to the geometry change than is the $1^1B_u^+$ state. Although the $1^1B_u^+$ state is found to be the lowest singlet excited state at the ground-state geometry in butadiene, the $2^1A_g^-$ 0–0 energy becomes lower by 0.44 eV than the $1^1B_u^+$ 0–0 energy. This is true for the emission energies. The $2^1A_g^-$ emission energy is lower by 0.45 eV than the $1^1B_u^+$ emission energy. It is suggested that the low-lying excited states of butadiene are twisted. Even in that case, the state ordering predicted in this study will be unaltered. Cave and Davidson [34] calculated the 0–0 transition energies of butadiene by CI4 using the C_{2h} geometries determined by a semiempirical method. Their 0–0 transition energies are 5.66 eV for $2^1A_g^-$ and 5.73 eV for $1^1B_u^+$. They also computed that the $2^1A_g^-$ 0–0 energy is lower than the $1^1B_u^+$ 0–0 energy but the energy difference is much smaller than ours.

For hexatriene, the present theory predicts the 0–0 energy as 4.84 eV for $1^1B_u^+$ and 4.15–4.17 eV for $2^1A_g^-$. Again, the $2^1A_g^-$ 0–0 energy is lower by about 0.7 eV than the $1^1B_u^+$ 0–0 energy. At the ground-state geometry, two states are predicted to

be almost degenerate. The present $1^1B_u^+$ 0–0 energy underestimates the experimental 0–0 energy of 4.93 eV [1] by 0.1 eV. Cave and Davidson [34] estimated the 0–0 energy to be 4.68 eV for $1^1B_u^+$ and 4.52 eV for $2^1A_g^-$. The state ordering is same as ours but their energy gap is again much smaller than our prediction.

Octatetraene is the first polyene for which we predict that the $2^1A_g^-$ state is the lowest excited singlet state at the ground-state geometry. The $2^1A_g^-$ state is predicted to lie by 0.20 eV lower than the $1^1B_u^+$ state at the ground-state geometry. The difference of the 0–0 energies to $2^1A_g^-$ and $1^1B_u^+$ is enlarged due to the sensitivity of the $2^1A_g^-$ state to the geometry variation. The computed $2^1A_g^-$ 0–0 energy is 0.84 eV lower than the $1^1B_u^+$ 0–0 energy. Reasonable agreement is found with experimental values which were obtained from extrapolation of the solution results to the gas phase [1, 14]. The present $2^1A_g^-$ 0–0 energy is only 0.09 eV lower than the experimental value. The $1^1B_u^+$ 0–0 energy is also in excellent agreement with the experimental estimate [1, 12, 14, 15]. The error is less than 0.1 eV. Cave and Davidson [41] obtained 0–0 transition energies of 4.15 eV for $2^1A_g^-$ and 4.56 eV for $1^1B_u^+$. They placed the $2^1A_g^-$ state much higher than ours. This error may be due to the result of an

inaccurate guess for the excited-state geometry that they employed. CASPT2 results [42] for the 0−0 transition energy are 3.61 eV for $2^1A_g^-$ and 4.35 eV for $1^1B_u^+$, which are close to the present results. As to the emission energy, we obtained 2.80 eV for $2^1A_g^-$ and 3.80 eV for $1^1B_u^+$. Bouwman et al. [79] found a weak fluorescence band from the $2^1A_g^-$ in the gas-phase octatetraene spectrum with a maximum near 2.80−2.90 eV. Petek et al. [81] recently showed the fluorescence maximum around 3.1 eV.

For decapentaene, the present calculations for the $2^1A_g^-$ state obtain a vertical excitation energy of 3.65 eV, a 0−0 transition energy of 2.99 eV, and an emission energy of 2.36 eV. The corresponding values for the $1^1B_u^+$ state are 4.05, 3.88, and 3.38 eV. The difference between the $2^1A_g^-$ and $1^1B_u^+$ 0−0 energies reaches 0.9 eV. Clearly, the relaxation of the excited-state geometries leads to the greater lowering for the $2^1A_g^-$ state than for the $1^1B_u^+$ state. Our theoretical values are slightly (by less than 0.14 eV) lower than the experimental ones [1, 12, 14]. Again, MRMP results with correction agree excellently with the experimental estimates.

As shown above, the $2^1A_g^-$ state is more sensitive to the geometry variation than is the $1^1B_u^+$ state, which places the $2^1A_g^-$ state significantly below the $1^1B_u^+$ state at the relaxed geometry. As to the 0−0 energy, there are some discrepancies between the theoretical and experimental estimates for ethene and butadiene. But the agreement is excellent for hexatriene and larger polyenes. Disagreement in the cases of ethene and butadiene may be the result of a planar guess for the excited-state geometry that we assumed. Figure 2 shows the 0−0 excitation energies of the low-lying $2^1A_g^-$ and $1^1B_u^+$ states with the number of carbon chains. The energy gap between two states increases with the carbon chains in going from butadiene to decapentaene. The present calculations confirm a general feature of polyenes that the $2^1A_g^-$ state has the lowest 0−0 transition energy.

Summary

Results are presented from MRMP calculations for low-lying $\pi \to \pi^*$ excited states of polyenes. Our focus was put on the two lowest-lying singlet excited states: the ionic *plus* $1^1B_u^+$ state and the
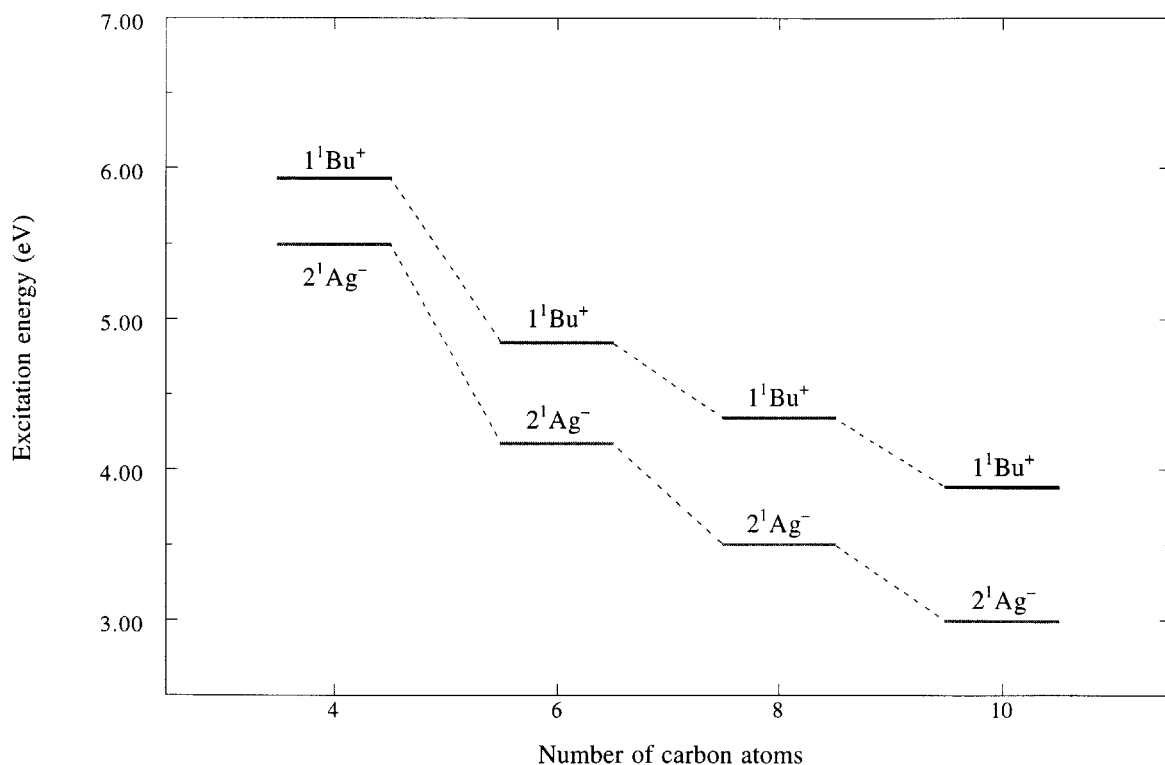

FIGURE 2. The 0−0 excitation energies to the two lowest polyene singlet states. MRMP results are corrected by taking into account the basis-set and active-space effects for hexatriene and larger polyenes.

covalent *minus* $2^1A_g^-$ state and their ordering. The basis-set and the active-space effects to the vertical excitation energies are found to be rather significant. Estimating these effects, we corrected the excitation energies for larger polyenes. We believe that the accuracy of the present method is sufficient to be able to discern the energy difference between the low-lying $1^1B_u^+$ and $2^1A_g^-$ states.

For butadiene, the $1^1B_u^+$ state is calculated to be slightly lower by 0.1 eV than the doubly excited $2^1A_g^-$ state at the ground-state equilibrium geometry. For hexatriene, our calculations predict the two states to be virtually degenerate. Octatetraene is the first polyene for which we predict that the $2^1A_g^-$ state is the lowest excited singlet state at the ground-state geometry. The present theory indicates that the $2^1A_g^-$ state lies clearly below the $1^1B_u^+$ state in decapentaene. Based on the present values, it is confirmed that the ordering of doubly excited $2^1A_g^-$ below $1^1B_u^+$ at the ground-state geometry is a general feature of polyenes, except in butadiene and hexatriene. The 0−0 transition and the emission energies are also calculated using the relaxed excited-state geometries. The $2^1A_g^-$ state is more sensitive to the geometry variation than is the $1^1B_u^+$ state, which places the $2^1A_g^-$ state significantly below the $1^1B_u^+$ state at the relaxed geometry. The present calculations suggest that the $2^1A_g^-$ state has the lowest 0−0 and emission energies for all the polyenes.

The present approach has proved to provide a systematic, quantitative understanding of the electronic structure and spectroscopy of linear polyenes. There also remain a number of significant challenges in polyene chemistry. One of the most important is *cis−trans* photoisomerization. Further work on the mechanism of *cis−trans* photoisomerization will be reported in the future.

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