

Correlation effects in the spectra of polyacenes

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In order to describe the electron correlation in the excited singlet π, π^* states of the polyacenes $[C_{4n+2}H_{2n+4}]$, we have carried out PPP-SCF-CI calculations including all single and double excitations in the CI expansion up to $n = 5$, including all triple excitations up to $n = 3$, and all quadruple excitations up to $n = 2$. Compared to previous CI descriptions which included single excitations only, e.g., the classic work of Pariser [J. Chem. Phys. 24, 250 (1956)], our calculations lead us to predict the following: (1) "new" excited states entailing the promotion of two electrons from the ground state (some of them predicted previously by other authors), and (2) a partial reordering of those (well-known) excited states already accounted for by a S-CI representation. Single and double excitations in a CI expansion (D-CI) satisfactorily describe the ordering of all excited states up to 7 eV; the effect of higher excitations is to correct the excitation energies overestimated by the D-CI description. Our predicted spectra provide a consistent assignment of all one- and two-photon spectral data but do not yield a quantitative agreement.

I. INTRODUCTION

The recent years have seen a revival of theoretical work on conjugated molecules prompted by observations of anomalies in the spectra of the polyenes which lead to the discovery of a low-lying state in these compounds. The quantumchemical explanation of this state forced the independent-electron theory, i. e., the molecular orbital theory, out of a long-held domain to give way to a more complete theory which takes better account of electron correlation in the excited states.¹

In this paper we want to study the effect of electron correlation in the polyacene class of conjugated molecules. Contrary to the polyene case, the absorption and emission spectra of the polyacenes apparently do not show any anomalies. The absorption spectra mainly consist of three bands corresponding to ${}^1B_{3u}^*$, ${}^1B_{2u}^*$, and ${}^1B_{3u}^*$ states (in the notation of the D_{2h} group).^{2,3} The successful description of these bands by Pariser's S-CI approximation⁴ propagated the widespread application of this method to the assignment of the spectra of conjugated molecules.⁵ However, the apparent success of the S-CI approximation seems to be due to the fact that electron correlation, neglected in this approach, strongly affects mainly those excited singlet states which are one-photon forbidden or weak^{6,7} and, hence, do not influence the main features of one-photon absorption spectra which the theoretical efforts quoted above^{4,5} dealt with exclusively.

A case at hand is the parent of the polyacene family, benzene. If one includes in addition to single also double excitations in a CI expansion, thereby partially accounting for electron correlation, a "new" ${}^1E_{2g}$ state appears in the calculated spectrum of benzene. This state is mainly comprised of double excitations from the SCF ground state. It had been predicted already in 1956 by Murrell and McEwen⁸ on the basis of a semiempirical PPP-SCF-CI study including selected single and double excitations, a prediction which has been confirmed since then by several more complete CI treatments.⁹

Until the existence of the one-photon-forbidden ${}^1E_{2g}$ state had been verified experimentally, the neglect of

electron correlation in Pariser's approach to the description of excited polyacene states was tolerated. However, evidence for the ${}^1E_{2g}$ state in benzene has been obtained recently. Bonneau *et al.*¹⁰ observed an $S_1 \rightarrow S_n$ absorption band at 2.53 eV which Birks¹¹ assigned to a ${}^1B_{2u} \rightarrow {}^1E_{2g}$ transition. This places the ${}^1E_{2g}$ state just above the intense ${}^1E_{1u}$ state at 6.9 eV. Johnson¹² assigned a band in the two-photon ionization spectrum of benzene at 6.33 eV to a g state. This state had been confused for a while with the higher ${}^1E_{2g}$ state. However, Twarowski and Kliger¹³ proved by means of a two-photon thermal lensing spectrum of benzene in solution that the g state at 6.33 eV has to be assigned to a Rydberg state of ${}^1E_{1g}$ symmetry. These authors also observed a strong two-photon absorption with onset at 6.9 eV, i. e., the ${}^1E_{2g}$ state. On the basis of these observations the following state ordering of benzene can be inferred:

$${}^1B_{2u} < {}^1B_{1u} < {}^1E_{1g} (\text{Rydberg}) < {}^1E_{1u} < {}^1E_{2g} . \quad (1)$$

The observation of the doubly excited ${}^1E_{2g}$ state of benzene strongly motivates a systematic study of correlation effects in the spectra of the polyacene family altogether. The quantum chemical method to be employed for the purpose of such study should, of course, reproduce the benzene state ordering (1).

The ${}^1E_{2g}$ state of benzene has been predicted also by the extensive *ab initio* study of Hay and Shavitt.¹⁴ However, this treatment lacks from a neglect of σ, π mixing and, therefore,¹⁵ attributes too much Rydberg character to the ionic¹⁶ ${}^1B_{1u}$ and ${}^1E_{1u}$ states. For a sufficiently extended *ab initio* treatment even the smallest aromatic molecule benzene has been "too large" so far. This predicament applies the more so to the larger polyacenes. For their spectra one has to rely at this point exclusively on semiempirical descriptions.

The benzene singlet state ordering (1) can be reproduced satisfactorily by a PPP-SCF-CI calculation including all excitations in the underlying minimum basis set.⁷ Of course, such description will not account for any Rydberg state. Koutecký *et al.*¹⁷ demonstrated that the ordering of the ${}^1E_{2g}$ state relative to the other benzene states is not much affected by the inclusion of higher

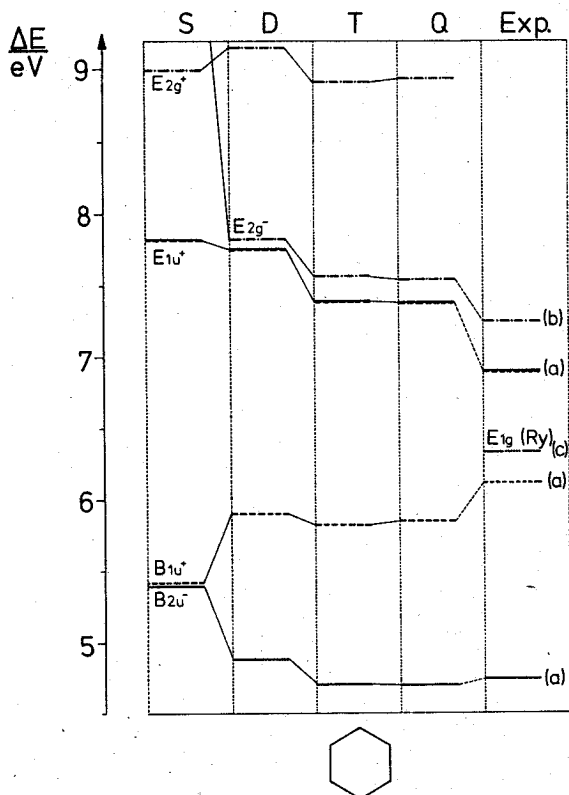


FIG. 1. Excitation energies of the lowest excited benzene singlet states obtained by different PPP-SCF-CI expansions (S: all single excitations, D: all single and double excitations etc., see text) and the respective spectral data; (a) Ref. 18; (b) Ref. 10; (c) Ref. 12.

than double excitations in a CI expansion, depending, however, critically on the semiempirical interaction parameters chosen for the PPP Hamiltonian. We will employ for our calculations the PPP Hamiltonian of Ref. 1 which describes satisfactorily benzene⁷ as well as the polyenes.¹

To illustrate what has been said above we have presented in Fig. 1 a comparison between benzene singlet excitation energies observed and those obtained from S-, D-, T-, and Q-CI calculations, including up to all single, double, triple, and quadruple excitations, respectively. The PPP-SCF-CI calculations are in reasonable agreement with the spectral observations, except that they do not account for the Rydberg $^1E_{1g}$ state.

The effect of electron correlation on the spectrum of benzene demonstrated by Fig. 1 certainly warrants a study also of larger aromatic systems. Therefore, we have extended the CI description underlying Fig. 1 to polyacenes: For naphthalene we included all single up to all quadruple excitations, for anthracene up to all triple excitations, and for tetracene and pentacene all single and double excitations. To our knowledge such systematic account of electron correlation effects on the polyacene spectra had not been given so far, although for naphthalene,^{6,19} anthracene,²⁰ and tetracene²¹ CI treatments including double excitations have been published. Furthermore, Gouyet and Prat²² have investigated correlation effects in some of the low-energy singlet states

of naphthalene, anthracene, and tetracene by a second order perturbation expansion. We will comment on all these investigations below. In Sec. II we will present the results of our own calculations, in Sec. III we will compare our predictions with the spectral data available and will add a short conclusion in Sec. IV.

II. THE INFLUENCE OF DOUBLE EXCITATIONS ON THE POLYACENE SPECTRA

In Figs. 2-5 we have presented the spectra of the polyacene singlet states predicted by our CI calculations. The results demonstrate clearly that the inclusion of double excitations has a strong effect on the level ordering for all molecules, naphthalene to pentacene. In going from a Pariser-type S-CI to a D-CI description the predominantly covalent (-) states are lowered in energy with respect to the ionic (+) states.³¹ This effect is more pronounced for the higher states and for the larger polyacenes. Also the states of $^1A_g^-$ symmetry, in particular the ground state, are more depressed than the $^1B_{1g}^-$, $^1B_{2u}^-$, and the $^1B_{3u}^-$ states.³² The overall pattern of the polyacene singlet states resulting from S-CI and D-CI calculations is illustrated in Fig. 6 presenting the energy levels relative to the SCF ground state. We would like now to discuss in some more detail the effect of higher excitations on the polyacene spectra, starting with the role of double excitations.

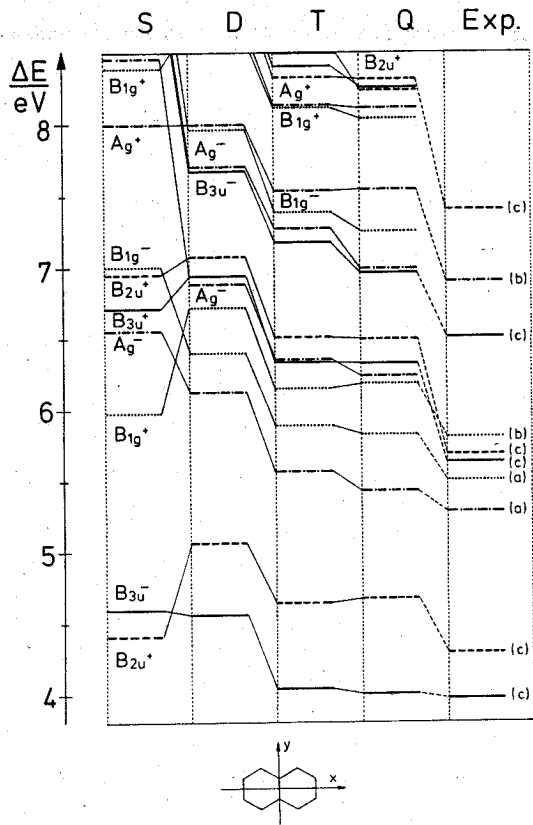


FIG. 2. Excitation energies of the lowest excited singlet states of naphthalene as predicted by different PPP-SCF-CI calculations and compared with spectral data; (a) Ref. 23; (b) Ref. 24; (c) Ref. 25.

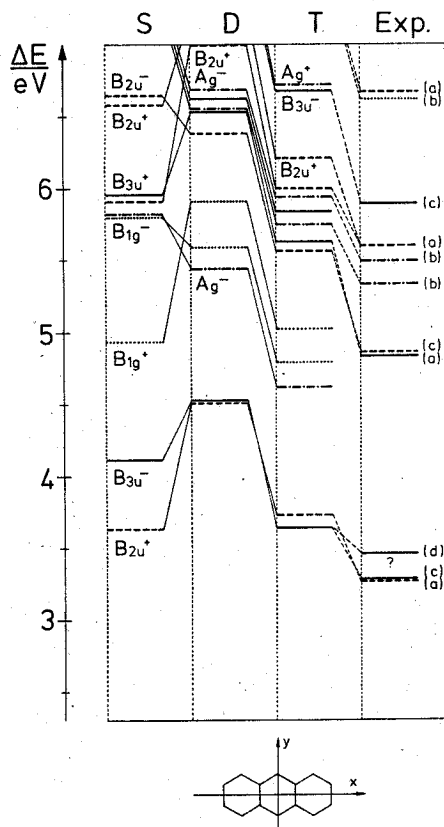


FIG. 3. Excitation energies of the lowest excited singlet states of anthracene as predicted by different PPP-SCF-CI calculations and spectral data; for a discussion of the spectral position of the $1^1B_{3u}^-$ state see text; (a) Ref. 25; (b) Ref. 24; (c) Ref. 26; (d) Ref. 27.

A. The relative order of the lowest g states

Previous S-CI studies had predicted for the lowest g states of the polyacenes the ordering $1^1B_{1g}^- < \{1^1B_{1g}^-, 2^1A_g^-\}$. The D-CI calculations yield, however, for all the polyacenes the $2^1A_g^-$ and $1^1B_{1g}^-$ states, the "relatives" of the 1^1E_{2g} benzene state, below the $1^1B_{1g}^-$ state. The resulting state ordering is $2^1A_g^- < 1^1B_{1g}^- < 1^1B_{1g}^+$. According to the D-CI description, the low-lying $2^1A_g^-$ and $1^1B_{1g}^-$ states approach the first excited singlet state $1^1B_{2u}^+$ for an increasing number of aromatic rings. For pentacene these states are predicted to constitute already the second and third excited singlet states below the $1^1B_{3u}^-$ state. A linear extrapolation of the approach to the $1^1B_{2u}^+$ state leads to the estimate for octacene that the $2^1A_g^-$ state constitutes the first excited singlet state in this molecule. As the Q-CI treatment depresses the $2^1A_g^-$ state further relative to the $1^1B_{2u}^+$ state, a level crossing may occur already for the smaller hexacene (cf. the energy gap between the $2^1A_g^-$ and $1^1B_{2u}^+$ state in the polyenes, Ref. 1).

The strong energy depression of the $2^1A_g^-$ and $1^1B_{1g}^-$ states in going from the S-CI to the D-CI description is indicative of an admixture of low-energy double excitations in the polyacene π system. Indeed, the $2^1A_g^-$ state of pentacene contains a 61% contribution of an electron configuration $|D\rangle$ which entails two π electrons being promoted from the highest occupied to the lowest unoc-

cupied orbital. The energy expectation value of this configuration $\langle D|H|D\rangle$ relative to the SCF ground state energy measures 4.6 eV, considerably less than the corresponding energy expectation value of 6.1 eV of the lowest $1^1A_g^-$ type single excitation. In view of this a misrepresentation of some low-lying electronic states by the Pariser-type S-CI approximation had to be expected.

The strong admixture of double excitations to the wave function of the $2^1A_g^-$ state of anthracene had been noted previously by Michl *et al.*²⁰ However, these authors included only a selection of single and double excitations in their CI expansion and predict the g state ordering $1^1B_{1g}^- < 1^1B_{1g}^+ < 2^1A_g^-$. Also the limitation of the CI expansion lead to a double excitation contribution to the $2^1A_g^-$ state of 36% only, whereas our more complete expansion attributes 49% double excited character to this state and places it below all other g states (see Fig. 3). This is to demonstrate the problems connected with any selection of higher excited configurations in a CI expansion. The individual contribution of any higher excitation as estimated by a perturbation theory argument may be small, nevertheless, because of the large number of such configurations these contributions can add up to a sizable overall energy depression.³³

The optical transitions to the low-lying $2^1A_g^-$ and $1^1B_{1g}^-$

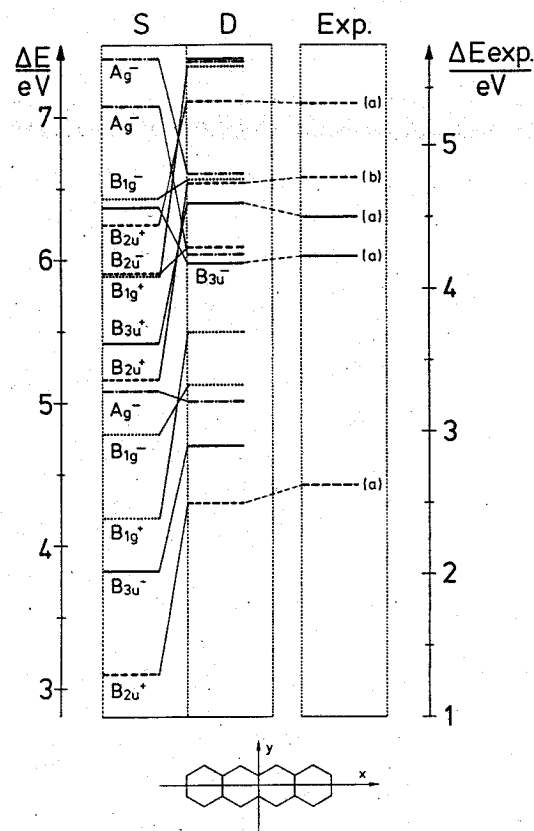


FIG. 4. Excitation energies of the lowest excited singlet states of tetracene as predicted by different PPP-SCF-CI calculations and spectral data; theoretical and experimental excitation energy scales refer to different zero levels to simplify comparison and to account for the overestimate of excitation energies in the D-CI approximation (cf. Sec. IID and Ref. 35); (a) Ref. 28; (b) Ref. 29.

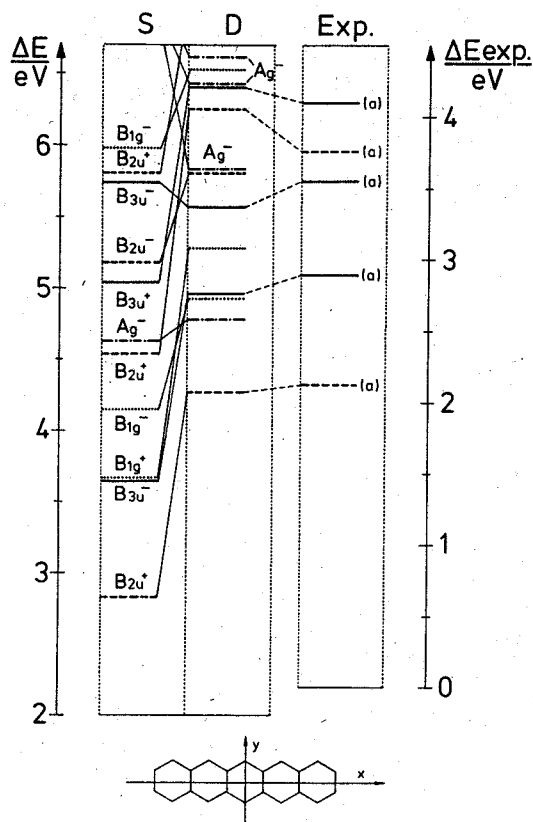


FIG. 5. Pentacene; (a) Ref. 30; for explanation see Fig. 4.

states of the polyacene family are one-photon forbidden and, therefore, do not appear in conventional optical absorption spectra. However, these transitions should be observable by two-photon spectroscopic methods (see below).

B. "New" states in the low energy regime

Beside the energy depression of the $2^1A_g^-$ and $1^1B_{1g}^-$ state the most important result of our D -CI calculations is the prediction for the larger polyacenes of three "new" singlet states below the strongly absorbing $1^1B_{3u}^+$ band. In the D -CI level scheme of naphthalene appears a $3^1A_g^-$ state just below the $1^1B_{3u}^+$ state. In anthracene the $3^1A_g^-$ state moves slightly above the $1^1B_{3u}^+$ state and a $1^1B_{2u}^-$ state below it. This state ordering has been predicted previously also by Michl *et al.*²⁰ In tetracene and pentacene the $1^1B_{2u}^-$ as well as the $3^1A_g^-$ and $2^1B_{3u}^-$ state come to lie below the $1^1B_{3u}^+$ state. Like the low-lying g states these states contain large contributions of double excited electron configurations. For example, the $2^1B_{3u}^-$ state of pentacene is composed to 60% of a linear combination involving the excitation promoting two electrons from the highest occupied orbital to the two lowest unoccupied orbitals and the alternancy symmetry conjugate³⁴ thereof.

A comparison of our CI results with the second order perturbation theory predictions of Gouyet and Prat²² reveals a systematic failure of the latter approach in that

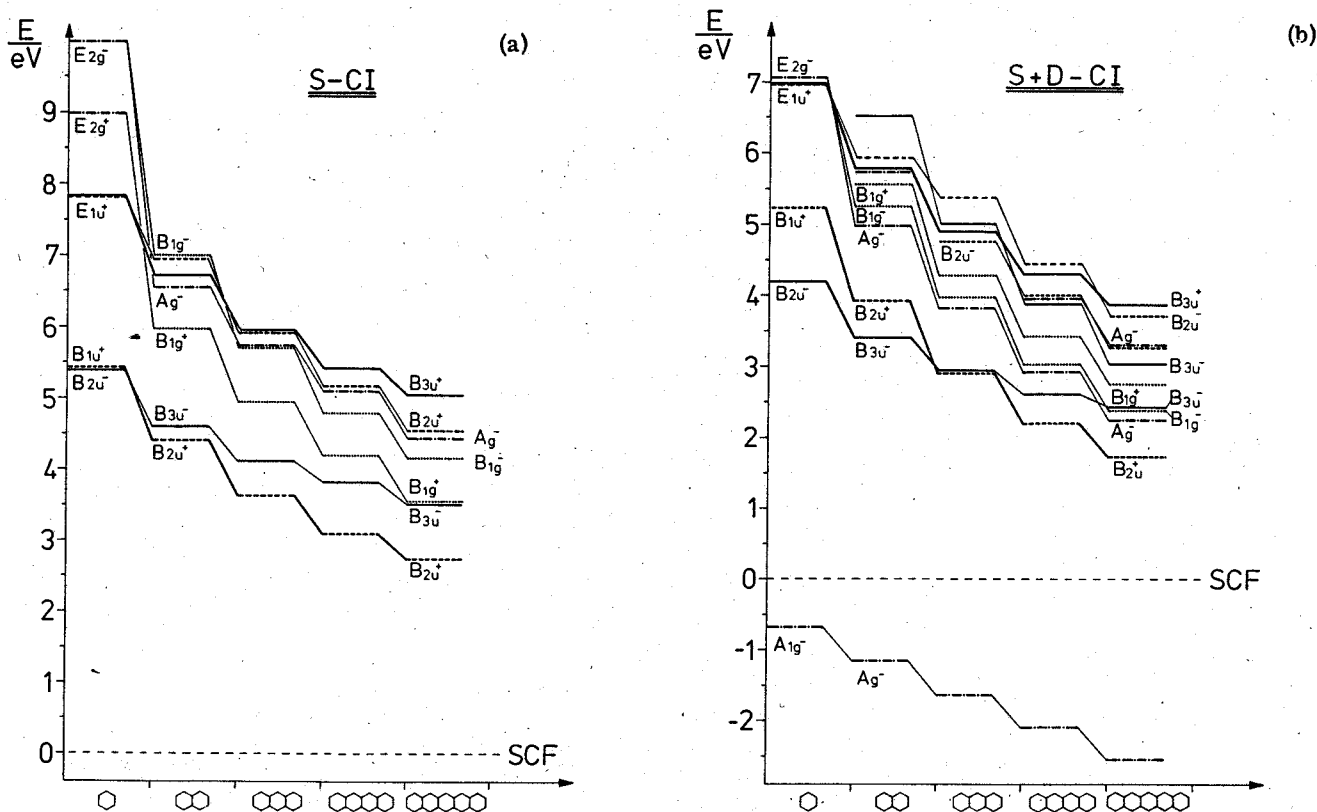


FIG. 6. Energy levels relative to the SCF ground state of the polyacene singlet states obtained by (a) S -CI and (b) D -CI expansions. (The numerical values of the energy levels can be obtained from us upon request.)

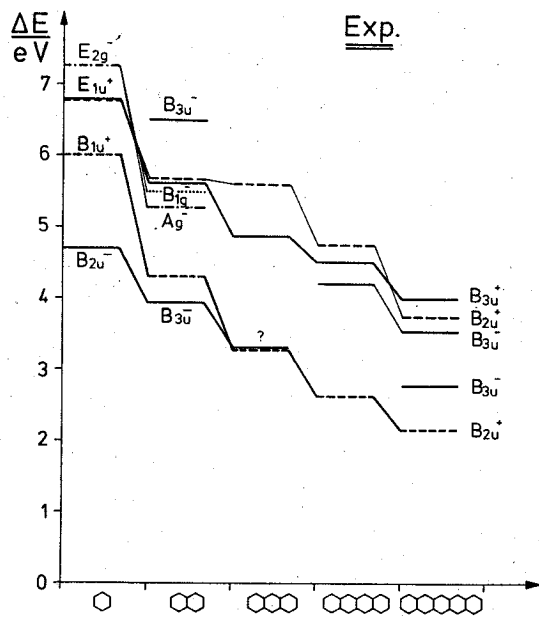


FIG. 7. Spectroscopic data on the singlet state excitation energies of the polyacenes.

it does not provide a complete description of the low-lying polyacene singlet states. The perturbation expansion starting from a single excited reference function did not always converge to the appropriate low-lying state, but rather to a higher state of the same symmetry type. For example, these calculations miss the low-lying, predominantly double excited, $2^1A_g^-$ and $3^1B_{3u}^-$ states. For tetracene a $2^1A_g^-$ state is predicted which corresponds to the $4^1A_g^-$ state of our D -CI description.

C. The ordering of the u states

A comparison of Figs. 6(a) and 6(b) proves that the inclusion of double excitations in a S -CI expansion also affects the energy gap between the singlet u states, despite their reasonable representation by the S -CI approach. The u state differences between Figs. 6(a) and 6(b) involve (1) the two lowest singlet u states $1^1B_{3u}^-$ and $1^1B_{2u}^+$ (together with the corresponding $1^1B_{2u}^-$ and $1^1B_{1u}^+$ benzene states), and (2) the two allowed states $1^1B_{3u}^-$ and $2^1B_{2u}^+$ derived from the $1^1E_{1u}^+$ benzene parent state. The spectroscopic information available is presented in Fig. 7.

The relative ordering of the $1^1B_{3u}^-$ and the $2^1B_{2u}^+$ states as predicted by our S -CI calculations agrees with the corresponding S -CI results of Pariser⁴ in that the $2^1B_{2u}^+$ state lies below the $1^1B_{3u}^-$ state for anthracene, tetracene, and pentacene. However, our D -CI calculations render this ordering for pentacene only. The prediction of this behavior is rather independent of the PPP parameters chosen. In contrast, the description of the $1^1B_{3u}^-$ and $1^1B_{2u}^+$ energy gap depends sensitively on the parameterization. A comparison of our S -CI results with those obtained by Pariser⁴ based on a different PPP Hamiltonian proves this point. Pariser's S -CI prediction of the $1^1B_{3u}^- - 1^1B_{2u}^+$ energy gap agreed with the spectral information. In our calculation this agreement is

achieved only upon the inclusion of double excitations in the CI expansion (cf. Figs. 6 and 7).

Similar considerations apply to the energy spacing between the $1^1B_{2u}^+$ and $1^1B_{3u}^-$ states which is overestimated by all our calculations. From the benzene CI studies by Koutecký *et al.*^{17(b)} it can be concluded that an appropriate parameterization (of a D -CI calculation, for instance) could have reproduced the spectroscopic values by rescaling the energy distances of all the excited states. However, in keeping with the model character of the PPP Hamiltonian, we have resisted the temptation of optimizing the agreement of predictions and spectral observations, and rather kept the parameterization adopted once.⁷

D. Overestimate of excitation energies

The D -CI method furnishes the proper ordering of the excited states, but fails in the quantitative prediction of excitation energies.^{1,35} The reason of this failure can be abstracted from Fig. 6. The D -CI ground state correlation energy decreases approximately in a size-consistent manner, i. e., linearly with the number of π electrons, whereas the correlation energies of the excited states (defined *ad hoc* as the difference between D -CI and S -CI energies of a state) are approximately constant. The D -CI description misses to account for the size-consistent contribution to these correlation energies.³⁵ The result is an excitation energy divergence with increasing size of the π system, most clearly reflected by the results in Figs. 2-5.

E. The influence of triple and quadruple excitations

In order to repair the excitation energy divergence inherent in the D -CI approach higher, at least triple and quadruple, excitations have to be included in a CI expansion.^{1,35} Indeed, our T -CI and Q -CI calculations yield an overall redshift of the excited states and, thereby, better excitation energies. The errors in the predicted excitation energies which remain, e.g., of the naphthalene $1^1B_{3u}^-$ state, are due to a large part to the PPP parameters chosen. Figures 3 and 4 also show that triple and quadruple excitations have only very small effects on the ordering of the excited states and their energy separation and, hence, reveal the great value of the D -CI approximation in this respect.

III. COMPARISON OF THEORETICAL PREDICTIONS AND SPECTRAL DATA

Our D -CI calculations of the polyacene spectra, which yielded extensive changes of the excited singlet state ordering from that predicted by former S -CI descriptions, call for a reconsideration of previous spectral assignments. For this purpose we recall that the symmetry classes of the polyacene states determine selection rules for spectroscopic transitions. One-photon transitions from the $1^1A_g^-$ ground state are solely allowed for u states, the corresponding two-photon transitions are allowed for g states only. Adhering to this classification we will first discuss assignments of one-photon transitions and then the assignments rendered possible

by the observation of two-photon and also $S_1 \rightarrow S_n$ processes.

A. Assignment of one-photon transitions to u states

For the most prominent features of the polyacene spectra, the L_a , L_b , and B_b bands, we adopt the assignment of Pariser to $1^1B_{2u}^+$, $1^1B_{3u}^-$, and $1^1B_{3u}^+$ states. The corresponding experimental excitation energies taken from Clar² and Klevens and Platt²⁵ are represented in Figs. 2–5 and in Fig. 7. A comparison of the experimental and theoretical data, even for our most complete Q -CI calculation on naphthalene, reveals a certain error of the predicted excitation energies (cf. Sec. IIC). Hence, our assignments will not entail a matching of these energies, but rather a matching of the relative ordering of the excited states.

In their absorption spectrum of *naphthalene* Klevens and Platt²⁵ observed beside the $1^1B_{2u}^+$, $1^1B_{3u}^-$, and $1^1B_{3u}^+$ bands two additional features at 6.51 eV and at about 7.4 eV. These authors assigned the latter more intense ($f_{\text{exp}}=0.6$) transition to a short-axis-polarized 1^1B_{2u} state and the first transition which appears as a broad and weak ($f_{\text{exp}}=0.2$) shoulder on the blue flank of the $1^1B_{3u}^+$ band ($f_{\text{exp}}=1.7$) to a forbidden 1^1A_g state. On the other hand, Pariser assigned the transition at 6.51 eV to the $2^1B_{2u}^+$ state. On the basis of our results we prefer the assignment of the weak 6.51 eV transition to the weak $2^1B_{3u}^-$ state and that at 7.4 eV to the $3^1B_{2u}^+$ state for which an oscillator strength $f_D=1.27$ has been evaluated in the D -CI approximation. We assume that the weaker absorption of the $2^1B_{2u}^+$ state ($f_D=0.85$) is hidden under the strong $1^1B_{3u}^+$ state ($f_D=1.92$). This assignment is in keeping with the linear dichroism measurements of Margulies and Yogev.²⁶ These authors found in the region of the main absorption band of naphthalene (beside the strong long-axis-polarized $1^1B_{3u}^+$ contribution with maximum at 5.63 eV) a weaker short-axis-polarized contribution which they assigned to a $1^1B_{2u}^+$ state at 5.68 eV.

In the spectroscopy of *anthracene* the search for the $1^1B_{3u}^-$ state near the $1^1B_{2u}^+$ band with onset at 3.27 eV (Ref. 25) seems to be the most controversial issue. The situation has been reviewed by Friedrich *et al.*³⁶ who on the basis of their low temperature polarized absorption and fluorescence spectra of anthracene in a host matrix assigned an excitation energy of about 3.6 eV to the $1^1B_{3u}^-$ state, the evidence being, however, rather circumstantial. Michl *et al.*²⁰ concluded from a linear dichroism study of anthracene in stretched polyethylene films and from an analysis of previous observations that there does not exist any undisputable evidence for this state. In contrast, Margulies and Yogev on the basis of linear dichroism measurements similar to those described in Ref. 20 argued that the $1^1B_{3u}^-$ state has its origin 80 cm^{-1} above the 0,0 band of the $1^1B_{2u}^+$ state and is responsible for the long-axis polarization observed in the absorption and emission bands of the $1^1F_{2u}^+$ state. However, these arguments have been criticized most recently by Steiner and Michl.²⁷ These authors on the basis of magnetic circular dichroism measurements suggest an excitation energy of 3.45 eV for the $1^1B_{3u}^-$ state.

Kleuens and Platt²⁵ observed to the blue of the $1^1B_{3u}^+$ state of anthracene two bands at 5.62 and at 6.66 eV with oscillator strength values $f_{\text{exp}}=0.23$ and $f_{\text{exp}}=0.65$, respectively. The anthracene spectra of Ref. 26 revealed that both bands are short-axis polarized. Hence, we assign the band at 5.62 eV to the two $2^1B_{2u}^+$ and $3^1B_{2u}^+$ states which are predicted to lie close together and to carry oscillator strength values $f_D=0.10$ and $f_D=0.37$, respectively. We attribute the band at 6.66 eV to the $4^1B_{2u}^+$ state predicted to be very intense ($f_D=1.31$). Between these bands Margulies and Yogev²⁶ observed a weak long-axis-polarized absorption at 5.9 eV which we ascribe to a $3^1B_{3u}^-$ state. [According to our calculations the $2^1B_{3u}^-$ state should be completely hidden by the intense ($f_D=2.37$) $1^1B_{3u}^+$ state.] Finally, these authors observed at 4.68 eV, partially hidden by the $1^1B_{3u}^+$ band, a very weak short-axis-polarized absorption which can be attributed to a $1^1B_{2u}^+$ state predicted by us.

Five singlet states are discernable in the absorption spectrum of *tetracene* ranging from 2.5 to 6.2 eV²⁸: S_1 (2.62 eV), S_2 (4.22 eV), S_3 (4.50 eV), S_5 (5.39 eV), and S_6 (5.86 eV). The absorption polarization spectrum by Zimmermann and Joop²⁹ indicates the existence of yet another state, S_4 (4.77 eV).²⁸ In agreement with the polarization behavior observed in Ref. 29 Pariser had assigned S_1 to the short-axis-polarized $1^1B_{2u}^+$ state and S_3 to the long-axis-polarized $1^1B_{3u}^+$ state. Pariser attributed S_2 to the $2^1B_{2u}^+$ state which in tetracene, as pointed out above, is predicted by an S -CI calculation below the $1^1B_{3u}^+$ state. However, Zimmermann and Joop assigned the degree of polarization of the $S_1 \rightarrow S_0$ fluorescence to be constant and negative throughout the S_2 and S_3 bands. This implies that the $S_0 \rightarrow S_2$ transition must be long-axis polarized, in contrast to Pariser's assignment. In keeping with this polarization behavior our results suggest to attribute S_2 to the $2^1B_{3u}^-$ state which is mainly comprised of double excited configurations.

Following the observations by Zimmermann and Joop we assign S_4 to the $2^1B_{2u}^+$ state. The bands S_5 and S_6 , observed 0.89 and 1.36 eV above the $1^1B_{3u}^+$ state, are assigned to the $3^1B_{2u}^+$ and the $4^1B_{2u}^+$ states which, according to our D -CI description, lie 0.70 and 1.68 eV above the $1^1B_{3u}^+$ state (the S_6 assignment is not presented in Fig. 4).

The absorption spectrum of *pentacene*³⁰ exhibits the prominent bands corresponding to the $1^1B_{2u}^+$ and $1^1B_{3u}^+$ states. The so-called³ L_b band ($1^1B_{3u}^-$) clearly discernable in benzene ($1^1B_{2u}^-$) and in naphthalene, but hidden in anthracene and tetracene, surfaces again in pentacene to the blue of $1^1B_{2u}^+$ at 2.89 eV in agreement with our description of this state. A weak absorption at 3.55 eV, i. e., 0.66 eV above the L_b ($1^1B_{3u}^-$) band seems to correspond to the S_2 state of tetracene assigned to $2^1B_{3u}^-$. Our D -CI calculation supports this correspondence in that it places the pentacene $2^1B_{3u}^-$ at 0.62 eV above the $1^1B_{3u}^+$ state. A rather intense broad shoulder to the red of the $1^1B_{3u}^+$ main absorption band of pentacene at 3.79 eV may be connected to the tetracene S_4 , i. e., $2^1B_{2u}^+$, which lies slightly to the blue of the intense tetracene $1^1B_{3u}^+$. This relationship is suggested by the D -CI predicted

crossing of the $1^1B_{3u}^+$ and $2^1B_{2u}^+$ in going from tetracene to pentacene. Our assignment of the pentacene 3.79 eV band to the $2^1B_{2u}^+$ state implies a short-axis polarization of this absorption and, hence, can be readily tested spectroscopically.

B. Assignment of two-photon and $S_1 \rightarrow S_n$ transitions to g states

We want to discuss now the information provided by two-photon excitation (TPE) as well as $S_1 \rightarrow S_n$ absorption spectra pertinent to the assignment of the g states of the polyacenes. To our knowledge experimental data exist for naphthalene and anthracene only.

The TPE spectra of polyacenes to this date seem to be crippled by experimental difficulties^{37,38} and lack of resolution. The three TPE spectra of *naphthalene* available until recently^{23,39,40} exhibit large discrepancies.³⁸ Drucker and McClain³⁹ observed on the background of a broad featureless two-photon band rising steadily from 4.5 to 5.8 eV a shoulder at 5.65 eV. Bergmann and Jortner⁴⁰ obtained a more structured two-photon spectrum in the range 3.8–5.6 eV exhibiting vibronically-induced two-photon transitions to the $1^1B_{3u}^+$ and $1^1B_{2u}^+$ states as well as two strong absorptions at 5.21 and 5.46 eV. The TPE spectrum by Mikami and Ito²³ taken over the energy range 3.7–6.2 eV is rather well resolved and shows beside vibronically-induced transitions to u -states intense bands at 5.28 and 5.5 eV. The most recent two-photon absorption measurements by Lynch and Lotem³⁸ based on coherent anti-Stokes Raman scattering corroborate the statements of Refs. 23 and 40 about the 5.0–5.5 eV range. Because of their large two-photon cross sections the two bands in this range have to be assigned to g^- rather than g^+ states as the latter render weak two-photon absorption only. Hence, these transitions should not be assigned to $1^1B_{1g}^+$ and $2^1A_g^+$ states as suggested in Refs. 23 and 40 on the basis of Pariser's description of naphthalene⁴ but rather to the two lowest g^- states $2^1A_g^-$ and $1^1B_{1g}^-$ predicted by our Q -CI calculation in the right energy range (see Fig. 2).

Bebelaar²⁴ recently studied the $S_1 \rightarrow S_n$ absorption of naphthalene in the 5.7–7.7 eV energy range. Beside a strong transition at 6.9 eV observed previously⁴¹ he found a broad and weak transition at 5.8 eV. Since S_1 in naphthalene corresponds to a $1^1B_{3u}^+$ state, $S_1 \rightarrow S_n$ transitions should be observable for $1^1B_{1g}^+$ and $1^1A_g^+$ states. Our Q -CI results assign the transition at 5.8 eV to the $1^1B_{1g}^+$ state and at 6.9 eV to the $1^1A_g^+$ state. Altogether it appears that the TPE and $S_1 \rightarrow S_n$ observations of naphthalene indicate the existence of g^- states at 5.28 and 5.50 eV and of a g^+ state at 5.8 eV in harmony with our Q -CI description, but in contrast to earlier^{4,5} S -CI treatments (cf. Sec. II A).

There exist only few observations connected with the g states of *anthracene*. The only TPE spectrum is that by Bergmann and Jortner⁴² in the range of 3.6–5.2 eV. This spectrum exhibits transitions in the range of the $2^1A_g^+$ and $2^1B_{1g}^+$ states predicted 0.90 and 1.10 eV above the $1^1B_{2u}^+$ state. However, in light of the aforementioned difficulties connected with TPE spectra, additional evidence for these states would be much welcomed. Informa-

tion on higher g^- states is contained in the $S_1 \rightarrow S_n$ absorption spectra of Beelaar²⁴ covering the energy range 5.3–7.7 eV. This author observed at 5.34 and 5.50 eV (i. e., 2.07 and 2.23 eV, respectively, above S_1) two weak bands which the author because of their slightly different degree of polarization assigned to $1^1A_g^-$ and $1^1B_{1g}^-$ states (though not excluding the possibility that the 5.50 eV band entails a vibrational state of the 5.34 eV band). As the degree of polarization for both bands is positive we prefer to assign these bands to the close-lying $3^1A_g^-$ and $4^1A_g^-$ states predicted by our T -CI calculation to lie 2.02 and 2.21 eV, respectively, above S_1 . At 6.62 eV, i. e., 3.4 eV above S_1 , Beelaar found a broad and intense band with a negative degree of polarization which he assigned to a $1^1B_{1g}^-$ state. Indeed, a corresponding $2^1B_{1g}^-$ state is predicted 3.6 eV above S_1 by our T -CI calculation.

IV. CONCLUSION

The inclusion of higher (at least all double) excitations in a CI expansion to account for electron correlation in excited states leads to the prediction of polyacene spectra which provide a consistent assignment of all one- and two-photon spectral data. In contrast, previous CI descriptions including only single excitations account for only a part of the low-energy excitations and also do not yield the right state ordering, and, thereby, fail a complete assignment of spectral transitions. However, the correlation effects in the polyacenes, as far as the number and low-energy position of new excitations is concerned, are not quite as dramatic as in the case of the polyenes. Triple and quadruple excitations were found to leave nearly unaltered the D -CI ordering of the polyacene excited states, but repair the general overestimate of excitation energies by the D -CI approach.

In our study we had to leave unassigned a number of singlet excitations predicted [cf. Figs. 6(b) and 7]. In this respect we hope that our calculations will stimulate further spectroscopic work.

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¹See, for example, the discussion in the preceding paper: P. Tavan and K. Schulten, *J. Chem. Phys.* 70, 5407 (1979).

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