

The $2^1A_g-1^1B_u$ energy gap in the polyenes: An extended configuration interaction study

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For a correct account of the ordering of excited states in the polyenes, in particular the low-lying 2^1A_g and 1^1B_u states, single as well as double excited configurations must be included in a CI expansion. However, for longer π systems such expansion shows, in contrast to spectroscopic observations, a divergence of excitation energies and a reversal of the 2^1A_g and 1^1B_u state ordering. We have therefore extended the CI expansion to include all triple and quadruple excitations for the polyene series C_nH_{n+2} , $n = 4,6,8,10,12$ and $n = 4,6,8,10$, respectively. In our calculations we employed a PPP model Hamiltonian. The extended CI expansions correct the faults of previous treatments and predict an increase of the $2^1A_g-1^1B_u$ energy gap with increasing polyene length in agreement with recent spectroscopic observations. The effect of higher excitations is mainly due to triple excitations involving three simultaneous spin flips of ground state electrons.

I. INTRODUCTION

The observation of the low-lying 2^1A_g state in diphenyloctatetraene by Hudson and Kohler¹ and the theoretical prediction of the general occurrence of this state in the polyenes^{2,3} started a new era of polyene spectroscopy. This is best illustrated by the spectroscopic data on the 2^1A_g state collected in Table I.

The theoretical explanation^{3,13,14} revealed the qualitative picture of the excited 2^1A_g state entailing two simultaneous triplet excitations combined to a singlet state.¹⁵ As a result single as well as double excited π -electron configurations must be included in a SCF-CI representation (D -CI) of this state. However, such D -CI treatment is found to fail for quantitative predictions as this method accounts for a large part of the ground state cor-

relation energy (though not in a size consistent manner) but only for a small part of the correlation energy of the excited states. The resulting ill behavior of the D -CI excitation energies, a divergence with increasing π system, is illustrated in Fig. 1 for the two lowest singlet excited states. In order to repair the excitation energy divergence, triple and quadruple excitations have to be included in a CI expansion.¹⁷

The D -CI results in Fig. 1 fail also in the description of the energy gap between the 1^1B_u and the 2^1A_g state in that a decrease of this gap upon increasing polyene length is predicted whereas the experimental observations in Table I show the opposite behavior. For a comparison of theory and experiment it must be kept in mind, however, that the observed energy gap between the $0,0$ transitions ground -1^1B_u and ground -2^1A_g have

TABLE I. Observation of the 2^1A_g state in the polyenes.

Molecule	$\Delta E^{00}/\text{eV}$		gap eV	Temperature °K	Matrix	Reference
	1A_g	1B_u				
Octatetraene	3.55	3.98	0.43	77	hexane	Gavin <i>et al.</i> (1978) ⁴
Octatetraene	3.54	3.96	0.42	4.2	octane	Granville <i>et al.</i> (1978) ⁵
Deca-2,4,6,8-tetraene	3.56	3.88	0.32	4.2	undecane	Andrews and Hudson (1978) ⁶
Decapentaene	3.03	3.67	0.64	4.2	nonane	Christensen (1978) ⁴
2,10-Dimethyldecapentaene	3.04	3.43	0.39	4.2	nonane	Christensen and Kohler (1975) ⁷
Dodecahexaene	2.68	3.31	0.63	4.2		Christensen (1978) ⁴
2,12-Dimethyltridecahexaene	2.70	3.20	0.50	4.2	decane	Christensen and Kohler (1976) ⁸
Diphenylhexatriene	3.12	3.22	0.10	4.2	hexane	Nikitina <i>et al.</i> (1976) ⁹
Diphenylhexatriene	3.11	3.23	0.12	77	EPA	Two photon, Fang <i>et al.</i> (1978) ¹⁰
Diphenyloctatetraene	2.80	3.01	0.21	4.2	pentadecane	Hudson and Kohler (1972) ^{1,11}
Diphenyloctatetraene	2.79	2.90	0.16	1.8	bibenzyl	Hudson and Kohler (1972) ^{1,11}
Diphenyloctatetraene	2.77	2.96	0.19	4.2	octane	Nikitina <i>et al.</i> (1976) ⁹
Diphenyloctatetraene	2.77	3.02	0.25	77	EPA	Two photon, Fang <i>et al.</i> (1977) ¹²

^aPrivate communication.

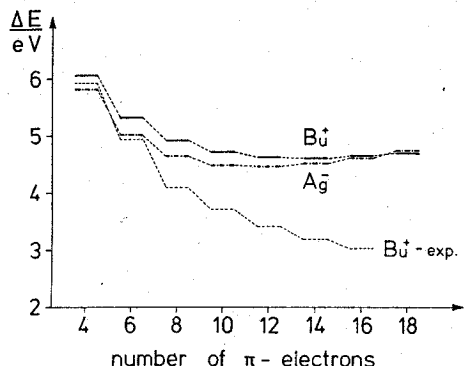


FIG. 1. Excitation energies of the two lowest polyene singlet states as predicted by a PPP-SCF-CI calculation including all single and double excitations; the experimental values are from Ref. 16; the PPP parameters employed are given in Sec. II B.

two possible contributions, one which arises from the energy gap existing for the molecule frozen in the ground state equilibrium geometry (i.e., the gap between the "vertical" transitions), and another from different energy yields in the excited 2^1A_g and 1^1B_u states when the molecule is relaxed from this geometry. In this paper we want to study only the first contribution to the 2^1A_g - 1^1B_u energy gap resulting from vertical transitions.¹⁶ We will show that the inclusion of higher (triple and quadruple) excitations in a CI treatment besides repairing the aforementioned excitation energy divergence leads to an increase of the 2^1A_g - 1^1B_u gap with increasing polyene length. The finding emerges that the low-lying 2^1A_g state contains important contributions from triple and quadruple excited configurations exceeding those of the nearby 1^1B_u state.

II. METHOD: PPP-SCF-CI INCLUDING UP TO QUADRUPLE EXCITATIONS

The effects of higher (double, triple...) excitations on the polyene spectra in particular and conjugated molecules in general have been described previously^{3,13} and will be described here by a PPP-parametrized many-electron Hamiltonian. The effects found^{3,13,17} are not artifacts of this semiempirical approach but have their analogues in *ab initio* calculations.^{14,19,20} Nevertheless do we like to comment shortly on the relationship between the two approaches.

A. Relationship to *ab initio* studies

In their extended *ab initio* CI study (full π -CI, frozen σ -core) on the excited π , π^* states of benzene, Hay and Shavitt¹⁹ voiced doubts about the value of semiempirical calculations even for the sake of only qualitative descriptions. These authors based their criticism on the finding that their calculations predict a much smaller number of low-lying valence states than the semiempirical calculations. This discrepancy seems to originate, however, from a shortcoming of "frozen σ -core *ab initio* π -CI" studies. In fact, a comparison of two *ab initio* studies on ethylene, one employing a frozen σ -core π -CI treatment,²¹ the other allowing for an all-valence-electron CI,²² reveals a change of Rydberg to

valence character for the 1^1B_u state upon inclusion of σ - π mixing. The valence character of the 1^1B_u state is in agreement with the observation of a small solvent-matrix shift for this band.²³ A similar situation holds for butadiene. Shih *et al.*²⁰ and Hosteny *et al.*¹⁴ found in their frozen σ -core studies beside the low-lying 2^1A_g valence state all the 1^1B_u states to be of Rydberg character. A recent all-valence-electron CI study by Buenker *et al.*²⁴ revealed, however, a Rydberg 1^1B_u state at 6.67 eV below the 2^1A_g valence state at 7.02 eV and a valence 1^1B_u state at 7.67 eV (which carries the main oscillator strength), i.e., two valence states like the semiempirical method.

This is not to say that the *ab initio* calculations do not have enormous merits beyond the simple semiempirical studies in the prediction of the valence 1^1A_g state and the Rydberg states which states seem to be very well described indeed. However, calculations such as that of Ref. 24 can hardly be applied to longer polyenes and, judged from the butadiene case, it seems that the semiempirical approach fares reasonably well in the prediction of 1^1A_g and 1^1B_u valence states.

Freed²⁵ recently addressed the question why semiempirical π -electron theories accounting for electron correlation in a minimum basis set provide reasonable results judged even on a quantitative scale. He argues that the semiempirical matrix elements, accounting for a correlation between π -electrons and core electrons as well as for excitations of the former electrons into higher orbitals, correctly assume a "softer" core- π -electron repulsion than that entering frozen core *ab initio* calculations. However, a semiempirical model Hamiltonian does not account for any variation in the π -electron-core correlation among different excited states. Furthermore, the possibility of $\sigma^* - \pi$ or $\pi^* - \sigma$ and Rydberg type excited states is not accounted for. Nevertheless, because of its great simplicity and its well-known success in spectral assignments the PPP-model Hamiltonian seems to be eminently suitable for a study of electron correlation effects in the excited states of conjugated molecules, it allows to focus on the many-electron effects and does not divert attention to problems arising from the size and shape of basis sets.

B. Parameterization of the PPP Hamiltonian

The PPP Hamiltonian has been employed in the following representation:

$$H = \sum_{n < m} R_{nm} + \sum_{m, \sigma} \left(-I - \sum_{n \neq m} R_{nm} \right) c_{m\sigma}^+ c_{m\sigma} + \sum_{\substack{n, m, \sigma \\ n \neq m}} t_{nm} c_{n\sigma}^+ c_{m\sigma} + \frac{1}{2} \sum_{\substack{n, m \\ \sigma, \sigma'}} R_{nm} c_{n\sigma}^+ c_{n\sigma} c_{m\sigma'}^+ c_{m\sigma'} \quad (1)$$

where the first term is to describe the nuclear repulsion, the second term the attraction between electrons and nuclei, the third the Hückel type electron delocalization and the last term the electron repulsion. $c_{m\sigma}^+$ ($c_{m\sigma}$) are Fermion creation (annihilation) operators which position the π -electrons in an orthonormal set of atomic orbitals. R_{nm} are the effective Coulomb repulsion integrals between orbitals at atoms n and m described by the formula (Ohno approximation)²⁶

$$R_{nm} = 14.397 \text{ eV} \{1.67 + r_{nm}^2\}^{-1/2}, \quad (2)$$

where r_{nm} is the atomic distance in Å. I stands for the effective ionization potential of a π electron at a carbon site chosen to be 11.16 eV and t_{nm} represents the resonance integrals between centers n and m

$$t_{nm} = \begin{cases} -2.6 \text{ eV} + 3.21(r_{nm} - 1.397) \text{ eV} & \text{for } n = m \pm 1 \\ 0 & \text{else} \end{cases} \quad (3)$$

The distance chosen for double bonds was $r_{nm} = 1.35$ Å, for single bonds $r_{nm} = 1.46$ Å. The sum in the last term of (1) excludes all terms $(n, \sigma) = (m, \sigma')$. This parameterization is identical with that of Ref. 13.

The PPP-model Hamiltonian (1) is known to yield for alternating hydrocarbons, like polyenes, in addition to the spin and spatial symmetries the so-called "Pariser alternancy symmetry" (Refs. 27 and 28) which classifies (-) states, e.g. the polyene $1^1A_g^-$ ground state, and (+) states e.g., the optically allowed $1^1B_u^+$ state. The latter two symmetry classes exhibit different behavior as far as the effect of electron correlation is concerned and, therefore, all states will be classified by their (+) or (-) alternancy symmetry from now on. In order to reduce computational effort we have taken advantage of all three symmetry types of the PPP Hamiltonian in our calculations.

C. Method for the evaluation of the Hamiltonian matrix

We have employed for the CI calculations a very efficient algorithm for the evaluation of the matrix elements of a general spin-free molecular Hamiltonian in a spin-coupled basis involving multiple excitations. This algorithm has been developed by us recently²⁹ and will be published in detail elsewhere. In short, irreducible products of second-quantized operators generating spin-adapted electron configurations are constructed according to the Serber scheme and normalized. The Hamiltonian operator is expanded in terms of related spin-coupled operators and the evaluation of matrix elements thereby reduced to the computation of scalar products between spin adapted configurations, a task solved by the theory of representations of the symmetric group and by application of Wick's theorem. This procedure leads to a small set of simple expressions for the matrix elements.

D. Localized SCF orbitals

For a characterization of correlation effects in polyenes in terms of electron configurations SCF orbitals localized around the ethylene moieties constituting the polyene chain proved to be suited best. For this purpose we employed such orbitals in some of our calculations. The algorithm for obtaining these localized orbitals has been presented and the resulting orbitals have been illustrated in Ref. 17.

III. RESULTS: CI DESCRIPTION INCLUDING UP TO ALL TRIPLE AND QUADRUPLE EXCITATIONS

To explore how higher excitations repair the ill behavior of D-CI descriptions, i.e., an excitation energy divergence and a decreasing $2^1A_g^- - 1^1B_u^+$ energy gap, we

have set out to evaluate the excited singlet states of the polyenes butadiene up to dodecahexaene in the T -CI approximation including all single, double, and triple excitations and up to decapentaene in the Q -CI approximation also including all quadruple excitations. Figures 2(a)-2(e) compare the resulting spectra with those predicted by S -CI (all single excitation CI) and D -CI (all single and double excitation CI) calculations.³⁰

A. General observations

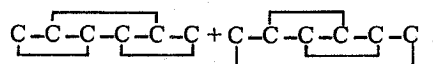
The following three observations regarding the main effect of triple and quadruple excitations on the predicted spectra of polyenes can be stated:

1. The inclusion of triple and quadruple excitations in the CI expansion leaves (nearly) unaltered the ordering of excited singlet states, proving thereby the value of the D -CI description.
2. It results in an overall redshift of the spectrum relative to the ground state. This redshift is the larger the higher the energy of the excited states and the longer the polyene chain, and (essentially) repairs the excitation energy divergence inherent in the D -CI approximation.
3. The inclusion of triple and quadruple excitations induces small changes in the relative energy distances of the excited states, an effect which becomes more important for longer polyenes.

A detailed analysis of Fig. 2 reveals a different behavior of the ionic³¹ (+) and the covalent³¹ (-) states upon inclusion of triple and quadruple excitations. The ionic states are being further redshifted (relative to the ground state) by triple excitations than the covalent states and are slightly blueshifted by quadruple excitations in contrast to the covalent excited states which are further redshifted. The net result is an approximate conservation of energy separation in going from a D -CI to a Q -CI description, an exception being the $2^1A_g^- - 1^1B_u^+$ energy gap.

B. The $2^1A_g^-$ state

Figure 2 shows that the covalent $2^1A_g^-$ state upon inclusion of triple excitations experiences about the same redshift as the higher ionic $1^1B_u^+$ state. This unexpected large redshift originates from only a few triple excitations. A CI expansion in terms of localized SCF orbitals identifies large contributions due to three simultaneous triplet single excitations of ethylene units coupled to form a total singlet state. Such configurations are generated from the antiferromagnetic ground state through three simultaneous spin flips in atomic orbitals. They correspond to linear combinations of valence bond structures like



Previous D -CI calculations had suggested that the $2^1A_g^-$ state is properly described already by double excitations involving only two simultaneous triplet excitations of ethylene units. Such configurations are obtained through

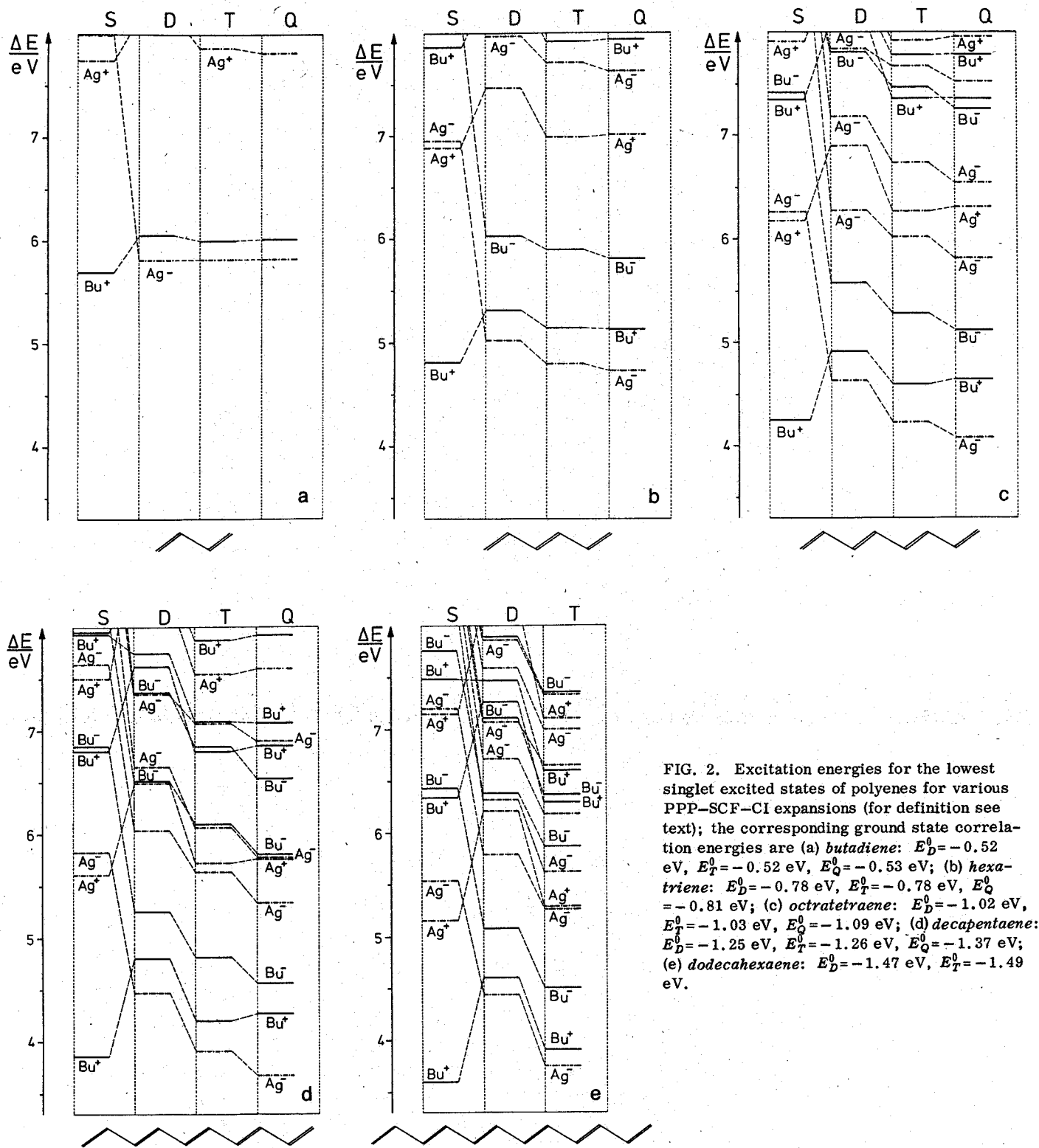
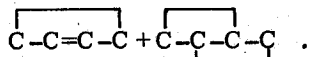


FIG. 2. Excitation energies for the lowest singlet excited states of polyenes for various PPP-SCF-CI expansions (for definition see text); the corresponding ground state correlation energies are (a) *butadiene*: $E_D^0 = -0.52$ eV, $E_T^0 = -0.52$ eV, $E_Q^0 = -0.53$ eV; (b) *hexatriene*: $E_D^0 = -0.78$ eV, $E_T^0 = -0.78$ eV, $E_Q^0 = -0.81$ eV; (c) *octatetraene*: $E_D^0 = -1.02$ eV, $E_T^0 = -1.03$ eV, $E_Q^0 = -1.09$ eV; (d) *decapentaene*: $E_D^0 = -1.25$ eV, $E_T^0 = -1.26$ eV, $E_Q^0 = -1.37$ eV; (e) *dodecahexaene*: $E_D^0 = -1.47$ eV, $E_T^0 = -1.49$ eV.

simultaneous spin flips in two atomic orbitals^{3,13,17} and correspond to valence bond structures like



Our Q -CI study reveals now that the correlation of electron spins in the excited $2^1A_g^-$ state involves more electrons than assumed previously. As an illustration we provide in Fig. 3 the main CI coefficients of the $1^1A_g^-$,

$2^1A_g^-$, and $1^1B_u^+$ states of hexatriene resulting from a localized SCF-orbital Q -CI description.

The inclusion of quadruple excitations further redshifts the $2^1A_g^-$ state like the other covalent (-) states whereas the $1^1B_u^+$ state together with the remaining ionic (+) states experiences a blueshift. The net effect of the Q -CI description compared to a D -CI description is an increase of the $2^1A_g^- - 1^1B_u^+$ energy gap.

C. The $2^1A_g^- - 1^1B_u^+$ energy gap

In Fig. 4 are presented the (vertical) excitation energies to the $2^1A_g^-$ and $1^1B_u^+$ states predicted from a Q-CI treatment. It can be observed that the $2^1A_g^- - 1^1B_u^+$ energy gap increases with increasing polyene chain from 0.19 to 0.60 eV, whereas a slight decrease from 0.25 to 0.23 eV results in a D-CI description (cf. Fig. 1). The increment of this gap as predicted by a Q-CI treatment is largest in going from butadiene to hexatriene (0.21 eV), somewhat smaller for the step to octatetraene (0.16 eV), and amounts to only 0.04 eV in going from octatetraene to decapentaene. The gap seems to reach a value of about 0.6 to 0.7 eV for very large polyenes.

IV. DISCUSSION: SPECTRAL DATA ON THE $2^1A_g^- - 1^1B_u^+$ ORDERING

A. Butadiene

Spectral observations pertinent to the ordering of the $2^1A_g^-$ and $1^1B_u^+$ states for unsubstituted polyenes are available for butadiene to dodecahexaene. McDiarmid³² assigned a series of sharp vibrational bands observed in the gas phase absorption spectrum of butadiene to the blue of the diffuse $1^1B_u^+$ band to a $2^1A_g^-$ state with origin at 6.2 eV. This observation is in agreement with an early gas phase spectrum by Price and Walsh³³ which exhibited a sharp feature at 6.25 eV which Mosher *et al.*³⁴ attributed to the $2^1A_g^-$ transition. However, this assignment has been revised recently. On the basis of a careful account of the vibrational structure connected with this transition McDiarmid concluded a Rydberg state responsible for these spectral features.³⁵ From a multiphoton ionization (MPI) spectrum of gas phase butadiene Johnson³⁶ concluded this Rydberg state to be of 1^1B_g symmetry. The MPI method detected no 1^1A_g excited state at lower energies than the 1^1B_g state although its existence at higher energies remained possible. Johnson's observations were corroborated by recent multiphoton studies of Vaida *et al.*³⁷ and the theoretical results of Buenker *et al.*²⁴ The latter authors assigned the $2^1A_g^-$

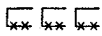
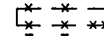
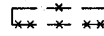

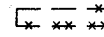
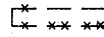

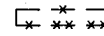
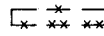
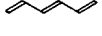
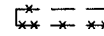
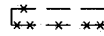

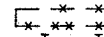
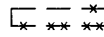

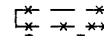

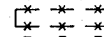
$1^1A_g^-$	$2^1A_g^-$	$1^1B_u^+$
 .959	 .312	 .476
 .139	 .253	 .336
 .133	 .251	 .325
 .133	 .251	 .325
 .197	 .197	 .200
 .119	 .119	
 .110	 .110	

FIG. 3. The main spin-coupled electron configurations and the corresponding Q-CI coefficients for the three lowest hexatriene singlet states. The configurations are defined over localized SCF orbitals (defined in Sec. IID) and are represented by the occupation of the corresponding ethylene energy levels. *T* denotes a triplet (single) excitation. *TT* denotes a pair and *TTT* a triple of such excitations coupled to an overall *singlet* state.

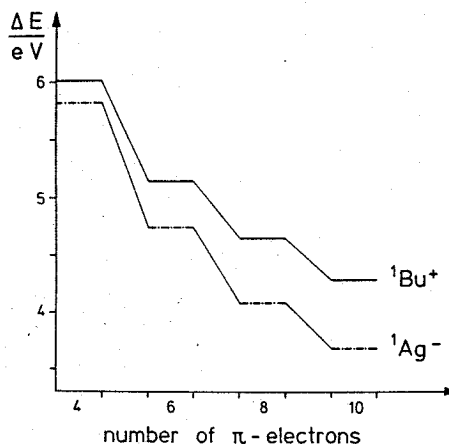


FIG. 4. Dependence of the excitation energies on the polyene length for the two lowest singlet states as described by a Q-CI expansion.

state to a spectral feature at 7.06 eV while Johnson³⁴ assigned it to a band at 6.66 eV with origin at 6.47 eV. Hence it appears to be quite certain that a low-lying $2^1A_g^-$ state exists in butadiene, however, several tenths of an eV above the optically allowed $1^1B_u^+$ π, π^* excitation.

B. Hexatriene

Gavin and Rice³⁸ did not succeed to observe the $2^1A_g^-$ state in the gas phase absorption spectrum of hexatriene. Andrews and Hudson³⁹ observed large differences in fluorescence lifetimes between steroids containing triene moieties of the 3-*cis* hexatriene type and of the 3-*cis*, 4*s-cis* type, and concluded that in hexatriene the $2^1A_g^-$ and $1^1B_u^+$ states are nearly degenerate crossing upon 4*s-trans* \rightarrow 4*s-cis* isomerization of the 3-*cis* compound.

C. Octatetraene, decapentaene, and dodecahexaene

There exist two most recent spectra of the $2^1A_g^-$ state in tetraenes. Incorporating deca-2, 4, 6, 8-tetraene in an *n*-undecane host at 4.2 °K Andrews and Hudson⁶ observed the $2^1A_g^-$ state with its origin about 0.3 eV below that of the $1^1B_u^+$ state. For octatetraene in an *n*-octane host at 4.2 °K Granville *et al.*⁵ found the origin of the $2^1A_g^-$ state at 3.54 eV, i. e., at 0.42 eV below the onset of the $1^1B_u^+$ band. The corresponding absorption and fluorescence spectra of both groups are remarkable in that they exhibit clearly the forbidden character of the 0,0 band and identify the modes on which the vibronic absorption intensity is built. Granville *et al.*⁵ also demonstrated that the 0,0 band of the $2^1A_g^-$ state is strongly two-photon allowed confirming thereby the 1^1A_g assignment. Previously, Gavin *et al.*⁴ had observed the octatetraene $2^1A_g^-$ state in a hexane solvent at 77 °K about 0.43 eV below the main absorption band originating from the $1^1B_u^+$ state. Extrapolating the room temperature solvent dependence of absorption and fluorescence maxima these authors predicted that in a gas phase situation the $2^1A_g^-$ state should be about 0.8 eV below the $1^1B_u^+$ state, however, a corresponding fluorescence of gas phase octatetraene could not be detected.

The position of the $2^1A_g^-$ state below the $1^1B_u^+$ state has been confirmed recently for decapentaene and dodecahexaene embedded in a Shpol'skii matrix at 4.2 °K by Christensen (private communication). These findings corroborate the observations of the $2^1A_g^-$ state below the $1^1B_u^+$ state in 2,10-dimethyldecapentaene by 0.39 eV (Ref. 7) and in 2,12-dimethyltridecahexaene by 0.50 eV (Ref. 8).

The spectral data obtained for the diphenylpolyenes will not be discussed here. A theoretical description of these compounds is presented in Ref. 40. There it has been shown that a *D*-CI treatment for these large π systems entailing 20 and more conjugated electrons predicts a low-lying doubly excited $1^1A_g^-$ state but fails to bring this state below the $1^1B_u^+$ state. An explanation may be that for such large electron systems correlation effects due to triple and quadruple excitations as discussed in Sec. III must not be neglected for a proper description of the $2^1A_g^-$ - $1^1B_u^+$ ordering as is also evidenced by the failure of the *D*-CI approximation for very long polyenes (see Fig. 1).

V. CONCLUSION

We have addressed in this paper the problem of the energy gap between the $2^1A_g^-$ and the $1^1B_u^+$ states in polyenes. The spectroscopic evidence that polyenes with four and more double bonds have the optically forbidden $2^1A_g^-$ state below the strongly absorbing $1^1B_u^+$ state is overwhelming. Our study demonstrated that higher (triple and quadruple) excitations are necessary (1) to avoid a strong excitation energy divergence inherent in the *D*-CI approach, and (2) for a proper description of the $2^1A_g^-$ - $1^1B_u^+$ energy gap. The excitation energy divergence of the *D*-CI approach, results from the imbalance in the description of correlation energies of ground and excited states.¹⁷ The imbalance Δ is most pronounced in the *D*-CI approximation

$$\Delta \sim -E_D^0,$$

(E_x^0 is the ground state correlation energy accounted for by a *X*-CI treatment), less so for the *Q*-CI approach

$$\Delta \sim E_D^0 - E_Q^0.$$

A method to repair this deficiency, the "Renormalized CI" method, has been suggested in Ref. 17 and will be applied to polyenes in a forthcoming publication (see also Ref. 29).

Our calculations indicate that the $2^1A_g^-$ - $1^1B_u^+$ energy gap increases in going from butadiene to hexatriene and to octatetraene to reach a saturation value of about 0.7 eV soon for larger polyenes such that the $2^1A_g^-$ state is well positioned above the ground state for very large polyenes. Assuming a $1^1A_g^-$ - $1^1B_u^+$ excitation energy of 2.2 eV for the infinite polyene the $2^1A_g^-$ state is estimated at about 1.5 eV in the asymptotic limit. This conjecture is at variance with the prediction⁴¹ for the Hubbard model (which keeps only one-center electron repulsion integrals and is amenable to an exact solution) of the existence of optically forbidden singlet states degenerate with the ground state. The longest polyene derivative for which the $2^1A_g^-$ state has been observed is β -carotene (11 con-

jugated double bonds) for which Thrash *et al.*⁴² by way of measuring Raman excitation profiles found a 0.43 eV gap. This value is close to the gap values of the shorter polyenes in Table I and, hence, seems to provide evidence for our conjecture.

A direct comparison of our results with spectral observations on the shorter polyenes is hampered by the fact that we have evaluated vertical transitions and that most data are on substituted polyenes. Substitution appears to affect the $2^1A_g^-$ - $1^1B_u^+$ level distance. In any case it seems that for butadiene the $2^1A_g^-$ state is predicted too low. This statement may apply to hexatriene, too. The agreement for octatetraene and decapentaene is satisfactory. Whatever improvement in the description of the $2^1A_g^-$ state for larger polyenes will be envisioned, the fact that higher excitations describing longer range spin coupling contribute significantly to this state must not be overlooked.

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